INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON SOLUBILITY DATA

SOLUBILITY DATA SERIES

Volume 56

ALCOHOLS WITH HYDROCARBONS

SOLUBILITY DATA SERIES

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY
IUPAC SECRETARIAT: Bank Court Chambers, 2-3 Pound Way
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SOLUBILITY DATA SERIES

Volume 56

ALCOHOLS WITH HYDROCARBONS

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OXFORD UNIVERSITY PRESS

IUPAC Solubility Data Series Rates for 1994

Subscriptions:	**UK and Europe**	**Rest of World**
Full subscription	£265	$395
Single volume	£75	$115

Reduced rates are available to members of IUPAC. Please apply directly to the publisher for details.

Prices include postage by surface mail or, for subscribers in the USA and Canada by Airfreight or in Japan, India, Australia and New Zealand by Air Speeded Post. Airmail rates are available on request.

The IUPAC Solubility Data Series is published quarterly in March, June, September and December by Oxford University Press. Subscription is $395 per year. Second Class postage paid at Newark, New Jersey. ISSN 0191-5622.

POSTMASTER: Send address corrections to IUPAC Solubility Data Series, c/o Virgin Mailing and Distribution, Cargo Atlantic, 10 Camptown Road, Irvington, New Jersey 07111-1105, USA.

New subscriptions may be registered at any time during the year but will be reckoned as running from January 1st of the year in which the subscription is received. Claims regarding non-receipt of issues must be received within 4 months of publication or date of order, whichever is later. Back issues are available—for information contact Journals Customer Services Department, Oxford University Press, Walton Street, Oxford OX2 6DP.

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Any enquires regarding this publication should be addressed to:
USA and Canada: Oxford University Press, 2001 Evans Road, Cary, NC 27513, USA.
Rest of World: Journals Customer Services Department, Oxford University Press, Walton Street, Oxford OX2 6DP, UK.

Printed and bound in Great Britain by Antony Rowe Ltd, Chippenham, Wiltshire

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INTRODUCTION TO THE SOLUBILITY DATA SERIES

SOLUBILITY OF LIQUIDS IN LIQUIDS

NATURE OF THE PROJECT

The Solubility Data project (SDP) has as its aim a comprehensive review of published data for solubilities of gases, liquids and solids in liquids or solids. Data of suitable precision are compiled for each publication on data sheets in a uniform format. The data for each system are evaluated and, where data from different sources agree sufficiently, recommended values are proposed. The evaluation sheets, recommended values, and compiled data sheets are published on consecutive pages.

This series is concerned primarily with liquid-liquid systems, but a limited number or related solid-liquid, fluid-fluid and multicomponent (organic-water-salt) systems are included where it is considered logical and appropriate. Solubilities at elevated and low temperatures and at elevated pressures have also been included, as it is considered inappropriate to establish artificial limits on the data presented if they are considered relevant or useful.

For some systems, the two components may be miscible in all proportions at certain temperatures and pressures. Data on reported miscibility gaps and upper and lower critical solution temperatures are included where appropriate and when available.

COMPILATIONS AND EVALUATIONS

The formats for the compilations and critical evaluations have been standardized for all volumes. A description of these formats follows.

Compilations

The format used for the compilations is, for the most part, self-explanatory. A compilation sheet is divided into boxes, with detailed contents described below.

Components: Each component is listed according to IUPAC name, formula, and Chemical Abstracts (CA) Registry Number. The Chemical Abstracts name is also included if this differs from the IUPAC name, as are trivial names if appropriate. IUPAC and common names are cross-referenced to Chemical Abstracts names in the System Index.

The formula is given either in terms of the IUPAC or Hill (1) system and the choice of formula is governed by what is usual for most current users: i.e., IUPAC for inorganic compounds, and Hill system for organic compounds. Components are ordered on a given compilation sheet according to:

(a) saturating components:
(b) non-saturating components in alphanumerical order;
(c) solvents in alphanumerical order.

The saturating components are arranged in order according to the IUPAC 18-column periodic table with two additional rows:

Columns 1 and 2:	H, alkali elements, ammonium, alkaline earth elements
Columns 3 to 12:	transition elements
Columns 13 to 17:	boron, carbon, nitrogen groups; chalcogenides, halogens
Column 18:	noble gases
Row 1:	Ce to Lu
Row 2:	Th to the end of the known elements, in order of atomic number.

Organic compounds within each Hill formula are ordered in the following succession:

(a) by degree of unsaturation
(b) by order of increasing chain length in the parent hydrocarbon
(c) by order of increasing chain length of hydrocarbon branches
(d) numerically by position of unsaturation
(e) numerically by position by substitution
(f) alphabetically by IUPAC name.

Example:

C_5H_8	cyclopentane
	2-methyl-1,3-butadiene
	1,4-pentadiene
	1-pentyne
C_5H_{10}	cyclopentane
	3-methyl-1-butene
	2-methyl-2-butene
	1-pentene
	2-pentene
C_5H_{12}	2,2-dimethylpropane
	2-methylbutane
	pentane
$C_5H_{12}O$	2,2-dimethyl-1-propanol
	2-methyl-1-butanol
	2-methyl-2-butanol
	3-methyl-1-butanol
	3-methyl-2-butanol
	1-pentanol
	2-pentanol
	3-pentanol
$C_6H_{12}O$	cyclohexanol
	4-methyl-1-penten-3-ol
	1-hexen-3-ol
	4-hexen-3-ol

Deuterated (^2H) compounds follow immediately the corresponding H compounds.

Original Measurements: References are abbreviated in the forms given by Chemical Abstracts Service Source Index (CASSI). Names originally in other than Roman alphabets are given as transliterated by Chemical Abstracts. In the case of multiple entries (for example, translations) an asterisk indicates the publication used for compilation of the data.

Variables: Ranges of temperature, pressure, etc. are indicated here.

Prepared by: The names of all compilers are given here.

Experimental Values: Components are described as (1), (2), etc., as defined in the "Components" box. Data are reported in the units used in the original publication, with the exception that modern names for units and quantities are used; e.g., mass per cent for weight per cent; mol dm^{-3} for molar; etc. In most cases, both mass and molar values are given. Usually, only one type of value (e.g., mass per cent) is found in the original paper, and the compiler has added the other type of value (e.g., mole per cent) from computer calculations based on 1989 atomic weights (2). Temperatures are expressed as t/°C, t/°F or T/K as in the original; if necessary, conversions to T/K are made, sometimes in the compilations, and always in the critical evaluation. However, the author's units are expressed according to IUPAC recommendations (3) as far as possible.

Errors in calculations, fitting equations, etc. are noted, and where possible corrected. Material inserted by the compiler is identified by the word "compiler" or by the compiler's name in parentheses or in a footnote. In addition, compiler-calculated values of mole or mass fractions are included if the original data do not use these units. If densities are reported in the original paper, conversions from concentrations to mole fractions are included, but otherwise this is done in the evaluation, with the values and sources of the densities being quoted and referenced.

Details of smoothing equations (with limits) are included if they are present in the original publication and if the temperature or pressure ranges are wide enough to justify this procedure and if the compiler finds that the equations are consistent with the data.

The precision of the original data is preserved when derived quantities are calculated, if necessary by the inclusion of one additional significant figure. In some cases graphs have been included, either to illustrate presented data more clearly, or if this is the only information in the original. Full grids are not usually inserted as it is not intended that users should read data from the graphs.

Method: The apparatus and procedure are mentioned briefly. Abbreviations used in Chemical Abstracts are often used here to save space, reference being made to sources of further detail if these are cited in the original paper.

Source and Purity of Materials: For each component, referred to as (1), (2), etc., the following information (in this order and in abbreviated form) is provided if available in the original paper: source and specified method of preparation; properties; degree of purity.

Estimated Error: If estimated errors were omitted by the original authors, and if relevant information is available, the compilers have attempted to estimate errors (identified by "compiler" or the compiler's name in parentheses or in a footnote) from the internal consistency of data and type of apparatus used. Methods used by the compilers for estimating and reporting errors are based on Ku and Eisenhart (4).

Comments and/or Additional Data: Many compilations include this section which provides short comments relevant to the general nature of the work or additional experimental and thermodynamic data which are judged by the compiler to be of value to the reader.

References: The format for these follows the format for the Original Measurements box, except that final page numbers are omitted. References (usually cited in the original paper) are given where relevant to interpretation of the compiled data, or where cross-reference can be made to other compilations.

Evaluations

The evaluator's task is to assess the reliability and quality of the data, to estimate errors where necessary, and to recommend "best" values. The evaluation takes the form of a summary in which all the data supplied by the compiler have been critically reviewed. There are only three boxes on a typical evaluation sheet, and these are described below.

Components: The format is the same as on the Compilation sheets.

Evaluator: The name and affiliation of the evaluator(s) and date up to which the literature was checked.

Critical Evaluation:

(a) Critical text. The evaluator checks that the compiled data are correct, assesses their reliability and quality, estimates errors where necessary, and recommends numerical values based on all the published data (including theses, reports and patents) for each given system. Thus, the evaluator reviews the merits or shortcomings of the various data. Only published data are considered. Documented rejection of some published data may occur at this stage, and the corresponding compilations may be removed.

The solubility of comparatively few systems is known with sufficient accuracy to enable a set of recommended values to be presented. Although many systems have been studied by at least two workers, the range of temperatures is often sufficiently different to make meaningful comparison impossible.

Occasionally, it is not clear why two groups of workers obtained very different but internally consistent sets of results at the same temperature, although both sets of results were obtained by reliable methods. In such cases, a definitive assessment may not be possible. In some cases, two or more sets of data have been classified as tentative even though the sets are mutually inconsistent.

(b) Fitting equations. If the use of a smoothing equation is justifiable the evaluator may provide an equation representing the solubility as a function of the variables reported on all the compilation sheets, stating the limits within which it should be used.

(c) Graphical summary. In addition to (b) above, graphical summaries are often given.

(d) Recommended values. Data are recommended if the results of at least two independent groups are available and they are in good agreement, and if the evaluator has no doubt as to the adequacy and reliability of the applied experimental and computational procedures. Data are reported as tentative if only one set of measurements is available, or if the evaluator considers some aspect of the computational or experimental method as mildly undesirable but estimates that it should cause only minor errors. Data are considered as doubtful if the evaluator considers some aspect of the computational or experimental method as undesirable but still considers the data to have some value where the order of magnitude of the solubility is needed. Data determined by an inadequate method or under ill-defined conditions are rejected. However, references to these data are included in the evaluation together with a comment by the evaluator as to the reason for their rejection.

(e) References. All pertinent references are given here, including all those publications appearing in the accompanying compilation sheets and those which, by virtue of their poor precision, have been rejected and not compiled.

(f) Units. While the original data may be reported in the units used by the investigators, the final recommended values are reported in SI units (3) when the data can be converted accurately.

QUANTITIES AND UNITS USED IN COMPILATION AND EVALUATION OF SOLUBILITY DATA

Mixtures, Solutions and Solubilities

A *mixture* (5, 6) describes a gaseous, liquid or solid phase containing more than one substance, where the substances are all treated in the same way.

A *solution* (5, 6) describes a liquid or solid phase containing more than one substance, when for convenience one of the substances, which is called the *solvent*, and may itself be a mixture, is treated differently than the other substances, which are called *solutes*. If the sum of the mole fractions of the solutes is small compared to unity, the solution is called a *dilute solution*.

The *solubility* of a solute 1 (solid, liquid or gas) is the analytical composition of a saturated solution, expressed in terms of the proportion of the designated solute in a designated solvent (7).

"Saturated" implies equilibrium with respect to the processes of dissolution and demixing; the equilibrium may be stable or metastable. The solubility of a substance in metastable equilibrium is usually greater than that of the same substance in stable equilibrium. (Strictly speaking, it is the activity of the substance in metastable equilibrium that is greater.) Care must be taken to distinguish true metastability from supersaturation, where equilibrium does not exist.

Either point of view, mixture or solution, may be taken in describing solubility. The two points of view find their expression in the reference states used for definition of activities, activity coefficients and osmotic coefficients. Note that the composition of a saturated mixture (or solution) can be described in terms of any suitable set of thermodynamic components.

Physicochemical Quantities and Units

Solubilities of solids have been the subject of research for a long time, and have been expressed in a great many ways, as described below. In each case, specification of the temperature and either partial or total pressure of the saturating gaseous component is necessary. The nomenclature and units follow, where possible, ref. (3)

A note on nomenclature. The nomenclature of the IUPAC Green Book (3) calls the solute cpmponent B and the solvent component A. In compilations and evaluations, the first-named component (component 1) is the solute, and the second (component 2 for a two-component system) is the solvent. The reader should bear these distinctions in nomenclature in mind when comparing equations given here with those in the Green Book.

1. *Mole fraction* of substance 1, x_1 or $x(1)$:

$$x_1 = n_1/\sum_{s=1}^{c} n_s \qquad [1]$$

where n_s is the amount of substance of s, and c is the number of distinct substances present (often the number of thermodynamic components in the system). *Mole per cent* of substance 1 is $100\,x_1$.

2. *Ionic mole fractions* of salt i, x_{i+}, x_{i-}:
For a mixture of s binary salts i, each of which ionizes completely into ν_{s+} cations and ν_{s-} anions, with $\nu_s = \nu_{s+} + \nu_{s-}$ and a mixture of p non-electrolytes j, of which some may be solvent components, a generalization of the definition in (8) gives:

$$x_{i+} = \frac{\nu_{i+}x_i}{1+\sum_{i=1}^{s}(\nu_i-1)x_s}, \quad x_{i-} = \frac{\nu_{i-}x_{i+}}{\nu_{i+}} \quad i = 1...s \qquad [2]$$

$$x_j' = \frac{x_j}{1+\sum_{i=1}^{s}(\nu_i-1)x_i}, \quad j = (s+1),...,p \qquad [3]$$

The sum of these mole fractions is unity, so that, with $c = s + p$,

$$\sum_{i=1}^{s}(x_{i+}+x_{i-})+\sum_{i=s+1}^{c}x_i' = 1 \qquad [4]$$

General conversions to other units in multicomponent systems are complicated. For a three-component system containing non-electrolyte 1, electrolyte 2 and solvent 3,

$$x_1 = \frac{\nu_{2+}x_1'}{\nu_{2+}-(\nu_2-1)x_{2+}} \qquad x_2 = \frac{x_{2+}}{\nu_{2+}-(\nu_2-1)x_{2+}} \qquad [5]$$

These relations are used in solubility equations for salts, and for tabulation of salt effects on solubilities of gases (see below).

3. *Mass fraction* of substance 1, w_1 or $w(1)$:

$$w_1 = g_1/\sum_{s=1}^{c} g_s \qquad [6]$$

where g_s is the mass of substance s. *Mass per cent* of substance 1 is 100 w_1. The equivalent terms *weight fraction*, *weight per cent* and *g (1)/100 g solution* are no longer used.

4. *Molality* of solute 1 in a solvent 2, m_1:

$$m_1 = n_1/n_2\, M_2 \qquad [7]$$

SI base units: mol kg^{-1}. Here, M_2 is the molar mass of the solvent.

5. *Aquamolality, Solvomolality* of substance 1 in a mixed solvent with components 2, 3 (9), $m_1^{(3)}$:

$$m_1^{(3)} = m_1\overline{M}/M_3 \qquad [8]$$

SI base units: mol kg^{-1}. Here, the average molar mass of the solvent is

$$\overline{M} = x_2'M_2+(1-x_2')M_3 \qquad [9]$$

and x_2' is the solvent mole fraction of component 2. This term is used most frequently in discussing comparative solubilities in water (component 2) and heavy water (component 3) and in their mixtures.

6. *Amount concentration* of solute 1 in a solution of volume V, c_1:

$$c_1 = [\text{formula of solute}] = n_1/V \qquad [10]$$

SI base units: mol m^{-3}. The symbol c_1 is preferred to [formula of solute], but both are used. The old terms *molarity*, *molar* and *moles per unit volume* are no longer used.

7. *Mass concentration* of solute 1 in a solution of volume V, ρ_1:SI base units: kg m^{-3}.

$$\rho_1 = g_1/V \qquad [11]$$

8. *Mole ratio*, $r_{n,12}$ (dimensionless)

$$r_{n,12} = n_1/n_2 \qquad [12]$$

Mass ratio, symbol $r_{g,12}$, may be defined analogously.

Mole and mass fractions are appropriate to either the mixture or the solution point of view. The other quantities are appropriate to the solution point of view only. Conversions between pairs of these quantities can be carried out using the equations given in Table 1 at the end of this Introduction. Other useful quantities will be defined in the prefaces to individual volumes or on specific data sheets.

9. *Density*, ρ:

$$\rho = g/V \qquad [13]$$

SI base units: kg m^{-3}. Here g is the total mass of the system.

10. *Relative density*, $d = \rho/\rho^{o}$: the ratio of the density of a mixture at temperature t, pressure p to the density of a reference substance at temperature t', pressure p'. For liquid solutions, the reference substance is often water at 4°C, 1 bar. (In some cases 1 atm is used instead of 1 bar.) The term *specific gravity* is no longer used.

Thermodynamics of Solubility

Thermodynamic analysis of solubility phenomena provides a rational basis for the construction of functions to represent solubility data, and thus aids in evaluation, and sometimes enables thermodynamic quantities to be extracted. Both these are often difficult to achieve because of a lack of experimental or theoretical activity coefficients. Where thermodynamic quantities can be found, they are not evaluated critically, since this task would involve examination of a large body of data that is not directly relevant to solubility. Where possible, procedures for evaluation are based on established thermodynamic methods. Specific procedures used in a particular volume will ybe described in the Preface to that volume.

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January, 1994

Table 1. Interconversions between Quantities Used as Measures of Solubility
c-component Systems Containing c - 1 Solutes i and Single Solvent c

	x_i	w_i	m_i	c_i
$x_i =$	x_i	$\dfrac{1}{1+\dfrac{M_i}{M_c}\left(\dfrac{1}{w_i}-1+\sum\limits_{j\neq i}^{c-1}\left(\dfrac{M_c}{M_j}-1\right)\dfrac{w_j}{w_i}\right)}$	$\dfrac{1}{1+\dfrac{1}{m_i M_c}+\sum\limits_{j\neq i}^{c-1}\dfrac{m_j}{m_i}}$	$\dfrac{1}{1+\dfrac{1}{M_c}\left(\dfrac{\rho}{c_i}-M_i\right)+\sum\limits_{j\neq i}^{c-1}\dfrac{c_j}{c_i}\left(1-\dfrac{M_j}{M_c}\right)}$
$w_i =$	$\dfrac{1}{1+\dfrac{M_c}{M_i}\left(\dfrac{1}{x_i}-1+\sum\limits_{j\neq i}^{c-1}\left(\dfrac{M_j}{M_c}-1\right)\dfrac{x_j}{x_i}\right)}$	w_i	$\dfrac{1}{1+\dfrac{1}{m_i M_i}\left(1+\sum\limits_{j\neq i}^{c-1}m_j M_j\right)}$	$\dfrac{c_i M_i}{\rho}$
$m_i =$	$\dfrac{1}{M_c\left(\dfrac{1}{x_i}-1-\sum\limits_{j\neq i}^{c-1}\dfrac{x_j}{x_i}\right)}$	$\dfrac{1}{M_i\left(\dfrac{1}{w_i}-1-\sum\limits_{j\neq i}^{c-1}\dfrac{w_j}{w_i}\right)}$	m_i	$\dfrac{1}{\dfrac{1}{c_i}\left(\rho-\sum\limits_{j\neq i}^{c-1}c_j M_j\right)-M_i}$
$c_i =$	$\dfrac{\rho}{M_i+M_c\left(\dfrac{1}{x_i}-1+\sum\limits_{j\neq i}^{c-1}\left(\dfrac{M_j}{M_c}-1\right)\dfrac{x_j}{x_i}\right)}$	$\dfrac{\rho w_i}{M_i}$	$\dfrac{\rho}{\dfrac{1}{m_i}\left(1+\sum\limits_{j\neq i}^{c-1}M_j m_j\right)+M_i}$	c_i

ρ - density of solution; M_i - molar masses of i. For relations for 2-component systems, set summations to 0.

PREFACE TO THE VOLUME

Scope of the Volume

This volume surveys solubility data which have been published in the open literature up to the end of 1988 for binary systems containing hydrocarbons and alcohols. The hydrocarbons include those with four or more carbon atoms and of all structural types (aliphatic, aromatic, unsaturated, etc.); i.e., all hydrocarbons which are liquids at room temperature and pressure. The alcohol in the binary pair is most commonly methanol, but some less systematic data exist for ethanol and a few higher alcohols such as benzyl alcohol. Altogether 120 systems containing 280 data sets are presented. From these, it has been possible to make critical evaluations for only 24 systems, which indicates the pronounced lack of data for alcohols other than methanol.

Components of these systems were (with one or two exceptions) always well-defined substances. Only numerical data are given because data published originally in graphical form are inherently imprecise, especially given the high precision of the tabulated data for many systems. The literature contains a large amount of imprecise and conflicting data. Where possible, recommended or tentative values of critical solution composition, critical solution temperature and mutual solubility, all at 0.1 MPa, are given, but and in many cases this cannot be done because of insufficient information.

This volume is the result of a careful search of the chemical literature. The goal of that search was to include all published data for the systems indicated in the title. Each Critical Evaluation includes a closing date for the literature for that system, generally December, 1988. In spite of these efforts, some published measurements may have been missed. The editors will appreciate having their attention brought to any omitted source of solubility data for inclusion in future volumes.

For purposes of comparison, the compilers and evaluators of this volume have, in so far as is possible, expressed all original results in mass percent and mole fraction as well as in the units given by the original investigators. Conversions, where they have been made, are clearly attributed to the compiler and the sources of any data not provided by the original investigators (such as density) are specified. Definitions of mass percent and mole fraction as well as their relation to other common measures of solubility are given in the *Introduction to the Solubility Data Series: Solubility of Liquids in Liquids* in this volume. A table of conversion formulas is included at the end of the *Introduction.*

General Properties of Systems Exhibiting Liquid-Liquid Equilibria

The alcohol-hydrocarbon systems all exhibit liquid-liquid equilibria, giving rise to a *coexistence* or *connodal* curve which is the locus of the ends of the tie-lines joining phases in equilibrium (at a given temperature) as a function of temperature. For a general discussion, see for example (ref. 1, 2); a schematic phase diagram which incorporates features found for the systems discussed in this volume is shown in Fig. 1. The coexistence curve separates homogeneous and metastable heterogeneous regions of the system. Within the coexistence curve lies the *spinodal* curve, which is the boundary between metastable and unstable regions of the system. With care, points between

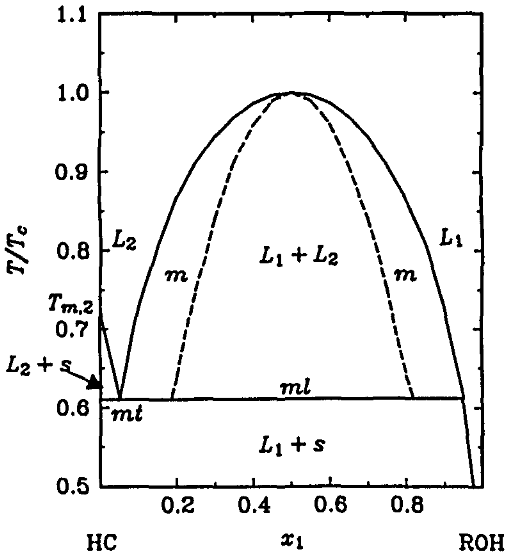

Fig. 1. Schematic phase diagram for a binary liquid-liquid system. L_1, L_2 - coexisting liquid phases; *s* - solid phase 2; *m* - metastable liquid region; *ml* - monotectic line; *mt* - monotectic point; $T_{m,2}$ - melting point of pure component 2.

the coexistence and spinodal curves can be reached experimentally, i.e., one liquid phase can become supersaturated with respect to the other. The coexistence and spinodal curves coincide at a *critical solution point*, which for alcohol-hydrocarbon systems, in the ranges of pressure which have been investigated, is always an *upper critical solution point*, which has an *upper critical solution temperature*, *UCST*, (sometimes referred to in the older literature as an "upper consolute temperature") and a corresponding *upper critical solution composition*. Points within the spinodal curve cannot be reached by experiment; the process of *spinodal decomposition* takes place in that region.

In principle, each of the two branches of the coexistence curve extends downwards from the critical solution point until the system reaches a *monotectic* point, where a pure solid phase and two conjugate liquid phases are in mutual equilibrium, and the end of the stable part of the solubility curve of the solid is reached. For alcohol-hydrocarbon systems, the monotectic has been observed in only one system, methanol-cyclohexane, on the cyclohexane-rich side of the phase diagram; the monotectic for the alcohol-rich branch would be expected to occur at a very much lower temperature because of the lower melting point of methanol.

Modern Theories of Critical Solution Behavior

The phenomenon of critical solution points is analogous to the phenomenon of the critical point in one-component systems, about which many precise data have been collected (ref. 2). Analogs also exist in solid-solid equilibria. This ubiquitous phenomenon has thus given rise to intense theoretical and experimental investigation, especially during the past 20 years. Classical thermodynamics predicts that the composition near the critical point is a quadratic function of temperature, i.e., the critical index β (see below) is exactly 1/2, but it has been known for a long time that the experimental value is closer to 1/3 (ref. 2). The classical thermodynamic theory assumes that the Gibbs energy is an analytic function of temperature and composition, so that a

Taylor expansion about the critical point is valid. The general conclusions of modern theory (ref. 3) are that the Gibbs energy is not analytic in the neighborhood of the critical solution point, as a result of long-range fluctuations in composition, but can be *scaled* in a region very near the critical point. The scaling equation is characterized by a universal *critical index*, β, defined by (ref. 2)

$$\beta = \lim_{T \to T_c} \left(\frac{\partial \ln[(x_i'' - x_i')]}{\partial \ln |T - T_c|} \right) \tag{1}$$

where $x_i'' - x_i'$ is the difference in mole fraction of component i between the more concentrated and the more dilute phases in equilibrium at temperature T, and T_c is the critical solution temperature.

At temperatures not far from the critical point, usually when $\theta = 1 - T/T_c > 10^{-3}$ (ref. 3), the classical thermodynamic description of the liquid-liquid equilibrium is expected to be valid. The following equation contains corrections to the scaling equation for the whole region (ref. 4):

$$x_i'' - x_i' = B_1|\theta|^{\beta} + B_2|\theta|^{\beta+w} + B_3|\theta|^{\beta+2w} + \dots \tag{2}$$

with the B_i constants. The locus of the bisector of the tie-lines (the *binodal* curve) defines a second critical index, α, through the equation

$$(x_i'' + x_i')/2 = x_{ci} + A_1|\theta|^{1-\alpha} + A_2|\theta| + A_3|\theta|^{1-\alpha+w} + \dots \tag{3}$$

where the empirical index $w = 0.5$ (but see ref. 4) is called the first Wegner correction term (ref. 5). Combining eqns. (1) and (2), as in ref. 6, gives

$$x_i = x_{ci} \pm (B_1/2)|\theta|^{\beta} \pm (B_2/2)|\theta|^{\beta+w} + A_1|\theta| \pm (B_3/2)|\theta|^{\beta+2w} + A_2|\theta|^{1-\alpha+w} \tag{4}$$

The form of eqn. (4) and the sequence of coefficients is derived from experience in fitting experimental data for this volume. In particular, powers of 1 and $1 - \alpha = 0.89$ in θ have been combined as a single power of unity.

Modern theories give $\beta = 0.329$, $\alpha = 0.11$ (ref. 7). In this volume, the slightly older theoretical value $\beta = 0.325 \pm 0.003$ will be used, as in most modern papers quoted herein.

Equation (4) gives a fitting equation for the coexistence curve in terms of the critical parameters α and β, the Wegner correctios w and arbitrary constants. The critical parameters can be given their theoretical values (which in some cases are not well known), or can be used as fitting parameters. It has been found (ref. 3) for the systems acetonitrile - cyclohexane and carbon tetrachloride - perfluoroheptane that an equation of the form (4) represents data very well over the whole experimental range of temperature. Although the classical equation is equally successful in representing the data, it gives, of course, a dependence on temperature which is inconsistent with theory very near the critical solution temperature. (For discussion of the theory of the "crossover" problem between scaling and classical equations, see ref. 8, and for practical consequences in fitting data see ref. 3.) Many data for methanol-hydrocarbon systems have been obtained within $\theta = 10^{-3}$ of the critical solution temperature. For that reason, fitting equations of the form (4) are used in this volume; their use in practice will be discussed briefly below.

Experimental Methods

Most solubility measurements of hydrocarbon-alcohol systems have been made in the temperature range which is considered to be "room temperature", i.e., 273 - 320 K. Except in more recent precise work, pressure has seldom been specified, and is assumed to be approximately 0.1 MPa (1 atm). There are two principal methods: isothermal equilibration and the cloud - point method. Isothermal equilibration of systems of known overall composition is carried out at a carefully-controlled temperature, and the equilibrated phases are analyzed by a variety of methods, physical or chemical. In the cloud-point method, systems of accurately-known composition are heated in a closed tube until the meniscus between coexisting phases just disappears. Heating and cooling over small intervals in temperature then establishes a point on the coexistence curve, occasionally with precision which approaches the mK range.

Both the isothermal equilibration and cloud-point methods are subject to errors arising from gravitational effects. In the isothermal equilibration method, if the whole of each phase is analyzed and the system is near the critical solution point, where the two coexisting phases have almost the same composition and density, the isothermal compressibility approaches an infinite value. Thus, just above the critical point, the fluid becomes compressed significantly by its own weight, and its density varies with height. At some particular height, there is a density equal to the critical density. In most experiments, only the average density (or composition) is measured, so there will be an apparent range of critical densities which will lead to a flat top in the coexistence curve. This phenomenon is very marked in gases (ref. 2), and more recent work has demonstrated its importance in liquid-liquid systems; for a review, see ref. 8. In the cloud-point method, on the other hand, the first nucleation of small droplets is observed visually at a given position in the sample container at which the pressure is higher at the surface of the liquid. An estimate of the effect of this pressure can be obtained from the measured value of $(\partial T_c/\partial p)_c$, which, for the system cyclohexane-methanol, has the value 3.30×10^{-7} K Pa^{-1} (ref. 6). In this system, critical solution temperatures have been measured to a precision of 10^{-4} K (ref. 5); a change in critical solution temperature of this magnitude will be caused by change in depth of 4 cm for a liquid density of 0.8 g cm^{-3}. Thus corrections must be made for any pressure head above the point of observation. In a sealed tube, where the pressure is unknown, the associated error in temperature is also unknown. In general, if care is taken in keeping the pressure constant, the cloud-point method is capable of greater precision than the isothermal equilibration method.

With either method, small amounts of impurities have a very large influence on the critical solution temperature, and a smaller influence on the critical solution composition (ref. 9, 10). Thermodynamics applied to the simple mixture model makes two general predictions about the effect of impurities. These predictions have been found in practice to apply to systems which are not simple mixtures, and thus are more general than it would appear. The predictions are (ref. 1):

> Introduction of a third component which is equally soluble in the first two components will lower the critical solution temperature, i.e. it will increase the mutual solubility.
>
> Introduction of a third component which is much less soluble in one of the first two components than in the other will always raise the critical solution temperature, i.e. there will be a decrease in mutual solubility.

The simple theory also predicts that, to a first approximation, the critical solution temperature varies linearly with mole fraction of impurity. For the alcohol-hydrocarbon systems, water is a common impurity which is difficult to remove from the starting products and difficult to avoid as a contaminant which enters during experimental manipulations. Because water is always much more soluble in alcohols than in hydrocarbons, contamination by water should lead to an increase in the critical solution temperature, other things being equal. Many examples of this behavior can be found in the alcohol-hydrocarbon systems, where the lowest critical solution temperature should be closest to the correct value, if water is the main impurity.

Yet another complication occurs in connection with the isothermal equilibration method. In a mixture of, for example, methanol and cyclohexane near the critical point, the slightly denser methanol-rich phase wets the walls of the container preferentially, and surrounds the cyclohexane-rich phase (ref. 11). Thus, location of the critical point by optical (including visual) methods can be difficult in cells with heights and widths of comparable dimensions.

Procedures Used in Critical Evaluations

1. *Fitting Equations for Coexistence Curves.* Equation (4) above is the basis of the fitting procedure used in the Critical Evaluations in this volume. Simple least-squares theory (ref. 12), as used by authors of recent papers (such as ref. 6), requires that all error should be in the dependent variable (x), with the independent variable (θ) known accurately. Since the temperature appears in a non-linear form in the fitting equation, an estimated value of T_c is used to calculate values of θ, then the value of parameter T_c is varied systematically until minimum standard error of estimate is found for x (see ref. 12). The error in T_c must be found by examining the variation in the standard error of estimate near its minimum value for various trial values of T_c.

In the cloud-point method, errors in composition (arising from weighing the components and in evaporation during transfer to the apparatus) can actually be comparable to errors in θ, but this is not usually the case. Clearly, a more general least-squares approach is indicated, in which errors in both temperature and composition are taken into account. Some limited progress in this direction has been made, e.g., by Aizpiri et al., ref. 13, but the whole question of a statistically valid approach to fitting experimental data to eqn. (4) appears to be a matter for further research.

For this volume the simpler approach, despite its shortcomings from the point of view of statistical theory, has been found to give excellent representations of the experimental data. In the Critical Evaluations, it would appear that more significant figures are given for the parameters of the fitting equations than are justified by the respective standard deviations. However, it should be noted that the errors in the parameters are highly correlated, and retention of the larger number of digits is necessary to achieve a correct calculation.

According to eqn. (4), the difference $x_1 - x_{c1}$ is a function of $\theta = 1 - T/T_c$ only, which suggests that variations in T_c and x_{c1} for different sets of data for a given system should be taken into account in large measure by plotting T/T_c against $x_1 - x_{c1}$, where T_c and x_{c1} are the values for each individual set; values of T/T_c are thus less than unity, and of x_{c1} generally in the range -0.5 to + 0.5. Hoelscher, Schneider and Ott (ref. 14) used a similar plot to compare phase diagrams of different methanol - *n*-alkane systems. In this volume, the method has been found to be useful in one case only, that of methanol - cyclohexane. The large effects of small amounts of impurities on T_c appear to have been eliminated, and comparisons among the sets of data have thus been facilitated.

2. *Correlations between Critical Solution Temperatures and Compositions and Chain Length in Systems of Alcohols and Homologous Series of Hydrocarbons*

Within a particular system, reported critical solution parameters and mutual solubilities show substantial scatter; as examples, see the Critical Evaluations for the systems methanol - cyclohexane and methanol - hexane. As noted above, both x_{c1} and (especially) T_c are very sensitive to the presence of impurities. Therefore, correlations of these quantities with a characteristic molecular parameter should prove useful as an indication of the consistency of the data and the presence of outliers. In making such comparisons, it should be noted that x_{c1} has been measured in the better experiments to about ± 0.001 at best, while T_c for between-laboratory and within-laboratory determinations can probably be defined to within only ± 0.1 K at best, even though average determinations within one laboratory have been recorded with uncertainties of only ± 0.001 K.

Haarhaus and Schneider, ref. 15, suggested that T_c is linear in ln *n* for methanol - *n*-alkane systems, where *n* is the number of carbon atoms in the chain. However, this dependence does not account for the expected asymptotic approach to a constant value at very high chain length. A more satisfactory dependence can be found from Flory-Huggins theory (ref. 16), from which the following equations may be derived:

$$1/T_c = (1/T_c^{\infty})[1+(1/\psi_1)(1/V_r^{1/2}+1/2V_r)] \qquad (5)$$

$$x_{c1} = \frac{1}{1+V_r^{-3/2}} \qquad (6)$$

where $V_r = V_{m,2}/V_{m,1}$ is the ratio of the molar volumes of pure liquids 2 and 1 at the temperature of interest (the number of lattice sites occupied by the chain in Flory-Huggins theory), T_c^{∞} is the critical temperature at infinite chain length, and ψ_1 is a parameter related to the non-ideal entropy of mixing. Sufficiently precise density data for calculation of the appropriate values of V_r at the critical solution temperature are not available for all alcohols and hydrocarbons of interest. In addition, the Flory-Huggins relations are not expected to hold for molecules of such different polarities as alcohols and hydrocarbons. Therefore, an approximate approach is indicated. For *n*-alkanes with sufficiently long chains, V_r is approximately linear to *n*, the number of carbon atoms in the hydrocarbon chain, and the dependence of V_r on temperature can be absorbed in the fitting coefficients. Thus, eqns. (7) and (8) below have been found to provide satisfactory semi-empirical relations for T_c and x_{c1}:

$$1/T_c = a + b/n^{1/2} \tag{7}$$

$$x_{c1} = c + d/n^{1/2} \tag{8}$$

where n is the number of carbon atoms in the n-alkane, T_c is the upper critical solution temperature of the system and x_{c1} is the critical mole fraction of methanol.

2.1 *Methanol-n-Alkane Series* In this series, values of T_c, x_{c1} and solubilities were compared over the range from butane to hexadecane, resulting in the rejection of some data as outliers. An example of rejected UCST data are those of Fischer and Neupauer, who measured the UCST of methanol with alkanes from pentane to undecane and found values much higher (e.g. in the system methanol - heptane 14.6 K higher) than the recommended or tentative values. For this reason, all their UCST data are considered unreliable and are rejected. Recommended or tentative values were derived from the reliable data for each system, as discussed in individual evaluations.

Least-squares fits to equations (7) and (8) give:

$$10^3\text{K}/T_c = 0.9888(0.011) + 5.5543(0.029)/n^{1/2} \tag{9}$$

$$x_{1c} = 1.2066(0.013) - 1.6071(0.034)/n^{1/2} \tag{10}$$

Numerical quantities in parentheses are estimated standard deviations of the fitting coefficients.

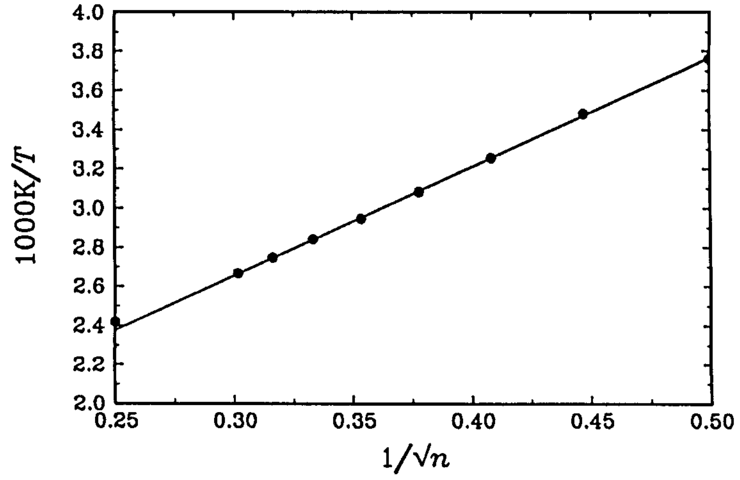

Fig. 2. Linear dependence of reciprocal of critical solution temperature on reciprocal square root of number of carbon atoms in methanol-*n*-alkane mixtures.

The standard errors of estimate are 0.0053 for eqn. (9) and 0.0054 for eqn. (10). The equations were constructed using all available values except those for *n*-hexadecane, which appear to be aberrant; T_c appears to be low by about 7 K and x_{c1} high by about 0.07. The recommended or tentative data for T_c and x_{1c} together with values calculated from the fitting equations are shown in Table 1; the linearity in $1/n^{1/2}$ is shown in figs. 2 and 3. Except for *n*-hexadecane, the calculated values of T_c deviate a maximum of 1.0 K from the recommended values, and the calculated values of x_{1c} deviate a maximum of 0.009 from the recommended or tentative values.

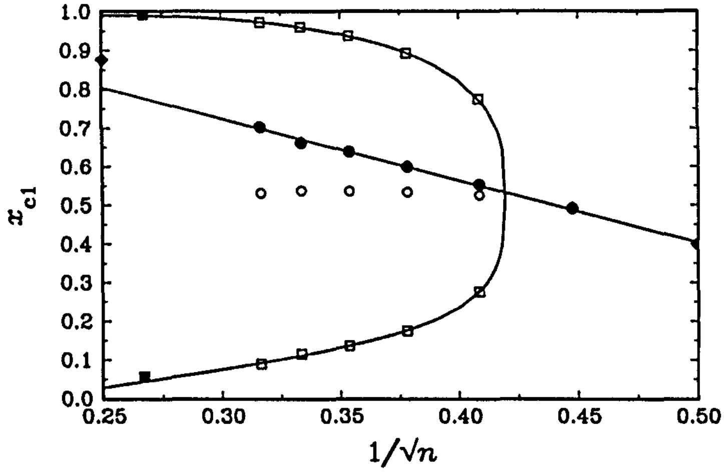

Fig. 3. Dependence of critical solution compositions and mutual solubilities at 300 K on reciprocal square root of carbon number for methanol-*n*-alkane systems. Critical solution compositions, x_{c1}: ●; solid line, fitting equation; note the aberrant point for hexadecane at ♦, $1/n^{1/2} = 0.25$ and two points for tetradecane, ■. Mutual solubilities: □, for methanol- and cyclohexane-rich branches; ○, diameter of "coexistence" curve; solid curve, fitting equation (see text).

Table 1.
Observed and calculated values of T_c, x_{c1} and mutual solubility at 300 K for the systems methanol-*n*-alkanes.

hydrocarbon	T_c/K		x_{1c}		x_1		x_2	
	obsd.	calc.	obsd.	calc.	obsd.	calc.	obsd.	calc.
butane	265.8	265.5	0.403	0.403	-	-	-	-
pentane	287.2	288.0	0.497	0.488	-	-	-	-
hexane	307.1	307.1	0.554	0.551	0.276	0.275	0.225	0.225
heptane	324.3	323.8	0.599	0.599	0.175	0.177	0.108	0.107
octane	339.4	338.7	0.639	0.638	0.136	0.137	0.063	0.063
nonane	351.9	352.1	0.662	0.671	0.115	0.111	0.040	0.040
decane	364.0	364.3	0.703	0.698	0.090	0.092	0.028	0.027
undecane	375.2	375.4	-	0.722	-	0.078	-	0.016
dodecane	-	385.8	-	0.743	-	0.071	-	0.011
tridecane	-	395.4	-	0.761	-	0.066	-	0.008
tetradecane	-	404.3	-	0.777	-	0.058	-	0.006
pentadecane	-	412.7	-	0.792	-	0.060	-	0.004
hexadecane	413.4	420.6	0.876	0.805	0.059	0.059	0.003	0.003

In fig. 3, recommended or tentative values of mutual solubilities at 300 K are plotted against $1/n_{1/2}$. According to the extended scaling equation, the composition is a function of $\theta = 1 - T/T_c$. The curve for the five hydrocarbons for which data are available can be rationalized by noting that both $1/T_c$ and x_{c1} are linear in $1/n_{1/2}$, so that introduction of these dependencies into the scaling equation at a fixed temperature T gives, at least approximately, an equation of the same form, but with $1/n_{1/2}$ replacing T_c. As usual, six parameters were needed to represent the data well, with values (and standard deviations in parentheses):

$$x_1 = x_{c1} \pm B_1\theta^{\beta} \pm B_2\theta^{\beta+w} + A_1\theta \pm B_3\theta^{\beta+2w} + A_2\theta^{1-\alpha+w} \tag{11}$$

where $\theta = |1 - (n_c/n)^{1/2}|$, + and - refer to the branches below and above the critical composition, and the constants have their theoretical values $\beta = 0.329$, $\alpha = 0.11$, $w = 0.5$. The constants (with standard deviations in parentheses) are:

$x_{c1} = 0.5180\ (0.0030)$ $(1/n_{1/2})_c = 0.419\ (0.001)$
$B_1 = 0.8859\ (0.018)$ $B_2 = -0.4140\ (0.1059)$ $B_3 = 0.0573\ (0.15)$
$A_1 = 0.4326\ (0.099)$ $A_2 = -0.6520\ (0.17)$ $s = 0.0025$
s is the standard error of estimate in composition.

The value of x_{c1} for hexadecane is evidently aberrant. Figure 3 also includes two non-evaluated solubilities for methanol-*n*-tetradecane, which fall close to the curve and thus appear to be of reasonable quality.

2.2 *Benzyl Alcohol-n-Alkane Series*

Values of the UCST for systems containing benzyl alcohol and alkanes from hexane to hexadecane were treated as described above for the methanol-*n*-alkane systems. These data were smoothed by the following equation:

$$10^3\mathrm{K}/T_c = 1.0338(0.021) + 5.4476(0.056)/n^{1/2} \tag{12}$$

The experimental UCST data together with the calculated values and smoothing curve are shown in Table 2. In this series of systems, the solubilities at the UCST were not of adequate quality for fitting.

Table 2. Experimental and smoothed values of T_c for the systems benzyl alcohol-*n*-alkane.

Hydrocarbon	T_c/K	
	obsd.	calc.
hexane	322.0-323.8	323.1
heptane	324.9-333.0	325.3
octane	327.7	328.4
nonane	-	332.2
decane	-	336.3
undecane	339.4	340.6
dodecane	345.1	345.0
tridecane	350.5	349.5
tetradecane	355.0	354.0
pentadecane	359.7	358.6
hexadecane	363.0	363.1

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August, 1994

COMPONENTS:

(1) Methanol-*d*; CDH_3O; [1455-13-6]

(2) Cyclohexane-d_{12}; C_6D_{12}; [1735-17-7]

EVALUATOR:

A. Skrzecz

Institute of Physical Chemistry
Polish Academy of Sciences
Warsaw, Poland

July, 1989

CRITICAL EVALUATION:

Solubilities and upper critical solution temperatures (UCST) for the system methanol-*d*-cyclohexane-d_{12} have been reported in the two references listed below:

Author(s)	T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Rabinovich 1971	317.3 UCST	-	-
2. Schoen 1986	314.935 UCST	0.516	0.516

Critical Solution Temperature and Composition

The values of Schoen et al., ref 2, is accepted as tentative because information is given about the method and degree of deuterization of components, and the value is consistent with other similar systems investigated by the authors. This information is lacking in ref 1.

Mutual Solubility

The authors give, for temperatures within about 0.3 K of the critical,

$$\Delta n = B_n | 1 - T/T_c |^{\beta}$$

where Δn is the difference in refractive index between coexisting phases, $B = 0.136 \pm 0.004$ is an amplitude constant, the critical index is $\beta = 0.323 \pm 0.004$, and the sample variance is 6.2×10^{-5}. The calibration factor for conversion to composition is unknown, so these data are given without further comment.

TENTATIVE DATA:

UCST: $T_c = 314.935 \pm 0.001$ K $x_{c1} = 0.516$

REFERENCES:

1. Rabinovich, I.B.; Tsvetkov, V.G. *Zh. Fiz. Khim.* 1971, *45*, 822.
2. Schoen, W.; Wiechers, R.; Woermann, D. *J. Chem. Phys.* 1986, *85*, 2922.

COMPONENTS:

(1) Methanol-*d*; CDH_3O; [1455-13-6]

(2) Cyclohexane-d_{12}; C_6D_{12}; [1735-17-7]

ORIGINAL MEASUREMENTS:

Rabinovich, I.B.; Tsvetkov, V.G.
Zh. Fiz. Khim. 1971, *45*, 822-3;
Russ. J. Phys. Chem. (Engl. Transl.) 1971, *45*, 814.

VARIABLES:

One temperature: 317 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 44.1°C.

Solubility data were presented on a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The temperature of appearance of turbidity was observed. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; purified by methods described in ref 1.
(2) source not specified; purified by methods described in ref 1.

ESTIMATED ERROR:

temp. ±0.1 K.

REFERENCES:

1. Rabinovich, I.B. *Vliyanie izitopii na fiziko-khimicheskie svoistva zhidkostei*, Izd. Nauka, Moskva, 1968.

COMPONENTS:

(1) Methanol-*d*; CDH_3O; [1455-13-6]

(2) Cyclohexane-d_{12}; C_6D_{12}; [1735-17-7]

ORIGINAL MEASUREMENTS:

Schoen, W.; Wiechers, R.;
Woermann, D.

J. Chem. Phys. 1986, *85*, 2922-8.

VARIABLES:

One temperature: 315 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 41.785°C at $x_1 = 0.516$.

The corresponding mass percentage, calculated by the compiler is $100w_1 = 26.8$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The differences of refractive index between two coexisting liquid phases were measured. The samples were prepared by mixing the required masses of components in a glove box. The deflection of a He/Ne laser beam after passing through the two compartments of the differential refractometer cell was measured as the distance necessary to shift the light detection unit. The refractive index of the coexisting phases was related to the composition by measuring several mixtures as function of temperature. The measurements were made over the range: UCST - 2 K.

SOURCE AND PURITY OF MATERIALS:

(1) Merck, Uvasol quality, degree of deuteration > 99 %; used as received.

(2) Merck, Uvasol quality, degree of deuteration > 99 %; used as received.

ESTIMATED ERROR:

temp. ±0.001 K (UCST),
±0.003 K (24 h stability).

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol-*d*; CDH_3O; [1455-13-6] (2) Hexane-d_{14}; C_6D_{14}; [21666-38-6]	Khurma, J.R.; Fenby, D.V. *Aust. J. Chem.* 1982, *35*, 1281-4.
VARIABLES:	**PREPARED BY:**
Temperature: 301 - 305 K	A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol-d and hexane-d_{14}

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
301.24	0.3333	-	14.15	-
303.29	-	0.6926	-	42.62
304.53	-	0.6301	-	35.96
304.59	0.4758	-	23.03	-
304.79	-	0.5939	-	32.53
304.84 UCST	0.560	0.560	29.6	29.6

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. Sample tubes containing mixtures of known composition were prepared by distillation under vacuum from the bulk degassed pure components and sealed. The phase separation was observed visually. The temperature of a silicone oil bath was controlled by a precision temperature controller (Tronac PTC 60) and measured with calorimeter thermometers which had been calibrated against a platinum resistance thermometer. For each sample the phase separation temperature was measured several times.

SOURCE AND PURITY OF MATERIALS:

(1) Merck, Sharpe and Dohme Canada Ltd, isotopic purity > 99 atom % D; dried over freshly activated molecular sieve type 3A, degassed by vacuum sublimation.

(2) Merck, Sharpe and Dohme Canada Ltd, isotopic purity > 98 atom % D; dried over freshly cut Na, degassed by vacuum sublimation.

ESTIMATED ERROR:

temp. ±0.02 K, ±0.06 K (UCST).

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Methanol-*d*; CDH_3O; [1455-13-6] (2) Cyclohexane; C_6H_{12}; [110-82-7]	A. Maczynski Institute of Physical Chemistry Polish Academy of Sciences Warsaw, Poland J.W. Lorimer Department of Chemistry The University of Western Ontario London, Ont., Canada July, 1989

CRITICAL EVALUATION:

Data on solubilities and upper critical solution temperatures (UCST) for the system methanol-*d* - cyclohexane are summarized in Table 1.

Table 1. Summary of solubility dat for the system methanol-*d* (1) - cyclohexane (2)

Author(s)	Range			
	T/K	p/MPa	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Cardinaud 1960	319.8 UCST		0.5	0.5
2. Rabinovich 1971	320.7 UCST		-	-
3. Schoen 1986	320.187 UCST		0.530	0.530
4. Singh 1987	316-321.307 UCST		0.354-0.514	0.514-0.757
	317.1-323.6	0.1-11.8	0.400-0.493	0.587 - 0.757

Critical Solution Temperature and Composition

The four reported values of UCST, ref. 1-4, vary over a range of 1.5 K. The values of Schoen and Wichers, ref. 3, and of Singh and Van Hook, ref 4, were determined with careful attention to details. However, only Singh and Van Hook have given details of the careful analysis by which the results were obtained, so their value, T_c = 321.307 K at 0.1 MPa, is considered as *tentative*.

The critical composition is reported in refs. 1, 3 and 4, and varies from x_1 = 0.5 to 0.530. The average of the values in refs. 3 and 4. For reasons given above, the value of Singh and Van Hook found by analysis of all data at all pressures, x_{1c} = 0.5140 ± 0.0006, is considered as *tentative*. Their value for data at 0.1 MPa alone is x_{1c} = 0.510 ± 0.002.

Mutual Solubility

The only data not at the critical solution point are those of Singh and Van Hook, who fitted their data using the equation

(continued)

CRITICAL EVALUATION: (continued)

$$x_1 = x_{1c} \pm A\,|1-T/T_c|^{\beta}$$

where + and - refer to the branches below and above the critical composition, $\beta = 0.340 \pm 0.013$, $A = 1.02 \pm 0.07$, $T_c/K = 321.307 \pm 0.001$, $x_{c1} = 0.510 \pm 0.002$, variance 3.2×10^{-5}. The evaluators find that this equation does not, in fact, predict the data correctly. An independent least-squares calculation with fixed T_c and β as given above yields $x_{c1} = 0.5083 \pm 0.0007$, $A = 1.0168 \pm 0.0046$, (std. error of estimate)$^2 = 2.9 \times 10^{-6}$. These recalculated values have been used to calculate the data in Table 2. Note that the value at $p = 0$ MPa is 0.032 K lower than any of the values at 0.1 MPa.

The data of Singh and Van Hook at high pressure are shown on the compilation sheets. At all pressures, their data are considered to be *tentative.*

Pressure coefficient of critical solution temperature

Singh and Van Hook also measured the value:

$$(\partial T_c/\partial p)_{x_c} = (3.173 \pm 0.012) \times 10^{-7}\ \text{K Pa}^{-1}$$

TENTATIVE DATA:

Table 2. Mutual solubilities in the system
methanol-*d* (1) - cyclohexane (2) at $p = 0.1$ MPa

T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
316.00	0.256	0.760
317.00	0.274	0.743
318.00	0.294	0.723
319.00	0.319	0.698
320.00	0.352	0.665
320.50	0.376	0.641
321.00	0.413	0.604
321.20	0.442	0.575
321.30	0.482	0.535
323.33	0.514 UCST	

The precision is estimated to be at least ± 0.002 in mole fraction. Note that the critical composition derived from the fitting equation (0.508) agrees well with that estimated by Singh and Van Hook for data at 0.1 MPa.

REFERENCES:

1. Cardinaud, R. *Bull. Soc. Chim. Fr.* <u>1960</u>, 622.
2. Rabinovich, I.B.; Tsvetkov, V.G. *Zh. Fiz. Khim.* <u>1971</u>, *45*, 822.
3. Schoen, W; Wiechers, R.; Woermann, D. *J. Chem. Phys.* <u>1986</u>, *85*, 2922.
4. Singh, R.R.; Van Hook, W.A. *J. Chem. Phys.* <u>1987</u>, *87*, 6097.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol-*d*; CDH_3O; [1455-13-6] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Cardinaud, R. *Bull. Soc. Chim. Fr.* 1960, 622-6.
VARIABLES: One temperature: 320 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 46.6°C at $x_1 = 0.5$.
The corresponding mass percentage, calculated by the compiler is 28 g(1)/100g sln.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
The cloud point method was used. The components were weighed in ampoules and protected against moisture. The influence of water impurity (0.004 mole fraction) was investigated. Solubility data were reported in a graph.

SOURCE AND PURITY OF MATERIALS:
(1) obtained in the laboratory; 97 - 98 % CH_3OD, boiled with Mg, distilled; b.p. 65.3 °C.
(2) source not specified; dried over $CaCl_2$, distilled over $Mg(ClO_4)_2$.

ESTIMATED ERROR:
temp. ±0.2 K.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol-*d*; CDH_3O; [1455-13-6] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Rabinovich, I.B.; Tsvetkov, V.G. *Zh. Fiz. Khim.* 1971, *45*, 822-3; *Russ. J. Phys. Chem. (Engl. Transl.)* 1971, *45*. 458.
VARIABLES: One temperature: 321 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 47.5°C.

Solubility data were presented on a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
The cloud point method was used. The temperature of appearance of turbidity was observed. No further details were reported.

SOURCE AND PURITY OF MATERIALS:
(1) source not specified; purified by methods described in ref 1.
(2) source not specified; purified by methods described in ref 1.

ESTIMATED ERROR:
temp. ±0.1 K.

REFERENCES:
1. Rabinovich, I.B. *Vliyanie izitopii na fiziko-khimicheskie svoistva zhidkostei*, Izd. Nayka, Moskva, 1968.

COMPONENTS:

(1) Methanol-*d*; CDH_3O; [1455-13-6]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Schoen, W.; Wiechers, R.;
Woermann, D.

J. Chem. Phys. 1986, *85*, 2922-8.

VARIABLES:

One temperature: 320 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 47.037°C at x_1 = 0.530.
The corresponding mass percentage, calculated by the compiler is
w_1 = 0.307.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The differences of refractive index between two coexisting liquid phases were measured. Samples were made by mixing the required nasses of components in a glove box. The The deflection of a He/Ne laser beam after passing through the two compartments of the differential refractometer cell was measured as the distance necessary to shift the light detection unit. The refractive index of the coexisting phases was related to the composition by measuring several mixtures as a function of temperature. The measurements were made over the range: UCST - 2 K.

SOURCE AND PURITY OF MATERIALS:

(1) Merck, Uvasol quality, degree of deuteration > 99 %; used as received.

(2) Aldrich, Gold Label quality, guaranteed purity > 99 %, water < 0.005 %; used as received.

ESTIMATED ERROR:

temp. ±0.008 K (UCST),
±0.003 K (24 h stability).

REFERENCES:

COMPONENTS:

(1) Methanol-*d*; CDH_3O; [1455-13-6]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Singh, R.R.; Van Hook, W.A.

J. Chem. Phys. 1987, *87*, 6097-110.

VARIABLES:

Temperature: 316 - 321 K
Pressure : 0.1 - 11.8 MPa

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol-*d* and cyclohexane

T/K	p/MPa	x_1	100 w_1 (compiler)
320.049	0.1	0.3539	17.70
320.854	0.1	0.3996	20.72
320.858	0.11	0.3996	20.72
321.768	3.23	0.3996	20.72
321.844	3.53	0.3996	20.72
322.841	6.39	0.3996	20.72
323.104	6.92	0.3996	20.72
322.199	4.48	0.3996	20.72
324.266	9.96	0.3996	20.72
324.756	11.77	0.3996	20.72
321.213	1.82	0.4339	23.13
321.173	0.1	0.4362	23.30
321.180	0.12	0.4362	23.30
321.196	0.14	0.4362	23.30
322.112	2.84	0.4362	23.30
321.984	2.45	0.4362	23.30
321.967	2.24	0.4362	23.30
321.306	0.1	0.4932	27.65
321.302	0.09	0.4932	27.65
321.307	1.16	0.4932	27.65

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The point at which the intensity of an emerging beam from a 3-mW He-Ne laser decreased to one-half its incident value was taken as the temperature of phase separation. For a run, the cell with magnetic stirrer was warmed to about 5-10 K above T_c and a sample, prepared gravimetrically, was added under vacuum. The pressure was set manually and the bath temperature then allowed to decrease at about 2-5 mK per min, while a computer continously monitored pressure, temperature and light intensity. The rapid change in intensity at the transition was used to instruct the computer to store the relevant data, then to warm the apparatus and repeat the experiment a preselected number of times. For details, see ref 1.

SOURCE AND PURITY OF MATERIALS:

(1) Aldrich Chemical Co.,isotopic purity 99.5 % D; purified over Mg-activated I_2, 2X dist. under dry Ar; no impurities by glc.
(2) Fisher Scientific, ASC grade; stored over Na wire, distilled in a spinning band column; no impurities by glc.

ESTIMATED ERROR:

temp. ±0.001 K (reproducibility);
pressure ±0.01 MPa.

REFERENCES:

1. Singh, R.R. *Thesis*, University of Tennesee, 1987.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol-*d*; CDH_3O; [1455-13-6]	Singh, R.R.; Van Hook, W.A.
(2) Cyclohexane; C_6H_{12}; [110-82-7]	*J. Chem. Phys.* <u>1987</u>, *87*, 6097-110.

EXPERIMENTAL VALUES: (continued)

Solubility of methanol-*d* and cyclohexane

T/K	p/MPa	x_1	100 w_1 (compiler)	
322.119	2.93	0.4932	27.65	
322.858	5.27	0.4932	27.65	
322.680	4.71	0.4932	27.65	
323.599	8.44	0.4932	27.65	
323.912	9.64	0.4932	27.65	
321.307	0.1	0.514	29.3	UCST calc. by authors for 0.1 MPa
321.138	0.1	0.5872	35.84	
321.936	2.61	0.5872	35.84	
322.214	3.55	0.5872	35.84	
321.988	2.88	0.5872	35.84	
317.969	0.1	0.7261	51.00	
317.970	0.09	0.7261	51.00	
318.468	1.97	0.7261	51.00	
320.357	8.04	0.7261	51.00	
320.333	7.98	0.7261	51.00	
316.050	0.1	0.7571	55.03	
317.163	3.38	0.7571	55.03	
317.167	3.35	0.7571	55.03	
318.118	6.03	0.7571	55.03	
319.177	9.265	0.7571	55.03	
319.108	9.05	0.7571	55.03	

COMMENTS AND ADDITIONAL DATA:

The authors give extensive analysis of their data, with fitting equations of the form

$$x_1 = x_{c1} \pm A|1-T/T_c^\circ|$$

$$T_c^\circ = T_c + cp$$

where T_c, T_c° are the critical solution temperatures at zero pressure and pressure p, x_{c1} is the critical composition, c = (3.173 ± 0.012) × 10^{-1} K MPa^{-1} is the pressure coefficient of T_c and A is an amplitude constant. For analysis of all data at all pressures, they find T_c/K = 321.326 ± 0.002, x_{c1} = 0.514 ± 0.002, while for data at 0.1 MPa alone, T_c/K = 321.307 ± 0.001, x_{c1} = 0.510 ± 0.002.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol-*d*; CDH_3O; [1455-13-6] (2) Hexane; C_6H_{14}; [110-54-3]	Khurma, J.R.; Fenby, D.V. *Aust. J. Chem.* 1982, *35*, 1281-4.
VARIABLES:	PREPARED BY:
Temperature: 297 - 308 K	A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol-*d* and hexane

T/K	x_1 (2)-rich phase	x_1 (1)-rich phase	$100\ w_1$ (compiler) (2)-rich phase	$100\ w_1$ (compiler) (1)-rich phase
296.80	0.2329	-	10.43	-
300.99	-	0.7798	-	57.59
304.45	-	0.7332	-	51.31
306.89	0.4546	-	24.22	-
307.23	-	0.6588	-	42.54
307.29	0.4942	-	27.26	-
307.46	-	0.5920	-	35.75
307.58	0.5462	-	31.58	-
307.59 UCST	0.560	0.560	32.8	32.8

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. Sample tubes containing mixtures of known composition were prepared by distillation under vacuum from the bulk degassed pure components and sealed. The phase separation was observed visually. The temperature of a silicone oil bath was controlled by a precision temperature controller (Tronac PTC 60) and measured with calorimeter thermometers which had been calibrated against a platinum resistance thermometer. For each sample the phase separation temperature was measured several times.

SOURCE AND PURITY OF MATERIALS:

(1) Merck, Sharpe and Dohme Canada Ltd, isotopic purity > 99 atom % D; dried over freshly activated molecular sieve type 3A, degassed by vacuum sublimation.

(2) Philips, research grade; dried over freshly-cut Na, degassed by vacuum sublimation.

ESTIMATED ERROR:

temp. ±0.02 K, ±0.04 K (UCST).

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Methanol-d_4 (methyl-d_3-alcohol-d); CD_4O; [811-98-3] (2) Cyclohexane; C_6H_{12}; [110-82-7]	A. Maczynski Institute of Physical Chemistry Polish Academy of Sciences Warsaw, Poland J.W. Lorimer Department of Chemistry The University of Western Ontario London, Ont., Canada July, 1989

CRITICAL EVALUATION:

Solubilities and upper critical solution temperatures (UCST) for the system methanol-d$_4$-cyclohexane were reported in the following two papers:

Author(s)	T/K	p/MPa	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Schoen 1986	342.922 UCST		0.530	0.530
2. Singh 1987	317.7-318.593 UCST	0.1	0.369-0.509	0.509-0.518
	317.1-323.6	2.5-11.1	0.369-0.515	0.515-0.628

Critical Solution Temperature and Composition

The two reported values of UCST, refs 1 and 2, are in poor agreement. The value T_c = 518.593±0.006 K at 0.1 MPa of Singh and Van Hook, ref 2, is considered as *tentative* because these workers reported greater care in the purification of the components and gave data over a wide range of temperature and pressure. Schoen et al., ref 1, used as-received chemicals, and did not report any procedures to remove water, which may account partially for their higher value.

The critical composition is reported in refs 1 and 2, and do not agree satisfactorily. For the reasons stated previously, the value x_c = 0.509 ±0.005 at 0.1 MPa of Singh and Van Hook is considered as *tentative.*

Mutual Solubility

Only Singh and Van Hook reported composition data below the critical temperature. They correlated their data with the equations

$$|x_1 - x_{c1}| = B|1 - T/T_c|^{\beta}$$

and

$$|x - x_{c1}| = B[1 - T/(T_c^o + cp)]^{\beta}$$

(continued)

CRITICAL EVALUATION: (continued)

where p is the pressure, $c = (3.173 \pm 0.012) \times 10^{-7}$ K Pa^{-1} is the pressure coefficient of the critical solution temperature. They give various sets of fitting parameters, as follows.

parameter	data for 0.1 MPa only (authors' Table II)	data for all pressures (authors' Table II)	fixed $\beta = 0.325$ (authors' Table III)
x_{c1}	0.509 ±0.005	0.515 ±0.001	0.514 0 ±0.000 6
B	0.95 ±0.02	1.28 ±0.07	1.18 ±0.037
β	0.325 ±0.034	0.338 ±0.008	(0.325)
T_c	318.593 ±0.006	318.597 ±0.002	318.601 ±0.002
T_c^o		318.574 ±0.002	318.569 ±0.002
variance	6.7×10^{-5}	4.8×10^{-5}	1.66×10^{-4}

The quantities T_c and T_c^o are the critical solution temperatures at 0.1 MPa and zero pressure. The evaluators find that large errors in composition arise from use of these equations, possibly because of excessive rounding of the B parameter. Thus, the equations should be used as rough guides only. For the data at 0.1 MPa and fixed $\beta = 0.325$, the evaluators find: $T_c = 318.601 \pm 0.001$ K, $B = 0.9362 \pm 0.020$, $x_{c1} = 0.4911 \pm 0.0017$, $s = 0.0050$ (variance 2.5×10^{-5}), values that are close to those of Singh and Van Hook, but which actually reproduce the experimental data better. The evaluators' parameters are recommended for calculations.

The complete high pressure data of Singh and Van Hook are shown on the compilation and should be considered as *tentative*.

REFERENCES:

1. Schoen, W.; Wiechers, R.; Woermann, D. *J. Chem. Phys.* 1986, *85*, 2922.
2. Singh, R.R.; Van Hook, W.A. *J. Chem. Phys.* 1987, *87*, 6097.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol-d_4 (methyl-d_3 alcohol-d); CD_4O; [811-98-3] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Schoen, W.; Wiechers, R.; Woermann, D. *J. Chem. Phys.* 1986, *85*, 2922-8.
VARIABLES:	PREPARED BY:
One temperature: 325 K	A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 51.772°C at x_1 = 0.530.
The corresponding mass percentage, calculated by the compiler is 32.6 g(1)/100g sln.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The differences of refractive index between two coexisting liquid phases were measured. Samples were made by mixing the required masses of components in a glove box. The deflection of a He/Ne laser beam after passing through the two compartments of a differential refractometer cell was measured as the distance necessary to shift the light detection unit. The refractive index of the coexisting phases was related to the composition by measuring several mixtures as a function of temperature. The measurements were made over the range: UCST - 2 K.

SOURCE AND PURITY OF MATERIALS:

(1) Merck, Uvasol quality, degree of deuteration > 99 %; used as received.

(2) Aldrich, Gold Label quality, guaranteed purity > 99 %, water < 0.005 %; used as received.

ESTIMATED ERROR:

temp. ±0.001 K (UCST),
±0.003 K (24 h stability).

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol-d_4 (methyl-d_3 alcohol-d); CD_4O; [811-98-3] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Singh, R.R.; Van Hook, W.A. *J. Chem. Phys.* 1987, *87*, 6097-110.
VARIABLES:	PREPARED BY:
Temperature: 318 - 319 K Pressure : 0.1 - 11.8 MPa	A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol-d_4 and cyclohexane

T/K	p/MPa	x_1	100 w_1 (compiler)	
317.666	0.1	0.3689	20.03	
318.945	4.13	0.3689	20.03	
320.350	8.56	0.3689	20.03	
318.176	0.1	0.4022	22.38	
319.375	3.88	0.4022	22.38	
320.718	8.11	0.4022	22.38	
318.553	0.1	0.4593	26.69	
319.803	4.04	0.4593	26.69	
321.215	8.49	0.4593	26.69	
318.596	0.1	0.4808	28.41	
319.596	3.27	0.4808	28.41	
320.708	6.87	0.4808	28.41	
318.593	0.1	0.514	31.2	UCST calculated by the authors
318.599	0.1	0.5176	31.50	
319.700	3.57	0.5176	31.50	
320.795	7.02	0.5176	31.50	
322.086	11.09	0.5176	31.50	
318.584	0.1	0.5488	34.26	
319.894	4.23	0.5488	34.26	
321.262	8.54	0.5488	34.26	

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The point at which the intensity of an emerging beam from a 3-mW He-Ne laser decreased to one-half its incident value was taken as the temperature of phase separation. For a run, the cell with magnetic stirrer was warmed to about 5-10 K above T_c and a sample, prepared gravimetrically, was added under vacuum. The pressure was set manually and the bath temperature then allowed to decrease at about 2-5 mK per min, while a computer continously monitored pressure, temperature and light intensity. The rapid change in intensity at the transition was used to instruct the computer to store the relevant data, then to warm the apparatus and repeat the experiment a preselected number of times. For details, see ref 1.

SOURCE AND PURITY OF MATERIALS:

(1) MSD Isotopes, isotopic purity 99 % D; purified over Mg -activated I_2, 2X dist. under dry Ar; no impurities by glc.
(2) Fisher Scientific, ASC grade; stored over Na wire, distilled in a spinning band column; no impurities by glc.

ESTIMATED ERROR:

temp. ±0.001 K (reproducibility); pressure ±0.01 MPa.

REFERENCES:

1. Singh, R.R. *Thesis*, University of Tennesee, 1987.

COMPONENTS:

(1) Methanol-d_4 (methyl-d_3 alcohol-d); CD_4O; [811-98-3]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Singh, R.R.; Van Hook, W.A.

J. Chem. Phys. **1987**, *87*, 6097-110.

EXPERIMENTAL VALUES: (continued)

Solubility of methanol-d_4 and cyclohexane

T/K	p/MPa	x_1	100 w_1 (compiler)
318.501	0.1	0.5794	37.12
319.425	3.01	0.5794	37.12
320.682	6.97	0.5794	37.12
318.103	0.1	0.6279	41.97
318.880	2.55	0.6279	41.97
320.416	7.39	0.6279	41.97

COMMENTS AND ADDITIONAL DATA:

The authors give extensive analysis of their data, with fitting equations of the form

$$x_1 = x_{c1} \pm A|1-T/T_c^{\circ}|$$

$$T_c^{\circ} = T_c + cp$$

where T_c, T_c° are the critical solution temperatures at zero pressure and pressure p, x_{c1} is the critical composition, c = (3.173 ± 0.012) × 10^{-1} K MPa^{-1} is the pressure coefficient of T_c and A is an amplitude constant. For analysis of all data at all pressures, they find T_c/K = 318.597 ± 0.002, x_{c1} = 0.514 ± 0.001, while for data at 0.1 MPa alone, T_c/K = 318.593 ± 0.006, x_{c1} = 0.515 ± 0.001.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Butane; C_4H_{10}; [106-97-8]

EVALUATOR:

A. Maczynski and A. Skrzecz
Institute of Physical Chemistry
Polish Academy of Sciences
Warsaw, Poland

J.W. Lorimer
Department of Chemistry
The University of Western Ontario
London, Ont., Canada

July, 1989

CRITICAL EVALUATION:

Table 1 gives solubilities and upper critical solution temperature (UCST) and compositions for the system methanol-butane which have been reported in the literature.

Table 1. Solubilities, critical solution temperatures and compositions in the system methanol(1) - butane (2)

Author(s)	Range			
	T/K	p/MPa	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Noda 1975	249.8-265.8 UCST		0.127-0.403	0.403-0.693
2. Haarhaus 1988	263.8-292.6 266.45 at 0.1 MPa	5-140	0.285-0.384	0.418-0.607

Critical solution temperature and composiition

Of the two values for each of these quantities, those of Noda are closest to the correlations discussed in the *Preface*, and are acceped as *tentative*: $T_c = 265.8$ K, $x_{c1} = 0.403$.

Mutual solubility

Noda et al., ref 1, reported solubility data at normal pressure. Haarhaus and Schneider, ref 2, extrapolated their data measured at high pressures to 0.1 MPa, and gave the results in terms of the Simon equation

$$T/\mathrm{K} = T_c/\mathrm{K} + k|x_1 - x_{c1}|^{\nu}$$

with

$$y = \alpha x_1/[1+x_1(\alpha+1)]$$
$$y_c = \alpha x_{c1}/[1+x_{c1}(\alpha-1)]$$

valid over the range $0.25 < x_1 < 0.6$ or $264 < T/\mathrm{K} < 266.45$, where

$T_c = 266.45$ K $k = -1425$ $\alpha = 9.02$ $x_{c1} = 0.399$ $\nu = 2.30$

(continued)

CRITICAL EVALUATION: (continued)

These data overlap those of Noda et al., which are shown in the figure along with the curve calculated from the results of Haarhaus and Schneider. Clearly, the two sets of data coincide satisfactorily in the region $0.3 < x_1 < 0.6$, but deviate significantly outside that range. Thus, the equations of Haarhaus and Schneider give *tentative* values in the range $0.3 < x_1 < 0.6$, with uncertainties of $\Delta T = 0.2$ K for given x_1, or $\Delta x_1 = 0.005$ for given T. Typical values are given in the table below.

Pressure Coefficient of Critical Solution Temperature

This quantity can be calculated from the fitting equations of Haarhaus and Schneider:

$$(\partial T/\partial p)_{x_c} = T_0/ac = 2.66\times10^{-7}\ \mathrm{K\ Pa^{-1}}$$

where T_0, a and c are constants given on the compilation sheet.

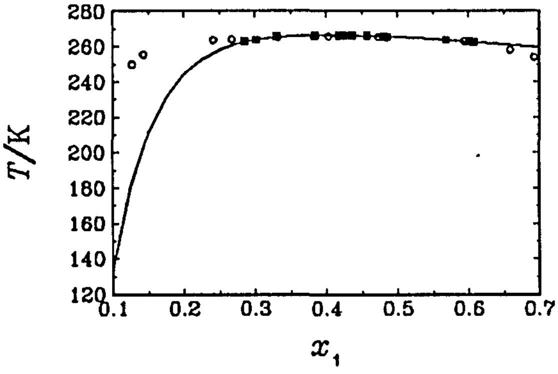

Fig. 1. Solubilities in the system methanol-butane at $p = 0.1$ MPa. Solid line and ■: results of Haarhaus and Schneider (extrapolated for $x_1 < 0.25$, > 0.6); ○, results of Noda et al.

TENTATIVE DATA:

x_1 (2)-rich phase	T/K	x_1 (1)-rich phase	T/K
0.30	264.0	0.40	266.45
0.35	266.1	0.41	266.44
0.36	266.2	0.42	266.41
0.37	266.4	0.43	266.36
0.38	266.4	0.44	266.28
0.39	266.4	0.45	266.19
0.403	265.8	0.50	265.41
(UCST)		0.55	264.25
		0.60	262.84

REFERENCES:

1. Noda, K.; Sato, K.; Nayatsuka, K.; Ishida, K. *J. Chem. Eng. Jpn.* 1975, *8*, 492.
2. Haarhaus, U.; Schneider, G.M. *J. Chem. Thermodyn.* 1980, *20*, 1121.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Butane; C_4H_{10}; [106-97-8]

ORIGINAL MEASUREMENTS:

Noda, K.; Sato, K.; Nagatsuka, K.; Ishida, K.

J. Chem. Eng. Jpn. 1975, *8*, 492-3.

VARIABLES:

Temperature: 250 - 266 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and butane

$t/°C$	100 w_1 (compiler)		x_1	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
-23.4	7.4	-	0.127	-
-19.2	-	55.4	-	0.693
-18.6	8.4	-	0.143	-
-15.0	-	51.6	-	0.659
-10.0	-	44.7	-	0.594
-9.5	14.9	-	0.241	-
-9.1	16.7	-	0.267	-
-8.1	-	34.2	-	0.485
-7.9	-	33.1	-	0.473
-7.8	21.5	-	0.332	-
-7.4 UCST	27.1	27.1	0.403	0.403

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; guaranteed reagent grade; used as received.

(2) Takachido Chemical Industry Co., Ltd., standard reagent; used as received.

ESTIMATED ERROR:

not specified

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Butane; C_4H_{10}; [106-97-8]

ORIGINAL MEASUREMENTS:

Haarhaus, U.; Schneider, G.M.

J. Chem. Thermodyn. 1988, *20*, 1121-9.

VARIABLES:

Temperature: 264 - 293 K
Pressure: 5 - 140 MPa

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and butane

T/K	p/MPa	x_1 (2)-rich phase	x_1 (1)-rich phase	100 w_1 (compiler) (2)-rich phase	100 w_1 (compiler) (1)-rich phase
263.8	5.0	-	0.607	-	46.0
264.2	5.0	0.285	0.601	18.0	45.4
265.2	5.0	0.302	0.568	19.3	42.0
266.3	5.0	-	0.523	-	37.7
266.8	5.0	-	0.486	-	34.3
267.0	5.0	-	0.481	-	33.8
267.1	5.0	0.330	-	21.4	-
267.5	5.0	-	0.436	-	29.9
267.6	5.0	-	0.424	-	28.9
267.6	5.0	-	0.418	-	28.4
267.7	5.0	-	0.457	-	31.7
267.8	5.0	0.384	-	25.6	-
264.8	10.0	-	0.607	-	46.0
265.2	10.0	-	0.601	-	45.4
265.4	10.0	0.285	-	18.0	-

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual measurements were performed in a modified optical high-pressure cell, similar to that described in ref 1, at constant pressures using a constant cooling rate. Methanol was drawn from a burette at room temperature; butane was condensed into the cell which was cooled to about 273 K. Precautions taken against contamination by water were as described in ref 2.

SOURCE AND PURITY OF MATERIALS:

(1) Reidel de Haen; used as received; purity > 99.5 mole % by glc, H_2O < 0.01 mole % by Karl Fischer titration.

(2) Messer-Griesheim; used as received; purity > 99.5 mole % by glc.

ESTIMATED ERROR:

sol. ±0.002 mole fraction;
temp. ±0.1-0.2 K (total accuracy)
pressure ±0.1 MPa at $p < 100$ MPa and ±0.5 MPa at $p > 100$ MPa.

REFERENCES:

1. Liphard, K.G.; Schneider, G.M. *J. Chem. Thermodyn.* 1975, *7*, 805.
2. Ott, J.B.; Hoelscher, I.F.; Schneider, G.M. *J. Chem. Thermodyn.* 1986, *18*, 815.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Butane; C_4H_{10}; [106-97-8]

ORIGINAL MEASUREMENTS:

Haarhaus, U.; Schneider, G.M.

J. Chem. Thermodyn. 1988, *20*, 1121-9.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and butane

T/K	*p*/MPa	x_1 (2)-rich phase	x_1 (1)-rich phase	100 w_1 (compiler) (2)-rich phase	100 w_1 (compiler) (1)-rich phase
266.3	10.0	-	0.568	-	42.0
266.4	10.0	0.302	-	19.3	-
267.5	10.0	-	0.523	-	37.7
268.1	10.0	-	0.486	-	34.3
268.3	10.0	-	0.481	-	33.8
268.4	10.0	0.330	-	21.4	-
268.8	10.0	-	0.436	-	29.9
268.8	10.0	-	0.424	-	28.9
268.9	10.0	-	0.418	-	28.4
269.0	10.0	0.384	0.457	25.6	31.7
267.0	20.0	-	0.607	-	46.0
267.4	20.0	-	0.601	-	45.4
267.9	20.0	0.285	-	18.0	-
268.6	20.0	-	0.568	-	42.0
268.8	20.0	0.302	-	19.3	-
269.8	20.0	-	0.523	-	37.7
270.4	20.0	-	0.486	-	34.3
270.6	20.0	-	0.481	-	33.8
270.7	20.0	0.330	-	21.4	-
271.2	20.0	-	0.436	-	29.9
271.2	20.0	-	0.424	-	28.9
271.2	20.0	-	0.418	-	28.4
271.3	20.0	-	0.457	-	31.7
271.4	20.0	0.384	-	25.6	-
271.2	40.0	-	0.607	-	46.0
271.3	40.0	-	0.601	-	45.4
272.2	40.0	0.285	-	18.0	-
273.0	40.0	-	0.568	-	42.0
273.3	40.0	0.302	-	19.3	-
274.1	40.0	-	0.523	-	37.7
274.8	40.0	-	0.486	-	34.3
274.9	40.0	-	0.481	-	33.8
275.0	40.0	0.330	-	21.4	-
275.5	40.0	-	0.436	-	29.9
275.5	40.0	-	0.424	-	28.9
275.6	40.0	-	0.457	-	31.7
275.6	40.0	-	0.418	-	28.4
275.7	40.0	0.384	-	25.6	-
274.9	60.0	-	0.607	-	46.0
275.1	60.0	-	0.601	-	45.4
276.1	60.0	0.285	-	18.0	-
277.0	60.0	-	0.568	-	42.0
277.3	60.0	0.302	-	19.3	-
278.1	60.0	-	0.523	-	37.7
278.7	60.0	-	0.486	-	34.3
278.9	60.0	-	0.481	-	33.8
279.1	60.0	0.330	-	21.4	-
279.5	60.0	-	0.436	-	29.9
279.5	60.0	-	0.424	-	28.9
279.6	60.0	-	0.457	-	31.7

(continued)

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Butane; C_4H_{10}; [106-97-8]

ORIGINAL MEASUREMENTS:

Haarhaus, U.; Schneider, G.M.

J. Chem. Thermodyn. 1988, *20*, 1121-9.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and butane

T/K	p/MPa	x_1 (2)-rich phase	x_1 (1)-rich phase	100 w_1 (compiler) (2)-rich phase	100 w_1 (compiler) (1)-rich phase
279.6	60.0	-	0.418	-	28.4
279.7	60.0	0.384	-	25.6	-
278.3	80.0	-	0.607	-	46.0
278.5	80.0	-	0.601	-	45.4
279.8	80.0	0.284	-	17.9	-
280.4	80.0	-	0.568	-	42.0
280.9	80.0	0.302	-	19.3	-
281.8	80.0	-	0.523	-	37.7
282.4	80.0	-	0.486	-	34.3
282.5	80.0	-	0.481	-	33.8
282.7	80.0	0.330	-	21.4	-
283.1	80.0	-	0.436	-	29.9
283.2	80.0	-	0.457	-	31.7
283.2	80.0	-	0.424	-	28.9
283.3	80.0	0.384	0.418	25.6	28.4
281.3	100.0	-	0.607	-	46.0
281.7	100.0	-	0.601	-	45.4
283.0	100.0	0.285	-	18.0	-
283.5	100.0	-	0.568	-	42.0
284.1	100.0	0.302	-	19.3	-
285.1	100.0	-	0.523	-	37.7
285.7	100.0	-	0.486	-	34.3
285.9	100.0	-	0.481	-	33.8
286.1	100.0	0.330	-	21.4	-
286.4	100.0	-	0.436	-	29.9
286.5	100.0	-	0.424	-	28.9
286.6	100.0	-	0.457	-	31.7
286.6	100.0	-	0.418	-	28.4
286.7	100.0	0.384	-	25.6	-
284.2	120.0	-	0.607	-	46.0
284.6	120.0	-	0.601	-	45.4
286.1	120.0	0.285	-	18.0	-
287.2	120.0	0.302	-	19.3	-
288.2	120.0	-	0.523	-	37.7
288.8	120.0	-	0.486	-	34.3
289.0	120.0	-	0.481	-	33.8
289.2	120.0	0.330	-	21.4	-
289.6	120.0	-	0.457	-	31.7
289.6	120.0	-	0.436	-	29.9
289.6	120.0	-	0.424	-	28.9
289.7	120.0	-	0.418	-	28.4
289.8	120.0	0.384	-	25.6	-
287.1	140.0	-	0.607	-	46.0
289.0	140.0	0.285	-	18.0	-
289.1	140.0	-	0.568	-	42.0
290.1	140.0	0.302	-	19.3	-
291.0	140.0	-	0.523	-	37.7
291.7	140.0	-	0.486	-	34.3
291.9	140.0	-	0.481	-	33.8
292.1	140.0	0.330	-	21.4	-
292.4	140.0	-	0.436	-	29.9
292.5	140.0	-	0.457	-	31.7
292.5	140.0	-	0.424	-	28.9
292.6	140.0	0.384	0.418	25.6	28.4

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1]	Haarhaus, U.; Schneider, G.M.
(2) Butane; C_4H_{10}; [106-97-8]	*J. Chem. Thermodyn.* 1988, *20*, 1121-9.

EXPERIMENTAL VALUES: (continued)

COMMENTS AND ADDITIONAL DATA:

Data for isopleths at high pressures were fitted to the Simon equation

$$p(x,T)/\text{MPa} = a[(T/T_0)^c-1]$$

From these equations, the corresponding (T, x) isobars were calculated and were fitted to the equation

$$T/\text{K} = T_c/\text{K}+k|y-y_c|^{\nu}$$

where

$$y = \alpha x_1/[1+x_1(\alpha-1)]$$
$$y_c = \alpha x_{c1}/[1+x_{c1}(\alpha-1)]$$

The coefficients found are (s = std. error of estimate):

x_1	T_0/K	a	c	s
0.285	262.92	131.4	7.66	0.21
0.302	263.85	122.8	8.02	0.14
0.330	265.82	139.7	7.35	0.12
0.384	266.47	135.7	7.56	0.16
0.418	266.29	131.0	7.72	0.13
0.424	266.31	136.8	7.52	0.10
0.436	266.22	133.7	7.62	0.12
0.457	266.43	135.6	7.60	0.15
0.481	265.71	137.0	7.48	0.10
0.486	265.54	137.9	7.45	0.04
0.568	263.75	112.7	8.78	0.35
0.601	262.98	167.1	6.83	0.17
0.607	262.52	141.3	7.72	0.37

p/MPa	T_c/K	k	α	x_{c1}	ν	s
0.1	266.45	-1425	9.02	0.399	2.30	0.17
5.0	267.81	-1173	8.70	0.399	2.24	0.17
10.0	268.96	-1440	7.46	0.399	2.42	0.16
20.0	271.32	-1192	6.11	0.400	2.46	0.15
40.0	275.61	-1292	5.01	0.401	2.62	0.14
60.0	279.58	-1902	5.16	0.400	2.76	0.16
80.0	283.25	-1300	4.25	0.402	2.70	0.16
100.0	286.59	-1615	4.34	0.401	2.77	0.15
120.0	289.69	-1849	4.44	0.400	2.80	0.15
140.0	292.57	-1555	4.19	0.400	2.76	0.15

Simon equations are also given for (p, x) pairs, which are of the same form as those for the (T, x) pairs.

COMPONENTS:	EVALUATOR:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclopentane; C_5H_{10}; [287-92-3]	A. Maczynski Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland. July 1989.

CRITICAL EVALUATION:

Table 1 gives solubilities and upper critical solution temperatures (UCST) and compositions for the system methanol - cyclopentane which have been reported in the literature.

Table 1. Solubilities, upper critical solution temperatures and compositions for the system methanol (1) - cyclopentane (2)

Authors	Range T/K		x_1 in (1)-rich phase
1. Fischer et al. 1949	312	UCST	-
2. Kiser et al. 1961	278.0 - 289.8	UCST	0.554 - 0.722

Fischer and Neupauer (ref 1) found UCST = 39.0°C by the cloud-point method in a micro melting-point apparatus with mg-sized samples. This value is rejected; the original paper is not compiled. All UCST reported in ref 1 for different alcohol - hydrocarbon systems are higher by about 10 - 20 K than the recommended values, which indicates significant contamination by impurities, probably water.

The data of Kiser et al. are accepted as tentative since their values for other systems are reliable.

TENTATIVE DATA:

T/K	x_1 in (1)-rich phase	
278	0.72	
283	0.67	
288	0.55	
289.8	0.47	UCST (critical composition estimated by Evaluator)

REFERENCES:

1. Fischer, R.; Neupauer, E. *Mikrochem. Ver. Mikrochim. Acta* 1949, *34*, 319.

2. Kiser, R.W.; Johnson, G.D.; Shetlar, M.D. *J. Chem. Eng. Data* 1961, *6*, 338.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclopentane; C_5H_{10}; [287-92-3]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.;

J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 276 - 290 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of cyclopentane in methanol

$t/_{\circ}\mathrm{C}$	mass(2)/vol(1)/g cm^3	100 w_1 (compiler)	x_2 (compiler)
5	68	46	0.28
10	86	52	0.33
15	140	64	0.45
16.6	UCST		

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method involved heating/cooling samples of known composition and noting the temp. of phase transition. The cloud point was more reproducible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. duPont de Nemours; dist.; $n_D(20^{\circ}C) = 1.3294$; b.p. 64.6°C, f.p. -99°C.

(2) Matheson, Coleman and Bell; used as received; $n_D(20^{\circ}C) = 1.4046$.

ESTIMATED ERROR:

soly. 2 %
temp. 0.2 K

REFERENCES:

1. *International Crirical Tables*. vol. 3. New York. 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Pentane; C_5H_{12}; [109-66-0]

EVALUATOR:

A. Skrzecz
Institute of Physical Chemistry
Polish Academy of Sciences
Warsaw, Poland

J.W. Lorimer
Department of Chemistry
The University of Western Ontario
London, Ont., Canada

July, 1989

CRITICAL EVALUATION:

Table 1 summarizes solubilities and upper critical solution temperatures (UCST) and compositions for the system methanol-pentane which have been reported in the literature.

Table 1. Solubility data for the system methanol (1) - pentane (2)

Author(s)	*T*/K	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Cornish 1934	286.4 and 287.90 UCST	-	-
2. Fischer 1949	311.2 UCST	-	-
3. Francis 1954	287.90 UCST	-	-
4. Kiser 1961	278-287.40 UCST	-	0.690-0.745
5. Haarhaus 1988	272-316 286.92 (UCST at 0.1 MPa)	0.209-0.492	0.492-0.789

Critical solution temperature and composition

Five values have been reported for T_c, but only one for x_{c1}. The values of T_c of Cornish et al., ref. 1, were obtained with two different samples, both of questionable purity. The UCST of Fischer and Neupauer, ref 2, is rejected, because all their values of UCST for different alcohol-hydrocarbon systems are higher by about 10-20 K than recommended values; the paper is not compiled. The value of Francis, ref. 3, was found using as-received methanol and pentane from an unspecified source. The average of the values of T_c of Kiser et al. and of Haarhaus and Schneider are considered as *tentative* because they were obtained through a carefully-conducted study with precautions to avoid contamination with water. As well, this value correlates reasonable with values for other hydrocarbons, as explained in the *Preface* to this volume. Thus, the *tentative* values are: $T_c = 287.2 \pm 0.3$ K, $x_{c1} = 0.497$.

Mutual solubility

Kiser et al., ref. 4, used distilled methanol but as-received pentane. Haarhaus and Schneider, ref 5, extrapolated their data measured at high pressures to 0.1 MPa, and gave the results in terms of the Simon equation

(continued)

CRITICAL EVALUATION: (continued)

$$T/\mathrm{K} = T_c/\mathrm{K} + k|x_1 - x_{c1}|^{\nu}$$

with

$$y = \alpha x_1/[1+x_1(\alpha+1)]$$
$$y_c = \alpha x_{c1}/[1+x_{c1}(\alpha-1)]$$

valid over the range $0.2 < x_1 < 0.8$ or $270 < T/\mathrm{K} < 286.92$, where
$T_c = 286.92$ K $\quad k = -883 \quad \alpha = 0.83 \quad x_{c1} = 0.497$

The solubility data of Kiser et al. are shown in the figure along with the curve calculated from the results of Haarhaus and Schneider. Clearly, the two data points of Kiser et al. are slightly higher than the curve; thus all composition data for this system must be considered as *tentative.*

The equations of Haarhaus and Schneider give *tentative* values in the range $0.2 < x_1 < 0.8$, with uncertainties of $\Delta T = 0.3$ K for given x_1, or $\Delta x_1 = 0.005$ for given T, and selected values are given in the table below. See the compilation sheets for the data of Haarhaus and Schneider at higher pressures, where the methods of fitting and extrapolation are described. These data were obtained under cafrefully-controlled conditions, and can be considered as tentative.

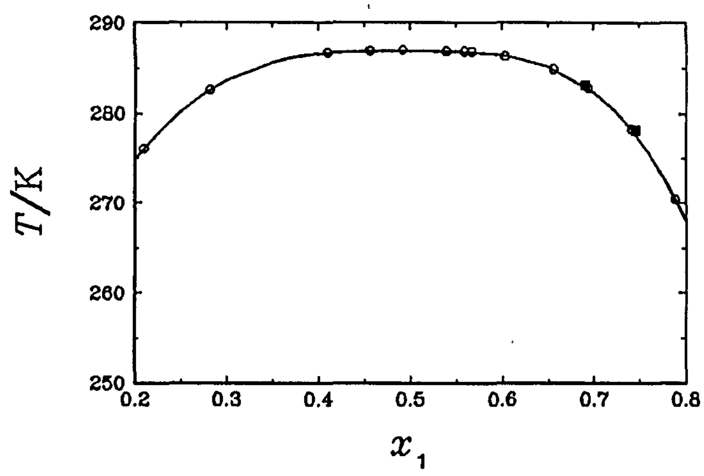

Fig. 1. Phase diagram of the system methanol-pentane at p = 0.1 MPa. Solid line and ○: results of Haarhaus and Schneider (extrapolated for x_1 < 0.25, > 0.6); ■, results of Kiser et al.

Pressure Coefficient of Critical Solution Temperature

This quantity can be calculated from the fitting equations of Haarhaus and Schneider:

$$(\partial T/\partial p)_{x_c} = T_0/ac = 3.26\times10^{-7}\ \mathrm{K\ Pa^{-1}}$$

where T_0, a and c are constants given on the compilation sheet.

(continued)

CRITICAL EVALUATION: (continued)

Table 2. Tentative mutual solubilities
in the system methanol (1) - pentane (2)

x_1 (2)-rich phase	T/K	x_1 (1)-rich phase	T/K
0.20	274.8	0.50	286.9
0.25	280.2	0.55	286.9
0.30	283.7	0.60	286.5
0.35	285.7	0.65	285.2
0.40	286.6	0.70	282.3
0.45	286.9	0.75	277
0.497 (UCST)	287.2	0.80	268.1

REFERENCES:

1. Cornish, R.E.; Archibald, R.C.; Murphy, E.A.; Evans, H.M. *Ind. Eng. Chem.* 1934, *26*, 397.
2. Fischer, R.; Neupauer, E. *Mikrochem. Ver. Mikrochim. Acta* 1949, *34*, 319.
3. Francis, A.W. *J. Am. Chem. Soc.* 1954, *76*, 393.
4. Kiser, R.W.; Johnson, G.D.; Shetlar, M.D. *J. Chem. Eng. Data* 1961, *6*, 338.
5. Haarhaus, U.; Schneider, G.M. *J. Chem. Thermodyn.* 1988, *20*, 1121.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Pentane; C_5H_{12}; [109-66-0]

ORIGINAL MEASUREMENTS:

Cornish, R.E.; Archibald, R.C.;
Murphy, E.A.; Evans, H.M.
Ind. Eng. Chem. 1934, *26*, 397-406.

VARIABLES:

Temperature: 286 and 288 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 14.75°C a) and 13.2°C b).

a), b) data for cyclohexane (2) from different sources; see "SOURCE AND PURITY OF MATERIALS" below.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was not specified.

SOURCE AND PURITY OF MATERIALS:

- (1) source not specified; distilled; ρ(25°C)/ρ(4°C) = 0.78656, (corrected for buoyancy), anhydrous.
- (2) a) Eastman Kodak Company (presumably from petroleum); dist., boiling range < 0.1 K.
  - b) source not specified; purified in the laboratory, less pure than a).

ESTIMATED ERROR:

not specified.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Pentane; C_5H_{12}; [109-66-0]

ORIGINAL MEASUREMENTS:

Francis, A.W.
J. Am. Chem. Soc. 1954, *76*, 393-5.

VARIABLES:

One temperature: 288 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 14.75°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The observations were madein narrow, graduated, glass-stoppered tubes immersed in a water bath in a large silvered Dewar flask. Mixtures were made up by volume from graduated pipets until cloudiness just disappeared or reappeared. The bath temperature was adjusted by addition of small quantities of cooler or warmer water and stirred several minutes.

SOURCE AND PURITY OF MATERIALS:

(1) J.T. Baker anhydrous, C.P.; used as received.

(2) source not specified.

ESTIMATED ERROR:

temp. ±0.2 K

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Pentane; C_5H_{12}; [109-66-0]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.; Shetlar, M.D.

J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 278 - 287 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of pentane in methanol

$t/°C$	g(2)/100 ml(1)	100 w_1 (compiler)	x_2 (compiler)
5	62.0	43.5	0.255
10	81.0	50.3	0.310
14.25	UCST		

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4°C) = 0.80999 - 9.253\ 10^{-4}\ (t/°C) - 4.1\ 10^{-7}\ (t/°C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; $n_D(20°C) = 1.3293$, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Eastman Organic Chemicals, technical grade; used as received; absence of unsaturated compounds by u.v. analysis, impurities ≤ 0.05 mole % (benzene) by glc analysis.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables vol. 3*, New York, 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Pentane; C_5H_{12}; [109-66-0]

ORIGINAL MEASUREMENTS:

Haarhaus, U.; Schneider, G.M.

J. Chem. Thermodyn. 1988, *20*, 1121-9.

VARIABLES:

Temperature: 272 - 316 K
Pressure: 5 - 140 MPa

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and pentane

T/K	p/MPa	x_1		100 w_1 (compiler)	
		(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
272.0	5.0	-	0.7889	-	62.40
277.6	5.0	0.2093	-	10.52	-
279.9	5.0	-	0.7408	-	55.93
284.2	5.0	0.2814	-	14.81	-
284.4	5.0	-	0.6931	-	50.07
286.5	5.0	-	0.6557	-	45.82
287.2	5.0	0.3459	-	19.02	-
287.9	5.0	-	0.6028	-	40.26
288.3	5.0	0.4101	-	23.59	-
288.4	5.0	-	0.5668	-	36.75
288.4	5.0	-	0.5589	-	36.01
288.5	5.0	0.4561	-	27.14	-
288.5	5.0	-	0.5396	-	34.23
288.6	5.0	0.4918	-	30.06	-
273.6	10.0	-	0.7889	-	62.40

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual measurements were performed in a modified optical high-pressure cell, similar to that described in ref 1, at constant pressures using a constant cooling rate. Components were drawn into a gas-tight syringe successively and mixed by shaking. The homogenous mixture was transferred into an evacuated cell at room temperature. The precautions taken against water contamination are described in ref 2.

SOURCE AND PURITY OF MATERIALS:

(1) Reidel de Haen; used as received; purity > 99.5 mole % by glc, H_2O < 0.01 mole % by the Karl Fischer titration.
(2) Fluka; used as received; purity > 99.5 mole % by glc.

ESTIMATED ERROR:

sol. ±0.0001 mole fraction;
temp. ±0.1-0.2 K (total accuracy);
pressure ±0.1 MPa at p < 100 MPa and ±5 MPa at p > 100MPa.

REFERENCES:

1. Liphard, K.G.; Schneider, G.M. *J. Chem. Thermodyn.* 1975, *7*, 805.
2. Ott, J.B.; Hoelscher, I.F.; Schneider, G.M. *J. Chem. Thermodyn.* 1986, *18*, 815.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1]	Haarhaus, U.; Schneider, G.M.
(2) Pentane; C_5H_{12}; [109-66-0]	*J. Chem. Thermodyn.* 1988, *20*, 1121-9.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and pentane

T/K	*p*/MPa	x_1		100 w_1 (compiler)	
		(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
279.1	10.0	0.2093	-	10.52	-
281.2	10.0	-	0.7408	-	55.93
285.7	10.0	0.2814	-	14.81	-
285.9	10.0	-	0.6931	-	50.07
287.9	10.0	-	0.6557	-	45.82
288.8	10.0	0.3459	-	19.02	-
289.4	10.0	-	0.6028	-	40.26
289.8	10.0	0.4101	-	23.59	-
289.9	10.0	-	0.5668	-	36.75
290.0	10.0	-	0.5589	-	36.01
290.0	10.0	0.4561	0.5396	27.14	34.23
290.1	10.0	0.4918	-	30.06	-
276.3	20.0	-	0.7889	-	62.40
281.7	20.0	0.2093	-	10.52	-
284.0	20.0	-	0.7408	-	55.93
288.5	20.0	-	0.6931	-	50.07
288.6	20.0	0.2814	-	14.81	-
290.6	20.0	-	0.6557	-	45.82
291.7	20.0	0.3459	-	19.02	-
292.3	20.0	-	0.6028	-	40.26
292.7	20.0	0.4101	0.5668	23.59	36.75
292.8	20.0	-	0.5589	-	36.01
292.9	20.0	0.4561	0.5396	27.14	34.23
293.0	20.0	0.4918	-	30.06	-
280.9	40.0	-	0.7889	-	62.40
286.6	40.0	0.2093	-	10.52	-
288.9	40.0	-	0.7408	-	55.93
293.5	40.0	-	0.6931	-	50.07
293.7	40.0	0.2814	-	14.81	-
295.5	40.0	-	0.6557	-	45.82
296.7	40.0	0.3459	-	19.02	-
297.4	40.0	-	0.6028	-	40.26
297.8	40.0	0.4101	0.5668	23.59	36.75
298.0	40.0	0.4561	0.5589	27.14	36.01
298.0	40.0	0.4918	0.5396	30.06	34.23
285.4	60.0	-	0.7889	-	62.40
291.1	60.0	0.2093	-	10.52	-
293.3	60.0	-	0.7408	-	55.93
298.0	60.0	-	0.6931	-	50.07
298.2	60.0	0.2814	-	14.81	-
299.9	60.0	-	0.6557	-	45.82
301.2	60.0	0.3459	-	19.02	-
301.8	60.0	-	0.6028	-	40.26
302.2	60.0	0.4101	0.5668	23.59	36.75
302.3	60.0	-	0.5589	-	36.01
302.4	60.0	-	0.5396	-	34.23
302.5	60.0	0.4561	0.4918	27.14	30.06
289.1	80.0	-	0.7889	-	62.40
294.9	80.0	0.2093	-	10.52	-
297.1	80.0	-	0.7408	-	55.93

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1]	Haarhaus, U.; Schneider, G.M.
(2) Pentane; C_5H_{12}; [109-66-0]	*J. Chem. Thermodyn.* 1988, *20*, 1121-9.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and pentane

T/K	*p*/MPa	x_1 (2)-rich phase	x_1 (1)-rich phase	100 w_1 (compiler) (2)-rich phase	100 w_1 (compiler) (1)-rich phase
302.0	80.0	-	0.6931	-	50.07
302.1	80.0	0.2814	-	14.81	-
303.9	80.0	-	0.6557	-	45.82
305.1	80.0	0.3459	-	19.02	-
305.8	80.0	-	0.6028	-	40.26
306.2	80.0	0.4101	0.5668	23.59	36.75
306.3	80.0	-	0.5589	-	36.01
306.4	80.0	-	0.5396	-	34.23
306.5	80.0	0.4561	0.4918	27.14	30.06
292.4	100.0	-	0.7889	-	62.40
298.3	100.0	0.2093	-	10.52	-
300.8	100.0	-	0.7408	-	55.93
305.5	100.0	-	0.6931	-	50.07
305.6	100.0	0.2814	-	14.81	-
307.6	100.0	-	0.6557	-	45.82
308.5	100.0	0.3459	-	19.02	-
309.4	100.0	-	0.6028	-	40.26
309.8	100.0	0.4101	0.5668	23.59	36.75
310.0	100.0	-	0.5589	-	36.01
310.0	100.0	-	0.5396	-	34.23
310.1	100.0	0.4561	0.4918	27.14	30.06
295.5	120.0	-	0.7889	-	62.40
303.9	120.0	-	0.7408	-	55.93
308.8	120.0	0.2814	0.6931	14.81	50.07
310.9	120.0	-	0.6557	-	45.82
311.9	120.0	0.3459	-	19.02	-
313.1	120.0	-	0.5668	-	36.75
313.2	120.0	0.4101	0.5589	23.59	36.01
313.3	120.0	-	0.5396	-	34.23
313.4	120.0	0.4561	0.4918	27.14	30.06
298.3	140.0	-	0.7889	-	62.40
304.5	140.0	0.2093	-	10.52	-
306.9	140.0	-	0.7408	-	55.93
311.7	140.0	-	0.6931	-	50.07
311.8	140.0	0.2814	-	14.81	-
313.9	140.0	-	0.6557	-	45.82
314.8	140.0	0.3459	-	19.02	-
315.7	140.0	-	0.6028	-	40.26
316.2	140.0	0.4101	0.5668	23.59	36.75
316.3	140.0	-	0.5589	-	36.01
316.3	140.0	-	0.5396	-	34.23
314.4	140.0	0.4561	0.4918	27.14	30.06

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1]	Haarhaus, U.; Schneider, G.M.
(2) Pentane; C_5H_{12}; [109-66-0]	*J. Chem. Thermodyn.* 1988, *20*, 1121-9.

EXPERIMENTAL VALUES: (continued)

COMMENTS AND ADDITIONAL DATA:

Data for isopleths at high pressures were fitted to the Simon equation

$$p(x,T)/\mathrm{MPa} = a[(T/T_0)^c-1]$$

From these equations, the corresponding (T, x) isobars were calculated and were fitted to the equation

$$T/\mathrm{K} = T_c/\mathrm{K}+k|y-y_c|^{\nu}$$

where

$$y = \alpha x_1/[1+x_1(\alpha-1)]$$
$$y_c = \alpha x_{c1}/[1+x_{c1}(\alpha-1)]$$

The coefficients found are (s = std. error of estimate):

x_1	T_0/K	a	c	s
0.2093	276.04	98.2	9.03	0.30
0.2814	282.60	89.1	9.61	0.09
0.3459	285.58	88.5	9.74	0.23
0.4101	286.70	96.2	9.17	0.11
0.4561	286.90	94.6	9.27	0.07
0.4918	287.00	95.1	9.27	0.05
0.5396	286.89	94.7	9.28	0.08
0.5589	286.85	96.5	9.18	0.13
0.5668	286.80	99.5	9.01	0.06
0.6028	286.35	96.7	9.16	0.05
0.6557	284.92	114.0	8.25	0.33
0.6931	282.81	100.2	8.98	0.27
0.7408	278.27	100.9	8.88	0.21
0.7889	270.41	87.4	9.73	0.41

p/MPa	T_c/K	k	α	x_{c1}	ν	s
0.1	286.92	-883	0.83	0.497	3.36	0.04
5.0	288.49	-899	0.83	0.496	3.37	0.04
10.0	290.03	-874	0.86	0.494	3.35	0.05
20.0	292.90	-860	0.91	0.490	3.34	0.06
40.0	298.00	-900	0.90	0.490	3.35	0.09
60.0	302.44	-886	0.91	0.489	3.35	0.10
80.0	306.42	-903	0.89	0.491	3.35	0.10
100.0	310.01	-924	0.87	0.493	3.35	0.10
120.0	313.33	-844	0.82	0.495	3.28	0.08
140.0	316.34	-906	0.85	0.494	3.32	0.09

Simon equations are also given for (p, x) pairs, which are of the same form as those for the (T, x) pairs.

COMPONENTS:	EVALUATOR:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane-d_{12}; C_6D_{12}; [1735-17-7]	A. Maczynski Institute of Physical Chemistry Polish Academy of Sciences Warsaw, Poland J.W. Lorimer The University of Western Ontario London, Ontario, Canada July, 1989

CRITICAL EVALUATION:

Table 1 gives solubilities, upper critical solution temperatures (UCST) and compositions for the system methanol-cyclohexane-d_{12} which have been reported in the literature.

Table 1. Solubilities, critical solution temperature and composition in the system methanol (1) - cyclohexane-d_{12} (2)

Author(s)	Range			
	T/K	p/MPa	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Rabinovich 1971	316.4 UCST		-	-
2. Houessou 1985	315.280 UCST		0.512	0.512
3. Schoen 1986	313.364 UCST		0.516	0.516
4. Singh 1987	310.3-314.935 UCST		0.315-0.514	0.514-0.630
	311.0-319.0	1.9-13.1	0.315-0.500	0.539-0.630

Critical Solution Temperature and Composition

The four reported values of UCST, ref 1-4, average 314.505 K, std. dev. 1.0 K, well outside the precision of the data; the value of Rabinovich, ref. 1, appears to be unacceptably high, and that of Schoen et al., ref. 3, too low. The values in refs. 2 and 4 were all obtained through carefully-conducted experiments; the differences may arise from varying amounts of water. Their average value T_c = 315.11 ± 0.24 K is considered to be *tentative*. However, the various values given by Singh and Van Hook should be taken into account, as discussed below.

The critical composition is reported in refs. 2-4. The data average $x_c = 0.514 \pm 0.002$, the spread being equal to the estimated error given by Singh and Van Hook; this value is *recommended.*

Mutual Solubility

Only Singh and Van Hook reported compositions below the critical temperature; Schoen et al. gave only differencs in refactive index. They correlated their data with the equations

(continued)

CRITICAL EVALUATION: (continued)

$$|x_1 - x_{c1}| = B|1 - T/T_c|^{\beta}$$

and

$$|x_1 - x_{c1}| = B[1 - T/(T_c^o + cp)]^{\beta}$$

where p is the pressure and $c = (3.173 \pm 0.012) \times 10^{-7}$ K Pa^{-1} is the pressure coefficient of the critical solution temperature. They give various sets of fitting parameters, as follows.

parameter	data for 0.1 MPa only (authors' Table II)	data for all pressures (authors' Table II)	fixed $\beta = 0.325$ (authors' Table III)
x_{c1}	0.515 ±0.003	0.517 ±0.001	0.514 0 ±0.000 6
B	1.09 ±0.12	1.22 ±0.06	0.968 ±0.025
β	0.355 ±0.026	0.317 ±0.010	
T_c/K	314.870 ±0.007		314.935 ±0.007
T_c^o/K		314.898 ±0.010	314.912 ±0.001
variance	5.8×10^{-5}	8.3×10^{-5}	1.66×10^{-4}

The quantities T_c and T_c^o are the critical solution temperatures at 0.1 MPa and zero pressure. The evaluators find that large errors in composition arise from use of these equations, possibly because of excessive rounding of the reported parameters. Thus, the equations should be used as rough guides only. For the data at 0.1 MPa and fixed $\beta = 0.325$, the evaluators find: $T_c = 314.863 \pm 0.001$ K, $B = 0.7493 \pm 0.038$, $x_{c1} = 0.5087 \pm .0045$, $s = 0.013$ (variance 1.7×10^{-4}), values that are within the error limits stated for the critical parameters in the section above, but which actially reproduce the experimental data better. The Evaluators' parameters are recommended for calculations.

The complete data of Singh and Van Hook at high pressures are shown on the compilation and should be considered as *tentative*.

REFERENCES:

1. Rabinovich, I.B.; Tsvetkov, V.G. *Zh. Fiz. Khim.* 1971, *45*, 822.
2. Houessou, C.; Guenoun, P.; Gastaud, P.; Perrot, F.; Beysens, D. *Phys. Rev. A* 1985, *32*, 1818.
3. Schoen, W; Wiechers, R.; Woermann, D. *J. Chem. Phys.* 1986, *85*, 2922.
4. Singh, R.R.; Van Hook, W.A. *J. Chem. Phys.* 1987, *87*, 6097.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane-d_{12}; C_6D_{12}; [1735-17-7]

ORIGINAL MEASUREMENTS:

Rabinovich, I.B.; Tsvetkov, V.G.

Zh. Fiz. Khim. 1971, *45*, 822-3; *Russ. J. Phys. Chem. (Engl. Transl.)* 1971, *45*, 814.

VARIABLES:

One temperature: 316 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 43.2°C.
Solubility data were presented on a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The temperature of appearance of turbidity was observed. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified; purified by methods described in ref 1.

ESTIMATED ERROR:

temp. ±0.1 K.

REFERENCES:

1. Rabinovich, I.B. *Vliyanie izitopii na fiziko-khimicheskie svoistva zhidkostei*, Izv. Nauka, Moskva, 1968.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane-d_{12}; C_6D_{12}; [1735-17-7]

ORIGINAL MEASUREMENTS:

Houessou, C.; Guenoun, P.; Gastaud, P.; Perrot, F.; Beysens, D.

Phys. Rev. A 1985, *32*, 1818-33.

VARIABLES:

One temperature: 315 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 42.130°C at 25.90 mass % methanol, or mole fraction (calculated by the compiler) $x_1 = 0.5121$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

An initially homogeneous mixture was quenched thermally through a few mK. If a ring of scattered light appeared (sign of spinodal decomposition) it was assumed that the initial temp. was T_c. Composition was determined by weighing to 0.1 mg. The coexistence curves were found as in ref. 1 from measured refractive index in both phases. Care was taken to avoid moisture and dust by baking syringes and cells under vacuum and working in a dust-free area.

SOURCE AND PURITY OF MATERIALS:

(1) Merck, guaranteed purity > 99.5%, water < 0.05%, acetone < 0.01%; used as received.

(2) Centre d'Etudes Nucléaires de Saclay, guaranteed purity 99.7%, impurities: water < 0.02%, acetone not detectable; used as received.

ESTIMATED ERROR: not specified

REFERENCES:

1. Jacobs, D.T.; Anthony, D.J.; Mockler, R.C.; O'Sullivan, W.J. *Chem. Phys.* 1977, *20*, 219.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane-d_{12}; C_6D_{12};
[1735-17-7]

ORIGINAL MEASUREMENTS:

Schoen, W.; Wiechers, R.;
Woermann, D.

J. Chem. Phys. 1986, *85*, 2922-8.

VARIABLES:

One temperature: 313 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 40.214°C at x_1 = 0.516.
The corresponding mass fraction, calculated by the compiler is
w_1 = 0.262.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The differences of refractive index between two coexisting liquid phases were measured. The samples were prepared by mixing the required weight of components in a glove box. The deflection of He/Ne laser beam after passing through the two compartments of the differential refractometer cell was measured as the distance necessary to shift the light detection unit. The refractive index of the coexisting phases was related to the composition by measuring several mixtures as a function of temperature. The measurements were made over the range: UCST - 2 K.

SOURCE AND PURITY OF MATERIALS:

(1) Merck, Uvasol quality, guaranteed purity > 99.7 %, water < 0.03 %; used as received.

(2) Merck, Uvasol quality, degree of deuteration > 99 %; used as received.

ESTIMATED ERROR:

temp. ±0.001 K (UCST),
±0.003 K (24 h stability).

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane-d_{12}; C_6D_{12}; [1735-17-7]

ORIGINAL MEASUREMENTS:

Singh, R.R.; Van Hook, W.A.

J. Chem. Phys. 1987, 87, 6097-110.

VARIABLES:

Temperature: 310 - 315 K
Pressure : 0.1 - 13.1 MPa

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol and cyclohexane-d_{12}

T/K	p/MPa	x_1	100 w_1 (compiler)
310.267	0.1	0.3147	13.26
311.009	1.92	0.3147	13.26
311.990	5.03	0.3147	13.26
312.871	7.85	0.3147	13.26
313.581	10.03	0.3147	13.26
314.551	0.1	0.4405	20.77
315.625	3.87	0.4405	20.77
315.611	3.82	0.4405	20.77
316.240	5.82	0.4405	20.77
317.239	8.90	0.4405	20.77
314.803	0.1	0.4649	22.44
315.730	2.74	0.4649	22.44
316.827	6.16	0.4649	22.44
318.744	9.03	0.4649	22.44
318.454	11.34	0.4649	22.44
314.863	0.1	0.4978	24.81
315.867	3.12	0.4978	24.81
317.102	7.01	0.4978	24.81
319.091	13.14	0.4978	24.81

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The point at which the intensity of an emerging beam from a 3-mW HeNe laser) becomes one-half of the incident was taken as the temperature of phase separation. For a run, the cell with magnetic stirrer was warmed to about 5-10 K above T_c and a sample prepared gravimetrically was added under vacuum. The pressure was set manually and the bath temperature then allowed to decrease at about 2-5 mK per min, while a computer continously monitored pressure, temperature and light intensity. The rapid change in intensity at the transition was used to instruct the computer to store the relevant data, then to warm the apparatus and repeat the experiment a preselected number of times. For details, see ref 1.

SOURCE AND PURITY OF MATERIALS:

(1) Fisher Scientific, ASC grade; refluxed over Mg activated withI_2, twice distilled under dry Ar; distilled in a spinning band column; no impurities by glc.

(2) MSD isotopes, isotopic purity 99% D; purified over Na wire; no impurities by glc.

ESTIMATED ERROR:

temp. ±0.001 K (reproducibility); pressure ±0.01 MPa.

REFERENCES:

1. Singh, R.R. *Thesis, University of Tennesee,* 1987.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1]	Singh, R.R.; Van Hook, W.A.
(2) Cyclohexane-d_{12}; C_6D_{12}; [1735-17-7]	*J. Chem. Phys.* <u>1987</u>, *87*, 6097-110.

EXPERIMENTAL VALUES: (continued)

Solubility of methanol and cyclohexane-d_{12}

T/K	p/MPa	x_1	100 w_1 (compiler)	
318.724	12.08	0.4978	24.81	
314.870	0.1	0.514	25.3	UCST calculated by the authors at 0.1 MPa
314.860	0.1	0.5388	28.00	
315.831	3.05	0.5388	28.00	
316.549	5.28	0.5388	28.00	
317.318	7.73	0.5388	28.00	
318.257	10.33	0.5388	28.00	
314.946	0.1	0.5400	28.10	
314.795	0.1	0.5694	30.57	
315.579	2.58	0.5694	30.57	
317.252	7.81	0.5694	30.57	
316.460	5.32	0.5694	30.57	
316.362	5.04	0.5694	30.57	
318.066	10.35	0.5694	30.57	
314.561	0.1	0.5809	31.58	
315.677	3.13	0.5809	31.58	
316.374	5.31	0.5809	31.58	
317.921	10.14	0.5809	31.58	
313.935	0.1	0.6300	36.18	
314.834	2.6	0.6300	36.18	
315.622	5.07	0.6300	36.18	
316.510	7.84	0.6300	36.18	
317.875	12.12	0.6300	36.18	

COMMENTS AND ADDITIONAL DATA:

The authors give extensive analysis of their data, with fitting equations of the form

$$x_1 = x_{c1} \pm A|1-T/T_c^\circ|$$

$$T_c^\circ = T_c + cp$$

where T_c, T_c° are the critical solution temperatures at zero pressure and pressure p, x_{c1} is the critical composition, $c = (3.173 \pm 0.012) \times 10^{-1}$ K MPa^{-1} is the pressure coefficient of T_c and A is an amplitude constant. For analysis of all data at all pressures, they find T_c/K = 314.935 ± 0.002, x_{c1} = 0.514 ± 0.001, while for data at 0.1 MPa alone, T_c/K = 314.870 ± 0.007, x_{c1} = 0.515 ± 0.003.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane-*d*$_{14}$; C_6D_{14}; [21666-38-6]

ORIGINAL MEASUREMENTS:

Khurma, J.R.; Fenby, D.V.

Aust. J. Chem. 1982, *35*, 1281-4.

VARIABLES:

Temperature: 302 - 304 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and hexane-*d*$_{14}$

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
302.34	0.3683	-	15.71	-
302.86	-	0.6793	-	40.37
304.11	0.4441	-	20.34	-
304.22	0.5091	-	24.89	-
304.25	0.5462	-	27.78	-
304.29	-	0.5986	-	32.28
304.30 UCST	0.560	0.560	28.9	28.9

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. Sample tubes containing mixtures of known composition were prepared by distillation under vacuum from the bulk degassed pure components and sealed. The phase separation was observed visually. The temperature of a silicone oil bath was controlled by a precision temperature controller (Tronac PTC 60) and measured with calorimeter thermometers which had been calibrated against a platinum resistance thermometer. For each sample the phase separation temperature was measured several times.

SOURCE AND PURITY OF MATERIALS:

(1) BDH Aristar grade, dried over freshly-activated molecular sieve type 3A, degassed by vacuum sublimation.

(2) Merck, Sharpe and Dohme Canada Ltd., isotopic purity > 98 atom % D; dried over freshly-cut Na, degassed by vacuum sublimation.

ESTIMATED ERROR:

temp. ±0.02 K, ±0.04 K (UCST).

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

EVALUATOR:

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The University of Western Ontario
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July, 1989

CRITICAL EVALUATION:

A survey of solubilities and upper critical solution temperatures (UCST) for the system methanol-cyclohexane which have been reported in the literature is given in Table 1.

Table 1. Summary of Solubility Data for the system methanol (1) - cyclohexane (2)

Author(s)	Range T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Timmermans 1922	332.6-354.1 UCST	-	-
2. Mondain-Monval 1926	322.2 UCST	-	-
3. Jones 1930	279.3-318.7 UCST	0.068-0.5053	0.5053-0.847
4. Cornish 1934	318.2, 293 UCST	-	-
5. Eckfeld 1943	302.3-318.3 UCST	0.146-0.482	0.507-0.805
6. Francis 1944	318 UCST	-	-
7. Francis 1944	318 UCST	-	-
8. Sieg 1951	319.0 UCST	-	-
9. Quantie 1954	322.4 UCST	0.534	0.534
10. Cardinaud 1960	319.6 UCST	0.5	0.5
11. Kiser 1961	288-318.9 UCST	-	0.733-0.859
12. Debye 1962	318.3 UCST	0.53	0.53
13. Marinichev 1965	308, 318	0.169-0.437	0.607-0.784
14. Gimler 1965	318.4 UCST	-	-
15. Roth 1966	264.2-437.3 [a]	0.122-0.500	0.635-0.912
16. Campbell 1967	313.2-319.2 UCST	0.228-0.433	0.588-0.739
17. Kurtynina 1968	298	0.112	0.830
18. Rudakovskaya 1968	293	0.112	0.845
19. Huang 1969	318.3 UCST	vol. fract. 0.286; x_1 = 0.517	
20. Sergeeva 1969	313	0.245	0.727
21. Warren 1969	318.4 UCST	vol. fract. 0.286; x_1 = 0.517	
22. Rabinovich 1971	319.0 UCST	-	-
23. Sergeeva 1971	298	0.075	0.821
24. Huang 1974	318.3 UCST	-	-

(continued)

CRITICAL EVALUATION: (continued)

Table 1 (continued). Summary of Solubility Data
for the system methanol (1) - cyclohexane (2)

Author(s)	Range		
	T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
25. Takeuchi 1975	298	0.129	0.825
26. Budantseva 1976	293	0.139	0.857
27. Sugi 1976	298	0.125	0.828
28. Jacobs 1977	318.6 UCST	0.517	0.517
29. Becker 1978	303.8-318.5 UCST	0.165-0.513	0.513-0.794
30. Scheibner 1978	318.2 UCST	0.518	0.518
31. Yosida 1978	318.2 UCST	-	-
32. Balasubramanian 1979	322.3 UCST	0.51	0.51
33. Nagata 1980	298	0.124	0.828
34. Nagata 1981	313.2	0.237	0.735
35. Eden 1982	318.2 UCST	0.518	0.518
36. Nagata 1983	298.2	0.125	0.829
37. Tveekrem 1983	322.9 UCST	0.521	0.521
38. Kopelman 1984	319.0 UCST	(28.98 vol %)	
39. Cohn 1984	320.6 UCST	(30.4 vol %)	
40. Nagata 1984	298.2	0.125	0.829
41. Nagata 1984	298.2	0.125	0.829
42. Houessou 1985	318.0 UCST	0.517	0.517
43. Schoen 1986	318.3 UCST	0.524	0.524
44. Hradetzky 1986	252.7-318.9 UCST	0.058-0.506	0.506-0.889
45. Singh 1986	318.8 UCST	0.508	0.508
46. Jacobs 1986	319.1 UCST	0.523	0.523
47. Schmidt 1986	318.7 UCST	-	-
48. Singh 1987	317.5-323.8 [b]	0.362-0.514	0.514-0.631
49. Aizpiri 1988	299.9-322.5 [c]	0.163-0.515	0.568-0.815
50. Ewing 1988	317.1-318.4	0.358-0.509	0.514-0.651
51. Brunner 1988	318.1 UCST	0.508	0.508

[a,b,c] At elevated pressures: [a] p = 0.1-563 MPa, [b] p = 0.1-12.6 MPa, [c] p = 0.1-14.4 MPa.

Critical Solution Temperature and Composition

Forty values of the UCST have been reported in refs. 1-12, 14, 16, 19, 21, 22, 24, 28-32, 35, 37-39, and 42-50. Timmermans, ref. 1, reported UCST as a function of pressure; extrapolation of his data by the evaluators indicated an unreasonably high value of the UCST, so these data are rejected. The remaining values are summarized in Table 2 in increasing order. One value of Cornish et al., ref. 4, was lower by more than 25 K, probably because of contamination of the cyclohexane with benzene.

(continued)

CRITICAL EVALUATION: (continued)

The critical solution temperature is extremely sensitive to impurities. All values higher than 319.1 K (refs. 2, 9, 32, 37, 39) can be rejected for one or more reasons: probable significant amounts of impurities (water, for example), lack of information about sources, unspecified purity of chemicals, or insufficient description of experimental methods. Similarly, all values below 318.3 K can be rejected for similar reasons; in these cases, examination of the data suggests that contamination by hydrocarbon impurities is a possibility.

The remaining 17 determinations lie in the range 318.25 to 319.094 K, and include all modern results of high precision. Their average and ± 1 standard deviation are: T_c = 318.70 ± 0.25 K, with 95 % confidence limits on the mean of ± 0.12 K. If only the precise results of Singh and Van Hook, refs. 45, 48, of Ewing et al., ref. 50, and of Aizpiri et al., ref. 49, are considered, the value is T_c = 318.61 ± 0.23 K, with 95 % confidence limits on the mean of ± 0.36 K. In conclusion, there is little to choose between the results of Singh and Van Hook on the one hand, and Ewing et al. and Aizpiri et al. on the other, so the present stage of knowledge suggests *recommendation* of the value;

$$T_c = 318.70 \pm 0.25 \text{ K}.$$

Table 2. Critical solution temperature in the system methanol-cyclohexane

T_c	Author	year	ref.
293	Cornish, Archibald	1934	4
316.2	Campbell, Kartzmark	1967	16
317.976	Houessou et al.	1985	42
318	Francis	1944	6
318	Francis	1944	7
318.1	Brunner	1988	51
318.193	Scheibner et al.	1978	30
318.2	Cornish, Archibald	1934	4
318.2	Eden	1982	35
318.25	Yosida, Ikushima	1978	31
318.285	Huang, Webb	1969	19
318.288	Schoen, Wiechers	1986	43
318.29	Eckfeld, Lucasse	1943	5
318.290	Huang et al.	1974	24
318.3	Debye et al.	1962	12
318.3	Roth et al.	1966	15[a]
318.3	Huang	1969	19
318.412	Ewing et al.	1988	50
318.422	Aizpiri et al.	1988	49
318.44	Warren, Webb	1969	21
318.5	Becker et al.	1978	29

(continued)

CRITICAL EVALUATION: (continued)

Table 2 (continued). Critical solution temperature in the system methanol-cyclohexane

T_c	Author	year	ref.
318.6	Cardinaud	1960	10
318.674	Jacobs et al.	1977	28
318.7	Schmidt	1986	47
318.72	Gimler et al.	1965	14
318.75	Jones, Amstell	1930	3
318.815	Singh, Van Hook	1987	48
318.816	Singh, Van Hook	1986	45
318.9	Kiser et al.	1961	11
318.93	Hradetsky, Bittrich	1986	44
318.98	Kopelman et al.	1984	38
319.0	Rabinovitch, Tsvetkov	1971	22
319.00	Sieg	1951	8
319.094	Jacobs	1986	46
319.2	Campbell, Kartzmark	1967	16
320.560	Cohn, Jacobs	1984	39
322.3	Mondain-Monval	1926	2
322.3	Balasubramanian, Mitra	1979	32
322.4	Quantie	1954	9
322.875	Tveekrem, Jacobs	1983	37

[a] From Evaluator's analysis

Twenty-five values of critical composition have been reported in refs. 3, 9, 10, 12, 19, 21, 28-30, 32, 35, 37-39, 42, 43, 45, 46, 48 and 51, or have been calculated by the evaluators from the solubility data of refs. 5, 15 and 16. The values lie between 0.496 and 0.534 mole fraction of methanol. Table 2 summarizes the values in increasing order. Values reported in volume per cent, refs. 19, 21, 38 and 39, have been converted to mole fractions by the evaluators, assuming that the volume fractions were calculated from the volumes of pure methanol and cyclohexane at 20°C, where the respective densities are 0.7865 and 0.7739 g cm^{-3}, from ref. 40. Values above mole fraction 0.521 were, in general, derived from experiments using as-received chemicals, or chemicals from unspecified sources (refs. 9, 37-39, 43, 46), and are rejected. The values of Cardinaud, ref. 10, and Quantie, ref. 9, are insufficiently precise to merit consideration. The value of Aizpiri et al. ref. 49, appears to be too low, although solubility data (refs. 5, 15, 16) analyzed by the evaluators gives some limited support for their value. Their favorable comparison of their value with that of Ewing et al., ref. 50, is based on an erroneous reading of the latter paper.

(continued)

CRITICAL EVALUATION: (continued)

However, they did point out the difficulty in deducing the critical composition from a coexistence curve which has such a flat top as that for methanol-cyclohexane. The remaining values give average abd standard deviation: x_{c1} = 0.5154 ± 0.0052, 95 % confidence limits ± 0.0028. If those values are omitted for which the corresponding critical solution temperature has been rejected, there is only a slight change: x_{c1} = 0.5124 ± 0.0053, 95 % confidence limits ± 0.0036. The present stage of knowledge suggests *recommendation* of the value;

$$x_{c1} = 0.515 \pm 0.005.$$

Table 3. Critical mole fraction of methanol in the system methanol-cyclohexane

x_{c1}	Author	year	ref.
0.489	Roth et al.	1966	15[a]
0.493	Campbell, Kartzmark	1967	16[a]
0.496	Eckfeld, Lucasse	1943	5[a]
0.4986	Aizpiri et al.	1988	49
0.5	Cardinaud	1960	10
0.5053	Jones, Amstell	1930	3
0.506	Hradetsky, Bittrich	1986	44
0.508	Singh, Van Hook	1986	45
0.508	Brunner	1988	51
0.50955	Ewing et al.	1988	50
0.514	Balusubramanian	1979	32
0.513	Becker et al.	1978	29
0.514	Singh, Van Hook	1987	48
0.5168	Jacobs et al.	1977	28
0.517	Huang, Webb	1969	19
0.517	Warren, Webb	1969	21
0.5172	Houessou et al.	1985	42
0.5179	Scheibner et al.	1978	30
0.518	Eden	1982	35
0.521	Tveekrem, Jacobs	1983	37
0.5214	Kopelman, Gammon	1984	38
0.5232	Jacobs	1986	46
0.524	Schoen, Wiechers	1986	43
0.53	Quantie	1954	9
0.538	Cohn, Jacobs	1984	39

[a] from Evaluator's analysis

(continued)

CRITICAL EVALUATION: (continued)

Mutual Solubility

Four hundred and twenty-five values of mutual solubilities have been reported in 23 publications, not including critical solution points; 249 of these are shown in fig. 1. Data from papers (refs. 17, 18, 20, 23, 25-27, 33, 34, 36, 40, 41) which are restricted to one or two temperatures have been combined for convenience in plotting, and are indicated by plus signs. Several of these (the data of ref. 26 and of ref. 23 for the cyclohexane-rich liquid) are clearly aberrant, and are rejected. The remaining 246 points lie in a band of vertical width about 3 K, which can arise in large part from differences in critical solution temperature.

The extensive data (176 points) of Ewing, Johnson and McGlashan (ref. 50) have not been included on the plot. The aim of their work was to examine the shape of the coexistence curve in the neighborhood of the critical solution point, and to this end the very precise measurements were restricted to a maximum of 1.3 K below the critical solution temperature. Thus these data would contribute simply to the density of points near the top of the curve in fig. 1, without contributing to our aim, which is to examine the whole coexistence curve.

In refs. 3, 5, 15, 16, 29, 44, 48 and 49, both solubility data and the coordinates of the critical solution point (determined either by the authors or the evaluators) are available. Therefore, these data from various sources can be compared by plotting T/T_c against $x_1 - x_{c1}$, which allows for differences in the critical coordinates, as discussed in the Preface to this volume. Although the remaining data (refs. 11, 13) may be of good quality, they cannot be compared because they belong to sets with unknown critical coordinates. The plot in reduced coordinates (fig. 2) shows that most of the selected data is of reasonable quality. (On the plot, the width of a symbol corresponds to ΔT = 1.6 K, Δx_1 = 0.0125.) Exceptions arise as follows. There are two aberrant points in the data of Jones and Amstell, ref. 3. The data of Roth et al., ref. 15, and of Singh and Van Hook, ref. 48, appear to require a value of x_{c1} larger by about 0.0125 (one symbol width) to bring them into line with the other data. While this would give a reasonable increase in the value of x_{c1} for the work of Roth et al., it would give an unreasonably high increase to the value of Singh and Van Hook, so we have preferred not to carry out this change. The points of Aizpiri et al., ref. 49, are centred well compared to the other points, but appear to be somewhat too broad at lower temperatures. These data have been extrapolated from higher pressures, and, while the experiments and analysis of the data were done with great care, the extrapolation procedure may not have been completely reliable.

The best results, which fortunately also cover the largest range of composition. appear to be those of Hradetsky and Bittrich, ref. 45, and these form the basis of the following fitting equation:

$$x_1 = x_{c1} \pm B_1\theta^{\beta} \pm B_2\theta^{\beta+w} + A_1\theta \pm B_3\theta^{\beta+2w} + A_2\theta^{1-\alpha+w}$$

where $\theta = |1 - T/T_c|$, + and - refer to the branches below and above the critical composition, and the constants have their theoretical values β = 0.329, α = 0.11, w = 0.5. The constants (with standard deviations in parentheses) are:

x_{c1} = 0.5066 (0.0023) T_c/K = 318.93 (0.3)
B_1 = 0.7010 (0.024) B_2 = 1.5034 (0.22) B_3 = -3.8731 (0.49)
A_1 = -1.1231 (0.21) A_2 = 1.9341 (0.46) s = 0.0077

s is the total standard error of estimate in composition. This equation is included in fig. 1. It should be noted that six coefficients are needed to obtain a good fit, but the almost-vertial intersection with the

(continued)

monotectic line appears to be slightly high (0.007 mole fraction) at the cyclohexane-rich end and slightly low by the same amount at the methanol-rich end. Thus the predicted values, especially at the lowest temperatures, should be interpreted with caution. Table 3 gives selected values calculated from the fitting equation. These can be *recommended* in the range of temperature given in the table, bearing in mind that the equilibrium temperatures are very sensitive to impurities.

Solubilities at high pressure, 0.1 to 612 MPa, were reported by Roth et al., ref. 15, Singh and Van Hook, ref. 48, and Aizpiri et al., ref. 49. However, because different regions of temperature and pressure were studied, a detailed evaluation is not possible. All of these high pressure values are accepted as *tentative.*

Table 4. Recommended values of solubility in the system methanol (1) - cyclohexane (2).

T/K	x_1	x_1
	(2)-rich phase	(1)-rich phase
280.0	0.068	0.877
285.0	0.081	0.865
290.0	0.097	0.851
295.0	0.115	0.835
300.0	0.138	0.816
305.0	0.169	0.792
310.0	0.214	0.758
315.0	0.298	0.703
318.70 ± 0.25	UCST	0.515 ± 0.005

Monotectic Point and Sub-monotectic Region

This system is the only alcohol-hydrocarbon system for which data are available for the monotectic, and these are contained in one paper only, that of Hradetsky and Bittrich, ref. 44. If the cocordinates of the ends of the monotectic line given by these workers are accepted, the sub-monotectic liquid phase (at high methanol content) can be fitted to a quadratic function:

$$T = T_{mt} + a(x_1 - x''_{mt}) + b(x_1 - x''_{mt})^2$$

with T_{mt} = 275.4 K, the monotectic temperature (found by graphical interpolation), constants (with standard deviations) a = -305 (68), b = -2860 (1600), and x_{mt}'' = 0.889 the mole fraction at the intersection of the coexistence and sub-monotectic curves. At the ends of the monotectic line, the three phases methanol-rich liquid, solid cyclohexane and methanol-poor liquid are in equilibrium; thus these points are isothermally invariant.

The melting curve of cyclohexane (at low methanol content) shows the point of inflection expected from a substance like cyclohexane with a low entropy of fusion (cf. ref. 52). This curve can be fitted accurately by a cubic equation which passes through $T_{m,2}$ = 279.6 K, the melting point of pure cyclohexane (at x_1 = 0), and x_{mt}' = 0.058, the mole fraction at the intersection of the monotectic line and the melting curve:

(continued)

CRITICAL EVALUATION: (continued)

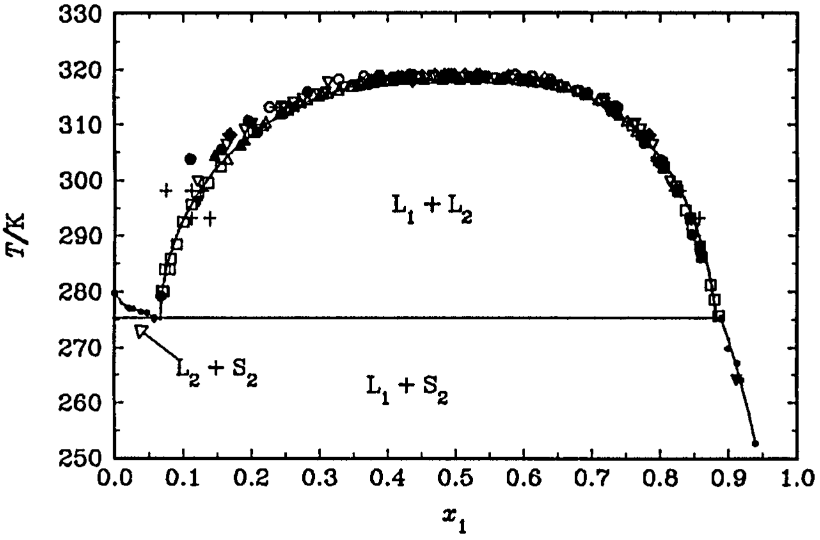

Fig. 1: Solubilities in the system methanol (1) - cyclohexane (2). Line: fitting equation (see text). The points are spaced so closely that identification is difficult; the plot is intended as an overall impression of the data.

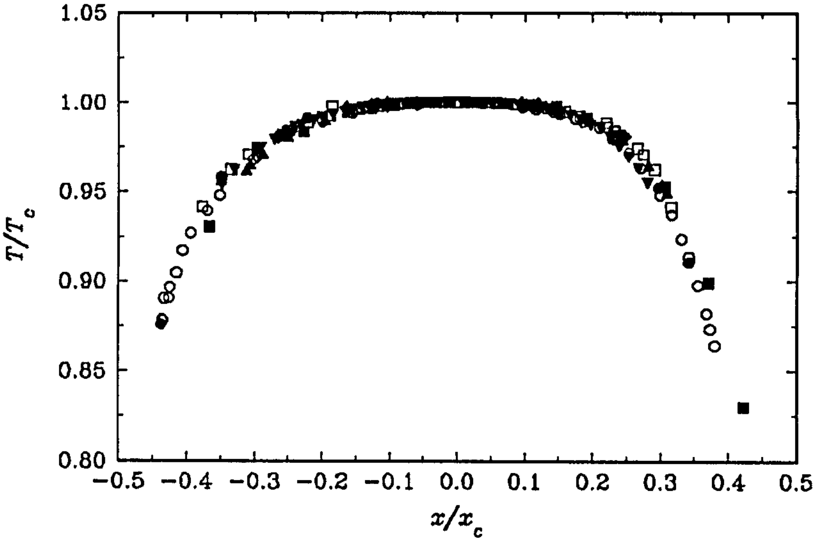

Fig. 2: Solubilities in the system methanol (1) - cyclohexane (2) in reduced coordinates T/T_c, $x_1 - x_{c1}$. Filled circles: ref. 3; open up triangles, ref. 5; filled squares, ref. 15; filled diamonds, ref. 16; filled down triangles, ref. 29; open circles, ref. 44; open up triangles, ref. 48; open squares, ref. 49.

(continued)

CRITICAL EVALUATION: (continued)

$$T = T_{m,2} + (T_{mt} - T_{m,2})(x_1/x'_{mt}) + cx_1(x_1 - x'_{mt}) + dx_1(x_1 - x'_{mt})^2$$

with constants $c = -535$ (520), $d = -4.73 \times 10^4$ (1.3×10^4). These data are *tentative*. As noted above, the compositions at the ends of the monotectic line differ by about 0.007 mole fraction from the extrapolated values of Hradetsky and Bittrich, ref. 44, who estimate the precision of their compositions to be 0.002-0.003. This precision is considered by these evaluators to be closer to 0.01 mole fraction.

The midpoint of the monotectic line, at $x_1 = 0.474$, lies at a lower value of x_1 than the critical solution composition, $x_{c1} = 0.515$, thus indicating that the coexistence curve is slightly asymmetric, in agreement with the measurements of Aizpiri et al., ref. 49.

Pressure coefficient of critical solution temperature

Three values have been reported; see Table 5.

Table 5. Pressure coefficient of critical solution temperature

$10^7 (\partial T_c/\partial p)_{xc}$/K Pa^{-1}	Authors	ref.
3.173 ± 0.012	Singh, Van Hook	48
3.42 ± 0.04 (quadratic fit)	Aizpiri et al.	49
3.21 ± 0.02 (linear fit to data)		
3.299 ± 0.048	Ewing et al.	50

The average of these, excluding the linear fit of Aizpiri et al. (which the authors consider less reliable), is $10^7 (\partial T_c/\partial p)_{xc}$/K Pa^{-1} = 3.30 ± 0.12; the result of Ewing et al. is almost exactly the mean of the other two. This average result is considered as *tentative*.

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CRITICAL EVALUATION: (continued)

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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Timmermans, J. **Arch. Neerland. Sci.* 1922, *6*, 147-51. *J. Chim. Phys.* 1923, *20*, 491.
VARIABLES: Temperature: 333 - 354 K Pressure: 4.9 - 98.1 MPa	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

USCT of methanol and cyclohexane

t/°C	p/atm	p/MPa (compiler)
59.45	50.	4.90
61.02	100.	9.81
63.98	200.	19.61
69.10	400.	39.23
75.26	700.	68.65
81.0	1000.	98.07

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was reported in ref 1.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, anhydrous; distilled over Na.

(2) source not specified; b.p. 80.75°C, f.p. 6.50°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Kohnstamm, P.; Timmermans, J. *Versl. Akad. Amsterdam* 1912, *21*, 783.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Mondain-Monval, P.

C.R. Hebd. Séances Acad. Sci. <u>1926</u>, *183*, 1104-6.

VARIABLES:

One temperature: 322 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 49.1°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was not specified.

SOURCE AND PURITY OF MATERIALS:

(1) Source not specified; b.p. 64.7°C
(2) Source not specified.

ESTIMATED ERROR:
not specified

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Cornish, R.E.; Archibald, R.C.; Murphy, E.A.; Evans, H.M.

Ind. Eng. Chem. <u>1934</u>, *26*, 397-406.

VARIABLES:

Temperature: 293, 318 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45.0°C a) and 20°C b) for cyclohexane (2) from different sources; see "SOURCE AND PURITY OF MATERIALS" below.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was not specified.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; distilled; $\rho(25^\circ C)/\rho(4^\circ C)$ = 0.78656 (corr. for buoyancy), anhydrous.
(2) a) Eastman Kodak Co., used as received.
b) Kahlbaum; used as received; probably contained benzene.

ESTIMATED ERROR:
not specified

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Jones, D.C.; Amstell, S.

J. Chem. Soc. 1930, 1316-23.

VARIABLES:

Temperature: 279 - 319 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and cyclohexane

$t/^\circ C$	100 w_1		x_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
6.1	2.70	-	0.0679	-
17.1	-	67.77	-	0.8467
30.40	-	60.60	-	0.8016
30.6	4.50	-	0.1101	-
32.3	6.60	-	0.1566	-
37.5	8.53	-	0.1967	-
40.05	-	51.04	-	0.7325
42.68	-	46.40	-	0.6945
42.80	13.07	-	0.2831	-
44.62	-	40.51	-	0.6414
45.10	18.75	-	0.3774	-
45.32	19.36	-	0.3867	-
45.45	20.74	33.82	0.4073	0.5731
45.52	-	30.85	-	0.5396
45.53	22.40	-	0.4312	-
45.56	-	30.14	-	0.5312
45.58	27.19	29.20	0.4952	0.5200
45.60 UCST	28.00	28.00	0.5053	0.5053

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. Known masses of components were sealed into tubes. To exclude moisture during the filling procedure and storage of reagents, the tubes were dried by heating with a blowpipe and kept in a desiccator and filling was accomplished inside dry-box (air blown through the box was dried by calcium chloride and phosphoric oxide). The thermometers used had been standardized at the NPL. The effect of water on the solubility curve was studied.

SOURCE AND PURITY OF MATERIALS:

(1) B.D.H., analytical reagent grade twice distilled, dried with aluminum amalgam, distilled, treated with freshly burnt lime, acetone free, twice distilled; b.p. 64.70°C.

(2) a) Poluenc Freres, "pur", m.p. 2.6°C; distilled; m.p. 6.48°C.
    b) Hopkin and Williams, "pure", m.p. 1.0°C; distilled; m.p. 6.48°C.
    c) synthetic material obtained by the catalytic method; m.p. 6.48°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Eckfeld, E.L.; Lucasse, W.W.

J. Phys. Chem. 1943, *47*, 164-83.

VARIABLES:

Temperature: 302 - 318 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and cyclohexane

t/°C	g(1)/100g sln		x_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
29.19	-	61.06	-	0.8046
30.46	-	60.05	-	0.7979
31.30	6.11	-	0.1460	-
33.19	7.88	-	0.1835	-
34.01	-	57.09	-	0.7775
34.13	8.19	-	0.1898	-
35.95	9.08	-	0.2078	-
38.62	-	52.12	-	0.7409
39.05	11.02	-	0.2455	-
42.05	14.01	-	0.2997	-
42.29	-	46.06	-	0.6916
44.15	18.16	-	0.3682	-
44.24	-	40.23	-	0.6387
44.81	-	21.17	-	0.6136
44.87	-	36.15	-	0.5979
45.07	-	33.18	-	0.5660
45.09	24.07	-	0.4543	-
45.14	-	30.09	-	0.5306
45.14	26.14	28.12	0.4818	0.5068
45.14 UCST	(by interpolation)		-	-

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The ampoules of about 4.5 mL capacity were filled very carefully with reagents in a dry chest with P_2O_5 to exclude atmospheric moisture, sealed and then placed into a water bath. Machinery for stirring the bath and shaking the ampoules was mounted on the top of the bath. A strong light mounted over the bath furnished "excellent conditions" for observing cloudiness and clearness in the ampoules. The temperature of clearing point was recorded. There was no change of the miscibility temperature over 2-month period.

Data are also given for the effects of added salt.

SOURCE AND PURITY OF MATERIALS:

(1) J.T.Baker Company (Phillipsburg New Jersey), c.p. analyzed grade purified by iodoform reaction to remove acetone, twice fractionated to remove water and residual salts, twice distilled from sodium methylate and then simply distilled; $\rho(25°C)/\rho(4°C) = 0.78654$ agreed with literature values.

(2) Dow Chemical Company (Midland, Michigan), commercial grade; nitrated to remove unsaturated compounds, washed with Na_2CO_3, and water, dried with anhydrous Na_2SO_4, distilled, dried with Na and distilled; f.p. 6.48 ±0.02°C.

ESTIMATED ERROR:

soly. ±0.03 g(1)/100g sln (compiler)
temp. ±0.02 K and ±0.01 K near the UCST (precision of the measurements).

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 764-71.
VARIABLES:	**PREPARED BY:**
One temperature: 318 K	A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temperature of disappearance or reappearance of the cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 1096-1104.
VARIABLES:	**PREPARED BY:**
One temperature: 318 K	A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents, about 1 mL of each, were introduced into a small tube and stirred with a thermometer while the tube was warmed gradually in a bath of water or glycerol or was cooled with ice or a bath of acetone and dry ice. The temperature of disappearance or reappearance of the cloud was read three or four times in each direction. The proportion of components was modified to obtain critical solution temperature.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; dried.

(2) source not specified; b.p. 80.8°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Sieg, L. *Chem.-Ing.-Tech.* 1951, *23*, 112-3.
VARIABLES: One temperature: 319 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45.85°C.

Mutual solubility was presented on a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The cloud point method was used. A mixture of known composition was sealed in an ampoule and the temperature of appearance or disappearance of turbidity was observed. The ampoules and pipettes were filled in a moistureless atmosphere over P_2O_5.	(1) source not specified; boiled with Mg, fractionated; physical properties were in agreement with literature values. (2) source not specified, pure grade fractionated; physical properties were in agreement with literature values.
	ESTIMATED ERROR: not specified.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Quantie, C. *Proc. Roy. Soc., Ser. A* 1954, *224*, 90-104.
VARIABLES: One temperature: 322 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 49.2°C at 39.4 g(1)/100g sln.

The corresponding mole fraction value, x_1, calculated by the compiler is 0.534.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The cloud point method was used. The method was based on the fact that the separation of a noncritical mixture in a vertical tube starts with the formation of a sharp boundary at the top or the bottom. If the mixture is very near the critical concentration, diffuse boundaries start at both ends. Finally, if the mixture has the critical composition and the rate of cooling is slow, a sharp boundary appears at a certain height at critical temperature which is nearly independent of further variation of temperature.	(1) source not specified. (2) source not specified.
	ESTIMATED ERROR: not specified.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Cardinaud, R. *Bull. Soc. Chim. Fr.* 1960, 622-6.
VARIABLES:	PREPARED BY:
One temperature: 319 K	A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45.4°C at x_1 = 0.5.

The corresponding mass percentage, calculated by the compiler is 28 g(1)/100g sln.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The cloud point method was used. The components were weighed in ampoules and protected against moisture. The influence of water impurity (0.004 mole fraction) was investigated. Solubility data were reported in a graph.	(1) source not specified, purity 99.5%; boiled with Mg, distilled b.p. 64.7 °C. (2) source not specified; dried over $CaCl_2$, distilled over $Mg(ClO_4)_2$.
	ESTIMATED ERROR:
	temp. ±0.2°C.
	REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.; Shetlar, M.D.

J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 288 - 319 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of cyclohexane in methanol

$t/°C$	g(2)/100 ml(1)	g(2)/100g sln (compiler)	x_2 (compiler)
15	34.4	30.2	0.141
20	38.4	32.7	0.156
25	43.5	35.6	0.174
30	50.3	39.2	0.197
35	60.	43.6	0.227
40	74.	48.9	0.267
45.75	UCST		

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$d/d(4°C) = 0.80999 - 9.253\ 10^{-4}\ (t/°C) - 4.1\ 10^{-7}\ (t/°C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; n_D^{20} 1.3293, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Matheson, Coleman and Bell, spectroquality; used as received contained no unsaturated material, estimated impurities <0.02 mole%; n_D^{20} 1.4259.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2°C.

REFERENCES:

1. *International Critical Tables vol. 3*, New York, 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Debye, P.; Chu, B.; Kaufmann, H.

J. Chem. Phys. 1962, *36*, 3378-81.

VARIABLES:

One temperature: 318 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45.15°C at 30 g(1)/100g sln.

The corresponding mole fraction value, x_1, calculated by the compiler is 0.53.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The critical opalescence of binary liquid mixtures was investigated. The solutions were prepared from weighed amounts of components. The temperatures of phase separation were determined in separate experiments by visual observation. The solutions were filtered directly into the scattering cell through a thermostatted glass frit. The scattering cell was fitted with a stopcock using a teflon plug. Evaporation was estimated at < 0.5%.

SOURCE AND PURITY OF MATERIALS:

(1) Mallinckrodt, analytical grade; dried with calcinated CaO, refluxed for one day with CaO and NaOH, fractionally distilled only one peak by glc.

(2) Matheson, Coleman, and Bell; passed through a column of silica gel, distilled; only one peak by glc.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Gimler, G.H.; Gilmore, W.;

Huang, J.; Webb, W.W.

Phys. Rev. Lett. 1965, *14*, 491-4.

VARIABLES:

One temperature: 318 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45.222°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The refractive index along the coexistance curve was measured. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; purified.

(2) source not specified; purified.

ESTIMATED ERROR:

temp. ±0.01°C.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Marinichev, A.N.; Susarev, M.P. * *Zh. Prikl. Khim. (Leningrad)* 1965, *38*, 1619-21; *J. Appl. Chem. (USSR)* 1965, *38*, 1582-4.
VARIABLES:	**PREPARED BY:**
Temperature: 308 and 318 K Pressure: 334, 520 mHg	A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and cyclohexane

$t/^{\circ}C$	p/mmHg	x_1		100 w_1 (compiler)	
		(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
35	333.5	0.169	0.784	7.19	58.02
45	519.9	0.437	0.607	22.81	37.03

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Liquid - liquid equilibrium and vapor - liquid equilibrium data were measured with a Bushmakin apparatus, ref 1 and 2. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; purified;b.p. 64.65°C, $n_D(20^{\circ}C)$ = 1.3286, $\rho(20^{\circ}C)/\rho(4^{\circ}C)$ = 0.7915.

(2) source not specified; purified; b.p. 80.75°C, $n_D(20^{\circ}C)$ = 1.4263, $\rho(20^{\circ}C)/\rho(4^{\circ}C)$ = 0.7786.

ESTIMATED ERROR:

not specified

REFERENCES:

1. Bushmakin, I.N.; Voeikova, E.D. *Zh. Obshch. Khim.* 1949, *19*, 1615.
2. Bushmakin, I.N. *Zh. Obshch. Khim.* 1959, *32*, 812.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Roth, K.; Schneider, G.; Franck, E.U.

Ber. Bunsenges. Phys. Chem. 1966, *70*, 5-10.

VARIABLES:

Temperature: 264 - 437 K
Pressure : 0.1 - 563 MPa

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol and cyclohexane

t/°C	p/MPa	x_1	100 w_1	
23.	0.1	0.122	5.	
37.4	49.0	0.122	5.	
45.2	82.5	0.122	5.	
48.	97.0	0.122	5.	a)
50.2	102.0	0.122	5.	b)
60.0	126.5	0.122	5.	b)
75.2	167.5	0.122	5.	b)
90.6	213.5	0.122	5.	b)
108.1	271.0	0.122	5.	b)
131.1	353.0	0.122	5.	b)
150.7	425.0	0.122	5.	b)
40.0	0.1	0.262	12.	
51.6	34.0	0.262	12.	
54.6	46.0	0.262	12.	
58.1	62.5	0.262	12.	
63.6	88.5	0.262	12.	
65.0	95.0	0.262	12.	
67.7	112.5	0.262	12.	
71.55	132.0	0.262	12.	
79.8	183.0	0.262	12.	

a) solid-liquid-liquid equilibrium (extrapolated by the authors)
b) solid-liquid equilibrium

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The visual direct observation method was used. A mixture of known composition was placed in a high pressure cell with a colorless sapphire window described in ref 1. The cell was thermostatted in an Al block; commercial high pressure equipment was used and pressure was measured by weight manometer. Two procedures were used: changes of temp. at constant pressure and changes of pressure at constant temp. Both methods gave similar results; the second was less time-consuming and was used in most cases). Each point was measured several times.

SOURCE AND PURITY OF MATERIALS:

(1) Merck, for analysis grade; twice distilled with Mg turnings; impurities 0.02 mole % by temperature-time freezing curve; m.p. -98.0 ±0.2°C.
(2) BASF; distilled, crystallized, distilled; impurities 0.06 mole% by temperature-time freezing curve; m.p. 6.50 ±0.05°C.

ESTIMATED ERROR:

soly. ±1 % (estimated precision);
temp. < ±0.1°C;
pressure: ±5 MPa (0-400 MPa), ±10 MPa (400-600 MPa).

REFERENCES:

1. Schneider, G. *Z. Phys. Chem. (Frankfurt)* 1963, 37, 333.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Roth, K.; Schneider, G.; Franck, E.U.

Ber. Bunsenges. Phys. Chem. 1966, *70*, 5-10.

EXPERIMENTAL VALUES: (continued)

Solubility of methanol and cyclohexane

$t/°C$	p/MPa	x_1	100 w_1	
80.4	189.0	0.262	12.	
81.2	193.0	0.262	12.	a)
82.2	196.0	0.262	12.	b)
85.2	206.0	0.262	12.	b)
95.5	242.0	0.262	12.	b)
99.9	257.0	0.262	12.	b)
115.5	316.0	0.262	12.	b)
142.0	432.0	0.262	12.	b)
44.7	0.1	0.395	20.	
60.4	53.0	0.395	20.	
65.1	75.5	0.395	20.	
68.7	93.0	0.395	20.	
73.9	120.5	0.395	20.	
78.4	147.0	0.395	20.	
82.5	172.0	0.395	20.	
85.4	196.0	0.395	20.	
90.1	222.0	0.395	20.	a)
90.6	226.0	0.395	20.	b)
95.2	240.0	0.395	20.	b)
100.3	258.0	0.395	20.	b)
108.0	290.0	0.395	20.	b)
121.5	346.0	0.395	20.	b)
140.9	443.0	0.395	20.	b)
45.3	0.1	0.500	27.5	
55.0	28.5	0.500	27.5	
60.2	49.0	0.500	27.5	
64.9	71.0	0.500	27.5	
70.4	97.5	0.500	27.5	
79.8	148.0	0.500	27.5	
84.8	179.5	0.500	27.5	
89.9	215.0	0.500	27.5	
92.5	229.0	0.500	27.5	a)
96.2	244.0	0.500	27.5	b)
97.3	248.0	0.500	27.5	b)
99.5	259.0	0.500	27.5	b)
106.0	283.0	0.500	27.5	b)
118.9	338.0	0.500	27.5	b)
131.2	397.0	0.500	27.5	b)
139.6	446.0	0.500	27.5	b)
164.1	593.0	0.500	27.5	b)
44.4	0.1	0.635	40.	
54.1	29.5	0.635	40.	
59.4	50.0	0.635	40.	
68.3	91.0	0.635	40.	
75.1	125.0	0.635	40.	
80.6	158.0	0.635	40.	
86.5	194.0	0.635	40.	
88.6	208.0	0.635	40.	
89.4	213.0	0.635	40.	
90.85	223.0	0.635	40.	
91.1	224.0	0.635	40.	a)
92.1	233.0	0.635	40.	
93.6	236.0	0.635	40.	b)
95.5	251.0	0.635	40.	b)
100.9	262.0	0.635	40.	b)

(continued)

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Roth, K.; Schneider, G.; Franck, E.U.

Ber. Bunsenges. Phys. Chem. 1966, *70*, 5-10.

EXPERIMENTAL VALUES: (continued)

Solubility of methanol and cyclohexane

$t/°C$	p/MPa	x_1	$100\ w_1$	
113.1	319.0	0.635	40.	b)
131.7	416.0	0.635	40.	b)
147.1	509.0	0.635	40.	b)
39.4	0.1	0.725	50.	
53.5	44.0	0.725	50.	
60.0	72.5	0.725	50.	
65.0	97.0	0.725	50.	
70.1	121.5	0.725	50.	
75.1	150.0	0.725	50.	
79.9	177.0	0.725	50.	
83.3	200.0	0.725	50.	a)
84.4	208.0	0.725	50.	
85.0	211.0	0.725	50.	
85.6	216.0	0.725	50.	
85.9	210.0	0.725	50.	b)
87.3	214.0	0.725	50.	b)
90.5	228.0	0.725	50.	b)
98.1	255.0	0.725	50.	b)
111.8	319.0	0.725	50.	b)
133.6	442.0	0.725	50.	b)
30.1	0.1	0.795	60.	
44.1	45.0	0.795	60.	
50.0	70.5	0.795	60.	
58.05	109.0	0.795	60.	
64.05	141.0	0.795	60.	
64.5	143.0	0.795	60.	a)
66.8	156.0	0.795	60.	
69.65	160.5	0.795	60.	b)
75.7	181.0	0.795	60.	b)
80.2	198.0	0.795	60.	b)
90.4	239.0	0.795	60.	b)
100.2	286.0	0.795	60.	b)
117.6	386.0	0.795	60.	b)
13.	0.1	0.860	70.	
29.	59.0	0.869	70.	a)
30.1	59.5	0.860	70.	b)
40.1	88.0	0.860	70.	b)
51.0	121.5	0.860	70.	b)
64.5	143.0	0.860	70.	b)
70.1	194.0	0.860	70.	b)
90.4	286.0	0.860	70.	b)
110.1	392.0	0.860	70.	b)
127.3	510.0	0.860	70.	b)
-9.	0.1	0.912	80.	b)
19.5	81.5	0.912	80.	b)
29.	59.0	0.912	80.	b)
35.3	133.0	0.912	80.	b)
50.2	191.0	0.912	80.	b)
70.3	289.0	0.912	80.	b)
90.9	416.0	0.912	80.	b)
112.6	612.0	0.912	80.	b)

COMMENTS: Mass per cent values are presumably primary data and are given in the same form as in original paper.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Campbell, A.N.; Kartzmark, E.M.

Can. J. Chem. 1967, *45*, 2433-9.

VARIABLES:

Temperature: 313 - 319 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and cyclohexane

$t/^\circ C$	$100\ w_1$		x_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
40.0	10.1	51.9	0.228	0.739
45.0	15.7	40.4	0.329	0.640
45.5	18.0	37.7	0.366	0.614
45.6	19.5	37.5	0.389	0.612
45.8	19.5	35.2	0.389	0.588
45.87	22.5	35.2	0.433	0.588
46.0	UCST (interpolated)	-	-	-

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. A heterogeneous mixture was stirred for at least 24 h in a vessel with a mercury seal and then allowed to settle for another 24 h until the meniscus was clearly defined. Samples of each phase were weighed, a weighed excess of the appropriate pure component was added to produce homogeneity and the mixture was analyzed by the refractive index method.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, highest purity obtainable; $n_D(25^\circ C)$ = 1.32693.

(2) source not specified, highest purity obtainable; $n_D(25^\circ C)$ = 1.42352.

ESTIMATED ERROR:

temp. ±0.01 K (precision of thermostating).

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Kurtynina, L.M.; Smirnova, N.A.; Andrukovich, P.F.

Khim. Termodin. Rastvorov 1968, (2), 43-52.

VARIABLES:

One temperature: 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol in cyclohexane, 25°C: x_1 = 0.112, 100 w_1 = 4.58 (compiler).
Solubility of cyclohexane in methanol, 25°C: x_2 = 0.170, 100 w_2 = 34.98 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. A flask containing a stirrer with Hg seal was used. An equimolar mixture was thermostatted and mixed for 2.5 h and then allowed to separate until both phases were clear.
Composition was measured by density, usinf a pycnometer.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, pure grade; distilled; b.p. 64.53°C, $n_D(20°C)$ = 1.3288, $\rho(25°C)/\rho(4°C)$ = 0.78674.
(2) source not specified, pure for analysis grade; distilled; b.p. 80.74°C, $n_D(20°C)$ = 1.4263, $\rho(25°C)/\rho(4°C)$ = 0.77375.

ESTIMATED ERROR:

density ±0.00005 g/mL.
solubility: no estimates possible.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Rudakovskaya, T.S.; Soboleva, S.A.; Timofeev, V.S.; Serafimov, L.A.

***Zh. Prikl. Khim. (Leningrad)* 1968, *41*, 1556-61; *J. Appl. Chem. (USSR)* 1968, *41*, 1479-82.

VARIABLES:

One temperature: 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol in cyclohexane, 25°C: 100 w_1 = 4.6, x_1 = 0.11 (compiler).

Solubility of cyclohexane in methanol, 25°C: 100 w_2 = 35.2, x_2 = 0.155 (compiler).

Data for the ternary system cyclohexane-methanol-vinyl acetate are also given.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A titration method, ref 1, was used.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; purified; 0.01 mass% H_2O; b.p. 64.5°C, $n_D(20^\circ C)$ = 1.3290.

(2) source not specified; purified; 0.01 mass% H_2O; b.p. 80.5°C, $n_D(20^\circ C)$ = 1.4262.

ESTIMATED ERROR:

not specified.
density ±0.00005 g/mL.
solubility: no estimates possible.

REFERENCES:

1. Alders, L. *Zhidkostnaya ekstraktsiya*, I.L., 1962.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

1. Huang, J.S.; Webb, W.W.
J. Chem. Phys. 1969, *50*, 3677-93.

2. Warren, C.; Webb, W.W.
J. Chem. Phys. 1969, *50*, 3694-700.

3. Huang, J.S.; Goldburg, W.I.; Bjerkaas, A.W.
Phys. Rev. Lett. 1974, *32*, 921-3.

VARIABLES:

One temperature: 318 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

UCST/°C	vol% MeOH	x_1 (compiler)	100 w_1 (compiler)	ref.
45.135	28.6	0.289	0.517	1
45.29	28.6	0.289	0.517	2
45.140	-	-	-	3

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

1. The reflectivity of the critical interface as a function of temperature at 632.8 nm from a He-Ne laser was measured. The critical mixture was prepared in a glass optical cell sealed at liquid N_2 temp. Before each reflectivity measurement, the sample was stirred in a thermostat for 8-12 h. Experiments were repeated several times after 8 and 72 h. A Beckmann thermometer calibrated against a NBS Pt resistance thermometer was used. Composition was measured at 20°C.

2. The meniscus profile was determined in a cubic glass cell containing the mixture, which was illuminated with parallel light, from a photograph. The cell was carefully cleaned and dried before filling, then was placed in the water bath.

3. The mixture, sealed in a glass tube and placed in a water bath, was illuminated with of a 15-mW He-Ne laser. The bath temperature was stabilized at the critical temperature and then quickly dropped to about 2 mK below this value. The dynamic light-scattering behavior of the mixture undergoing phase separation near the critical point was studied.

SOURCE AND PURITY OF MATERIALS:

(1) Fisher Scientific Company, Analytical Reagent-grade, purity 99.9 %; twice distilled with Mg.

(2) Phillips Petroleum Company, purity > 99.99 %; used as received.

ESTIMATED ERROR:

temp. ±0.001 K for refs 1, 3; ±0.01 K for ref 2.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

1. Sergeeva, V.F.; Eskareva, L.A.
Zh. Obshch. Khim. 1969, *39*, 731-4; *Russ. J. Gen. Chem.* 1969, *39*, 697-9.

2. Sergeeva, V.F.; Eskareva, L.A.; Usmanova, I.Z.; Glybovskaya, V.A.
Zh. Obshch. Khim. 1971, *41*, 1895-9; *Russ. J. Gen. Chem.* 1971, *41*, 1908-11.

VARIABLES:

Temperature: 298, 313 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and cyclohexane

Coexisting phases ′ and ″

t°C	x_1′	x_2″	100 w_1′	100 w_2″	ref.
25	0.075	0.179	2.99	36.4	2
40	0.2451	0.2738	11.00	49.76	1

Data for the ternary systems cyclohexane-methanol-stearic acid and cyclohexane-methanol-naphthalene are also given in refs 1 and 2, resp.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used, with analyses by refractometry.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; anhydrous, dist. over Na; $n_D(20^{\circ}C)$ = 1.3288, $\rho(20^{\circ}C)/\rho)4^{\circ}$^C) = 0.7912.
(2) source not specified; treated with H_2SO_4 and HNO_3, washed with alkali and H_2O, dried over anhydrous Na_2SO_4, dist. over Na; m.p. 6.2°C, $n_D(20^{\circ}C)$ = 1.4262, $\rho(20^{\circ}C)/\rho)4^{\circ}$^C) = 0.7787.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Rabinovich, I.B.; Tsvetkov, V.G.
Zh. Fiz. Khim. 1971, *45*, 822-3;
Russ. J. Phys. Chem. (Engl. Transl.) 1971, *45*, 814.

VARIABLES:

One temperature: 319 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45.8°C. Solubility data are graphical only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The temperature of appearance of turbidity was observed. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1), (2) sources not specified; purified as described in ref 1.

ESTIMATED ERROR:

temp. ±0.1 K.

REFERENCES:

1. Rabinovich, I.B. *Vliyanie izitopii na fiziko-. khimicheskie svoistva zhidkostei*, Izd. Nauka, Moskva, 1968.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Budantseva, L.S.; Lesteva, T.M.; Nemtsov, M.S.
Zh. Fiz. Khim. 1976, *50*, 1343-4;
Russ. J. Phys. Chem. (Engl. Transl.) 1976, *50*, 814; **Dep. Doc. VINITI* 1976, 438.

VARIABLES:

One temperature: 293 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES: Solubilities, 20°C:

methanol in cyclohexane: x_1 = 0.1390, 100 w_1 = 5.790 (compiler);
cyclohexane in methanol: x_2 = 0.1430, 100 w_2 = 30.47 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used, with analyses by glc. Measurements only for ternary systems are described.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.
(2) source not specified; dist., purity > 99.9%

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Takeuchi, S.; Nitta, T.; Katayama, T.

J. Chem. Ind. Jpn. 1975, *8*, 248-50.

VARIABLES:

One temperature: 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities at 25°C:

methanol in cyclohexane: $x_1 = 0.1291$, $100\ w_1 = 5.34$ (compiler).

cyclohexane in methanol: $x_2 = 0.1752$, $100\ w_2 = 35.81$ (compiler).

Data are also given for the ternary system methanol-cyclohexane-cyclopentane.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used, with components handled under dry N_2. A 30-mL tube with screw cap, and containing 15 mL mixture, was thermostated at 25°C in a liquid paraffin bath, shaken violently after thermal equilibration, then let stand for > 6 h. 1 mL samples were removed with preheated syringes, transferred to tubes with 0.5 mL toluene to prevent phase separation, and analyzed by glc (Shimadzu glc GC-4A, integrator ITG-2A).

SOURCE AND PURITY OF MATERIALS:

(1) Merck Uvasol, spectral grade, dried with molecular sieve 3A, dist.; small imputity by glc (area ratio 1:700).

(2) Wako Pure Chemical Ind., ltd., guaranteed grade; dried with molecular sieve 4A, dist.; no impurities by glc.

ESTIMATED ERROR:

not specified

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Sugi, H.; Nitta, T.; Katayama, T.

J. Chem. Ind. Jpn. 1975, *9*, 12-6.

VARIABLES:

One temperature: 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities at 25°C:

methanol in cyclohexane: $x_1 = 0.1250$, $100\ w_1 = 5.158$ (compiler).

cyclohexane in methanol: $x_2 = 0.1717$, $100\ w_2 = 35.25$ (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A titration method similar to that of ref 1 was used. A pre-weighed amount of homogeneous liquid mixture was placed in a thermostated 100-mL flask fitted with a cap through which two piston burets were inserted. One component was titrated to a turbid endpoint, then the other was added until turbidity disappeared. The procedure was repeated several times.

SOURCE AND PURITY OF MATERIALS:

(1) Wako Chemical Ind., Ltd., spectrograde reagent, dried with molecular sieve 3A, fractionated.

(2) Wako Chemical Ind., ltd., guaranteed reagent; dried with molecular sieve 4A, fractionated.

ESTIMATED ERROR:

temp. ±0.01 K

REFERENCES:

1. Othmer, D.F.; White, R.E.; Trueger, E. *Ind. Eng. Chem.* 1941, *33*, 1240.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Jacobs, D.T.; Anthony, D.J.;
Mockler, R.C.; O'Sullivan, W.J.
Chem. Phys. 1977, *20*, 219-26.

VARIABLES:

One temperature: 319 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45.474°C at 28.94 g(1)/100g sln.

The corresponding mole fraction value, x_1, calculated by the compiler is 0.5168.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The refractive index was measured as a function of temperature in one- and two- phase region. A heated aluminium cell of an equilateral triangle shape with a one inch hole bored parallel to the base and held by two optically flat pieces of glass sealed with teflon was used. The temperature was monitored with a thermistor. Before filling, the cell was baked overnight in an oven at 110°C and then cooled in a dry box (dry nitrogen atmosphere and desiccant). The components were separately syringed into the cell while in the dry box and the cell was sealed and weighed.

SOURCE AND PURITY OF MATERIALS:

(1) Fischer, spectranalyzed grade, purity 99.95%; used as received; the major impurity was water.

(2) Fischer, spectranalyzed grade, purity 99.98%, used as received; the major impurity was water; n_D^{25} 1.4232.

ESTIMATED ERROR:

soly. ±0.03% by weight of water in the fluid;
temp. ±0.015°C.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Scheibner, B.A.; Sorensen,C.M.;
Jacobs, D.T.; Mockler, R.C.;
O'Sullivan, W.J.
Chem. Phys. 1978, *31*, 209-16.

VARIABLES:

One temperature: 318 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45.043°C at 29.03 g(1)/100g sln.

The corresponding mole fraction value, x_1, calculated by the compiler is 0.5179.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The sample cell consisted of two pyrex spheres joined by a length of precision bore tubing. The total mass of the sample was 40.238 g. The sample cell was filled in a dry box under a nitrogen atmosphere heated to well above critical temperature (T_c), shaken vigorously and then mounted in a well stirred oil bath at a temperature 5 K above T_c. After several days of equilibration the critical point was located.

SOURCE AND PURITY OF MATERIALS:

(1) Fisher, "spectranalyzed", purity 99.95%; d_4^{20} 0.7914.

(2) Fisher, "spectranalyzed", purity 99.98%; d_4^{20} 0.7786.

ESTIMATED ERROR:

temp. ±0.001 K;
composition ±0.02 g(1)/100g sln.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Becker, F.; Kiefer, M.; Rhensius, P.
Spoerner, A.; Steiger, A.
Z. Phys. Chem. (Wiesbaden) 1978,
112, 139-52.

VARIABLES:

Temperature: 304 - 318 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and cyclohexane

t/°C	x_1		g(1)/100g sln (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
30.70	0.165	-	7.00	-
31.10	-	0.794	-	59.5
33.30	0.184	-	7.91	-
33.60	-	0.780	-	57.4
35.75	-	0.766	-	55.5
36.80	0.217	-	9.54	-
37.30	0.222	-	9.80	-
37.55	-	0.752	-	53.6
38.80	0.242	-	10.84	-
39.05	-	0.739	-	51.9
39.55	0.254	-	11.48	-
40.20	0.263	-	11.96	-
40.40	-	0.724	-	50.0
40.95	0.273	-	12.51	-
41.40	0.283	-	13.06	-
41.45	-	0.710	-	48.2

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A cylindrical glass vessel of 5 mL capacity containing a capillary for mixture injections, a tube for resistance thermometer, tubes for in- and output of dry nitrogen, magnetic stirrer, a jacket for flow of thermostating liquid and external vacuum jacket was used. The light beam going through the liquid fell on phototransistor (Simens BPX 81 III) and was registered. The signal was smaller by 20-40% when second phase begin to appear.

SOURCE AND PURITY OF MATERIALS:

(1) Merck, for analysis grade; dried over $CaCl_2$, fractionated; b.p. 64.5°C at 752 Torr, n_D^{20} 1.3286.

(2) Merck, for analysis grade; purified by column chromatography on silica gel and then on basic aluminium oxide; f.p. 6.60°C, n_D^{20} 1.4264.

ESTIMATED ERROR:

soly. ±0.001 mole fraction;
temp. ±0.05°C, ±0.01°C (stability of thermostating).

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Becker, F.; Kiefer, M.; Rhensius, P. Spoerner, A.; Steiger, A. *Z. Phys. Chem. (Wiesbaden)* 1978, *112*, 139-52.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and cyclohexane

t/°C	x_1		g(1)/100g sln (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
42.15	0.300	-	14.03	-
42.45	-	0.695	-	46.5
42.70	0.313	-	14.78	-
43.15	-	0.680	-	44.7
43.20	0.329	-	15.73	-
43.70	-	0.666	-	43.2
43.85	0.347	-	16.83	-
44.10	0.358	-	17.51	-
44.15	-	0.656	-	42.1
44.40	0.372	-	18.40	-
44.60	0.382	-	19.05	-
44.60	-	0.637	-	40.1
44.75	0.393	-	19.78	-
44.90	-	0.619	-	38.2
44.95	0.409	-	20.85	-
45.05	-	0.603	-	36.6
45.15	0.423	0.590	21.82	35.4
45.20	0.436	0.576	22.74	34.1
45.25	-	0.563	-	32.9
45.30	0.451	-	23.82	-
45.30	0.463	-	24.71	-
45.30	-	0.551	-	31.8
45.35	0.475	-	25.62	-
45.35	0.487	-	26.55	-
45.35	0.499	-	27.49	-
45.35	-	0.539	-	30.8
45.35	-	0.525	-	29.6
45.35 UCST	0.513	0.513	28.6	28.6

COMPONENTS: (1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	ORIGINAL MEASUREMENTS: Yosida, Y.; Ikushima, A. *J. Phys. Soc. Jpn.* 1978, *45*, 1949-56.
VARIABLES: One temperature: 318 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 318.25 K.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: The intensity of the Rayleigh scattering was measured near the critical point. The critical temperature corresponded to the maximum scattering intensity.	SOURCE AND PURITY OF MATERIALS: (1) Dotite Spectrozole; used as received. (2) Dotite Spectrozole; used as received.
	ESTIMATED ERROR: temp. ±0.01 K.
	REFERENCES:

COMPONENTS: (1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	ORIGINAL MEASUREMENTS: Balasubramanian, D.; Mitra, P. *J. Phys. Chem.* 1979, *83*, 2724-7.
VARIABLES: One temperature: 322 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 49.1°C at x_1 = 0.51.

The corresponding mass percentage, calculated by the compiler is 28 g(1)/100g sln.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: The method was described in ref 1. The experiments were conducted with sealed tubes to avoid moisture contamination. No further details were reported.	SOURCE AND PURITY OF MATERIALS: (1) source not specified, the best analytical grade available; used as received. (2) source not specified, the best analytical grade available; used as received.
	ESTIMATED ERROR: not specified.
	REFERENCES: 1. Hales, B.J.; Bertrand, G.L.; Hepler, L.G. *J. Phys. Chem.* 1960, *70*, 3970.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	1. Nagata I.; Katoh, K. *Thermochim. Acta* 1980, *39*, 45-62. 2. Nagata, I.;Katoh, K.; Koyabu, J. *Thermochim. Acta* 1981, *47*, 225-33. 3. Nagata, I.; Ohta, T. *J. Chem. Eng. Data* 1983, *28*, 256-9.
VARIABLES:	PREPARED BY:
Temperature: 298, 313 K	A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and cyclohexane
Coesisting phases ' and "

$t/^\circ C$	x_1'	x_2''	$100\ w_1'$	$100\ w_2''$	ref
25	0.1244	0.1715	5.132	35.22	1
40	0.2371	0.2652	10.58	48.66	2
25	0.1250	0.1713	5.160	35.19	3

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Titration and analytical methods were used. On the flat, polished upper face of an equilibrium vessel was a lid fitted with a Teflon O-ring and held tightly by bolts. The lid contained two feed tubes, two sampling tubes, a thermistor and a pressure measuring tube connected to a Hg manometer. The lower sampling tube was pressurized with N_2. The vessel was immersed in a water thermostat. During titration, component 2 was added from a buret to a known amount of component 1 until the mixture became turbid. In the analytical method a mixture was stirred for 2 h and after complete separation samples were taken by preheated hypodermic syringes and analyzed by glc.

SOURCE AND PURITY OF MATERIALS:

(1) Wakoh Chemical Co., spectrograde; used as received; $n_D(25^\circ C) = 1.32658$.
(2) Wakoh Chemical Co., spectrograde; used as received or dist.; $n_D(25^\circ C) = 1.42352$.

ESTIMATED ERROR:

temp. ±0.01 K.
solubility ±0.002 mole fraction.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Eden, D.

Rev. Sci. Instrum. 1982, *53*, 105-6.

VARIABLES:

One temperature: 318 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45.05°C at an unspecified composition.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The turbidity of a sample of known composition was measured at 632.8 nm in a specially-constructed cell. The components were introduced with syringes, then the cell was sealed by a stopcock and placed in a water bath. No further details are given.

SOURCE AND PURITY OF MATERIALS:

(1), (2) sources not specified, dry.

ESTIMATED ERROR:

temp. ±0.0015 K;

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Kopelman, R.B.; Gammon, R.W.;
Moldover, M.R.

Phys. Rev. 1984, *29A*, 2048-53.

VARIABLES:

One temperature: 319 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45.83°C at 0.2898 volume fraction of methanol.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The turbidity of a mixture close to the critical point was measured. A thin cell (0.2 mm optical path) with a very small volume (0.08 mL) was used to avoid multiple scattering. The "momentary" critical temperature method which exploited the rapid thermal response of the inner stages of the thermostat and the sample as well as the secular increase in critical temperature was selected. The thermostat was set to a temperature just above the expected critical temperature and the turbidity was monitored. The critical concentration was determined by observing the behavior of the meniscus near the critical temperature. Care was taken to avoid contact of components with moisture.

SOURCE AND PURITY OF MATERIALS:

(1) Baker, analyzed grade "photorex" < 0.02 % water impurity; used as received.

(2) Mallinkrodt, "SpectrAR" spectrophotometric grade; < 0.02 % water impurity; used as received.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]
(2) Cyclohexane; C_6H_{12}; [110-82-7]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Tveekrem, J.L.; Jacobs, D.T.
Phys. Rev. 1983, *27A*, 2773-6.

VARIABLES:

Effect of water on T_c and x_c

PREPARED BY:

J.W. Lorimer and A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 49.725°C at 29.3 g(1)/100g sln.

The corresponding mole fraction value, x_1, calculated by the compiler is 0.521.

For additions of water, the following results were found:

water concentration		t_c/°C	β	ϕ_c
vol.%	x_3			
0.05	0.002	49.725	0.325	0.302
0.45	0.018	65.597	0.338	0.319
0.65	0.025	72.494	0.338	0.323
0.85	0.033	79.465	0.344	0.331

Mole fraction of water, x_3, was calculated by compiler from volume fraction ϕ_3, by assuming no volume of mixing and tabulated densities for pure components:

$$x_3 = \frac{\phi_3[V_2 + x_1(V_1 - V_2)]}{V_3 - \phi_3(V_3 - V_2)}$$

where V_i is the molar volume for pure component i.
The data in the table were fitted with the scaling equation

$$\Delta n = b\ (1 - T/T_c)^{\beta}$$

by least squares, with Δn the difference in refractive index between coexisting phases, b a constant and β the critical index. The relative changes of T_c and ϕ_c were found to be linear in vol % H_2O, and proportional to one another:

$$\phi_c/\phi_{co} - 1 = k(T_c/T_{co} - 1)$$

with k = 1.0 and subscript *co* indicating the critical value with no added water.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The refractive index difference between two phases, which is proportional to the difference in volume fraction between the phases, was used as a measure. Before filling, the cell was baked overnight and allowed to cool in a dry nitrogen atmosphere. The total volume of the mixture was 6.2 mL. The method was described in ref 1. The influence of impurity effects of water on the critical temperature was measured.

SOURCE AND PURITY OF MATERIALS:

(1) Matheson, Coleman, and Bell, spectrophotometric grade; used as received.

(2) Matheson, Coleman, and Bell, spectrophotometric grade; used as received.

ESTIMATED ERROR:

temp. ±0.0015 K;
composition ±0.1 g(1)/100g sln,
impurities 0.05 ±0.1 vol % of H_2O.

REFERENCES:

1. Jacobs, D.T.
J. Phys. Chem. 1982, *86*, 1895.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

(3) Acetone (2-propanone, dimethyl ketone); C_3H_6O; [67-64-1]

ORIGINAL MEASUREMENTS:

Cohn, R.H.; Jacobs, D.T.

J. Chem. Phys. 1984, *80*, 856-9.

VARIABLES:

Effect of acetone (3) on T_c and x_c

PREPARED BY:

A. Skrzecz and J.W. Lorimer

EXPERIMENTAL VALUES:

The UCST was reported to be 47.410°C at volume fraction of methanol 0.304 = 29.6 ±0.1 g(1)/100g sln = 0.525 mole fraction (mole fraction by compiler).

For additions of acetone, the following results were found:

acetone concentration vol.%	x_3	t_c/°C	β	ϕ_c
0.00	0.0000	47.410	0.329	0.304
0.52	0.0053	45.560	0.330	0.301
1.05	0.0107	43.853	0.337	0.299
1.53	0.0155	42.33	-	0.296

Mole fraction of acetone, x_3, was calculated by compiler from volume fraction ϕ_3, by assuming no volume of mixing and tabulated densities for pure components:

$$x_3 = \frac{\phi_3[V_2 + x_1(V_1 - V_2)]}{V_3 - \phi_3(V_3 - V_2)}$$

where V_i is the molar volume for pure component i.
The data in the table were fitted with the scaling equation

$$\Delta n = a\ ((T_c - T)/T_c)^{\beta}$$

by least squares, with Δn the difference in refractive index between coexisting phases, a a constant and β the critical index. The relative changes of T_c and ϕ_c were found to be proportional:

$$\phi_c/\phi_{co} - 1 = k(T_c/T_{co} - 1)$$

with k = 1.0 and subscript *co* indicating the critical value with no added acetone.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The refractive index method was used. The fluids were put into a cell which was sealed to prevent evaporation or contamination. The refractive index of each phase (as a measure of volume fraction) was determined at 632.8 nm with resolution of 0.00015.
The coexistence curve as a function of refractive index was presented graphically. The influence of impurities (acetone) was tested.

SOURCE AND PURITY OF MATERIALS:

(1) J.T. Baker, spectrophotometric grade; used as received.

(2) Kodak, spectrophotometric grade; used as received.

ESTIMATED ERROR:

soly. ±0.002 volume fraction at UCST
temp. ±0.0015 K (experimental),
±0.015 K (UCST).

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

1. Nagata I.

   Fluid Phase Equilib. 1984, *18*, 83-92.

2. Nagata, I.

   J. Chem. Thermodyn. 1984, *16*, 737-41.

VARIABLES:

One temperature: 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and cyclohexane
Coesisting phases ′ and ″

$t/^\circ C$	x_1'	x_2''	$100\ w_1'$	$100\ w_2''$	ref
25	0.1248	0.1714	5.149	35.20	1
25	0.1251	0.1712	5.163	35.17	2

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The turbidity titration method was used. For details, see ref 1.

SOURCE AND PURITY OF MATERIALS:

(1) Wakoh Pure Chemical Industries Ltd., spectrograde; dried over CaO, dist.; $\rho(25^\circ C) = 0.7865$.
(2) Wakoh Pure Chemical Industries Ltd., special grade; dist.; $\rho(25^\circ C) = 0.7739. = 1.42352$.

ESTIMATED ERROR:

temp. ±0.01 K.
solubility < ±0.001 mole fraction.

REFERENCES:

1. Nagata, I.; Katoh, K.; *Thermochim. Acta* 1980, *39*, 45.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Houessou, C.; Guenoun, P.; Gastaud, P.; Perrot, F.; Beysens, D.

Phys. Rev. A 1985, *32*, 1818-33.

VARIABLES:

One temperature: 318 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 44.826°C at 28.97 g(1)/100g sln.

The corresponding mole fraction value, x_1, calculated by the compiler is 0.5172.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

An initially homogeneous mixture was thermally quenched through a few mK. If a ring of scattered light appeared indicating spinodal decomposition, then it was assumed that initial temperature was T_c. The mass composition of the mixture was determined by weighing with a resolution of 0.1 mg. The coexistence curves were determined, as in ref 1, by measuring the refractive index in both phases in the inhomogeneous region. During the operations care was taken to avoid moisture and dust by baking the syringes and cells over night under vacuum and preparing the mixtures in a dust-free area.

SOURCE AND PURITY OF MATERIALS:

(1) Merck, guaranteed purity > 99.5% main impurities: ethanol < 0.1%, water < 0.05%, acetone < 0.01%; used as received.

(2) Eastman Kodak company, < 0.02% of water; used as received.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Jacobs, D.T.; Anthony, D.J.; Mockler, R.C.; O'Sullivan, W.J. *Chem. Phys.* 1977, *20*, 219.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Singh, R.R.; van Hook, A.

J. Chem. Thermodyn. 1986, *18*, 1021-4.

VARIABLES:

One temperature: 319 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 318.816 K at $x_1 = 0.508$.

The corresponding mass percentage, calculated by the compiler is 28.2 g(1)/100g sln.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was not described. Neither pure liquid nor mixtures were exposed to the atmosphere at any time. Degassing was carried out using at least five free-pump-thaw cycles with a pumping pressure of 0.001 Pa or less. The mean value was reported. The gas effect on liquid-liquid critical point was studied.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; dried over molecular sieve, fractionated, distilled from magnesium turning under argon atmosphere.

(2) source not specified; fractionated, degassed, dried numerous times over fresh sodium

ESTIMATED ERROR:

temp. ±0.002 K.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Hradetzky, G.; Bittrich, H.-J.

Int. Data Ser., Sel. Data Mixtures, Ser. A 1986, 218.

VARIABLES:

Temperature: 275 - 319 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and cyclohexane

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
275.61	-	0.8862	-	74.78
278.55	-	0.8793	-	73.50
280.05	0.0716	-	2.85	-
280.15	0.0699	-	2.78	-
281.25	-	0.8737	-	72.48
283.95	0.0732	-	2.92	-
284.05	0.0800	-	3.20	-
285.95	0.0817	-	3.28	-
286.25	-	0.8616	-	70.33
288.45	0.0910	-	3.67	-
291.35	-	0.8475	-	67.91
292.55	0.0998	-	4.05	-
294.61	-	0.8372	-	66.19
295.65	0.1117	-	4.57	-
298.91	-	0.8222	-	63.78

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud-point method was used. Glass ampoules of about 20 mL capacity filled with known masses of pure components and sealed carefully to avoid contamination with moisture were immersed in a water thermostat equipped with a Hg-in-glass thermometer (ASMW, certified by the Bureau of Standards, GDR). Phase changes were observed visually as the mixture was cooled at 0.02 K/min Weighings accurate to 0.0001 g. Readings accurate to within 0.01 K. Reproducibility of temp. better than 0.03 K. Critical solution temp. and composition determined graphically using Caillet-Mathias rule. Monotectic temp. and compositions determined graphically.

SOURCE AND PURITY OF MATERIALS:

(1) VEB Leuna Werke (Leuna, GDR), stated purity > 99.9 mass %; used as received; < 50 mg/kg water as determined by Karl Fischer method.

(2) VEB Laborchemie (Apolda, GDR), analytical grade; washed with H_2SO_4, fractionally dist., dried over molecular sieve type 3A; purity 99.9 mole % by capillary glc (no aromatic impurities).

ESTIMATED ERROR:

soly. ±0.0005 mole fraction, ±0.002 (monotectic (1)-rich phase), ±0.003 mole fraction (UCST, monotectic, (2)-rich phase);

temp. ±0.03 K (LLE, UCST), ±0.1 K (SLE - (1)-rich phase), ±0.2 K (SLE - (2)-rich phase), ±0.3 K monotectic temp

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Hradetsky, G.; Bittrich, H.-J. *Int. Data ser., Sel. Data Mixtures, Ser. A.* <u>1986</u>, 218.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and cyclohexane

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
299.55	0.1364	-	5.67	-
302.35	0.1545	-	6.50	-
302.37	-	0.8050	-	61.12
307.13	-	0.7767	-	56.98
308.69	0.2036	-	8.87	-
308.75	0.2042	-	8.90	-
309.21	0.2093	-	9.16	-
309.85	-	0.7595	-	54.59
312.43	-	0.7372	-	51.64
312.48	-	0.7352	-	51.39
312.67	-	0.7343	-	51.27
312.99	0.2525	-	11.40	-
314.43	-	0.7156	-	48.93
315.45	-	0.6911	-	46.00
315.53	-	0.6918	-	46.08
315.57	0.3065	-	14.40	-
316.10	-	0.6797	-	44.69
316.87	-	0.6571	-	42.18
317.00	0.3505	-	17.04	-
317.15	-	0.6493	-	41.35
317.67	-	0.6217	-	38.49
318.15	-	0.6028	-	36.62
318.45	0.4133	-	21.15	-
318.64	0.4476	-	23.58	-
318.73	-	0.5435	-	31.19
318.85	0.4670	-	25.01	-
318.93	0.4861	-	26.48	-
318.93	0.4940	-	27.10	-
318.93 UCST	0.5060	0.5060	28.06	28.06

Liquidus curves of methanol and cyclohexane

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
252.65	-	0.9391	-	85.45
264.15	-	0.9190	-	81.20
267.15	-	0.9132	-	80.02
269.85	-	0.8999	-	77.39
275.4 a)	0.058	0.889	2.29	75.3
276.2	0.0473	-	1.855	-
276.4	0.0386	-	1.506	-
277.0	0.0269	-	1.041	-
277.0	0.0216	-	0.834	-
277.2	0.0202	-	0.779	-
279.6	0.0000	-	0.000	-

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Jacobs, D.T.

Phys. Rev. A 1986, *33*, 2605-11.

VARIABLES:

One temperature: 319 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45.944°C at 29.41 g(1)/100g sln.

The corresponding mole fraction value, x_1, calculated by the compiler is 0.5232.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The turbidity above upper critical consolute point was measured. The transmitted light intensity of a laser beam (Melles Griot 05-LLP-831 3mW polarized He-Ne laser, 632.8 nm) compared to the incident light intensity was used to determine an effective extinction. The composition was prepared by weight. The components were loaded into the cell in a dry box under dry N_2 atmosphere. The cell was immersed in a well stirred water bath, the temperature was monitored.

SOURCE AND PURITY OF MATERIALS:

(1) Baker Photrex, purity 99.9+%, less than 0.05% H_2O; used as received.

(2) Kodak Spectro ACS, purity 99.9+% less than 0.02% H_2O; used as received.

ESTIMATED ERROR:

soly. ±0.05 g(1)/100g sln;
temp. ±0.001 K (UCST).

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Schmidt, J.W.

J. Chem. Phys. 1986, *85*, 3631-5.

VARIABLES:

One temperature: 319 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45.5°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The UCST was located by using bulk index of refraction measurements. Upon comparison with ref 1, author estimated that there was about 0.01% H_2O in the sample.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, purity 99.8% with < 0.1% H_2O.

(2) source not specified, contain < 0.02% H_2O.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Eckfeld, E.L.; Lucasse, W.W. *J. Chem. Phys.* 1943, *47*, 164.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Schoen, W.; Wiechers, R.;

Woermann, D.

J. Chem. Phys. 1986, *85*, 2922-8.

VARIABLES:

One temperature: 318 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 45.138°C at x_1 = 0.524.

The corresponding mass percentage, calculated by the compiler is 29.5 g(1)/100g sln.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The differences of refractive index between two coexisting liquid phases were measured. The samples were prepared by mixing the required weight of components in a glove box. The deflection of a He/Ne laser beam after passing through the two compartments of the differential refractometer cell was measured as the distance necessary to shift the light detection unit. The refractive index of the coexisting phases was related to the composition by measuring several mixtures as function of temperature. The measurements were made over the range: UCST - 2 K.

SOURCE AND PURITY OF MATERIALS:

(1) Merck, Uvasol quality, guaranteed purity > 99.7 %, water < 0.03 %; used as received.

(2) Aldrich, Gold Label quality, guaranteed purity > 99 %, water < 0.005 %; used as received.

ESTIMATED ERROR:

temp. ±0.002 K (UCST),
±0.003 K (24 h stability).

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Brunner, E.

J. Chem. Thermodyn. 1988, *20*, 439-45.

VARIABLES:

One temperature: 318 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 318.10 K at x_1 = 0.508.

The corresponding mass percentage, calculated by the compiler is 28.2 g(1)/100g sln.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The effect of small amounts of dissolved gases and water on critical temperature was investigated. Critical temperature was determined visually as the temperature slowly decreased (cooling rate <0.0002 K/s). The reported UCST was the value for water-free mixture extrapolated from four series (each of four or five measurements) of experiments with known concentrations of water.

SOURCE AND PURITY OF MATERIALS:

(1) Merck; used as received; purity 99.99 mole % by glc, 0.004 mole % of H_2O by the Karl Fischer method.

(2) BASF, purity 99.7 wt%; distilled; purity 99.94 mole% by glc, 0.0075 mole % of H_2O by the Karl Fischer method.

ESTIMATED ERROR:

temp. ±0.05 K (UCST water-free),
±0.01 K (reproducibility).

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Singh, R.R.; Van Hook, W.A.

J. Chem. Phys. 1987, *87*, 6097-110.

VARIABLES:

Temperature: 318 - 319 K
Pressure : 0.1 - 12.6 MPa

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol and cyclohexane

T/K	*p*/MPa	x_1	100 w_1 (compiler)
317.541	0.1	0.3617	17.75
317.938	0.1	0.3715	18.37
318.541	0.1	0.4158	21.32
319.252	2.02	0.4158	21.32
320.050	4.67	0.4158	21.32
320.745	6.98	0.4158	21.32
321.332	9.04	0.4158	21.32
321.268	8.76	0.4158	21.32
321.200	8.52	0.4158	21.32
318.502	0.1	0.4216	21.72
318.652	0.1	0.4305	22.35
319.771	3.44	0.4305	22.35
320.642	6.18	0.4305	22.35
320.645	6.18	0.4305	22.35
320.638	6.15	0.4305	22.35
321.586	9.17	0.4305	22.35
322.307	11.56	0.4305	22.35
322.288	11.39	0.4305	22.35
322.246	11.23	0.4305	22.35
322.216	11.14	0.4305	22.35

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The point at which the intensity of an emerging beam from a 3-mW He-Ne laser decreased to one-half its incident value was taken as the temperature of phase separation. For a run, the cell with magnetic stirrer was warmed to about 5-10 K above T_c and a sample, prepared gravimetrically, was added under vacuum. The pressure was set manually and the bath temperature then allowed to decrease at about 2-5 mK per min, while a computer continously monitored pressure, temperature and light intensity. The rapid change in intensity at the transition was used to instruct the computer to store the relevant data, then to warm the apparatus and repeat the experiment a preselected number of times. For details, see ref 1.

SOURCE AND PURITY OF MATERIALS:

(1) Aldrich Chemical Co.,isotopic purity 99.5 % D; purified over Mg-activated I_2, 2X dist. under dry Ar; no impurities by glc.
(2) Fisher Scientific, ASC grade; stored over Na wire, distilled in a spinning band column; no impurities by glc.

ESTIMATED ERROR:

temp. ±0.001 K (reproducibility); pressure ±0.01 MPa.

REFERENCES:

1. Singh, R.R. *Thesis*, University of Tennesee, 1987.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Singh, R.R.; Van Hook, W.A.

J. Chem. Phys. 1987, *87*, 6097-110.

EXPERIMENTAL VALUES: (continued)

Solubility of methanol and cyclohexane

T/K	p/MPa	x_1	100 w_1 (compiler)	
318.709	0.1	0.4404	23.05	
319.647	3.07	0.4404	23.05	
320.473	5.63	0.4404	23.05	
321.694	9.59	0.4404	23.05	
322.411	11.82	0.4404	23.05	
322.533	12.06	0.4404	23.05	
318.761	0.1	0.4520	23.90	
319.763	3.19	0.4520	23.90	
320.715	6.44	0.4520	23.90	
320.758	6.53	0.4520	23.90	
321.663	9.36	0.4520	23.90	
322.638	12.55	0.4520	23.90	
322.625	12.49	0.4520	23.90	
318.799	0.1	0.4704	25.27	
318.805	0.1	0.4841	26.32	
319.768	3.07	0.4841	26.32	
320.673	5.95	0.4841	26.32	
321.519	0.88	0.4841	26.32	
321.488	8.50	0.4841	26.32	
321.493	8.51	0.4841	26.32	
322.613	12.17	0.4841	26.32	
318.793	0.1	0.4899	26.77	
318.815	0.1	0.4940	27.10	
319.796	3.05	0.4940	27.10	
319.770	2.94	0.4940	27.10	
319.752	2.74	0.4940	27.10	
320.829	6.16	0.4940	27.10	
320.785	5.94	0.4940	27.10	
322.067	10.01	0.4940	27.10	
322.064	9.99	0.4940	27.10	
322.155	10.20	0.4940	27.10	
322.805	12.32	0.4940	27.10	
318.785	0.1	0.4993	25.52	
318.815	0.1	0.514	28.7	UCST calc. by authors at 0.1 mPa
318.803	0.1	0.5318	30.19	
319.704	2.86	0.5318	30.19	
320.780	6.20	0.5318	30.19	
321.745	9.31	0.5318	30.19	
322.467	11.78	0.5318	30.19	
322.457	11.73	0.5318	30.19	
321.797	9.54	0.5318	30.19	
318.800	0.1	0.5363	30.57	
319.782	3.13	0.5363	30.57	
320.787	6.26	0.5363	30.57	

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Singh, R.R.; Van Hook, W.A. *J. Chem. Phys.* 1987, *87*, 6097-110.

EXPERIMENTAL VALUES: (continued)

Solubility of methanol and cyclohexane

T/K	p/MPa	x_1	100 w_1 (compiler)
321.728	9.23	0.5363	30.57
321.691	9.09	0.5363	30.57
318.714	0.1	0.5783	34.30
318.661	0.1	0.5886	35.26
319.623	2.69	0.5886	35.26
320.700	6.09	0.5886	35.26
318.130	0.1	0.6315	39.48

COMMENTS AND ADDITIONAL DATA:

The authors give extensive analysis of their data, with fitting equations of the form

$$x_1 = x_{c1} \pm A|1-T/T_c^{\circ}|$$

$$T_c^{\circ} = T_c + cp$$

where T_c, T_c° are the critical solution temperatures at zero pressure and pressure p, x_{c1} is the critical composition, $c = (3.173 \pm 0.012) \times 10^{-1}$ K MPa^{-1} is the pressure coefficient of T_c and A is an amplitude constant. For analysis of all data at all pressures, they find T_c/K = 318.827 ± 0.005, x_{c1} = 0.514 ± 0.00, while for data at 0.1 MPa alone, T_c/K = 318.815 ± 0.003, x_{c1} = 0.511 ± 0.002.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Aizpiri, A.G.; Rubio, R.G.;
Diaz Peña, M.

J. Chem. Phys. 1988, *88*, 1934-43.

VARIABLES:

Temperature: 300 - 323 K
Pressure: 0.1 - 14.4 MPa

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol and cyclohexane

T/K	p/MPa	x_1	100 w_1 (compiler)
306.720	1.01	0.1630	6.90
307.218	2.64	0.1630	6.90
307.781	4.49	0.1630	6.90
308.300	6.28	0.1630	6.90
308.808	8.09	0.1630	6.90
309.321	9.80	0.1630	6.90
309.863	11.69	0.1630	6.90
310.246	13.05	0.1630	6.90
310.521	1.13	0.2041	8.89
310.984	2.72	0.2041	8.89
311.516	4.49	0.2041	8.89
311.990	6.23	0.2041	8.89
312.463	7.79	0.2041	8.89
312.874	9.15	0.2041	8.89
313.284	10.62	0.2041	8.89
313.646	11.95	0.2041	8.89
313.943	13.03	0.2041	8.89
313.479	0.78	0.2468	11.09
313.971	2.28	0.2468	11.09
314.385	3.56	0.2468	11.09
314.810	4.87	0.2468	11.09
315.247	6.25	0.2468	11.09
315.481	6.99	0.2468	11.09
315.872	8.28	0.2468	11.09
316.363	9.87	0.2468	11.09

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A mixture of known composition was prepared gravimetrically, placed in a thick-walled glass tube (see ref 1), degassed and trapped under vacuum. At a fixed temp., pressure was adjusted until turbidity was observed. Temp. was then increased and the procedure repeated. Each reading was repeated 3-5 times. Smoothed data were estimated by the authors for selected isobars using
$x_1 = A_0 + A_1\, t + A_2\, t^{1-\alpha} + A_3\, t^{\beta}$
where $t = (T_c - T)/T_c$, $\alpha = 0.110$, $\beta = 0.325$. Each branch of the curve was fitted independently.

SOURCE AND PURITY OF MATERIALS:

(1) Fluka puriss., 0.05% H_2O; and Carlo Erba RS-ACS, purity >99.9%; both samples had no impurities by glc; kept under dry N_2 and molecular sieves 3A.
(2) Merck, purity 99.5%; no organic impurities by glc; kept under dry N_2 and molecular sieves 4A.

ESTIMATED ERROR:

temp. ±0.001 K;
pressure ±0.01 MPa;
soly. ±0.1 mass % (compiler)
±0.0005 mole fraction (UCST) at p = 0.1 MPa.

REFERENCES:

1. De Loos, T.W.; van der Krooi, H.J.; Poot, W.; Ott, P.L. *Delft Prog. Rep.* 1983, *8*, 200.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Aizpiri, A.G.; Rubio, R.G.; Diaz Peña, M. *J. Chem. Phys.* <u>1988</u>, *88*, 1934-43.

EXPERIMENTAL VALUES: (continued)

Solubility of methanol and cyclohexane

T/K	p/MPa	x_1	100 w_1 (compiler)
316.685	10.94	0.2468	11.09
316.951	11.81	0.2468	11.09
317.299	12.97	0.2468	11.09
314.425	1.15	0.2611	11.86
314.764	2.01	0.2611	11.86
315.495	4.51	0.2611	11.86
316.205	6.86	0.2611	11.86
316.728	8.35	0.2611	11.86
317.277	10.29	0.2611	11.86
317.700	11.82	0.2611	11.86
315.922	0.88	0.2991	13.98
316.389	2.18	0.2991	13.98
316.778	3.31	0.2991	13.98
317.361	4.99	0.2991	13.98
317.843	6.43	0.2991	13.98
318.156	7.36	0.2991	13.98
318.562	8.60	0.2991	13.98
318.981	9.87	0.2991	13.98
319.351	11.01	0.2991	13.98
319.674	12.02	0.2991	13.98
320.059	13.22	0.2991	13.98
317.286	0.40	0.3538	17.25
317.620	1.41	0.3538	17.25
317.898	2.24	0.3538	17.25
318.162	3.04	0.3538	17.25
318.463	3.96	0.3538	17.25
318.797	4.97	0.3538	17.25
319.199	6.18	0.3538	17.25
319.535	7.24	0.3538	17.25
319.881	8.32	0.3538	17.25
320.258	9.48	0.3538	17.25
320.772	11.07	0.3538	17.25
321.141	12.24	0.3538	17.25
321.376	12.99	0.3538	17.25
317.853	0.50	0.3791	18.86
318.198	1.47	0.3791	18.86
318.673	2.91	0.3791	18.86
319.031	4.01	0.3791	18.86
319.411	5.20	0.3791	18.86
319.863	6.54	0.3791	18.86
320.272	7.82	0.3791	18.86
320.718	9.23	0.3791	18.86
321.179	10.73	0.3791	18.86
321.524	11.86	0.3791	18.86
321.867	13.03	0.3791	18.86
318.156	0.68	0.3997	20.22
318.493	1.68	0.3997	20.22
318.826	2.69	0.3997	20.22
319.241	3.97	0.3997	20.22
319.677	5.31	0.3997	20.22
320.107	6.64	0.3997	20.22
320.515	7.93	0.3997	20.22
320.894	9.13	0.3997	20.22
321.293	10.42	0.3997	20.22
321.659	11.61	0.3997	20.22

(continued)

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Aizpiri, A.G.; Rubio, R.G.;
Diaz Peña, M.

J. Chem. Phys. 1988, *88*, 1934-43.

EXPERIMENTAL VALUES: (continued)

Solubility of methanol and cyclohexane

T/K	p/MPa	x_1	100 w_1 (compiler)
321.963	12.61	0.3997	20.22
322.048	12.88	0.3997	20.22
318.376	0.66	0.4199	21.60
318.800	1.92	0.4199	21.60
319.084	2.82	0.4199	21.60
319.428	3.86	0.4199	21.60
319.513	4.14	0.4199	21.60
319.949	5.52	0.4199	21.60
320.480	7.11	0.4199	21.60
320.842	8.24	0.4199	21.60
321.167	9.28	0.4199	21.60
321.613	10.71	0.4199	21.60
321.976	11.89	0.4199	21.60
322.268	12.86	0.4199	21.60
318.552	0.85	0.4409	23.09
318.855	1.74	0.4409	23.09
319.301	3.13	0.4409	23.09
319.656	4.22	0.4409	23.09
320.041	5.39	0.4409	23.09
320.509	6.79	0.4409	23.09
320.870	8.00	0.4409	23.09
321.228	9.07	0.4409	23.09
321.619	10.28	0.4409	23.09
321.932	11.31	0.4409	23.09
322.398	12.89	0.4409	23.09
318.664	0.96	0.4489	23.67
319.032	2.04	0.4489	23.67
319.398	3.14	0.4489	23.67
319.851	4.53	0.4489	23.67
320.232	5.69	0.4489	23.67
320.644	6.97	0.4489	23.67
320.961	7.97	0.4489	23.67
321.366	9.27	0.4489	23.67
321.788	10.62	0.4489	23.67
322.120	11.71	0.4489	23.67
322.478	12.88	0.4489	23.67
318.471	0.92	0.4809	26.07
319.069	1.73	0.4809	26.07
319.486	2.97	0.4809	26.07
319.831	4.05	0.4809	26.07
320.283	5.41	0.4809	26.07
320.624	6.47	0.4809	26.07
320.964	7.50	0.4809	26.07
321.366	9.27	0.4809	26.07
321.788	10.62	0.4809	26.07
322.120	11.71	0.4809	26.07
322.478	12.60	0.4809	26.07
318.638	0.57	0.5151	28.80
318.790	1.01	0.5151	28.80
319.081	1.81	0.5151	28.80
319.464	2.95	0.5151	28.80
319.777	3.90	0.5151	28.80
320.164	5.09	0.5151	28.80
320.584	6.39	0.5151	28.80
320.978	7.60	0.5151	28.80

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Aizpiri, A.G.; Rubio, R.G.; Diaz Peña, M. *J. Chem. Phys.* 1988, *88*, 1934-43.

EXPERIMENTAL VALUES: (continued)

Solubility of methanol and cyclohexane

T/K	p/MPa	x_1	100 w_1 (compiler)
321.440	9.07	0.5151	28.80
321.774	10.18	0.5151	28.80
322.114	11.28	0.5151	28.80
322.522	12.61	0.5151	28.80
318.569	0.70	0.5446	31.29
319.034	2.06	0.5446	31.29
319.418	3.23	0.5446	31.29
319.819	4.43	0.5446	31.29
320.211	5.61	0.5446	31.29
320.599	6.79	0.5446	31.29
320.994	8.04	0.5446	31.29
321.383	9.23	0.5446	31.29
321.791	10.54	0.5446	31.29
322.156	11.74	0.5446	31.29
322.541	12.99	0.5446	31.29
318.412	0.62	0.5685	33.40
318.820	1.82	0.5685	33.40
319.197	2.96	0.5685	33.40
319.603	4.22	0.5685	33.40
320.031	5.54	0.5685	33.40
320.399	6.67	0.5685	33.40
320.778	7.87	0.5685	33.40
321.155	9.06	0.5685	33.40
321.498	10.14	0.5685	33.40
321.852	11.28	0.5685	33.40
322.306	12.77	0.5685	33.40
318.404	1.02	0.5822	34.66
318.800	2.17	0.5822	34.66
319.204	3.42	0.5822	34.66
319.642	4.75	0.5822	34.66
320.073	6.06	0.5822	34.66
320.509	7.45	0.5822	34.66
320.938	8.79	0.5822	34.66
321.378	10.23	0.5822	34.66
321.752	11.42	0.5822	34.66
322.159	12.72	0.5822	34.66
318.011	0.44	0.6003	36.38
318.346	1.45	0.6003	36.38
318.713	2.56	0.6003	36.38
319.089	3.70	0.6003	36.38
319.417	4.72	0.6003	36.38
319.743	5.73	0.6003	36.38
320.183	7.08	0.6003	36.38
320.608	8.43	0.6003	36.38
320.899	9.36	0.6003	36.38
321.326	10.74	0.6003	36.38
321.674	11.87	0.6003	36.38
321.966	12.83	0.6003	36.38
317.597	0.69	0.6283	39.16
318.004	1.92	0.6283	39.16
318.394	3.05	0.6283	39.16
318.848	4.44	0.6283	39.16
319.215	5.59	0.6283	39.16
319.614	6.79	0.6283	39.16
320.018	8.01	0.6283	39.16
320.404	9.25	0.6283	39.16
320.793	10.43	0.6283	39.16
321.289	12.02	0.6283	39.16
321.594	12.99	0.6283	39.16
316.913	0.52	0.6577	42.25

(continued)

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Aizpiri, A.G.; Rubio, R.G.;
Diaz Peña, M.

J. Chem. Phys. 1988, *88*, 1934-43.

EXPERIMENTAL VALUES: (continued)

Solubility of methanol and cyclohexane

T/K	p/MPa	x_1	100 w_1 (compiler)
317.291	1.61	0.6577	42.25
317.636	2.62	0.6577	42.25
318.081	3.97	0.6577	42.25
318.498	5.21	0.6577	42.25
318.794	6.12	0.6577	42.25
319.227	7.45	0.6577	42.25
319.342	7.82	0.6577	42.25
319.827	9.36	0.6577	42.25
320.184	10.50	0.6577	42.25
320.655	12.01	0.6577	42.25
321.076	13.42	0.6577	42.25
316.116	0.38	0.6882	45.66
316.510	1.45	0.6882	45.66
317.010	2.87	0.6882	45.66
317.433	3.92	0.6882	45.66
317.973	5.41	0.6882	45.66
318.640	7.58	0.6882	45.66
319.150	9.02	0.6882	45.66
319.823	11.05	0.6882	45.66
320.290	12.35	0.6882	45.66
321.035	14.36	0.6882	45.66
315.037	0.96	0.7091	48.13
315.425	2.11	0.7091	48.13
316.020	4.15	0.7091	48.13
316.605	6.02	0.7091	48.13
317.115	7.58	0.7091	48.13
317.607	8.94	0.7091	48.13
318.033	10.24	0.7091	48.13
318.175	10.63	0.7091	48.13
318.666	12.10	0.7091	48.13
318.902	12.84	0.7091	48.13
319.173	13.73	0.7091	48.13
313.591	0.62	0.7296	50.67
313.910	1.60	0.7296	50.67
314.298	2.80	0.7296	50.67
314.749	4.21	0.7296	50.67
315.178	5.58	0.7296	50.67
315.519	6.66	0.7296	50.67
315.852	7.76	0.7296	50.67
316.124	8.63	0.7296	50.67
316.467	9.74	0.7296	50.67
316.723	10.56	0.7296	50.67
317.060	11.65	0.7296	50.67
317.372	12.68	0.7296	50.67
309.502	1.37	0.7685	55.83
310.035	2.85	0.7685	55.83
310.366	4.03	0.7685	55.83
310.875	5.85	0.7685	55.83
311.456	8.03	0.7685	55.83
311.956	9.39	0.7685	55.83
312.465	11.11	0.7685	55.83
313.086	12.96	0.7685	55.83
299.930	0.65	0.8151	62.66
300.542	2.59	0.8151	62.66
301.230	4.73	0.8151	62.66
301.589	5.89	0.8151	62.66
302.168	7.62	0.8151	62.66
302.718	9.59	0.8151	62.66
303.022	10.61	0.8151	62.66

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Aizpiri, A.G.; Rubio, R.G.; Diaz Peña, M. *J. Chem. Phys.* 1988, *88*, 1934-43.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and cyclohexane (smoothed data)

T/K	*p*/MPa	x_1 (2)-rich phase	x_1 (1)-rich phase	100 w_1 (compiler) (2)-rich phase	100 w_1 (compiler) (1)-rich phase
299.748	0.1	0.1212	0.8141	4.99	62.51
306.443	0.1	0.1641	0.7896	6.95	58.83
309.154	0.1	0.1900	0.7728	8.20	56.43
310.225	0.1	0.2023	0.7643	8.81	55.25
313.263	0.1	0.2468	0.7318	11.09	50.95
313.409	0.1	0.2495	0.7298	11.23	50.70
314.072	0.1	0.2621	0.7199	11.91	49.46
314.726	0.1	0.2762	0.7087	12.69	48.09
315.639	0.1	0.2990	0.6898	13.97	45.85
316.025	0.1	0.3102	0.6802	14.62	44.74
316.774	0.1	0.3359	0.6575	16.15	42.23
317.186	0.1	0.3533	0.6414	17.22	40.51
317.398	0.1	0.3637	0.6316	17.87	39.49
317.719	0.1	0.3822	0.6137	19.06	37.69
317.898	0.1	0.3946	0.6012	19.88	36.47
317.962	0.1	0.3996	0.5961	20.22	35.98
318.099	0.1	0.4118	0.5836	21.05	34.79
318.186	0.1	0.4208	0.5740	21.67	33.91
318.231	0.1	0.4261	0.5684	22.04	33.40
318.309	0.1	0.4367	0.5569	22.79	32.36
318.361	0.1	0.4452	0.5474	23.40	31.53
318.375	0.1	0.4478	0.5445	23.59	31.28
318.476	0.1	0.4747	0.5135	25.60	28.67
318.498	0.1	0.4859	0.5002	26.46	27.59
318.422 UCST	0.1	0.4986	0.4986	27.46	27.46
300.040	1.0	0.1115	0.8120	4.56	62.18
306.719	1.0	0.1626	0.7894	6.88	58.80
309.426	1.0	0.1903	0.7732	8.21	56.48
310.486	1.0	0.2029	0.7651	8.83	55.36
313.551	1.0	0.2480	0.7328	11.16	51.08
313.719	1.0	0.2510	0.7305	11.31	50.79
314.370	1.0	0.2633	0.7208	11.98	49.57
315.020	1.0	0.2769	0.7096	12.72	48.19
315.969	1.0	0.3001	0.6898	14.03	45.85
316.344	1.0	0.3108	0.6804	14.65	44.77
317.081	1.0	0.3356	0.6578	16.13	42.26
317.485	1.0	0.3523	0.6419	17.16	40.56
317.702	1.0	0.3628	0.6318	17.82	39.51
318.028	1.0	0.3814	0.6134	19.01	37.66
318.197	1.0	0.3931	0.6016	19.78	36.50
318.264	1.0	0.3983	0.5962	20.13	35.98
318.402	1.0	0.4106	0.5836	20.96	34.79
318.486	1.0	0.4193	0.5745	21.56	33.95
318.542	1.0	0.4260	0.5675	22.03	33.31
318.605	1.0	0.4345	0.5584	22.63	32.50
318.670	1.0	0.4452	0.5470	23.40	31.49
318.680	1.0	0.4470	0.5449	23.53	31.31
318.789	1.0	0.4761	0.5132	25.71	28.64
318.817	1.0	0.4908	0.4969	26.85	27.33
318.728 UCST	1.0	0.4986	0.4986	27.46	27.46
300.521	2.5	0.1196	0.8138	4.92	62.46
307.174	2.5	0.1623	0.7896	6.87	58.83
309.878	2.5	0.1885	0.7731	8.13	56.47
310.922	2.5	0.2007	0.7650	8.73	55.34
314.043	2.5	0.2470	0.7321	11.10	50.99

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Aizpiri, A.G.; Rubio, R.G.; Diaz Peña, M. *J. Chem. Phys.* 1988, *88*, 1934-43.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and cyclohexane (smoothed data)

T/K	*p*/MPa	x_1 (2)-rich phase	x_1 (1)-rich phase	100 w_1 (compiler) (2)-rich phase	100 w_1 (compiler) (1)-rich phase
314.200	2.5	0.2499	0.7299	11.26	50.71
314.860	2.5	0.2627	0.7202	11.94	49.49
315.509	2.5	0.2768	0.7092	12.72	48.15
316.496	2.5	0.3018	0.6887	14.13	45.72
316.874	2.5	0.3130	0.6792	14.78	44.63
317.593	2.5	0.3379	0.6573	16.27	42.20
317.984	2.5	0.3543	0.6421	17.28	40.58
318.205	2.5	0.3650	0.6319	17.95	39.52
318.536	2.5	0.3837	0.6134	19.16	37.66
318.695	2.5	0.3945	0.6024	19.88	36.58
318.762	2.5	0.3995	0.5972	20.21	36.08
318.875	2.5	0.4089	0.5872	20.85	35.13
318.984	2.5	0.4193	0.5758	21.56	34.07
319.041	2.5	0.4256	0.5688	22.00	33.43
319.097	2.5	0.4325	0.5609	22.49	32.72
319.179	2.5	0.4448	0.5466	23.37	31.46
319.184	2.5	0.4456	0.5456	23.43	31.37
319.303	2.5	0.4759	0.5081	25.69	28.23
319.329	2.5	0.4917	0.4873	26.92	26.57
319.245	UCST 2.5	0.4986	0.4986	27.46	27.46
301.311	5.0	0.1143	0.8122	4.68	62.22
307.922	5.0	0.1623	0.7899	6.87	58.87
310.632	5.0	0.1886	0.7740	8.13	56.60
312.098	5.0	0.2055	0.7626	8.96	55.02
314.848	5.0	0.2454	0.7332	11.02	51.13
314.994	5.0	0.2479	0.7312	11.15	50.88
315.657	5.0	0.2601	0.7214	11.80	49.64
316.325	5.0	0.2739	0.7101	12.56	48.26
317.359	5.0	0.2994	0.6884	13.99	45.68
317.751	5.0	0.3110	0.6783	14.66	44.53
318.427	5.0	0.3346	0.6571	16.07	42.18
318.807	5.0	0.3510	0.6421	17.07	40.58
319.033	5.0	0.3623	0.6315	17.78	39.48
319.365	5.0	0.3825	0.6125	19.08	37.57
319.511	5.0	0.3933	0.6022	19.80	36.56
319.578	5.0	0.3988	0.5969	20.16	36.05
319.723	5.0	0.4124	0.5837	21.09	34.80
319.800	5.0	0.4210	0.5754	21.68	34.03
319.859	5.0	0.4285	0.5681	22.21	33.37
319.911	5.0	0.4359	0.5608	22.73	32.71
320.008	5.0	0.4531	0.5439	23.98	31.22
320.011	5.0	0.4538	0.5432	24.03	31.16
320.137	5.0	0.4960	0.5013	27.26	27.68
320.148	5.0	0.5039	0.4935	27.89	27.06
320.049	UCST 5.0	0.4986	0.4986	27.46	27.46
302.841	10.0	0.1191	0.8136	4.90	62.43
309.381	10.0	0.1618	0.7903	6.85	58.93
312.141	10.0	0.1880	0.7734	8.10	56.51
313.110	10.0	0.1990	0.7659	8.64	55.47
316.402	10.0	0.2465	0.7311	11.08	50.86
316.551	10.0	0.2491	0.7290	11.21	50.60
317.182	10.0	0.2611	0.7197	11.86	49.43
317.956	10.0	0.2775	0.7065	12.76	47.82
319.022	10.0	0.3047	0.6839	14.30	45.17
319.441	10.0	0.3171	0.6725	15.02	43.88

(continued)

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Aizpiri, A.G.; Rubio, R.G.; Diaz Peña, M.

J. Chem. Phys. 1988, *88*, 1934-43.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and cyclohexane (smoothed data)

T/K	p/MPa	x_1 (2)-rich phase	x_1 (1)-rich phase	100 w_1 (compiler) (2)-rich phase	100 w_1 (compiler) (1)-rich phase
320.024	10.0	0.3380	0.6548	16.28	41.93
320.426	10.0	0.3551	0.6393	17.33	40.29
320.651	10.0	0.3662	0.6291	18.03	39.24
320.954	10.0	0.3837	0.6125	19.16	37.57
321.100	10.0	0.3937	0.6029	19.82	36.63
321.165	10.0	0.3986	0.5981	20.15	36.17
321.315	10.0	0.4114	0.5855	21.02	34.97
321.390	10.0	0.4189	0.5780	21.53	34.27
321.451	10.0	0.4257	0.5711	22.01	33.64
321.517	10.0	0.4341	0.5625	22.60	32.86
321.597	10.0	0.4466	0.5495	23.50	31.71
321.619	10.0	0.4507	0.5452	23.80	31.34
321.726	10.0	0.4815	0.5120	26.12	28.54
321.736	10.0	0.4869	0.5060	26.54	28.06
321.666	UCST 10.0	0.4986	0.4986	27.46	27.46
303.728	13.0	0.1306	0.8130	5.41	62.34
310.232	13.0	0.1663	0.7886	7.06	58.68
313.046	13.0	0.1904	0.7716	8.22	56.26
313.933	13.0	0.1997	0.7650	8.68	55.34
317.304	13.0	0.2454	0.7308	11.02	50.82
317.468	13.0	0.2483	0.7286	11.17	50.55
318.052	13.0	0.2590	0.7203	11.74	49.51
318.934	13.0	0.2773	0.7058	12.75	47.74
319.986	13.0	0.3041	0.6838	14.26	45.16
320.501	13.0	0.3201	0.6702	15.20	43.62
320.952	13.0	0.3365	0.6559	16.18	42.05
321.381	13.0	0.3552	0.6393	17.34	40.29
321.597	13.0	0.3662	0.6293	18.03	39.26
321.863	13.0	0.3820	0.6145	19.05	37.77
322.019	13.0	0.3929	0.6041	19.77	36.75
322.083	13.0	0.3979	0.5993	20.10	36.28
322.238	13.0	0.4116	0.5858	21.03	35.00
322.315	13.0	0.4196	0.5777	21.58	34.25
322.378	13.0	0.4271	0.5702	22.11	33.56
322.467	13.0	0.4397	0.5572	23.00	32.39
322.514	13.0	0.4478	0.5486	23.59	31.63
322.546	13.0	0.4543	0.5417	24.07	31.03
322.628	13.0	0.4785	0.5152	25.89	28.81
322.655	13.0	0.4939	0.4976	27.09	27.38
322.576	UCST 13.0	0.4986	0.4986	27.46	27.46

COMMENTS AND ADDITIONAL DATA:

The authors fitted the experimental isopleths to an equation

$$t/^{\circ}\mathrm{C} = a + b(p/\mathrm{MPa}) + c(p/\mathrm{MPa})^2$$

and obtained the parameters by the method of maximum likelihood. They next fitted the calculated isobars for each branch of the coexistence curve with the equation

$$\lambda = A_0 + A_1\theta + A_2\theta^{1-\alpha} + B\theta^{\beta}$$

where the composition variable λ was taken as either the mole or volume fraction of methanol; mole fraction was found to be preferable; the scaled temperature is $\theta = |1 - T/T_c|$.

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Aizpiri, A.G.; Rubio, R.G.; Diaz Peña, M. *J. Chem. Phys.* 1988, *88*, 1934-43.

EXPERIMENTAL VALUES: (continued)

They found the exponents to have the renormalization group values ($\beta = 0.325$, $\alpha = 0.110$). The values of T_c at rounded pressures are included in the tables for smoothed data.

The critical solution temperature was found to increase quadratically with pressure, and has errors ± 0.005-0.010 K. The critical solution composition used in the tables of rounded values is an average for all pressures and both branches. The errors in these data (± 0.004-0.006), and inconsistent values for the two branches, masked any dependence on pressure.

The diameter of the coexistence curve was found to decrease non-linearly with decreasing temperature at all pressures; i.e., the critical composition, as mole fraction of methanol, decreases with decreasing temperature.

Pressure dependence of critical solution temperature

The increase in T_c with pressure was found to be

$$(\partial T_c/\partial p)_{x_c} = (3.42 \pm 0.04) \times 10^{-7}\ \mathrm{K\ Pa^{-1}}$$

from a quadratic fit to the data, or $(3.21 \pm 0.02) \times 10^{-7}$ K $\mathrm{Pa^{-1}}$ for a linear fit. The quadratic fit was found to represent the data better.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Ewing, M.B.; Johnson, K.A.; McGlashan, M.L. *J. Chem. Thermodyn.* 1988, *20*, 49-62.
VARIABLES:	PREPARED BY:
Temperature: 317 - 319 K	A. Skrzecz, J.W. Lorimer

EXPERIMENTAL VALUES:

Mutual solubility from expts. in calorimeter - run c

T/K	x_1 (2)-rich phase	 (1)-rich phase	100 w_1 (compiler) (2)-rich phase	 (1)-rich phase
317.1813	0.35239	-	17.161	-
317.1813	0.35239	-	17.161	-
317.3065	0.35767	-	17.492	-
317.3513	-	0.64936	-	41.351
317.4277	0.36313	-	17.836	-
317.4370	-	0.64616	-	41.012
317.5200	-	0.64291	-	40.669
317.5290	0.36828	-	18.164	-
317.6034	-	0.63954	-	40.316
317.6313	0.37336	-	18.490	-
317.6763	-	0.63621	-	39.970
317.7206	0.37841	-	18.816	-
317.7450	-	0.63268	-	39.605
317.8073	0.38332	-	19.137	-
317.8182	-	0.62919	-	39.247
317.8842	-	0.62557	-	38.878
317.8862	0.38826	-	19.461	-
317.9447	-	0.62196	-	38.514
317.9598	0.39321	-	19.789	-
318.0073	-	0.61815	-	38.131
318.0246	0.39789	-	20.102	-
318.0605	-	0.61435	-	37.753
318.1065	-	0.61048	-	37.371
318.1374	0.40709	-	20.723	-
318.1561	-	0.60653	-	36.983
318.1859	0.41197	-	21.057	-
318.1987	-	0.60246	-	36.587
318.2268	0.41620	-	21.348	-
318.2287	-	0.59932	-	36.284
318.2569	-	0.59618	-	35.983

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
The isothermal displacement calorimeter and the dilution glass dilatometer (ref 1,2) were filled with a known amount of one component at a temperature about 2 K below UCST and the second component was injected until the two-phase region was reached. The mixture was heated until transparency and the mean temperature (within 0.2 mK) at which fine droplets appeared and disappeared was noted. In the calorimeter, temp. was measured with a bead thermistor calibrated against a Pt resistance thermometer (to 0,2 mK). Methanol could have some contact with air and therefore the mixture could contain some moisture.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified; dried, degassed as in ref 1.

ESTIMATED ERROR:

temp. < ±0.001 K (total error estimated by authors).

REFERENCES:

1. Ewing, M.B.; Johnson, K.A.; McGlashan, M.L. *J. Chem. Thermodyn.* 1985, *17*, 513; 1987, *19*, 949.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Cyclohexane; C_6H_{12}; [110-82-7]

ORIGINAL MEASUREMENTS:

Ewing, M.B.; Johnson, K.A.; McGlashan, M.L.

J. Chem. Thermodyn. 1988, *20*, 49-62.

EXPERIMENTAL VALUES: (continued)

Mutual solubility from experiments in calorimeter - run c

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
318.2641	0.42040	-	21.639	-
318.2820	-	0.59302	-	35.681
318.2997	0.42464	-	21.935	-
318.3057	-	0.58974	-	35.370
318.3269	-	0.58646	-	35.062
318.3321	0.42944	-	22.273	-
318.3475	-	0.58309	-	34.746
318.3607	0.43317	-	22.538	-
318.3650	-	0.57969	-	34.430
318.3796	-	0.57632	-	34.119
318.3834	0.43726	-	22.829	-
318.3893	-	0.57391	-	33.898
318.3988	-	0.57152	-	33.679
318.4062	0.44137	-	23.125	-
318.4077	-	0.56923	-	33.471
318.4152	-	0.56671	-	33.242
318.4223	-	0.56432	-	33.027
318.4256	0.44546	-	23.421	-
318.4285	-	0.56155	-	32.778
318.4401	0.44926	-	23.697	-
318.4412	-	0.55679	-	32.354
318.4456	-	0.55423	-	32.128
318.4519	-	0.55167	-	31.902
318.4555	0.45320	-	23.986	-
318.4557	-	0.54905	-	31.673
318.4606	-	0.54640	-	31.442
318.4667	0.45716	-	24.279	-
318.4673	-	0.54372	-	31.209
318.4720	-	0.54101	-	30.975
318.4728	0.46088	-	24.555	-
318.4769	-	0.53854	-	30.763
318.4795	-	0.53548	-	30.502
318.4809	0.46469	-	24.840	-
318.4825	-	0.53264	-	30.260
318.4867	0.46834	-	25.115	-
318.4888	-	0.52982	-	30.022
318.4900	0.47194	-	25.388	-
318.4915	-	0.52700	-	29.785
318.4946	0.47563	-	25.669	-
318.4956	0.47921	-	25.944	-
318.4964	0.48263	-	26.208	-
318.4978	-	0.52409	-	29.541
318.4988	0.48600	-	26.470	-
318.4992	0.49276	-	27.000	-
318.4995	0.49607	-	27.261	-
318.4997	0.50574	-	28.035	-
318.5002	0.50264	-	27.786	-
318.5006	0.51205	-	28.547	-
318.5009	0.50893	-	28.293	-
318.5010	-	0.52113	-	29.295
318.5011	0.48947	-	26.741	-
318.5016	0.51516	-	28.802	-
318.5020	-	0.51812	-	29.046

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Ewing, M.B.; Johnson, K.A.; McGlashan, M.L. *J. Chem. Thermodyn.* 1988, *20*, 49-62.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and cyclohexane
from experiments in dilatometer - run d1

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
317.1663	0.35822	-	17.526	-
317.3088	0.36424	-	17.907	-
317.3290	-	0.64894	-	41.307
317.4580	-	0.64401	-	40.785
317.4587	0.37173	-	18.385	-
317.6782	-	0.63396	-	39.737
317.7254	0.38771	-	19.425	-
317.7837	-	0.62828	-	39.154
317.8496	-	0.62438	-	38.758
317.8640	0.39590	-	19.969	-
317.9171	0.39903	-	20.178	-
317.9613	0.40283	-	20.434	-
317.9700	-	0.61647	-	37.964
318.0360	-	0.61109	-	37.431
318.0388	0.40959	-	20.894	-
318.0741	0.41334	-	21.151	-
318.0902	-	0.60626	-	36.957
318.1697	0.42450	-	21.926	-
318.1750	-	0.59631	-	35.995
318.2040	0.42796	-	22.169	-
318.2164	-	0.59160	-	35.547
318.2483	0.43418	-	22.609	-
318.2545	-	0.58567	-	34.987
318.2865	0.44036	-	23.052	-
318.2866	-	0.57944	-	34.407
318.3017	0.44324	-	23.260	-
318.3189	0.44987	-	23.742	-
318.3300	-	0.56848	-	33.403
318.3407	0.45173	-	23.878	-
318.3437	-	0.56451	-	33.044
318.3489	-	0.56230	-	32.845
318.3517	0.45488	-	24.110	-
318.3626	-	0.55724	-	32.394
318.3689	-	0.55265	-	31.989
318.3747	0.45862	-	24.387	-
318.3785	-	0.54684	-	31.480
318.3856	0.46346	-	24.748	-
318.3940	-	0.53631	-	30.572
318.3942	0.46812	-	25.098	-
318.4022	-	0.53102	-	30.123
318.4037	0.47417	-	25.558	-
318.4062	-	0.52600	-	29.701
318.4092	0.47855	-	25.893	-
318.4124	-	0.51839	-	29.068
318.4149	0.48423	-	26.332	-
318.4150	-	0.51443	-	28.742
318.4193	-	0.49832	-	27.440
318.4193	-	0.49325	-	27.038
318.4196	-	0.48995	-	26.779

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Ewing, M.B.; Johnson, K.A.; McGlashan, M.L. *J. Chem. Thermodyn.* 1988, *20*, 49-62.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and cyclohexane
from experiments in dilatometer - run d2

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
317.0601	-	0.65144	-	41.573
317.2494	-	0.64188	-	40.561
317.3468	0.37286	-	18.458	-
317.4808	-	0.63287	-	39.625
317.5199	0.38535	-	19.270	-
317.6402	-	0.62628	-	38.951
317.6830	0.39265	-	19.752	-
317.7717	-	0.61690	-	38.006
317.9037	-	0.60641	-	36.972
317.9583	-	0.60177	-	36.521
317.9654	0.41745	-	21.434	-
318.0248	-	0.59492	-	35.862
318.0715	-	0.58813	-	35.219
318.0879	0.43353	-	22.563	-
318.1182	-	0.58145	-	34.594
318.1347	0.44356	-	23.283	-
318.1418	-	0.57573	-	34.065
318.1769	-	0.56604	-	33.182
318.1830	0.45314	-	23.982	-
318.2089	-	0.55541	-	32.232
318.2161	0.46368	-	24.764	-
318.2255	-	0.54842	-	31.618
318.2370	0.47392	0.53717	25.538	30.646
318.2413	-	0.52952	-	29.996
318.2442	-	0.52260	-	29.417
318.2447	-	0.51361	-	28.675
318.2504	0.48594	-	26.465	-
318.2563	-	0.50176	-	27.715
318.2540	-	0.57461	-	33.962
318.2826	-	0.56740	-	33.305
318.2890	0.45742	-	24.298	-
318.3024	-	0.55884	-	32.536
318.3071	0.46275	-	24.695	-
318.3196	-	0.55187	-	31.920
318.3268	0.47191	-	25.385	-
318.3286	-	0.54124	-	30.995
318.3389	-	0.53531	-	30.487
318.3393	0.48129	-	26.104	-
318.3454	-	0.52449	-	29.574
318.3462	0.48760	-	26.595	-
318.3481	-	0.51902	-	29.120
318.3484	-	0.50971	-	28.357
318.3485	-	0.51376	-	28.687
318.3486	-	0.50555	-	28.020

COMMENTS AND ADDITIONAL DATA:

The authors give a careful analysis of their data based on the fitting equation

$$x = x_c \pm (B_1/2)\,|t|^{\beta} + A_1|t|^{1-\alpha} + A_2|t| \pm (B_2/2)\,|t|^{\beta+w} + A_3|t|^{1-\alpha+w}$$

where current theoretical values for the critical exponents $\alpha = 0.11$, $\beta = 0.325$ and the first Wegner exponent $w = 0.5$ were used, x_c is the critical mole fraction of cyclohexane, ± refers to the two branches of the coexistence curve and $t = T/T_c - 1$. They found that mole fraction was a better order parameter than mass fraction.

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Ewing, M.B.; Johnson, K.A.; McGlashan, M.L. *J. Chem. Thermodyn.* 1988, *20*, 49-62.

EXPERIMENTAL VALUES: (continued)

For the combined runs in the dilatometer, they found the following coefficients (± 1 std. dev.) by least squares and by varying T_c until minimum standard error of estimate in x was found.

$x_c = 0.50955 \pm 0.00039$ $B_1/2 = 0.8794 \pm 0.0071$
$A_2 = 0.59 \pm 0.24$ $B_2/2 = 0.37 \pm 0.16$
$s(x) = 0.00213$ $T_c/\mathrm{K} = 318.412 \pm 0.001$

The authors also determined directly the effect of pressure on the temperature of phase separation, as given in the table below.

Effect of pressure on phase separation of methanol and cyclohexane

x_1	$(p - p^\circ)/\mathrm{kPa}$	T/K
0.63466	74.1	317.5015
	62.3	317.4990
	48.4	317.4911
	32.4	317.4860
0.55766	69.9	318.2303
	58.0	318.2268
	45.4	318.2202
	32.6	318.2163
0.60466	66.4	318.2734
	55.4	318.2691
	45.0	318.2641
	30.7	318.2610
0.50177	64.8	318.3119
	50.6	318.3076
	56.5	318.3025
	18.5	318.2695
	10.2	318.2940
0.49964	71.4	318.3137
	60.1	318.3112
	44.7	318.3080
	33.5	318.3059
	20.9	318.2971
0.43580	73.9	318.1093
	59.8	318.1048
	45.7	318.0999
0.38761	40.7	317.5325
	27.5	317.5300
	12.4	317.5240

These results were fitted to the equation:

$$T/\mathrm{K} = a + b(p - p^\circ)$$

with $p^\circ = 100$ kPa. From the three values of b nearest the critical composition, they recommend:

$$(\partial T_c/\partial p)_{x=x_c} = (3.299 \pm 0.048) \times 10^{-7}\ \mathrm{K\ Pa^{-1}}$$

Note: The authors give results as mole fraction of cyclohexane, rather than mole fraction of methanol, as given here.

COMPONENTS:	EVALUATOR:
(1) Methanol; CH_4O; [67-56-1] (2) Methylcyclopentane; C_6H_{12}; [96-37-7]	A. Maczynski and A. Skrzecz Institute of Physical Chemistry Polish Academy of Sciences Warsaw, Poland J.W. Lorimer Department of Chemistry The University of Western Ontario London, Ont., Canada July, 1989

CRITICAL EVALUATION:

Data on solubilities and upper critical solution temperature (UCST) for the system methanol (1) - methylcyclopentane (2) were reported in the following two papers.

Author(s)	Range T/K		x_1 in (1)-rich phase
1. Fischer 1949	320.4	UCST	-
2. Kiser 1961	278.2 - 305.3	UCST	0.651 - 0.848

Critical Solution Temperature and Composition

The UCST by Fischer and Neupauer, ref 1, is rejected; the paper is not compiled. All values of UCST reported in ref 1 for different alcohol- hydrocarbon systems are higher by about 10-20 K than the recommended or tentative values, which suggests presence of significant amounts of inpurities, mainly water.

The value of Kiser et al., 305.3 K, is accepted as *tentative* since values from this source are reliable for other systems.

Mutual Solubilities

Only data for the methanol-rich phase are available. The data of Kiser et al. in the table are accepted as *tentative* since values from this source are reliable for other systems. The table gives these tentative data together with those calculated from the fitting equation:

$$x_1 = x_{c1} - B_1\theta^{\beta} - B_2\theta^{\beta+w}$$

where $\theta = |1 - T/T_c|$, the indices have their theoretical values $\beta = 0.329$, $w = 0.5$, and the value of T_c was constrained to be 305.3 K. The constants (with standard deviations in parentheses) are:

$x_{c1} = 0.455\ (0.014)$ $B_1 = 1.039\ (0.072)$ $B_2 = -0.57\ (0.15)$ $s = 0.003$

(continued)

CRITICAL EVALUATION: (continued)

s is the standard error of estimate in composition. The equation is valid for the temperature range 278 - 305 K, but note that evaluation of the critical solution composition involves a somewhat long extrapolation in composition.

Tentative values of solubility for the system
methanol (1) - methylcyclopentane (2)

T/K	x_1 in (1)-rich phase obs.	calc.	
278.2	0.848	0.850	
283.2	0.835	0.831	
288.2	0.807	0.809	
293.2	0.777	0.779	
298.2	0.736	0.735	
303.2	0.651	0.651	
305.3	-	0.455±0.014	UCST

REFERENCES:

1. Fischer, R.; Neupauer, E. *Mikrochim. Acta* 1949, *34*, 319.
2. Kiser, R.W.; Johnson, G.D.; Shetlar, M.D. *J. Chem. Eng. Data* 1961, *6*, 338.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Methylcyclopentane; C_6H_{12}; [96-37-7]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.; Shetlar, M.D.

J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 278 - 305 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methylcyclopentane in methanol

$t/^\circ C$	g(2)/100 mL(1)	100 w_1 (compiler)	x_2 (compiler)
5	38.0	32.1	0.152
10	41.5	34.1	0.165
15	50.0	38.6	0.193
20	59.5	42.9	0.223
25	74.	48.5	0.264
30	110.	58.5	0.349
32.1	UCST		

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4^\circ C) = 0.80999 - 9.253\ 10^{-4}\ (t/^\circ C) - 4.1\ 10^{-7}\ (t/^\circ C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; $n_D(20^\circ C) = 1.3293$, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Matheson, Coleman and Bell; used as received; a trace of benzene and 1.5 mole % of unsaturated impurities by u.v. analysis; n^{20}_D 1.37500.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables* vol. *3*, New York, 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) 2,2-Dimethylbutane; C_6H_{14}; [75-83-2]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.; Shetlar, M.D.

J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 278 - 287 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of 2,2-dimethylbutane in methanol

$t/°C$	g(2)/100 ml(1)	100 w_1 (compiler)	x_2 (compiler)
5	59.	42.3	0.214
10	80.	50.0	0.271
14.2	U C S T		

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4°C) = 0.80999 - 9.253\ 10^{-4}\ (t/°C) - 4.1\ 10^{-7}\ (t/°C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; $n_D(20°C) = 1.3293$, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Matheson, Coleman and Bell; used as received; 0.1 mole % of impurities of unsaturated compounds by u.v. analysis; $n_D(20°C) = 1.36885$.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables* *vol. 3*, New York, 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) 2,3-Dimethylbutane; C_6H_{14}; [79-29-8]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.; Shetlar, M.D.

J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 278 - 294 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of 2,3-dimethylbutane in methanol

t/°C	g(2)/100 mL(1)	100 w_1 (compiler)	x_2 (compiler)
5	49.5	38.1	0.186
10	59.3	42.5	0.216
15	76.	48.8	0.262
20	170.	68.2	0.444
20.4	UCST		

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4^{\circ}C) = 0.80999 - 9.253\ 10^{-4}\ (t/^{\circ}C) - 4.1\ 10^{-7}\ (t/^{\circ}C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; $n_D(20^{\circ}C) = 1.3293$, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Matheson, Coleman and Bell; used as received; a trace of benzene and 1.5 mole % of unsaturated impurities by u.v. analysis; $n_D(20^{\circ}C) = 1.37500$.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables vol. 3*, New York, 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

EVALUATOR:

A. Skrzecz
Institute of Physical Chemistry
Polish Academy of Sciences, Warsaw, Poland

J.W. Lorimer
Department of Chemistry
The University of Western Ontario
London, Ont., Canada

July, 1989

CRITICAL EVALUATION:

A survey of solubilities and upper critical solution temperatures (UCST) and compositions for the system methanol-hexane which have been reported in the literature is given in Table 1.

Table 1. Summary of solubility data for the system methanol (1) - hexane (2)

Author(s)	*T*/K	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Rothmund 1898	278-316	0.077-0.444	0.540-0.895
2. Bingham 1907	316.0 UCST	-	-
3. Schuekarew 1910	317.0 UCST	-	-
4. Howard 1926	309-315.2 UCST	0.271-0.598	-
5. Rising 1928	309.7	0.62 (from vol %)	-
6. Ferguson 1932	315.6 UCST	-	-
7. Cornish 1934	303.3 and 305 UCST	-	-
8. Ssementschenko 1934	305.7 UCST	-	-
9. Francis 1944	308 UCST	-	-
10. Sieg 1951	308.0 UCST	-	-
11. Suhrmann 1951	303-307.8 UCST	- vol %	- vol %
12. Smirnov 1954	309.8 UCST	-	-
13. Quantie 1954	301.3 UCST	0.5654	0.5654
14. Kogan 1956	275-293	0.104-0.181	0.816-0.889
15. Kiser 1961	278-306.4 UCST	-	0.717-0.870
16. Savini 1965	298-306.9 UCST	0.270-0.560	0.560-0.791
17. Myers 1966	309.6 UCST		
18. Schmidt 1969	293-307.7 UCST	0.193-0.553	0.553-0.822
19. Rudakovskaya 1972	285-293	0.126-0.204	0.821-0.857
20. Sergeeva 1973	298	0.210	0.791
21. Radice 1975	255-298	0.052-0.232	0.802-0.932
22. Budantseva 1976	293	0.236	0.839
23. Balasubramanian 1979	306.9 UCST	0.40	0.40
24. Skripov 1980	308.08 UCST	0.4133	0.4133
25. Grekova 1981	309.3	0.539	-

(continued)

CRITICAL EVALUATION: (continued)

Table 1 (continued). Summary of solubility data for the system methanol (1) - hexane (2)

Author(s)	T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
26. Khurma 1982	298-306.70 UCST	0.255-0.560	0.560-0.774
27. Alekhin 1983	308.0 UCST	0.547	0.547
28. Kasapova 1983	299-307.40 UCST	0.251-0.5695	0.5695-0.765
29. Hoelscher 1986	280-340 [a]	0.219-0.540	0.540-0.806
	307.2 UCST	0.535	
30. Hradetzky 1986	245-306.75 UCST	0.047-0.546	0.546-0.930
31. Nagata 1987	298	0.255	0.799

[a] At elevated pressures, p = 0.1 - 151 MPa; critical values at 0.1 MPa.

(continued)

Critical Solution Temperature and Composition

The 24 values of critical solution temperature which have been reported vary over the range 307 to 316 K (see Table 2, where they are arranged in order). Of these, values greater than 304 K are from work done before 1932 (refs. 2, 3, 4, 6), all of which are deficient in specifying materials or method, and are rejected. Similarly, all values less than 306.4 K (refs. 7, 8, 13) or greater than 307.8 K (refs. 9, 10, 12, 17, 24, 25, 27) were also obtained using chemicals from unspecified sources or using unspecified methods, and are rejected. The remaining nine values (from refs. 11, 15, 16, 18, 23, 26, 28, 29, 30) give an average T_c = 307.1 ± 0.5 K (std. dev.). What appear to be the results obtained using the most care (refs. 27-29) give: T_c = 307.1 ± 0.3 K, i.e., with a slightly improved standard deviation. The result using the nine values is *recommended*: T_c = 307.1 ± 0.5 K

The 11 values of critical composition which have been reported vary from x_{c1} = 0.40 to 0.570 (Table 3, again arranged in order). If values less than 0.40 (refs. 22, 23) are rejected, the average is 0.553. If those values are rejected for which the corresponding critical solution temperatures are also rejected (refs. 13, 24, 26), the remaining six values give the *recommended* value x_{c1} = 0.554 ± 0.013.

Table 2. Critical solution temperature
in the system methanol-hexane

T_c	Author	year	ref.
301.3	Quantie	1954	13
303.3	Cornish	1934	7
305	Cornish	1934	7
305.7	Ssmentschenko	1934	8
306.4	Kiser et al.	1961	15
306.70	Khurma, Fenby	1982	26
306.75	Hradetsky, Bittrich	1986	30
306.9	Savini et al.	1965	16

(continued)

CRITICAL EVALUATION: (continued)

Table 2 (continued). Critical solution temperature in the system methanol-hexane

T_c	Author	year	ref.
306.9	Balasubramanian, Mitra	1979	23
307.2	Hoelscher et al.	1986	27
307.40	Kasapova et al.	1983	28
307.7	Schmidt et al.	1969	18
307.8	Suhrmann, Walter	1951	11
308	Francis	1944	9
308.0	Sieg	1951	10
308.0	Alekhin et al.	1983	27
308.09	Skripov et al.	1980	24
309.3	Grekova et al.	1981	25
309.6	Myers et al.	1966	17
309.8	Smirnov, Predvoditelev	1954	12
315.2	Howard, Patterson	1907	2
315.6	Ferguson	1932	6
316.0	Bingham	1910	3
317.0	Schuekarew	1910	3

Table 3. Critical mole fraction of methanol in the system methanol-hexane

x_{c1}	Author	year	ref.
0.40	Balasubramanian, Mitra	1979	23
0.413	Skripov et al.	1980	24
0.535	Hoelscher et al.	1986	29
0.539	Grekova et al.	1981	25
0.546	Hradetsky, Bittrich	1986	30
0.547	Alekhin et al.	1983	27
0.553	Schmidt et al.	1969	18
0.560	Savini et al.	1965	16
0.560	Khurma, Fenby	1982	26
0.5654	Quantie	1954	13
0.5695	Kasapova et al.	1983	28

(continued)

CRITICAL EVALUATION: (continued)

Mutual Solubility

One hundred and thirty-seven values of mutual solubilities have been reported in 15 publications, not including critical solution points; most of these are shown in fig. 1. The exceptions are the values of Rising, ref. 5, for which the composition is given as an equal-volume mixture, and the values of Suhrmann, ref. 11, which are also given as volume ratios. These data are rejected. It is clear from the figure that the older data of Rothmund, ref. 1 (■ in fig. 1), and of Howard and Patterson, ref. 3 (crosses), as well as the modern data of Nagata, ref. 31 ("ant" in the figure) are aberrant, and are rejected. For the hexane-rich phase, fig. 1 shows that the datum of Sergeeva and Ustanova, ref. 20 (|) is aberrant, and is therefore rejected. The values of Hoelscher et al. (●), which were extrapolated from experimental solubilities at high pressures, appear to be in serious error, especially at $x_1 = 0.2$ and 0.8; all values are rejected. Note that this conclusion places their solubilities at high pressures in question, especially far from the critical solution point; their coexistence curve is probably too narrow at all pressures.

Other questionable (and therefore rejected) values are from Kogan et al., ref. 14 (too broad a coexistence curve), Radice and Knickle, ref. 21, except for one value at 255 K.

The most consistent of the remaining 90 points are those of Khurma and Fenby, ref. 26, and of Hradetsky and Bittrich, ref. 30. The latter cover the widest range of composition, and were used to construct a fitting equation:

$$x_1 = x_{c1} \pm B_1\theta^{\beta} \pm B_2\theta^{\beta+w} + A_1\theta \pm B_3\theta^{\beta+2w} + A_2\theta^{1-\alpha+w}$$

ywhere $\theta = |1 - T/T_c|$, + and - refer to the branches below and above the critical composition, and the constants have their theoretical values $\beta = 0.329$, $\alpha = 0.11$, $w = 0.5$. The constants (with standard deviations in parentheses) are:

$x_{c1} = 0.5501\ (0.0020)$	$T_c/\mathrm{K} = 306.74\ \mathrm{K}\ (1.2\ \mathrm{K})$	
$B_1 = 0.8472\ (0.20)$	$B_2 = 0.1100\ (0.15)$	$B_3 = -0.6908\ (0.28)$
$A_1 = -1.254\ (0.13)$	$A_2 = 1.6950\ (0.28)$	$s = 0.0070$

s is the total standard error of estimate in composition. Table 4 gives *recommended* values calculated from this equation.

The only data measured at high pressures are those of Hoelscher et al., ref. 29, up to 151 MPa; they are considered as *tentative*.

Table 4. Recommended values of solubility in the system methanol (1) - hexane (2).

T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
255.0	0.0453	0.9234
260.0	0.0573	0.9150
270.0	0.0855	0.8956
275.0	0.1024	0.8841
265.0	0.0706	0.9058

(continued)

CRITICAL EVALUATION: (continued)

Table 4 (continued). Recommended values of solubility in the system methanol (1) - hexane (2).

280.0	0.1221	0.8709
285.0	0.1457	0.8553
290.0	0.1752	0.8363
295.0	0.2151	0.8115
300.0	0.2764	0.7752
305.0	0.4011	0.6988
306.0	0.4514	0.6594
306.8	0.546	0.546 UCST

Pressure coefficient of critical solution temperature

Two values are available: $(\partial T_c/\partial p)_{xc} = (3.38 \pm 0.12) \times 10^{-7}$ K Pa^{-1} from Myers et al., ref. 7, and K Pa^{-1} calculated from the fitting data of Hoelscher et al., ref. 29, 3.58×10^{-7} K Pa^{-1}, with unknown certainty. The average of these values, 3.5×10^{-7} K Pa^{-1}, may be taken as a *tentative* value

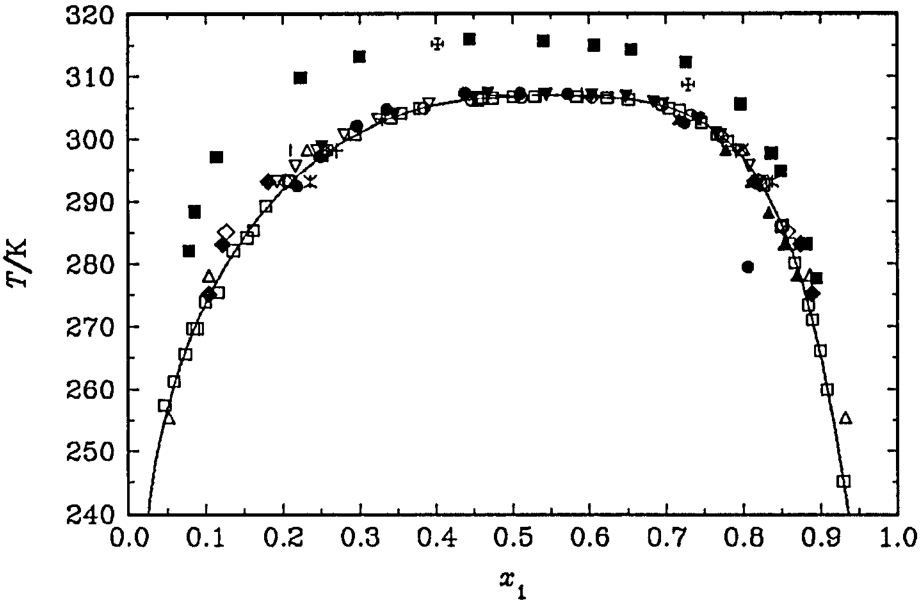

Fig. 1: Solubilities in the system methanol (1) - hexane (2). Line: fitting equation (see text). Points and reference: ■, 1; cross, 4; ♦, 14; ▲, 15; +, 16; ▽, 18; ◇, 19; |, 20; △, 21; ×, 22; ○, 26; ▼, 28; ●, 29; □, 30; ant, 31. The plot gives an overall impression of the data.

(continued)

CRITICAL EVALUATION: (continued)

REFERENCES:

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2. Bingham, E.C. *Am. Chem. J.* <u>1907</u>, *37*, 549.
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30. Hradetzky, G.; Bittrich, H.-J. *Int. Data Ser., Sel. Data Mixtures, Ser. A* <u>1986</u>, 216.
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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Hexane; C_6H_{14}; [110-54-3]	Rothmund, V. *Z. Phys. Chem.* 1898, *26*, 433-92.
VARIABLES:	**PREPARED BY:**
Temperature: 278 - 316 K	A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and hexane

$t/^{\circ}C$		100 w_1		x_1 (compiler)	
		(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
4.45	±0.25	-	75.96	-	0.8947
9.00	±0.60	3.02	-	0.0773	-
9.95	±0.35	-	73.60	-	0.8823
15.22	±0.28	3.35	-	0.0853	-
21.67	±0.28	-	67.75	-	0.8496
23.95	±0.35	4.56	-	0.1139	-
24.52	±0.22	-	65.60	-	0.8368
32.40	±0.20	-	59.39	-	0.7973
36.60	±0.30	9.65	-	0.2232	-
39.17	±0.17	-	49.60	-	0.7258
40.05	±0.20	13.76	-	0.3003	-
41.10	±0.10	-	41.33	-	0.6545
41.82	±0.12	-	36.44	-	0.6066
42.52	±0.12	-	30.41	-	0.5403
42.85	±0.15	22.89	-	0.4439	-

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The cloud point method was used. The measurements were carried out in thick-walled glass capillaries. The temperatures of appearance and disappearance of turbidity were observed and the mean value was adopted.	(1) source not specified, pure grade; purified with I_2 and NaOH, distilled, dried with CaO, distilled over $Ba(OH)_2$ and then over Na. (2) Kahlbaum, synthetic; dried over $CaCl_2$, twice fractionated over Na.
	ESTIMATED ERROR: temp.: see above.
	REFERENCES:

COMPONENTS: (1) Methanol; CH_4O; [67-56-1] (2) Hexane; C_6H_{14}; [110-54-3]	ORIGINAL MEASUREMENTS: Bingham, E.C. *Am. Chem. J.* 1907, *37*, 549-57.
VARIABLES: One temperature: 316 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 42.8°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: The components were added from burettes to thick-walled glass tubes of about 2 mm internal diameter and 6-7 mm long which were sealed. The tubes and the components during the adding procedure were protected from moisture. No further details were reported.	SOURCE AND PURITY OF MATERIALS: (1) Kahlbaum, the best provided; used as received. (2) Kahlbaum, the best provided; used as received. ESTIMATED ERROR: not specified. REFERENCES:

COMPONENTS: (1) Methanol; CH_4O; [67-56-1] (2) Hexane; C_6H_{14}; [110-54-3]	ORIGINAL MEASUREMENTS: Schuekarew, A. *Z. Phys. Chem.* 1910, *71*, 90-108.
VARIABLES: One temperature: 317 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 43.8°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: The method was not specified. Only measurements of vapor pressure were reported.	SOURCE AND PURITY OF MATERIALS: (1) source not specified, without acetone; distilled over Na; constant boiling temperature. (2) source not specified; b.p. 69°C, $\rho(17°C) = 0.6632$. ESTIMATED ERROR: not specified. REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Howard, E.J.; Patterson, W.H.

J. Chem. Soc. (London) 1926, *129*, 2787-91.

VARIABLES:

Temperature: 309, 315 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol in hexane

$t/^{\circ}C$	$100\ w_1$	x_1 (compiler)
35.5	50.	0.729
42.0 UCST	20.	0.402

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Experiments were carried out in stoppered tubes of thick glass to to avoid evaporation and water absorption. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, practically water free by means of the solubility curve in ref 1.

(2) obtained by fractional dist. of petrol; b.p. range 68-69°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Rothmund, *Z. Phys. Chem.* 1898, *26*, 433.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Hexane; C_6H_{14}; [110-54-3]	Rising, M.M.; Hicks, J.S. *J. Am. Chem. Soc.* 1928, *48*, 1929-33.
VARIABLES:	**PREPARED BY:**
Temperature: 309, 315 K	A. Skrzecz

EXPERIMENTAL VALUES:

Solubility at 36.55°C: methanol in hexane, 1 vol.(1) in 2 vol.(2) or 100 w_1 = 38, x_1 = 0.62 (compiler), using $\rho(1)(20°C)$ = 0.79129, $\rho(2)(20°C)$ = 0.65925 by ref 1.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A mixture of known composition was slowly cooled and warmed in a test tube and the appearance and disappearance of turbidity was observed visually.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, treated with lime; $\rho(15°C)$ = 0.79578.
(2) synthetic; b.p. range 68.6-69.0°C; used as received.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. *Selected Values of Properties of Hydrocarbons and Related Compounds*. API Project 44, TRC, Texas A & M Univ. 1973.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Ferguson, J.B.

J. Phys. Chem. 1932, *36*, 1123-28.

VARIABLES:

Temperature: 316 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 42.4°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The sealed tube method was used. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) Kahlbaum's best grade; dried over freshly ignited lime for three weeks, distilled; b.p. 45°C at 327.9 mm Hg.

(2) Eastman Kodak, synthetic; washed with 95% H_2SO_4, distilled H_2O, dilute $KMnO_4$, distilled H_2O, dried with Na, distilled; b.p. 45°C at 333.0 mm Hg.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Ssementschenko, W.; Gratschewa, S.; Davidoffskaja, E.

Kolloid. Z. 1934, *68*, 275-86.

VARIABLES:

One temperature: 306 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 32.55°C.

(The aritmetic mean value of three experiments viz.,: 32.5, 32.1 and 33.05°C was reported.)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The experiments were conducted in sealed ampoules and the temperature of water thermostat was observed. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; twice distilled over Mg.

(2) Kahlbaum; fractionated; b.p. range 66-67°C.

ESTIMATED ERROR:

temp. ±0.1 K (deviation of thermostat temperature).

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Cornish, R.E.; Archibald, R.C.; Murphy, E.A.; Evans, H.M.

Ind. Eng. Chem. 1934, *26*, 397-406.

VARIABLES:

Temperature: 303 and 305 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 32°C a) and 30.1°C b).

a), b) data for hexane (2) from different sources; see "SOURCE AND PURITY OF MATERIALS" below.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was not specified.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; distilled; $\rho(25°C) = 0.78656$, (corrected fo air buoyancy), anhydrous.

(2) Eastman Kodak Company, synthetic (presumably from propyl iodide).

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*, 764-71.

VARIABLES:

One temperature: 308 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 35°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temperature of disappearance or reappearance of the cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) obtained from petroleum.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Sieg, L.

Chem.-Ing.-Tech. 1951, *23*, 112-3.

VARIABLES:

One temperature: 308 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 34.8°C.

Mutual solubility was presented on a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A mixture of known composition was sealed in an ampoule and the temperature of appearance or disappearance of turbidity was observed. The ampoules and pipettes were filled in a moistureless atmosphere over P_2O_5.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; boiled with Mg, fractionated; physical properties were in agreement with literature values.

(2) prepared from C_3H_7I; fractionated; physical properties were in agreement with literature values.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Suhrmann, R.; Walter, R.

Abh. Braunschweig. Wiss. Ges. 1951, *3*, 135-52.

VARIABLES:

Temperature: 303 - 308 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and hexane

$t/°C$	vol % of (1)		100 w_1 (compiler)		x_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
29.9	-	40.0	-	44.5	-	0.683
32.1	-	35.0	-	39.3	-	0.635
33.8	20.0	-	23.1	-	0.447	-
33.9	-	30.0	-	34.0	-	0.581
34.5	24.0	27.6	27.5	31.4	0.505	0.552
34.6 UCST	25.9	25.9	29.6	29.6	0.531	0.531

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A mixture of known composition was prepared from microburettes which were closed by tube with silica gel or $CaCl_2$. A sample was heated to homogeneity and then temperature of cloud point was observed in a thermostat. The influence of the third component on UCST was observed. The data were reported in vol % measured at 20°C.

SOURCE AND PURITY OF MATERIALS:

(1) Riedel de Haen and Merck, for analysis grade; dried through two weeks over $CaCl_2$, distilled several times over $Mg(ClO_4)_2$; b.p. 64.78°C, $n(18°C) = 1.3292$, $\rho(20°C) = 0.7950 - 0.7955$.

(2) Ruhrchemie Holten; distilled three times; $\rho(20°C) = 0.6608$.

ESTIMATED ERROR:

temp. ±0.1 K.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Quantie, C.

Proc. Roy. Soc. London ser. A 1954, *224*, 90-104.

VARIABLES:

One temperature: 301 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

UCST = 28.1°C at 100 w_1 = 32.6 or x_1 = 0.565 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The method was based on the fact that the separation of a noncritical mixture in a vertical tube starts with the formation of a sharp boundary at the top or the bottom. If the mixture is very near the critical concentration, diffuse boundaries start at both ends. Finally, if the mixture has the critical composition and the rate of cooling is slow, a sharp boundary appears at a certain height at the critical temperature which is nearly independent of further variation of temperature.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Smirnov, B.A.; Predvoditelev, A.A.

Zh. Fiz. Khim. 1954, *28*, 906-13.

VARIABLES:

One temperature: 310 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 36.6°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was not specified.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, technical grade; three times distilled; $\rho/\rho(20°C)$ = 0.7914.

(2) VNII Khimgaz; b.p. 68.8°C, $\rho/\rho(20°C)$ = 0.6604.

ESTIMATED ERROR:

temp. ±0.3 K.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Kogan, V.B.; Deizenrot, I.V.;

Kul'byaeva, T.A.; Fridman, V.M.

Zh. Prikl. Khim. 1956, *29*, 1387-92.

VARIABLES:

Temperature: 275 - 293 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and hexane

$t/^{\circ}C$	$100\ w_1$		x_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
2	4.14	74.92	0.1041	0.8893
10	4.92	72.11	0.1222	0.8743
10 a)	4.9	72.2	0.122	0.875
20 a)	7.6	62.2	0.181	0.816

a) from hexane - methanol - water ternary equilibrium data.

(1)-rich phase was observed to be the lower layer.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. The two-phase mixture was periodically shaken in a thermostatted buret with with water jacket for several hours. The phases were removed for analysis after separation. Methanol was determined twice by reaction with phthalic anhydride.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, pure grade; distilled; < 0.01% of water; $n(20^{\circ}C) = 1.3391$.

(2) source not specified; used as received; b.p. 68.7°C, $n(20^{\circ}C) = 1.3753$.

ESTIMATED ERROR:

soly. < ±1% (relative error of methanol concentration);
temp. ±0.05 K.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.;
Shetlar, M.D.

J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 278 - 306 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of hexane in methanol

$t/^\circ C$	g(2)/100 ml(1)	100 w_1 (compiler)	x_2 (compiler)
5	32.4	28.7	0.130
10	37.0	31.6	0.147
15	42.7	34.9	0.166
20	49.5	38.5	0.189
25	60.4	43.4	0.222
30	80.	51.5	0.283
33.2	UCST		

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4^\circ C) = 0.80999 - 9.253\ 10^{-4}\ (t/^\circ C) - 4.1\ 10^{-7}\ (t/^\circ C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; $n_D(20^\circ C) = 1.3293$, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Fisher certified; used as received; absence of unsaturated compounds by u.v. analysis, without impurities by glc analysis, estimated impurities < 0.05 mole %; $n_D(20^\circ C) = 1.3794$.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables vol. 3*, New York, 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Savini, L.G.; Winterhalter, D.R.; Van Ness, H.C.

J. Chem. Eng. Data 1965, *10*, 171-2.

VARIABLES:

Temperature: 298 - 307 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and hexane

$t/^\circ C$	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
25	0.270	0.791	12.09	58.46
30	0.330	0.745	15.48	52.07
33.7	0.535	0.590	29.96	34.86
33.7 a)	0.560	0.560	32.12	32.12

a) interpolated UCST.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isothermal dilution calorimeter for heat of mixing determination was used. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) Fisher Scientific Co., certified reagent; purity > 99.9%; b.p. 64.4 ±0.05°C; used as received.

(2) Philips Petroleum Co., pure grade, purity > 99 mole %; distilled; purity 99.9% by glc.

ESTIMATED ERROR:

Accuracy of results to well within ±1%.

REFERENCES:

COMPONENTS: (1) Methanol; CH_4O; [67-56-1] (2) Hexane; C_6H_{14}; [110-54-3]	ORIGINAL MEASUREMENTS: Myers, D.B.; Smith, R.A.; Katz, J. Scott, R.L. *J. Phys. Chem.* 1966, *70*, 3341-3.
VARIABLES: One temperature: 310 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 309.6 K at 1 atm.

The derivative dT_c/dP was determined to be 0.0338 ± 0.0012 K/bar.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The synthetic method was used. The apparatus was the same as used in ref 1. Mixtures were contained over Hg in a glass tube attached to a stainless steel U tube. Pressure up to 10 MPa was applied from a nitrogen cylinder. Samples were observed through a window in a plywood box. Critical phenomena were determined while slowly stirring the mixture with a glass-enclosed magnetic bar and while cooling the bath at a rate of 0.1°C per min or less. Three to eleven points were determined.

SOURCE AND PURITY OF MATERIALS:

(1) not specified.

(2) not specified.

ESTIMATED ERROR:

temp. ±0.05 K.

REFERENCES:

1. Furrow, S.D.
   M.S. Thesis, University of Maine 1962.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Schmidt, R.; Werner, G.; Schuberth, H

Z. Phys. Chem. <u>1969</u>, *242*, 381-90.

VARIABLES:

Temperature: 293 - 308 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and hexane

t/°C	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
20.0	0.193	0.822	8.17	63.2
22.5	0.217	0.808	9.34	61.0
25.0	0.245	0.792	10.77	58.6
27.5	0.280	0.771	12.63	55.6
30.0	0.324	0.743	15.13	51.8
32.5	0.391	0.696	19.27	46.0
34.5 UCST	0.553	0.553	31.5	31.5

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The temperature of turbidity was observed in sealed ampoules. The experimental results were symmetrized by the method of Malesinska, ref 1, and the smoothed values were reported.

SOURCE AND PURITY OF MATERIALS:

(1) VEB Leuna-Werke 'Walter Ulbricht'; boiled with Mg, fractionated; n_D(15°C) = 1.3306, ρ(20°C) = 0.7914, b.p. 64.50°C.

(2) VEB Synthesewerk Schwarzheide; fractionated; b.p. 68.70°C, n_D(15°C) = 1.3776, ρ(20°C) = 0.6590.

ESTIMATED ERROR:

temp. ±0.15 K (difference between experimental and calculated temperature).

REFERENCES:

1. Malesinska, B.; Malesinski, W. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* <u>1960</u>, *3*, 61.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Rudakovskaya, T.S.; Vinogradova, L.I.; Timofeev, V.S.; Serafimov, L.A.

Sb. Nauch. Tr. Ivanov. Energ. Inst. 1972, (14), 249-55.

VARIABLES:

Temperature: 285 and 293 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and hexane

$t/^\circ C$	$100\ w_1$		x_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
12.	5.1	69.0	0.126	0.8569
20.	8.7	63.0	0.204	0.8208

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The titration method was used.
No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; purified; b.p. 64.5°C, n^{20} 1.3290.
(2) source not specified; purified; b.p. 68.8°C, n^{20} 1.3746.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Budantseva, L.S.; Lesteva, T.M.; Nemtsov, M.S.
Zh. Fiz. Khim. 1976, *50*, 1343-44; *Russ. J. Phys. Chem. (Engl. Transl.)* 1976, *50*, 814; **Dep. Doc. VINITI* 1976, 438.

VARIABLES:
One temperature: 293 K

PREPARED BY:
A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities at 20°C:
methanol in hexane: x_1 = 0.2360, w_1 = 10.30 (compiler).
hexane in methanol: x_2 = 0.1610, w_1 = 34.04 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
The analytical method was used. Hexane was analyzed by gas chromatography. The measurements were described for ternary systems only.

SOURCE AND PURITY OF MATERIALS:
(1) source not specified.
(2) source not specified; distilled; purity > 99.9%.

ESTIMATED ERROR:
not specified.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Sergeeva, V.F.; Ustanova, I.Z.
Zh. Obshch. Khim. 1973, *43*, 1878-81; *J. Gen. Chem. USSR (Engl. Transl.)* 1973, *43*, 1866-8.

VARIABLES:
One temperature: 298 K

PREPARED BY:
A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities at 20°C:
methanol in hexane: x_1 = 0.210, w_1 = 8.99 (compiler).
hexane in methanol: x_2 = 0.209, w_1 = 41.54 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
The method was not specified.

SOURCE AND PURITY OF MATERIALS:
(1), (2) source not specified; purified and dried; physical properties agreed with literature.

ESTIMATED ERROR:
not specified

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Radice, F.C.; Knickle, H.N.

J. Chem. Eng. Data 1975, *20*, 371-2.

VARIABLES:

Temperature: 255 - 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and hexane

t/°C		100 w_1		x_1	
		(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
-17.8	±0.5	1.98	83.68	0.0515	0.9324
5.0	±0.25	4.12	74.36	0.1036	0.8864
25.0	±0.25	10.11	60.04	0.2322	0.8016

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. The cells were charged with about 15 mL of mixture of approx. 70 mass % hexane, then they were tightly closed, shaken periodically and placed in a constant temperature bath for more than 3 h. Samples of each layer were analyzed by glc.
Data for the ternary system methanol - hexane - 2-propanol are also given.

SOURCE AND PURITY OF MATERIALS:

(1) Phillips Petroleum Co., pure grade; purity > 99.5% by glc; used as received.

(2) Phillips Petroleum Co., pure grade; purity > 99.0% by glc; used as received.

ESTIMATED ERROR:

soly. < ±0.01% (relative error of analysis);
temp.: see above.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Balasubramanian, D.; Mitra, P.

J. Phys. Chem. 1979, *83*, 2724-7.

VARIABLES:

One temperature: 307 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 33.7°C at x_1 = 0.40.

The corresponding mass percentage, calculated by the compiler, is 100 w_1 = 20.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was described in ref 1. Experiments were conducted with sealed tubes to avoid moisture contamination. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified; the best analytical grade available; used as received.

ESTIMATED ERROR:

not specified

REFERENCES:

1. Hales, B.J.; Bertrand, G.L.; Hepler, L.G. J. Phys. Chem. 1960, *70*, 3970.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Skripov, V.P.; Vitkalov, V.S.; Kolpakov, Yu. D.

Zh. Fiz. Khim. 1980, *54*, 1754-8; *Russ. J. Phys. Chem. (Engl. Transl.)* 1980, *54*, 997-9.

VARIABLES:

One temperature: 307 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 34.93°C at w_1 = 34.55.
The corresponding mole fraction, calculated by the compiler, is x_1 = 0.5867.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Light scattering near the critical point was observed in a glass ampoule of 70 mm length and 9 mm diameter with magnetic stirrer when equilibrium was stabilized after a change in temp. The system was thermostatted for 30-40 h.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified.

ESTIMATED ERROR:

temp. ±0.003 K.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Grekova, I.G.; Shimanskaya, E.T.;

Shimanskii, Yu.I.

Ukr. Fiz. Zh. 1981, *26*, 283-7.

VARIABLES:

One temperature: 309 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The solubility was reported to be 36.12°C at w_1 = 30.6.
The corresponding mole fraction, calculated by the compiler,
is x_1 = 0.539.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The optical schlieren method of Töpler, ref 1, was used. The measurements were made to study a gravitational effect near the critical liquid-liquid point.

SOURCE AND PURITY OF MATERIALS:

(1) not specified; distilled.

(2) not specified; distilled.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Shimanska, O.T.; Shimanski, Yu.I. *Visn. Kiev. Univ., Ser. Fiz.* 1967, (7), 35.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Alekhin, A.D.; Barkov, M.G.;

Kuleshova, N.P.

Ukr. Fiz. Zh. 1983, *28*, 68-72.

VARIABLES:

One temperature: 308 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 34.8°C at w_1 = 31.0.
The corresponding mole fraction, calculated by the compiler,
is x_1 = 0.547.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The light scattering method was used. The apparatus and procedure were described in ref 1.
The insensitivity of scattering light at the angle of 90 degree was measured.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified.

ESTIMATED ERROR:

temp. ±0.005 K.

REFERENCES:

1. Alekhin, A.D.; Krupskii, N.P. *Fiz. zhidkogo sostoyaniya* 1975, 3, 48.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Khurma, J.R.; Fenby, D.V.

Aust. J. Chem. 1982, *35*, 1281-4.

VARIABLES:

Temperature: 298 - 307 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and hexane

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
297.89	0.2551	-	11.30	-
300.25	-	0.7737	-	55.97
303.73	-	0.7327	-	50.48
304.93	0.3845	-	18.85	-
305.32	-	0.6945	-	45.81
306.14	0.4466	-	23.08	-
306.62	0.5120	-	28.06	-
306.66	-	0.6038	-	36.17
306.66	-	0.5880	-	34.67
306.70 UCST	0.560	0.560	32.1	32.1

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. Sample tubes containing mixtures of known composition were prepared by distillation under vacuum from the bulk degassed pure components and sealed. Phase separation was observed visually. The temperature of a silicone oil bath was controlled by a precision temperature controller (Tronac PTC 60) and measured with calorimeter thermometers which had been calibrated against a platinum resistance thermometer. For each sample the phase separation temp. was measured several times.

SOURCE AND PURITY OF MATERIALS:

(1) B.D.H., Aristar grade; dried over freshly activated molecular sieve type 3A, degassed by vacuum sublimation.

(2) Phillips, research grade; dried over freshly cut Na, degassed by vacuum sublimation.

ESTIMATED ERROR:

temp. ±0.02 K, ±0.04 K (UCST).

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Kasapova, N.L.; Pozharskaya, G.I.; Kolpakov, Yu.D.; Skripov, V.P.

Zh. Fiz. Khim. 1983, *57*, 2182-5.

VARIABLES:

Temperature: 299 - 307 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and hexane

T/K	x_1		100 w_1	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
298.85	0.2515	-	11.09	-
300.95	-	0.7655	-	54.80
303.20	-	0.7411	-	51.52
303.95	0.3462	-	16.43	-
305.89	-	0.6835	-	44.50
306.71	0.4498	-	23.29	-
306.79	-	0.6484	-	40.67
307.03	-	0.6032	-	36.08
307.06	0.5442	-	30.72	-
307.37	0.4680	-	25.30	-
307.40 UCST	0.5695	0.5695	32.94	32.94

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The optical method was used, ref 1. The ampoules with the mixture were prepared in liquid nitrogen. They were heated in a thermostat, mixed with a magnetic stirrer and then slowly cooled with the step of 0.005 - 0.01 K up to the temperature in which the insensitivity of the scattered light was changed. The mean of two experiments was reported. The wavelengths of 0.578, 0.546 and 0.436 were used.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; distilled with Mg.

(2) source not specified, chemical pure by chromatography; used as received.

ESTIMATED ERROR:

temp. ±0.01 K.

REFERENCES:

1. Vitkalov, V.S.; Kolpakov, Yu.D. in the book: *Teplofizika i termodinamika*, UNTs AN SSSR, Sverdlovsk 1974, 27.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Hoelscher, I.F.; Schneider, G.M.; Ott, J.B.

Fluid Phase Equilib. 1986, *27*, 153-69.

VARIABLES:

Temperature: 280 - 340 K
Pressure: 0.1 - 151 MPa

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol and hexane

T/K	p/MPa	x_1	100 w_1 (compiler)	
307.2	0.1	0.54	30.4	UCST extrapolated
292.7	1.0	0.219	9.4	
295.0	10.0	0.219	9.4	
297.4	20.0	0.219	9.4	
299.7	30.0	0.219	9.4	
301.7	40.0	0.219	9.4	
303.9	49.9	0.219	9.4	
305.9	59.9	0.219	9.4	
309.4	80.0	0.219	9.4	
312.6	99.8	0.219	9.4	
315.6	120.8	0.219	9.4	
318.3	140.3	0.219	9.4	
319.8	150.4	0.219	9.4	
297.5	1.0	0.249	11.0	
300.0	10.0	0.249	11.0	

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A high-pressure optical cell (ref 1) with sapphire windows with sandwich seals Al-to-Au-to-Al and magnetic stirring was used. Pressure was measured by Heise gauge calibrated calibrated against a dead-weight gauge, temperature by chromel-to-alumel thermocouple calibrated against certified platinum res. thermometer. Equilibrium temps. were found from visual observation of phase separation as the sample was cooled. The composition was determined from the volumes added to the cell. Special precautions were taken to exclude moisture from the samples. Data for 0.1 MPa were extrapolated.

SOURCE AND PURITY OF MATERIALS:

(1) Fisher, purity 0.999 mole fraction; distilled twice over Na in 2 m column packed with glass helices; purity > 0.9999 mole fraction by glc analysis.

(2) Phillips, research grade; purity 0.9989 mole fraction by glc analysis; used as received.

ESTIMATED ERROR:

temp. ±0.2 K, ±0.1 K at p = 0.1 MPa.
pressure ±0.2 MPa.
composition ±0.005 mole fraction.

REFERENCES:

1. Liphard, K.G.; Schneider, G.M. *J. Chem. Thermodyn.* 1975, 7, 805.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Hoelscher, I.F.; Schneider, G.M.; Ott, J.B.

Fluid Phase Equilib. 1986, *27*, 153-69.

EXPERIMENTAL VALUES: (Continued)

Solubility of methanol and hexane

T/K	p/MPa	x_1	100 w_1 (compiler)
302.8	20.0	0.249	11.0
305.2	30.0	0.249	11.0
307.7	40.0	0.249	11.0
310.0	50.0	0.249	11.0
312.0	60.0	0.249	11.0
315.7	80.0	0.249	11.0
318.9	100.3	0.249	11.0
322.0	120.4	0.249	11.0
324.9	140.5	0.249	11.0
326.5	150.4	0.249	11.0
302.1	1.0	0.297	13.6
305.1	10.0	0.297	13.6
308.0	20.0	0.297	13.6
310.4	30.0	0.297	13.6
312.6	40.0	0.297	13.6
315.1	50.0	0.297	13.6
317.3	60.0	0.297	13.6
321.1	80.0	0.297	13.6
324.8	100.4	0.297	13.6
328.1	120.3	0.297	13.6
331.3	140.3	0.297	13.6
332.7	150.1	0.297	13.6
305.0	1.0	0.336	15.8
307.8	10.0	0.336	15.8
310.7	20.0	0.336	15.8
313.4	30.0	0.336	15.8
316.0	40.0	0.336	15.8
318.3	50.0	0.336	15.8
320.6	60.0	0.336	15.8
324.6	79.9	0.336	15.8
328.4	100.4	0.336	15.8
331.8	120.5	0.336	15.8
335.1	140.3	0.336	15.8
336.6	150.4	0.336	15.8
307.6	1.0	0.438	22.5
310.6	10.0	0.438	22.5
313.6	20.0	0.438	22.5
316.4	29.9	0.438	22.5
319.0	40.0	0.438	22.5
321.4	50.0	0.438	22.5
323.7	59.9	0.438	22.5
327.9	80.0	0.438	22.5
331.7	100.8	0.438	22.5
335.2	120.8	0.438	22.5
338.1	140.3	0.438	22.5
339.6	149.9	0.438	22.5
307.5	1.0	0.510	27.9
310.5	10.0	0.510	27.9
313.6	20.0	0.510	27.9
316.5	30.0	0.510	27.9

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Hexane; C_6H_{14}; [110-54-3]	Hoelscher, I.F.; Schneider, G.M.; Ott, J.B. *Fluid Phase Equilib.* 1986, *27*, 153-69.

EXPERIMENTAL VALUES: (Continued)

Solubility of methanol and hexane

T/K	*p*/MPa	x_1	100 w_1 (compiler)
319.1	40.0	0.510	27.9
321.5	50.0	0.510	27.9
323.7	60.0	0.510	27.9
327.9	80.0	0.510	27.9
331.7	100.4	0.510	27.9
335.0	120.0	0.510	27.9
338.1	140.3	0.510	27.9
339.6	150.4	0.510	27.9
307.5	1.0	0.572	33.2
310.5	10.0	0.572	33.2
313.6	20.0	0.572	33.2
316.4	30.0	0.572	33.2
319.1	40.0	0.572	33.2
321.4	50.0	0.572	33.2
323.7	60.0	0.572	33.2
327.8	80.0	0.572	33.2
331.6	100.5	0.572	33.2
335.0	120.3	0.572	33.2
337.9	140.3	0.572	33.2
339.3	150.4	0.572	33.2
302.9	1.0	0.724	49.4
306.0	10.0	0.724	49.4
309.0	20.0	0.724	49.4
311.6	30.0	0.724	49.4
313.8	40.0	0.724	49.4
316.1	50.0	0.724	49.4
317.9	60.0	0.724	49.4
321.4	80.0	0.724	49.4
324.4	100.6	0.724	49.4
326.7	120.3	0.724	49.4
329.0	140.5	0.724	49.4
330.0	150.5	0.724	49.4
279.9	1.1	0.806	60.7
282.7	10.0	0.806	60.7
285.4	20.0	0.806	60.7
288.2	30.1	0.806	60.7
290.8	40.0	0.806	60.7
293.2	50.0	0.806	60.7
295.5	59.9	0.806	60.7
299.7	79.9	0.806	60.7
303.4	100.3	0.806	60.7
307.1	120.1	0.806	60.7
310.2	139.8	0.806	60.7
311.8	149.9	0.806	60.7
311.8	149.9	0.806	60.7

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Hexane; C_6H_{14}; [110-54-3]	Hoelscher, I.F.; Schneider, G.M.; Ott, J.B. *Fluid Phase Equilib.* 1986, *27*, 153-69.

EXPERIMENTAL VALUES: (Continued)

COMMENTS AND ADDITIONAL DATA:

Data for isopleths at high pressures were fitted to the Simon equation

$$p(x,T)/\text{MPa} = a[(T/T_0)^c-1]$$

From these equations, the corresponding $(T,\ x)$ isobars were calculated and were fitted to the equation

$$T/\text{K} = T_c/\text{K}+k|y-y_c|^{\nu}$$

where

$$y = \alpha x_1/[1+x_1(\alpha-1)]$$
$$y_c = \alpha x_{c1}/[1+x_{c1}(\alpha-1)]$$

The coefficients found are (s = std. error of estimate):

x_1	T_0/K	a	c	s/K
0.219	292.4	114.66	9.38	0.07
0.249	297.1	92.07	10.36	0.13
0.297	302.0	105.63	9.15	0.12
0.336	304.7	103.36	9.02	0.04
0.438	307.3	89.26	9.87	0.03
0.510	307.2	84.87	10.17	0.02
0.572	307.1	81.21	10.50	0.04
0.724	302.5	48.70	16.12	0.08
0.806	279.5	109.69	7.88	0.07

p/MPa	T_c/K	k	α	x_{c1}	ν	s
0.1	307.2	-4420	0.596	0.535	4.280	0.10
25	315.1	-4540	0.589	0.539	4.252	0.16
50	321.5	-3649	0.638	0.533	4.087	0.19
75	326.9	-2828	0.709	0.525	3.900	0.19
100	331.6	-2225	0.790	0.517	3.718	0.18
125	335.8	-1791	0.880	0.508	3.544	0.15
150	339.6	-1472	0.978	0.500	3.378	0.13

Equations are also given for $(p,\ x)$ pairs, which are of the same form as those for the $(T,\ x)$ pairs.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-82-7]

ORIGINAL MEASUREMENTS:

Hradetzky, G.; Bittrich, H.-J.

Int. Data Ser., Sel. Data Mixtures, Ser. A 1986, 216.

VARIABLES:

Temperature: 245 - 307 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and hexane

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
245.15	-	0.9300	-	83.16
257.37	0.0467	-	1.79	-
259.85	-	0.9086	-	78.71
261.25	0.0590	-	2.28	-
265.59	0.0730	-	2.84	-
266.07	-	0.8997	-	76.93
269.63	0.0884	-	3.48	-
269.65	0.0835	-	3.28	-
270.95	-	0.8899	-	75.03
273.35	-	0.8849	-	74.08
273.97	0.0992	-	3.93	-
275.49	0.1154	-	4.63	-
280.11	-	0.8665	-	70.70
282.17	0.1356	-	5.51	-
283.15	-	0.8600	-	69.55
284.20	0.1536	-	6.32	-

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud-point method was used. Glass ampoules of about 20 mL capacity filled with known masses of pure components and sealed carefully to avoid contamination with moisture were immersed in a water thermostat equipped with a Hg-in-glass thermometer (ASMW, certified by the Bureau of Standards, GDR). Phase changes were observed visually as the mixture was cooled at 0.02 K/min Weighings accurate to 0.0001 g. Readings accurate to within 0.01 K. Reproducibility of temp. better than 0.03 K. Critical solution temp. and composition determined graphically using Caillet-Mathias rule.

SOURCE AND PURITY OF MATERIALS:

(1) VEB Leuna Werke (Leuna, GDR), stated purity > 99.9 mass %; used as received; < 50 mg/kg water as determined by Karl Fischer method.

(2) VEB Laborchemie (Apolda, GDR), analytical grade; washed with H_2SO_4, fractionally dist., dried over molecular sieve type 3A; purity 99.9 mole % by capillary glc (no aromatic impurities).

ESTIMATED ERROR:

soly. ±0.0002 mole fraction,
±0.004 mole fraction for UCST.

temp. ±0.03 K

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexane; C_6H_{14}; [110-54-3]

ORIGINAL MEASUREMENTS:

Hradetzky, G.; Bittrich, H.-J.

Int. Data Ser., Sel. Data Mixtures, Ser. A 1986, 216.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and hexane

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
285.39	0.1616	-	6.69	-
285.85	-	0.8494	-	67.71
286.15	-	0.8516	-	68.09
289.25	0.1783	-	7.47	-
292.55	-	0.8274	-	64.06
292.81	-	0.8229	-	63.34
293.15	0.2104	-	9.01	-
293.41	0.2074	-	8.87	-
297.27	0.2523	-	11.15	-
298.15	0.2583	-	11.46	-
299.63	-	0.7805	-	56.94
300.67	-	0.7675	-	55.10
300.75	0.2942	-	13.42	-
302.60	-	0.7466	-	52.28
303.33	0.3415	-	16.17	-
304.05	0.3547	-	16.97	-
304.48	-	0.7180	-	48.63
304.85	0.3796	-	18.53	-
304.90	-	0.7043	-	46.97
306.20	0.4551	-	23.70	-
306.21	-	0.6512	-	40.97
306.37	0.4610	-	24.13	-
306.49	0.4736	-	25.07	-
306.57	-	0.6236	-	38.12
306.64	0.4983	-	26.97	-
306.71	0.5005	-	27.14	-
306.72	0.5296	-	29.51	-
306.73	-	0.5840	-	34.30
306.75 UCST	0.546	0.546	30.9	30.9

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Hexane; C_6H_{14}; [110-54-3]	Nagata, I. *Thermochim. Acta* 1987, *114*, 227-38.
VARIABLES: One temperature: 298 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubilities at 25°C:

methanol in hexane: $x_1 = 0.2550$, $100\ w_1 = 9.74$ (compiler).

hexane in methanol: $x_2 = 0.2005$, $100w_2 = 40.28$ (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. A two-phase mixture in an equilibrium cell of volume 70 mL was stirred intensely for 2 h and then was allowed to settle for 2 h within a thermostatted water bath. Both phases were withdrawn with Hamilton syringes and analyzed by glc (Shimadzu GC-8C and integrator Shimadzu C-E1B). Four analyses were made for each phase.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, C.P.grade; dried over CaO, distilled; no impurities by glc; density at 25°C was in agreement with literature value.

(2) source not specified; no impurities by glc; density at 25°C agreed with values in literature; used as received.

ESTIMATED ERROR:

soly. ±0.002 mole fraction (reproducibility);
temp. ±0.01 K.

REFERENCES:

COMPONENTS: (1) Methanol; CH_4O; [67-56-1] (2) 2-Methylpentane; C_6H_{14}; [107-83-5]	ORIGINAL MEASUREMENTS: Myers, D.B.; Smith, R.A.; Katz, J. Scott, R.L. *J. Phys. Chem.* 1966, *70*, 3341-3.
VARIABLES: One temperature: 306 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 305.8 K at 1 atm.

The derivative dT_c/dP was determined to be 0.0330 ± 0.0009 K/bar.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The synthetic method was used. The apparatus was the same as used in ref 1. Mixtures were contained over Hg in a glass tube attached to a stainless steel U tube. Pressure up to 10 MPa was applied from a nitrogen cylinder. Samples were observed through a window in a plywood box. Critical phenomena were determined while slowly stirring the mixture with a glass-enclosed magnetic bar and while cooling the bath at a rate of 0.1°C per min or less. Three to eleven points were determined.

SOURCE AND PURITY OF MATERIALS:

(1) not specified.

(2) not specified.

ESTIMATED ERROR:

temp. ±0.05 K.

REFERENCES:

1. Furrow, S.D.
M.S. Thesis, University of Maine 1962.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) 3-Methylpentane; C_6H_{14}; [96-14-0]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.; Shetlar, M.D.

J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 278 - 300 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of 3-methylpentane in methanol

t/°C	g(2)/100 ml(1)	100 w_1 (compiler)	x_2 (compiler)
5	38.9	32.6	0.152
10	45.0	36.0	0.173
15	53.0	40.0	0.198
20	65.	45.1	0.234
25	91.	53.6	0.301
27.2	UCST		

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4^\circ C) = 0.80999 - 9.253\ 10^{-4}\ (t/^\circ C) - 4.1\ 10^{-7}\ (t/^\circ C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; $n_D(20^\circ C) = 1.3293$, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Matheson, Coleman and Bell; used as received; $n_D(20^\circ C) = 1.3762$

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables vol. 3*, New York, 1933.

COMPONENTS:	EVALUATOR:
(1) Methanol; CH_4O; [67-56-1] (2) 1-Heptene; C_7H_{14}; [592-76-7]	A. Maczynski Institute of Physical Chemistry Polish Academy of Sciences Warsaw, Poland July, 1989

CRITICAL EVALUATION:

The upper critical solution temperature (UCST) for the system methanol (1)-1-heptene (2) was reported in the two following papers:

Author(s)	T/K	
1. Francis 1944	285	UCST
2. Pavlova 1975	271.6	UCST

The UCST data of Francis, ref 1, and Pavlova et al., ref 2, are treated as tentative. Although the values differ by 13 K, there is no valid criterion for preferring one over the other.

REFERENCES:

1. Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 764.
2. Pavlova, O.P.; Gaile, A.A.; Proskuryakov, K.A.; Li, I.F. *Zh. Fiz. Khim.* 1975, *49*, 2874.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) 1-Heptene; C_7H_{14}; [592-76-7]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*, 764-71.

VARIABLES:

One temperature: 285 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 12°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temperature of disappearance or reappearance of the cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, "substancially pure"; used as received.

(2) obtained by the Grignard reaction; purified; $\rho(20^{\circ}C) = 0.6980$, b.p. range 93 - 93.5°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) 1-Heptene; C_7H_{14}; [592-76-7]

ORIGINAL MEASUREMENTS:

Pavlova, O.P.; Gaile, A.A.;

Proskuryakov, K.A.; Li, I.F.

Zh. Fiz. Khim. 1975, *49*, 2874-6.

VARIABLES:

One temperature: 272 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be -1.6°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was not specified.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Methylcyclohexane; C_7H_{14};
[108-87-2]

EVALUATOR:

A. Skrzecz and A. Maczynski
Institute of Physical Chemistry
Polish Academy of Sciences
Warsaw, Poland

J.W. Lorimer
Department of Chemistry
The University of Western Ontario
London, Ont., Canada

July, 1989

CRITICAL EVALUATION:

Table 1 lists reported solubilities, upper critical solution temperatures (UCST) and compositions for the system methanol (1) - methylcyclohexane (2).

Table 1. Solubilities, upper critical solution temperatures and compositions for the system methanol (1) - methylcyclohexane (2)

Author(s)	T/K	Range x_1 (2)-rich phase	 x_1 (1)-rich phase
1. Francis 1944	320 UCST	-	-
2. Francis 1944	320 UCST	-	-
3. Sieg 1951	317.7 UCST	-	-
4. Francis 1954	319 UCST	-	-
5. Kiser 1961	278-319.2 UCST	-	0.769-0.902
6. Schmidt 1969	293.2-318.2 UCST	0.132-0.566	0.566-0.865
7. Nagata 1984	298.2	0.174	0.855

Critical Solution Temperature and Composition

The UCST values of Francis, refs. 1, 2, 4, were obtained with either as-received chemicals or chemicals from unspecified sources; these data are unreliable. The values of Sieg, ref. 3, and Schmidt et al., ref. 6, were found using purified chemicals; Sieg reported precautions to keep the system anhydrous. Kiser et al., ref. 5, used purified methanol, but as-received methylcyclohexane. Schmidt et al. give more extensive solubility data near the critical point, and appear to have carried out more careful work. Therefore, their value, T_c = 318.2 K, is *tentative*.

Mutual Solubilities

Thirty values have been reported, in addition to data for critical solution points. These are plotted in fig. 1. The data of Schmidt et al., ref. 6, cover a large range of temperature. Kiser et al.,

(continued)

CRITICAL EVALUATION: (continued)

ref 5, reported solubility of methylcyclohexane in methanol only and found values lower than those in ref. 6 by about 0.005 mole fraction at all measured temperatures; these data are probably within the range of expected error. (The width of a symbol on the plot is 1.6 K or 0.0125 mole fraction.) The two values of Nagata, ref 7, obtained with chemicals used as received from unspecified sources, are higher by 0.01-0.02 mole fraction than those of Schmidt et al., and are rejected. The data from ref. 6 are considered as *tentative*.

The data of Schmidt et al. were fitted to the equation

$$x_1 = x_{c1} \pm B_1\theta^{\beta} \pm B_2\theta^{\beta+w} + A_1\theta \pm B_3\theta^{\beta+2w} + A_2\theta^{1-\alpha+w}$$

where $\theta = |1 - T/T_c|$, + and - refer to the branches below and above the critical composition, and the indices have their theoretical values $\beta = 0.325$, $\alpha = 0.11$, $w = 0.5$. The constants (with standard deviations in parentheses) are:

$x_{c1} = 0.5618$ (0.0003)	$T_c/K = 317.93$ (0.055)	
$B_1 = 0.9346$ (0.014)	$B_2 = -0.3759$ (0.11)	$B_3 = 0.1358$ (0.23)
$A_1 = -2.6154$ (0.045)	$A_2 = 4.8821$ (0.11)	$s = 0.0005$

s is the total standard error of estimate in temperature and composition, assuming equal weights for each; the term in A_2 is necessary to obtain a good fit. Vlaues calculated from this equation are given in Table 2 below.

Table 2. Tentative solubilities in the system methanol-methylcyclohexane

T/K	x_1 (2)-rich phase	x_1 (1)-rich phase	
295.0	0.140	0.858	
300.0	0.171	0.841	
305.0	0.209	0.819	
310.0	0.259	0.789	
315.0	0.342	0.737	
318.2	0.566	0.566	UCST

REFERENCES:

1. Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 764.
2. Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 1096.
3. Sieg, L. *Chem.-Ing.-Tech.* 1951, *23*, 112.
4. Francis, A.W. *J. Am. Chem. Soc.* 1954, *76*, 393.
5. Kiser, R.W.; Johnson, G.D.; Shetlar, M.D. *J. Chem. Eng. Data* 1961, *6*, 338.
6. Schmidt, R.; Werner, G.; Schuberth, H. *Z. Phys. Chem.* 1969, *242*, 381.
7. Nagata, I. *J. Chem. Thermodyn.* 1984, *16*, 737.

(continued)

CRITICAL EVALUATION: (continued)

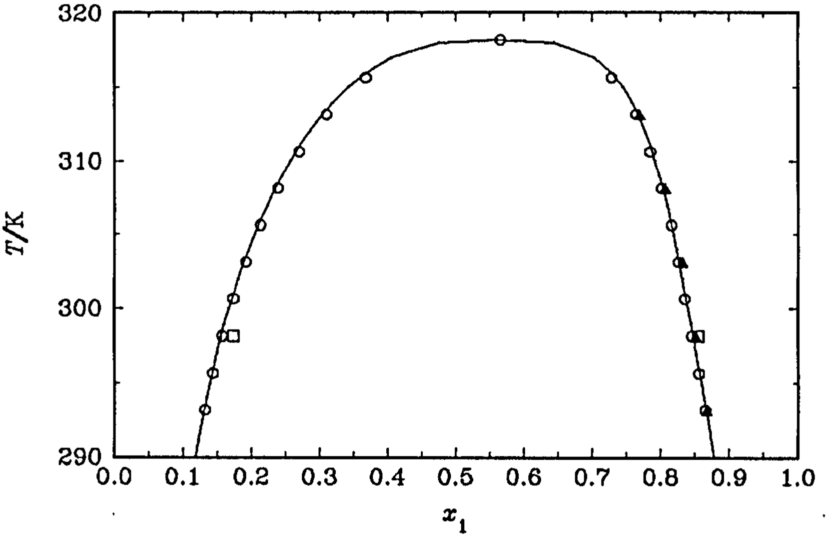

Fig. 1. Solubilities in the system methanol (1) - methylcyclohexane (2). Line: fitting equation (see text). Points and reference: ▲, ref. 5: ○, ref. 6; □, ref. 7.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Methylcyclohexane; C_7H_{14}; [108-87-2]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*, 764-71.

VARIABLES:

One temperature: 320 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 47°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temperature of disappearance or reappearance of the cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, "substancially pure"; used as received.

(2) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Methylcyclohexane; C_7H_{14}; [108-87-2]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*, 1096-1104.

VARIABLES:

One temperature: 320 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 47°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents, about 1 mL of each, were introduced into a small tube and stirred with a thermometer while the tube was warmed gradually in a bath of water or glycerol or was cooled with ice or a bath of acetone and dry ice. The temperature of disappearance or reappearance of the cloud was read three or four times in each direction. The proportion of components was modified to obtain critical solution temperature.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; dried.

(2) source not specified; b.p. 100.8°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Methylcyclohexane; C_7H_{14}; [108-87-2]	Sieg, L. *Chem.-Ing.-Tech.* 1951, *23*, 112-3.
VARIABLES: One temperature: 318 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 44.5°C.

Mutual solubility was presented on a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A mixture of known composition was sealed in an ampoule and the temperature of appearance or disappearance of turbidity was observed. The ampoules and pipettes were filled in a moistureless atmosphere over P_2O_5.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; boiled with Mg, fractionated; physical properties were in agreement with literature values.

(2) source not specified, pure grade; fractionated; physical properties were in agreement with literature values.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Methylcyclohexane; C_7H_{14}; [108-87-2]	Francis, A.W. *J. Am. Chem. Soc.* 1954, *76*, 393-5.
VARIABLES: One temperature: 319 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 46°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The observations were made in narrow graduated glass stoppered tubes immersed in a water bath in a large silver Dewar flask. Compositions were made up by volume from graduated pipettes until cloudiness just disappeared or reappeared. The bath temperature was adjusted by addition of small quantities of cooler or warmer water and stirred several minutes.

SOURCE AND PURITY OF MATERIALS:

(1) J.T. Baker, anhydrous, chemical pure grade; used as received.

(2) source not specified.

ESTIMATED ERROR:

temp. ±0.2°C.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Methylcyclohexane; C_7H_{14}; [108-87-2]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.; Shetlar, M.D.

J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 278 - 319 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methylcyclohexane in methanol

$t/^\circ C$	g(2)/100 ml(1)	100 w_1 (compiler)	x_2 (compiler)
5	26.9	25.0	0.0983
10	29.8	27.1	0.108
15	33.2	29.4	0.120
20	37.2	32.0	0.133
25	42.2	34.9	0.149
30	48.8	38.4	0.169
35	57.5	42.5	0.194
40	70.9	47.9	0.231
46.0	UCST		

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4^\circ C) = 0.80999 - 9.253 \times 10^{-4} (t/^\circ C) - 4.1 \times 10^{-7} (t/^\circ C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore was chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; $n_D(20^\circ C) = 1.3293$, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Matheson, Coleman and Bell, spectroquality; used as received; $n_D(20^\circ C) = 1.42315$.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables vol. 3*, New York, 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Methylcyclohexane; C_7H_{14}; [108-87-2]

ORIGINAL MEASUREMENTS:

Schmidt, R.; Werner, G.; Schuberth, H.

Z. Phys. Chem. 1969, *242*, 381-90.

VARIABLES:

Temperature: 293 - 318 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and methylcyclohexane

$t/^\circ C$	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
20.0	0.132	0.865	4.73	67.6
22.5	0.144	0.856	5.20	66.0
25.0	0.158	0.846	5.77	64.2
27.5	0.174	0.836	6.43	62.5
30.0	0.192	0.826	7.20	60.8
32.5	0.213	0.815	8.12	59.0
35.0	0.239	0.801	9.30	56.8
37.5	0.270	0.785	10.77	54.4
40.0	0.310	0.764	12.79	51.4
42.5	0.368	0.729	15.97	46.7
45.0 UCST	0.566	0.566	29.9	29.9

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The temperature of turbidity was observed in sealed ampoules. The experimental results were symmetrized by the method of Malesinska ref 1, and the smoothed values were reported.

SOURCE AND PURITY OF MATERIALS:

(1) VEB Leuna-Werke 'Walter Ulbricht'; boiled with Mg, fractionated; b.p. 64.50°C, n_D^{15} 1.3306, d^{20} 0.7914.

(2) VEB Buna-Werke Schkopau; fractionated; b.p. 100.93°C, n_D^{15} 1.4257, d^{20} 0.7692.

ESTIMATED ERROR:

temp. ±0.15 K (difference between experimental and calculated temperature).

REFERENCES:

1. Malesinska, B.; Malesinski, W. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* 1960, *3*, 61.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Methylcyclohexane; C_7H_{14}; [108-87-2]	Nagata, I. *J. Chem. Thermodyn.* 1984, *16*, 737-41.
VARIABLES:	PREPARED BY:
One temperature: 298 K	A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubilities at 25°C:

methanol in methylcyclohexane: x_1 = 0.1739, 100 w_1 = 6.428 (compiler).

methylcyclohexane in methanol: x_2 = 0.1453, 100w_2 = 34.25 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The turbidity titration method was used. Details of the measurements are given in ref 1.	(1), (2) source not specified, A two-phase mixture in an spectrograde; densities agreed with values in literature; used as received.
	ESTIMATED ERROR:
	temp. ±0.01 K.
	REFERENCES:
	1. Nagata, I.; Katoh, K. *Thermochim. Acta* 1980, *39*, 45.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

EVALUATOR:

A. Skrzecz
Institute of Physical Chemistry
Polish Academy of Sciences
Warsaw, Poland

J.W. Lorimer
Department of Chemistry
The University of Western Ontario
London, Ont., Canada

July, 1989

CRITICAL EVALUATION:

Solubilities and upper critical solution temperatures (UCST) for the system methanol (1) - heptane (2) have been reported in the references listed below.

Table 1. Summary of solubility data for the system methanol (1) - heptane (2)

Author(s)		Range	
	T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Cornish 1934	324.7 UCST	-	-
2. Francis 1944	324 UCST	-	-
3. Fischer 1949	338.7 UCST	-	-
4. Sieg 1951	324.2 UCST	-	-
5. Francis 1954	324 UCST	-	-
6. Kogan 1956	275-313	0.098-0.240	0.866-0.934
7. Tagliavini 1958	291-323	0.104-0.433	0.756-0.911
8. Kiser 1961	278-324.4 UCST	-	0.843-0.933
9. Chernova 1965	325.1 UCST	0.6291	0.6291
10. Savini 1965	303-318	0.210-0.317	0.822-0.879
11. Sergeeva 1973	298	0.130	0.900
12. Viswanathan 1973	325.02 UCST	0.6135	0.6135
13. Budantseva 1976	293-313	0.176-0.295	0.835-0.912
14. Hradetzky 1986	254-324.06 UCST	0.036-0.610	0.610-0.956
15. Letcher 1986	298	0.176	-
16. Ott 1986	320-357 [a]	0.296-0.579	0.579-0.787
	324.5 UCST	0.588	
17. Ranjan 1986	325.060, 325.68 UCST	-	-
18. Higashiuchi 1987	298-323	0.153-0.453	0.790-0.900
19. Nagata 1987	298	0.158	0.893

[a] At elevated pressures, p = 0.1-151 MPa; UCST at 0.1 MPa.

(continued)

CRITICAL EVALUATION: (continued)

Critical Solution Temperature and Composition

Twelve values of the UCST have been reported, ranging from 324.0 to 338.7 K; see Table 1. The value of Fischer and Neupauer, ref 3, was rejected, and is not compiled; all values in ref. 3 for different alcohol-hydrocarbon systems are higher by about 10-20 K than recommended or tentative values, which indicates presence of significant impurities, probably water. The values of Francis, refs. 2, 5, appear reliable, but are less precise. The remaining values are clustered in two groups. One group of four values (refs. 9, 12, 17) shows an average T_c = 325.2 ± 0.3 K (std. dev.), but all are rejected because of use of unpurified chemicals from unspecified sources or lack of precautions to eliminate water, or both. The other group of five values (refs. 1, 4, 8, 14, 16) shows an average T_c = 324.4 ± 0.3 K (std. dev.). The value of Cornish, ref. 1, was obtained with unspecied materials and by an unspecified method, and is rejected. The remaining four values give a *recommended* value:

$$T_c = 324.3 \pm 0.2 \text{ K } (\pm 1 \text{ std. dev.}).$$

Only four values of the critical comosition are reported (Table 1). Again, two groups of two each are found. The two higher values (refs. 9, 12) are rejected for the same reasons as the corresponding critical solution temperatures. The average of the two lower values (refs. 14, 16) gives a standard deviation within the authors' estimated precision. This value is therefore *recommended*:

$$x_{c1} = 0.599 \pm 0.016 \ (\pm 1 \text{ std. dev.})$$

Mutual Solubility

One hundred and fifteen values of mutual solubilities have been reported in 11 publications, not including critical solution points; these are shown in fig. 1. Inspection of the plot indicates that, except for points at the three highest mole fractions of ethanol, all data of both Kogan et al., ref. 6, and of Tagliavini and Arich, ref. 7, are clearly aberrant, and are rejected. Similarly, one of the four values of Savini et al., ref. 10, one of the two values of Sergeeva et al., ref. 11, all the values of Budantseva et al., ref. 13, the value of Letcher et al., ref. 15, and seven of the values on the methanol-rich side and near the critical solution temperature of Higashuichi et al., ref. 18, are rejected.

Of the remaining 88 values, the data of Ott et al., ref. 16 (extrapolated from high pressures) are close to those of Hradetsky and Bittrich, ref. 14. The respective critical solution temperatures agree to 0.3 K, so adjustment for this reason would not bring the two sets of results into coincidence. (The width of a symbol in fig. 1 is ΔT = 1.6 K, Δx_c = 0.0125.) Therefore, for construction of the fitting equation, all 88 points were used. The equation is:

$$x_1 = x_{c1} \pm B_1\theta^{\beta} \pm B_2\theta^{\beta+w} + A_1\theta \pm B_3\theta^{\beta+2w} + A_2\theta^{1-\alpha+w}$$

where $\theta = |1 - T/T_c|$, + and - refer to the branches below and above the critical composition, and the constants have their theoretical values β = 0.329, α = 0.11, w = 0.5. The constants (with standard deviations in parentheses) are:

x_{c1} = 0.5903 (0.0062)	T_c/K = 324.01 K (0.02 K)	
B_1 = 0.7508 (0.058)	B_2 = 0.7327 (0.40)	B_3 = -1.5583 (0.68)
A_1 = -1.3605 (0.34)	A_2 = 1.6335 (0.65)	s = 0.029

s is the total standard error of estimate in composition. This equation has been used to calculate the *recommended* values in Table 2 below, whose acuracy is estimated to be ± 0.001 in mole fraction.

The only measurements at high pressure are those of Ott et al., ref 8, up to 151 MPa.

(continued)

CRITICAL EVALUATION: (continued)

Consequently, these data (which can be found on the compilation sheets) are considered as *tentative*. These workers extrapolated their data measured at high pressures to 0.1 MPa, and gave the results in terms of the equation

$$T/\mathrm{K} = T_c/\mathrm{K} + k|x_1 - x_{c1}|^{\nu}$$

with

$$y = \alpha x_1/[1+x_1(\alpha+1)]$$
$$y_c = \alpha x_{c1}/[1+x_{c1}(\alpha-1)]$$

The equation is valid over the range $0.2 < x_1 < 0.8$ or $270 < T/\mathrm{K} < 286.92$, where, at 0.1 MPa, $\nu = 3.780$ $T_c = 324.5$ K $k = -1755$ $\alpha = 0.500$ $x_{c1} = 0.588$ See the compilation sheets for the data of Ott et al. at higher pressures, where the methods of fitting and extrapolation are described.

Pressure Coefficient of Critical Solution Temperature

This quantity can be calculated from the fititng equations of Ott et al.:

$$(\partial T_c/\partial p)_{x_c} = T_o/ac = 3.65\times10^{-7}\ \mathrm{K\ Pa^{-1}}$$

where T^o, a, c are constants given on the compilation sheet.

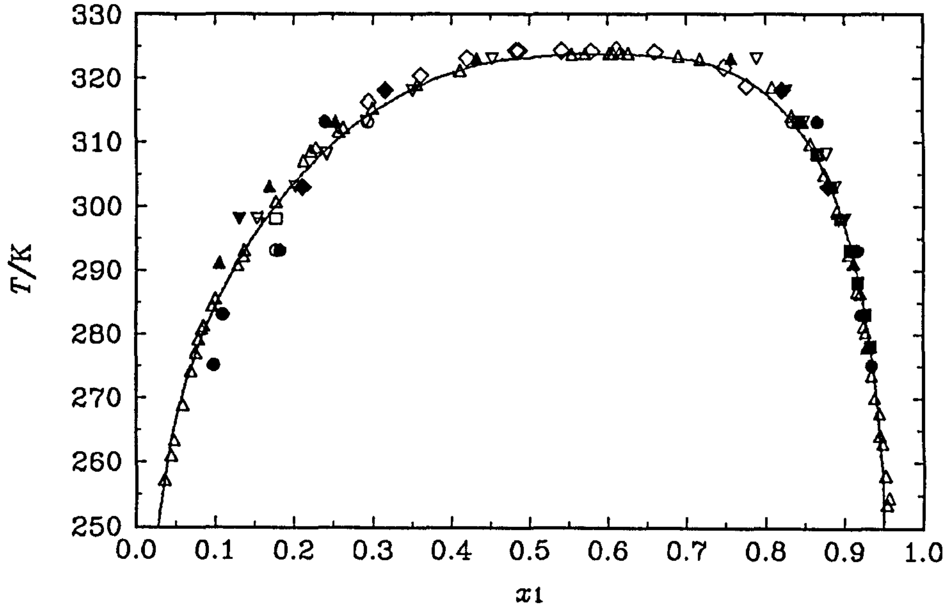

Fig. 1. Solubilities in the system methanol (1) - heptane (2). Line: fitting equation (see text). Points and reference: Points and reference: ●, 6; , 7; ■, 8; ♦, 10; , 11; o, 13; ▵, 14; □, 15; ◇, 16; ▿, 18; +, 19. The plot gives an overall impression of the data.

(continued)

CRITICAL EVALUATION: (continued)

Table 2. Recommended values of solubility in the system methanol (1) - heptane (2)

T/K	x_1 (2)-rich phase	x_1 (1)-rich phase	
250.0	0.028	0.950	
260.0	0.039	0.947	
270.0	0.058	0.940	
280.0	0.084	0.930	
285.0	0.102	0.923	
290.0	0.122	0.915	
295.0	0.147	0.905	
300.0	0.175	0.892	
305.0	0.209	0.875	
310.0	0.251	0.853	
315.0	0.305	0.823	
320.0	0.382	0.772	
324.0	0.565	0.616	
324.3	0.599	0.599	UCST

REFERENCES:

1. Cornish, R.E.; Archibald, R.C.; Murphy, E.A.; Evans, H.M. *Ind. Eng. Chem.* 1934, *26*, 397.
2. Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 764.
3. Fischer, R.; Neupauer, E. *Mikrochem. Ver. Mikrochim. Acta* 1949, *34*, 319.
4. Sieg, L. *Chem.-Ing.-Tech.* 1951, *23*, 112.
5. Francis, A.W. *J. Am. Chem. Soc.* 1954, *76*, 393-5.
6. Kogan, V.B.; Deizenrot, I.V.; Kul'byaeva, T.A.; Fridman, V.M. *Zh. Prikl. Khim.* 1956, *29*, 1387.
7. Tagliavini, G.; Arich, G. *Ric. Sci.* 1958, *28*, 1902-10.
8. Kiser, R.W.; Johnson, G.D.; Shetlar, M.D. *J. Chem. Eng. Data* 1961,*6*, 338.
9. Chernova, N.I. *Zh. Fiz. Khim.* 1965, *39*, 2388.
10. Savini, L.G.; Winterhalter, D.R.; Van Ness, H.C. *J. Chem. Eng. Data* 1965, *10*, 171.
11. Sergeeva, V.F.; Ustanova, I.Z. *Zh. Obshch. Khim.* 1973, *43*, 1878.
12. Viswanathan, B.; Govidarajan, K.; Gopal, E.S.R. *Indian J. Pure Appl. Phys.* 1973, *11*, 157.
13. Budantseva, L.S.; Lesteva, T.M.; Nemstov, M.S. *Zh. Fiz. Khim.* 1976, *50*, 1344; *Deposited Doc. VINITI* 1976, 437.
14. Hradetzky, G.; Bittrich, H.-J. *Int. Data Ser., Sel. Data Mixtures, Ser. A* 1986, 217.
15. Letcher, T.M.; Wootton, S.; Shuttleworth, B.; Heyward, C. *J. Chem. Thermodyn.* 1986, *18*, 1037.
16. Ott, J.B.; Hoelscher, I.F.; Schneider, G.M. *J. Chem. Thermodyn.* 1986, *18*, 815.
17. Ranjan, M.; Jayalaxmi, V.; Vani, V.; Gopal, E.S.R. *Indian J. Phys.* 1986, *60A*, 98-109.
18. Higashiuchi, H.; Sukuragi, Y.; Iwai, Y.; Arai, Y.; Nagatani, M. *Fluid Phase Equilib.* 1987, *36*, 35.
19. Nagata, I. *Thermochim. Acta* 1987, *114*, 227.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Cornish, R.E.; Archibald, R.C.;
Murphy, E.A.; Evans, H.M.
Ind. Eng. Chem. 1934, *26*, 397-406.

VARIABLES:

One temperature: 325 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 51.5°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was not specified.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; distilled; $\rho(25°C)/\rho(4°C) = 0.78656$, (corrected for air buoyancy), anhydrous.

(2) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Francis, A.W.
Ind. Eng. Chem. 1944, *36*, 764-71.

VARIABLES:

One temperature: 324 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 51°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temperature of disappearance or reappearance of the cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, "substancially pure"; used as received.

(2) obtained from Jeffrey pine, no more information.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Francis, A.W.

J. Am. Chem. Soc. 1954, *75*, 393-5.

VARIABLES:

One temperature: 324 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 51°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. Observations were amde in narrow graduated glass-stoppered tubes immersed in a water bath in a large silvered Dewar. Compositions were made up by volume from graduated pipets until cloudiness just disappeared or reappeared. The bath temp. was afjusted by adding small amounts of cooler or warmer water and stirring several minutes.

SOURCE AND PURITY OF MATERIALS:

(1) J.T. Baker, anhydrous, CP grade; used as received.

(2) source not specified.

ESTIMATED ERROR:

temp. ±0.2 K.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Sieg, L.

Chem.-Ing.-Tech. 1951, *23*, 112-3.

VARIABLES:

One temperature: 324 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 51.0°C.

Mutual solubility was presented on a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A mixture of known composition was sealed in an ampoule and the temp. of appearance or disappearance of turbidity was observed. The ampoules and pipets were filled in moisture-free atmosphere over P_2O_5.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; boiled with Mg, fractionated; physical properties were in agreement with literature values.

(2) source not specified, pure grade; fractionated; physical properties were in agreement with literature values.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Kogan, V.B.; Deizenrot, I.V.;

Kul'byaeva, T.A.; Fridman, V.M.

Zh. Prikl. Khim. 1956, *29*, 1387-92.

VARIABLES:

Temperature: 275 - 313 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and heptane

$t/^\circ C$	$100\ w_1$		x_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
2	3.36	81.90	0.0981	0.9340
10	3.75	78.91	0.1086	0.9213
10 a)	3.8	79.0	0.110	0.922
20	6.6	77.6	0.181	0.916
20 a)	6.6	77.7	0.181	0.916
40	9.19	67.4	0.2404	0.866

a) from heptane - methanol - water ternary equilibrium data.

(1)-rich phase was observed to be the lower layer.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. The two-phase mixture was periodically shaken in a thermostatted buret with water jacket for several hours. The phases were removed for analysis after separation. Methanol was determined in duplicate by reaction with phthalic anhydride.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, pure grade; distilled; < 0.01% of water; $n_D(20^\circ C) = 1.3391$.

(2) source not specified; used as received; b.p. 98.4°C, $n_D(20^\circ C) = 1.3877$.

ESTIMATED ERROR:

soly. < ±1% (relative error of methanol concentration); temp. ±0.05 K.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Tagliavini, G.; Arich, G.

Ric. Sci. <u>1958</u>, *28*, 1902-10.

VARIABLES:

Temperature: 291 - 323 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and heptane

t/°C	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
18.	0.1045	0.9110	3.60	76.60
30.	0.1681	0.8835	6.07	70.80
40.	0.2536	0.8486	9.80	64.19
50.	0.4326	0.7563	19.60	49.81

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. The procedure and apparatus were described in ref 1. Composition was determined from refractive index calibration curves for homogeneous mixtures. Data were reported together with ternary system heptane - methanol - morpholine.

SOURCE AND PURITY OF MATERIALS:

(1) Merck, purified by ref 2, distilled over Na; ρ(15°C) = 0.79360, n_D(20°C) = 1.32860.

(2) Philips; analyzed acc. to ref 3, purity 99.95%; n_D(20°C) = 1.38767.

ESTIMATED ERROR:

soly. ±0.0002 mole fraction.

REFERENCES:

1. Tagliavini, G.; Arich, G.; Biancani, M. *Ann. Chim.* <u>1955</u>, *45*, 292.
2. Gillo, L. *Ann. Chim.* <u>1939</u>, *12*, 281.
3. Anderson, J.A.; Zerwekh, C.F. *Anal. Chem.* <u>1949</u>, *21*, 911.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.; Shetlar, M.D.

J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 278 - 324 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of heptane in methanol

t/°C	g(2)/100 ml(1)	100 w_1 (compiler)	x_2 (compiler)
5	18.1	18.3	0.0670
10	20.0	20.0	0.0740
15	22.5	22.0	0.0829
20	25.4	24.3	0.0931
25	28.7	26.7	0.1045
30	32.7	29.5	0.1180
35	37.8	32.7	0.1346
40	45.0	36.8	0.1567
51.2	UCST		

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4°C) = 0.80999 - 9.253\ 10^{-4}\ (t/°C) - 4.1\ 10^{-7}\ (t/°C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; $n_D(20°C) = 1.3293$, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Eastman Organic Chemicals; used as received; 0.8 mole % of impurity, probably unsaturated by u.v. analysis; $n_D(20°C) = 1.3879$.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables vol. 3*, New York, 1933.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Heptane; C_7H_{16}; [142-82-5]	Savini, L.G.; Winterhalter, D.R.; Van Ness, H.C. *J. Chem. Eng. Data* 1965, *10*, 171-2.
VARIABLES:	**PREPARED BY:**
Temperature: 303 and 318 K	A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and heptane

$t/^\circ C$	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
30	0.210	0.879	7.83	69.91
45	0.317	0.822	12.92	59.62

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isothermal dilution calorimeter for heat of mixing determination was used. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) Fisher Scientific Co., certified reagent; purity > 99.9%; b.p. 64.4 ±0.05°C; used as received.

(2) Philips Petroleum Co., pure grade; purity > 99 mole %, trace of impurities by glc; used as received.

ESTIMATED ERROR:

Accuracy of results to well within ±1%.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Heptane; C_7H_{16}; [142-82-5]	Chernova, N.I. *Zh. Fiz. Khim.* 1965, *39*, 2388-93; *Russ. J. Phys. Chem. (Engl. Transl.)* 1965, *39*, 1275-8.
VARIABLES:	**PREPARED BY:**
One temperature: 325 K	A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 51.9°C at w_1 = 35.05 or x_1 = 0.6921 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The mixtures of known composition were prepared in ampoules which after cooling in liquid nitrogen were sealed. The moment of appearance of the second phase as drops was reported. Temperature was measured with a Beckmann thermometer. The measured UCST using three methanol samples of different purity was reported to be 55, 52.5, 50.4°C. The calculated UCST with "pure" methanol obtained after data analysis is reported above. The solubility data were reported in a plot.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, chemical pure grade; used as received.

(2) source not specified, chemical pure grade; used as received.

ESTIMATED ERROR:

soly. w_1 = ±0.05.
temp. ±0.1 K.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Heptane; C_7H_{16}; [142-82-5]	Sergeeva, V.F.; Ustanova, I.Z. *Zh. Obshch. Khim.* <u>1973</u>, *43*, 1878-81; *J. Gen. Chem. USSR (Engl. Transl.)* <u>1973</u>, *43*, 1866-8.
VARIABLES:	PREPARED BY:
One temperature: 298 K	A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities at 25°C:

methanol in heptane: $x_1 = 0.130$, or $100\ w_1 = 4.56$ (compiler).
heptane in methanol: $x_2 = 0.100$, or $100\ w_2 = 25.8$ (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The method was not specified.	(1), (2) source not specified; purified, dried; physical properties agreed with data in literature.
	ESTIMATED ERROR: not specified.
	REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Viswanathan, B.; Govidarajan, K.; Gopal, E.S.R.

Indian J. Pure Appl. Phys. 1973, *11*, 157-62.

VARIABLES:

One temperature: 325 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

UCST = 51.87°C at x_1 = 0.6135 or 100 w_1 = 33.67 (compiler).

Solubility data in the range 50.6 - 51.87°C were presented in a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A mixture of known composition was sealed in a small glass bulb of size 8-10 mL. Phase transition was observed during slow cooling in a thermostat (ref 1-3). Critical temp. and composition were found from a cube-root fit to the data.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified; analytical reagent grade.

ESTIMATED ERROR:

soly. ±0.0015 mole fraction (UCST); temp. ±0.002°C (stability of thermostating), ±0.05°C (UCST).

REFERENCES:

1. Gambhir, R.D.; Viswanathan, B.; Gopal, E.S.R. *Indian J. Appl. Phys.* 1971, *9*, 787.
2. Gopal, R.; Rice, O.K. *J. Chem. Phys.* 1955, *23*, 2428.
3. Viswanathan, B.; Gambhir, R.D.; Gopal, E.S.R. *J. Chem. Phys.* 1970, *53*, 4405.

COMPONENTS:
(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:
Budantseva, L.S.; Lesteva, T.M.; Nemtsov, M.S.
Zh. Fiz. Khim. 1976, *50*, 1344; *Russ. J. Phys. Chem. (Engl. Transl.)* 1976, *50*, 814; **Dep. Doc. VINITI* 1976, 437.

VARIABLES:

Temperature: 293 and 313 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and heptane

$t/^\circ C$	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
20	0.1760	0.9120	6.39	76.82
40	0.2950	0.8350	11.80	61.81

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
The analytical method was used. Hydrocarbon was analysed by glc according to ref 1.

SOURCE AND PURITY OF MATERIALS:
(1), (2) source not specified.

ESTIMATED ERROR:
not specified

REFERENCES:
1. Budantseva, L.S.; Lesteva, T.M.; Nemtsov, M.S. *Zh. Fiz. Khim.* 1976, *50*, 1343; *Dep. Doc. VINITI* 1976, 438.

COMPONENTS:
(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:
Letcher, T.M.; Wootton, S.; Shuttleworth, B.; Heyward, C.
J. Chem. Thermodyn. 1986, *18*, 1037-42.

VARIABLES:

One temperature: 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility at 298.2 K:
methanol in heptane: x_1 = 0.176, or w_1 = 6.39 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method adopted from ref. 1 was used. One of the components was added to a weighed mixture in a 100 mL long-necked flask until one drop caused the clear solution to become cloudy. The flask was immersed in a controlled water bath and shaken continuously. Data for the ternary system heptane-methanol-water are also given.

SOURCE AND PURITY OF MATERIALS:

(1) Carlo Erba, analytical grade, purity 99.5 mole %; purified by passing through columns containing silica gel and basic alumina.
(2) Merck, Uvasol grade; dried with Mg-activated with I_2, distilled.

ESTIMATED ERROR:
soly. ±0.005 mole fraction

REFERENCES:
1. Briggs, S.W.; Comings, E.W. *Ind. Eng. Chem.* 1943, *35*, 411.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Hradetzky, G.; Bittrich, H.-J.

Int. Data Ser., Sel. Data Mixtures, Ser. A 1986, 217.

VARIABLES:

Temperature: 254 - 324 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and heptane

T/K	x_1		$100\ w_1$ (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
253.65	-	0.9540	-	86.90
254.60	-	0.9560	-	87.42
257.25	0.0358	-	1.17	-
258.05	-	0.9509	-	86.10
261.06	0.0436	-	1.44	-
263.05	-	0.9480	-	85.36
263.43	0.0483	-	1.60	-
264.18	-	0.9449	-	84.58
267.70	-	0.9440	-	84.35
268.91	0.0588	-	1.96	-
270.05	-	0.9380	-	82.87
273.60	-	0.9343	-	81.97
274.21	0.0690	-	2.32	-
277.10	0.0755	-	2.54	-
278.01	-	0.9286	-	80.62
279.24	0.0791	-	2.67	-

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud-point method was used. Glass ampoules of about 20 mL capacity filled with known masses of pure components and sealed carefully to avoid contamination with moisture were immersed in a water thermostat equipped with a Hg-in-glass thermometer (ASMW, certified by the Bureau of Standards, GDR). Phase changes were observed visually as the mixture was cooled at 0.02 K/min Weighings accurate to 0.0001 g. Readings accurate to within 0.01 K. Reproducibility of temp. better than 0.03 K. Critical solution temp. and composition determined graphically using Caillet-Mathias rule. Monotectic temp. and compositions determined graphically.

SOURCE AND PURITY OF MATERIALS:

(1) VEB Leuna Werke (Leuna, GDR), stated purity > 99.9 mass %; used as received; < 50 mg/kg water as determined by Karl Fischer method.

(2) ALFA (Ventron Div. Danvers, USA), "ultrapure" grade; dried over molecular sieve type 3A; purity 99.86 mole % by capillary glc.

ESTIMATED ERROR:

soly. ±0.0002 mole fraction,
±0.006 mole fraction for UCST;
temp. ±0.03 K

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [110-82-7]

ORIGINAL MEASUREMENTS:

Hradetsky, G.; Bittrich, H.-J.

Int. Data ser., Sel. Data Mixtures, Ser. A. 1986, 217.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and heptane

T/K	x_1		g(1)/100g sln (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
280.50	-	0.9270	-	80.24
280.86	0.0830	-	2.81	-
281.30	-	0.9241	-	79.56
281.39	0.0850	-	2.88	-
284.55	0.0960	-	3.28	-
285.55	0.1000	-	3.43	-
286.50	-	0.9200	-	78.62
286.83	-	0.9155	-	77.60
290.95	0.1282	-	4.49	-
292.31	0.1346	-	4.74	-
292.55	-	0.9051	-	75.31
293.16	0.1364	-	4.81	-
299.33	-	0.8899	-	72.10
300.80	0.1762	-	6.40	-
305.05	-	0.8737	-	68.87
307.21	0.2113	-	7.89	-
308.65	0.2208	-	8.31	-
309.20	0.2272	-	8.59	-
309.71	-	0.8565	-	65.62
311.75	0.2573	-	9.97	-
312.31	0.2636	-	10.27	-
314.15	-	0.8340	-	61.64
315.39	0.3004	-	12.07	-
318.59	-	0.8019	-	56.42
319.03	0.3573	-	15.09	-
321.20	0.4116	-	18.28	-
323.09	-	0.7174	-	44.80
323.35	0.5015	-	24.34	-
323.52	-	0.6899	-	41.57
323.80	0.5544	-	28.46	-
323.92	0.5712	-	29.87	-
323.94	-	0.6256	-	34.82
324.04	0.6023	-	32.63	-
324.04	0.6069	-	33.05	-
324.06	-	0.6147	-	33.78
324.06 UCST	0.610	0.610	33.3	33.3

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Ott, J.B.; Hoelscher, I.F.; Schneider, G.M.

J. Chem. Thermodynamics 1986, *18*, 815-26.

VARIABLES:

Temperature: 317 - 357 K
Pressure: 0.1 - 151 MPa

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol and heptane

T/K	p/MPa	x_1	100 w_1 (compiler)
320.3	0.1	0.7871	54.17
321.3	0.1	0.3913	17.05
324.4	0.1	0.6493	37.19
319.5	10.1	0.296	11.9
322.1	20.0	0.296	11.9
324.6	30.0	0.296	11.9
326.7	40.0	0.296	11.9
328.8	50.0	0.296	11.9
331.1	60.1	0.296	11.9
334.4	80.0	0.296	11.9
337.4	100.3	0.296	11.9
339.9	120.3	0.296	11.9
342.3	140.3	0.296	11.9
343.2	150.4	0.296	11.9
320.8	1.0	0.362	15.4

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A high-pressure optical cell (ref 1) with sapphire windows with sandwich seals Al-to-Au-to-Al and magnetic stirring was used. Pressure was measured by Heise gauge calibrated calibrated against a dead-weight gauge, temperature by chromel-to-alumel thermocouple calibrated against certified platinum res. thermometer. Equilibrium temps. were found from visual observation of phase separation as the sample was cooled. The composition was determined from the volumes added to the cell. Special precautions were taken to exclude moisture from the samples. Data for 0.1 MPa were extrapolated.

SOURCE AND PURITY OF MATERIALS:

(1) Fisher, purity 0.999 mole fraction; distilled twice over Na in 2 m column packed with glass helices; purity > 0.9999 mole fraction by glc analysis.

(2) Phillips, research grade; purity 0.9989 mole fraction by glc analysis; used as received.

ESTIMATED ERROR:

temp. ±0.2 K, ±0.1 K at p = 0.1 MPa.
pressure ±0.2 MPa.
composition ±0.005 mole fraction, ±0.0005 mole fraction at 0.1 MPa.

REFERENCES:

1. Liphard, K.G.; Schneider, G.M. *J. Chem. Thermodyn.* 1975, *7*, 805.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Ott, J.B.; Hoelscher, I.F.; Schneider, G.M.

J. Chem. Thermodynamics 1986, *18*, 815-26.

EXPERIMENTAL VALUES: (Continued)

Solubility of methanol and heptane

T/K	p/MPa	x_1	100 w_1 (compiler)
323.7	10.0	0.362	15.4
326.7	20.0	0.362	15.4
329.3	30.0	0.362	15.4
331.8	40.0	0.362	15.4
334.1	50.0	0.362	15.4
336.3	60.0	0.362	15.4
340.0	80.0	0.362	15.4
343.6	100.7	0.362	15.4
346.6	120.2	0.362	15.4
349.8	140.8	0.362	15.4
351.2	150.4	0.362	15.4
323.5	1.0	0.421	18.9
326.4	10.0	0.421	18.9
329.5	20.1	0.421	18.9
332.1	30.1	0.421	18.9
334.6	40.1	0.421	18.9
337.0	50.0	0.421	18.9
339.2	60.0	0.421	18.9
343.0	79.8	0.421	18.9
347.1	100.0	0.421	18.9
350.6	120.5	0.421	18.9
353.6	139.7	0.421	18.9
355.3	150.6	0.421	18.9
324.7	1.0	0.483	23.0
328.0	10.1	0.483	23.0
330.8	20.0	0.483	23.0
333.7	30.0	0.483	23.0
336.4	40.2	0.483	23.0
338.7	50.0	0.483	23.0
341.0	60.1	0.483	23.0
345.2	80.4	0.483	23.0
349.0	100.3	0.483	23.0
352.3	120.3	0.483	23.0
355.6	140.4	0.483	23.0
357.0	150.4	0.483	23.0
324.8	1.0	0.487	23.3
327.7	10.1	0.487	23.3
330.7	20.0	0.487	23.3
333.8	30.1	0.487	23.3
336.4	40.1	0.487	23.3
338.7	50.1	0.487	23.3
340.9	60.0	0.487	23.3
345.1	80.1	0.487	23.3
349.0	100.8	0.487	23.3
352.4	120.6	0.487	23.3
355.6	140.2	0.487	23.3
357.0	150.3	0.487	23.3
324.7	1.0	0.541	27.4
327.9	10.0	0.541	27.4
330.9	20.0	0.541	27.4

(continued)

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Ott, J.B.; Hoelscher, I.F.; Schneider, G.M.

J. Chem. Thermodynamics 1986, *18*, 815-26.

EXPERIMENTAL VALUES: (Continued)

Solubility of methanol and heptane

T/K	p/MPa	x_1	100 w_1 (compiler)
333.8	30.0	0.541	27.4
336.4	40.0	0.541	27.4
338.9	50.0	0.541	27.4
341.1	60.0	0.541	27.4
345.4	79.9	0.541	27.4
349.1	100.1	0.541	27.4
352.7	120.3	0.541	27.4
355.7	140.5	0.541	27.4
357.3	150.4	0.541	27.4
324.7	1.0	0.579	30.5
327.9	10.2	0.579	30.5
331.0	20.1	0.579	30.5
333.9	30.0	0.579	30.5
336.5	40.1	0.579	30.5
338.9	50.1	0.579	30.5
341.2	60.1	0.579	30.5
345.4	80.1	0.579	30.5
349.2	100.6	0.579	30.5
352.6	120.6	0.579	30.5
355.6	140.8	0.579	30.5
357.2	150.6	0.579	30.5
324.8	1.0	0.611	33.4
327.9	10.0	0.611	33.4
331.1	20.1	0.611	33.4
334.0	30.0	0.611	33.4
336.7	40.1	0.611	33.4
339.1	50.1	0.611	33.4
341.3	60.2	0.611	33.4
345.4	80.0	0.611	33.4
349.2	100.3	0.611	33.4
352.6	119.8	0.611	33.4
355.8	140.7	0.611	33.4
357.3	150.9	0.611	33.4
324.5	1.0	0.660	38.3
327.6	10.1	0.660	38.3
330.7	20.0	0.660	38.3
333.6	30.1	0.660	38.3
336.2	40.0	0.660	38.3
338.6	50.0	0.660	38.3
340.8	60.0	0.660	38.3
345.0	79.9	0.660	38.3
348.7	100.3	0.660	38.3
352.1	120.3	0.660	38.3
355.1	140.5	0.660	38.3
356.6	150.6	0.660	38.3
322.3	1.0	0.748	48.7
325.0	10.0	0.748	48.7
327.9	20.1	0.748	48.7
330.6	30.0	0.748	48.7
332.8	40.0	0.748	48.7
335.2	50.0	0.748	48.7
337.2	60.0	0.748	48.7
340.6	80.0	0.748	48.7
343.9	100.8	0.748	48.7
346.7	120.5	0.748	48.7

(continued)

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Ott, J.B.; Hoelscher, I.F.; Schneider, G.M.

J. Chem. Thermodynamics 1986, *18*, 815-26.

EXPERIMENTAL VALUES: (Continued)

Solubility of methanol and heptane

T/K	p/MPa	x_1	100 w_1 (compiler)
349.1	140.1	0.748	48.7
350.1	149.8	0.748	48.7
319.5	1.0	0.777	52.7
322.5	10.1	0.777	52.7
325.1	20.0	0.777	52.7
327.9	30.1	0.777	52.7
330.1	40.1	0.777	52.7
332.0	50.0	0.777	52.7
334.0	60.0	0.777	52.7
337.2	80.0	0.777	52.7
339.9	100.6	0.777	52.7
341.9	120.5	0.777	52.7
343.0	140.5	0.777	52.7
343.7	150.7	0.777	52.7

COMMENTS AND ADDITIONAL DATA:

Data for isopleths at high pressures were fitted to the Simon equation

$$p(x,T)/\mathrm{MPa} = a[(T/T_0)^c - 1]$$

From these equations, the corresponding (T, x) isobars were calculated and were fitted to the equation

$$T/\mathrm{K} = T_c/\mathrm{K} + k|y - y_c|^{\nu}$$

where

$$y = \alpha x_1/[1 + x_1(\alpha - 1)]$$

$$y_c = \alpha x_{c1}/[1 + x_{c1}(\alpha - 1)]$$

The coefficients found are (s = std. error of estimate):

x_1	T_0/K	a	c	s/K
0.296	316.3	63.38	14.81	0.41
0.362	320.5	84.36	11.27	0.09
0.421	323.2	100.37	9.72	0.07
0.483	324.4	88.03	10.42	0.06
0.487	324.4	90.13	10.25	0.08
0.541	324.4	86.03	10.49	0.05
0.579	324.3	81.38	10.88	0.05
0.611	324.5	82.78	10.78	0.06
0.660	324.1	80.09	11.09	0.03
0.748	321.8	65.16	14.12	0.10
0.777	318.8	33.91	22.02	0.36

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Heptane; C_7H_{16}; [142-82-5]	Ott, J.B.; Hoelscher, I.F.; Schneider, G.M. *J. Chem. Thermodynamics* 1986, *18*, 815-26.

EXPERIMENTAL VALUES: (Continued)

p/MPa	T_c/K	k	α	x_{c1}	ν	s
0.1	324.5	-1755	0.500	0.588	3.780	0.16
25	332.5	-568	0.650	0.580	3.059	0.11
50	339.0	-700	0.617	0.579	3.086	0.07
75	344.5	-926	0.584	0.578	3.167	0.05
100	349.2	-1294	0.566	0.576	3.303	0.07
125	353.4	-1823	0.547	0.575	3.451	0.08
150	357.1	-2218	0.551	0.573	3.526	0.10

Equations are also given for (p, x) pairs, which are of the same form as those for the (T, x) pairs.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Ranjan, M.; Jayalaxmi, V.; Vani, V,; Guha, S,; Gopal, E.S.R.

Indian J. Phys. 1986, *60A*, 98-109.

VARIABLES:

One temperature: 325 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 325.60 K and 325.68 K a).

a) data for a stirred sample; see "METHOD/APPARATUS/PROCEDURE" below.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The electrical resistance of the binary liquid mixture at its critical composition as a function oftemp. at kHz frequency was studied. The resistance was measured in the one- and two-phase regions. The experiments were done over a range 3 K above and 2 K below T_c. Two pair of stainless steel electrodes coated with Pt black were fixed on either side of the center of a Pyrex glass cell 3.5 cm high. Electrodes had diameter 2.5 cm, separation 1 mm. The resistance value from one pair of electrodes was normalized relative to the other pair. The observed anomaly in resistance, in the range 15 to -15 mK around T_c, was attributed to the gravity effect. Similar experiments were done with samples (a) stirred at about 1 rev/min.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Higashiuchi, H.; Sukuragi, Y.;

Iwai, Y.; Arai, Y.; Nagatani, M.

Fluid Phase Equilib. 1987, *36*, 35-47.

VARIABLES:

Temperature: 298 - 323 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and heptane

$t/^{\circ}C$	x_1		$100\ w_1$ (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
25.00	0.1530	0.8995	5.46	74.11
30.00	0.2004	0.8871	7.42	71.53
35.00	0.2412	0.8764	9.23	69.39
40.00	0.2925	0.8491	11.68	64.28
45.00	0.3515	0.8264	14.77	60.35
50.00	0.4527	0.7897	20.92	54.56

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. Thermostatically controlled double-walled glass cells which were similar to that of ref 1 were used. Samples of both phases in equilibrium were carefully withdrawn with a precision syringe and the compositions were determined by gas chromatogrphy with FID. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, guaranteed reagent grade, purity > 99%; used as received.

(2) source not specified, guaranteed reagent grade, purity > 99%; used as received.

ESTIMATED ERROR:

soly. ±1% (accurancy);
temp. ±0.05 K (thermostating).

REFERENCES:

1. Fabries, J.-F.; Gustin, J.-L.; Renon, H. *J. Chem. Eng. Data* 1977, *22*, 303

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Nagata, I.

Thermochim. Acta 1987, *114*, 227-38.

VARIABLES:

One temperature: 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities 25°C

methanol in heptane: x_1 = 0.1582, w_1 = 5.67 (compiler).

heptane in methanol: x_2 = 0.1074. w_2 = 27.34 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. A two-phase mixture in an equilibrium cell of volume 70 mL was stirred intensely for 2 h and then was allowed to settle for 2 h within a thermostatted water bath. Both phases were withdrawn with Hamilton syringes and analyzed by glc (Shimadzu GC-8C and integrator Shimadzu C-E1B). Four analyses were made for each phase.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, C.P.grade; dried over CaO, distilled; no impurities by glc; density at 25°C was in agreement with literature value.

(2) source not specified; no impurities by glc; density at 25°C was in agreement with literature values; used as received.

ESTIMATED ERROR:

soly. ±0.002 mole fraction (reproducibility);
temp. ±0.01 K.

REFERENCES:

COMPONENTS: (1) Methanol; CH_4O; [67-56-1] (2) 2,2,3-Trimethylbutane; C_7H_{16}; [464-06-2]	ORIGINAL MEASUREMENTS: Sieg, L. *Chem.-Ing.-Tech.* <u>1951</u>, *23*, 112-3.
VARIABLES: One temperature: 301 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 28.2°C.

Mutual solubility was presented on a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: The cloud point method was used. A mixture of known composition was sealed in an ampoule and the temp. of appearance or disappearance of turbidity was observed. The ampoules and pipets were filled in a moisture-free atmosphere over P_2O_5.	SOURCE AND PURITY OF MATERIALS: (1) source not specified; boiled with Mg, fractionated; physical properties agreed with values in literature. (2) source not specified, pure grade; fractionated; physical properties agreed with values in literature.
	ESTIMATED ERROR: not specified.
	REFERENCES:

COMPONENTS: (1) Methanol; CH_4O; [67-56-1] (2) 2,5-Dimethyl-1,5-hexadiene (diisobutene); C_8H_{14}; [627-58-7]	ORIGINAL MEASUREMENTS: Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 764-71.
VARIABLES: One temperature: 273 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 0°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temperature of disappearance or reappearance of the cloudiness was read two or three times in each direction.	SOURCE AND PURITY OF MATERIALS: (1), (2) source not specified. ESTIMATED ERROR: not specified. REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) 3-Methylheptane; C_8H_{18}; [589-81-1]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.; Shetlar, M.D.

J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 278 - 333 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of 3-methylheptane in methanol

$t/^\circ C$	g(2)/100 ml(1)	100 w_1 (compiler)	x_2 (compiler)
5	15.4	16.1	0.0509
10	17.0	17.5	0.0562
15	19.0	19.3	0.0628
20	21.2	21.1	0.0699
25	24.2	23.5	0.0794
30	27.4	26.0	0.0895
35	31.4	28.8	0.1018
40	36.5	32.1	0.1170
60.2	UCST		

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4^\circ C) = 0.80999 - 9.253\ 10^{-4}\ (t/^\circ C) - 4.1\ 10^{-7}\ (t/^\circ C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; $n_D(20^\circ C) = 1.3293$, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Matheson, Coleman and Bell; used as received; 0.3 mole % of unsaturated compounds by u.v. analysis; $n_D(20^\circ C) = 1.3984$.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables vol. 3*, New York, 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Octane; C_8H_{18}; [111-65-9]

EVALUATOR:

A. Skrzecz
Institute of Physical Chemistry
Polish Academy of Sciences
Warsaw, Poland

J.W. Lorimer
Department of Chemistry
The University of Western Ontario
London, Ont., Canada

July, 1989

CRITICAL EVALUATION:

A survey of solubilities and upper critical solution temperatures (UCST) and compositions for the system methanol (1) - octane (2) which have been reported in the literature is given in Table 1.

Table 1. Summary of solubility data in the system methanol (1) - octane (2)

Author(s)	Range T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Fischer 1949	355.2 UCST	-	-
2. Sieg 1951	339.9 UCST	-	-
3. Kogan 1956	275-318	0.074-0.215	0.914-0.955
4. Kiser 1961	278-338.9 UCST	-	0.914-0.959
5. Sergeeva 1973	298	0.100	0.937
6. Budantseva 1976	293	0.155	0.960
7. Iwai 1986	298	0.141	0.940
8. Ott 1986	324-372 [a] 339.3 UCST	0.304-0.603	0.646-0.825
9. Higashiuchi 1987	298-333	0.118-0.416	0.837-0.940
10. Nagata 1987	298	0.097	0.937

[a] At elevated pressures, p = 0.1-151 MPa; UCST at 0.1 MPa.

Critical Solution Temperature and Composition

Four values have been reported for the UCST. The value of Fischer and Neupauer, ref 1, is rejected. All values of UCST reported in ref. 1 for different alcohol-hydrocarbon systems are higher by about 10-20 K than the recommended or tentative values, which suggests presence of significant amounts of impurities, mainly water. The values of Sieg, ref. 2, Kiser et al., ref. 3, and Ott et al., ref. 8, agree remarkably well; their average (with ± 1 std. dev.) is *recommended*:

$$T_c = 339.4 \pm 0.5 \text{ K}$$

(continued)

CRITICAL EVALUATION: (continued)

The critical solution composition was given by Ott et al., ref. 8, as $x_{c1} = 0.639$ at 0.1 MPa; this value is considered as *tentative* in view of the care taken in its determination.

Mutual Solubility

Sieg, ref. 1, gave mutual solubilities from 293 K to the UCST in graphical form only; these are rejected. The remaining data 58 data which have been reported are plotted in fig. 1, from which it is seen that the data of Kogan et al., ref. 3, at low methanol content, and one value at high methanol content, should be rejected. Similarly, the two values of Kiser et al., ref. 8, the high methanol value of Sergeeva, ref. 5, al data of Bundantseva et al., ref. 6, and the high methanol values of Iwai, ref. 7, and of Nagata, ref. 10, also appear to be aberrant, and are rejected. The remaining 46 values have been fitted to the equation:

$$x_1 = x_{c1} \pm B_1\theta^{\beta} \pm B_2\theta^{\beta+w} + A_1\theta \pm B_3\theta^{\beta+2w} + A_2\theta^{1-\alpha+w}$$

where $\theta = |1 - T/T_c|$, + and - refer to the branches below and above the critical composition, and the constants have their theoretical values $\beta = 0.329$, $\alpha = 0.11$, $w = 0.5$. The constants (with standard deviations in parentheses) are:

$x_{c1} = 0.6285$ (0.0034) $T_c/\mathrm{K} = 339.46$ K (0.01)
$B_1 = 0.7117$ (0.033) $B_2 = 0.6939$ (0.25) $B_3 = -1.3085$ (0.22)
$A_1 = -1.2182$ (0.44) $A_2 = 1.1928$ (0.43) $s = 0.011$

s is the total standard error of estimate in composition. This equation is plotted in fig. 1, and is used to calculate the *recommended* values in Table 2. The estimated accuracy of the data in Table 2 is 0.001 in mole fraction.

The only data reported at high pressures are those of Ott et al., ref 8, up to 151 MPa. Consequently, these data (which can be found on the compilation sheets) are considered as *tentative*. Ott, Hoelscher and Schneider, ref. 8, extrapolated their data measured at high pressures to 0.1 MPa, and gave the results in terms of the Simon equation

$$T/\mathrm{K} = T_c/\mathrm{K} + k|x_1 - x_{c1}|^{\nu}$$

with

$$y = \alpha x_1/[1+x_1(\alpha+1)]$$
$$y_c = \alpha x_{c1}/[1+x_{c1}(\alpha-1)]$$

valid over the range $0.2 < x_1 < 0.8$ or $270 < T/\mathrm{K} < 286.92$, where
$T_c = 286.92$ K $k = -883$ $\alpha = 0.83$ $x_{c1} = 0.497$

Pressure Coefficient of Critical Solution Temperature

This quantity can be calculated from the fitting equations of Ott et al.:

$$(\partial T/\partial p)_{x_c} = T_0/ac = 3.64\times10^{-7}\ \mathrm{K\ Pa^{-1}}$$

where T_0, a and c are constants given on the compilation sheet.

(continued)

CRITICAL EVALUATION: (continued)

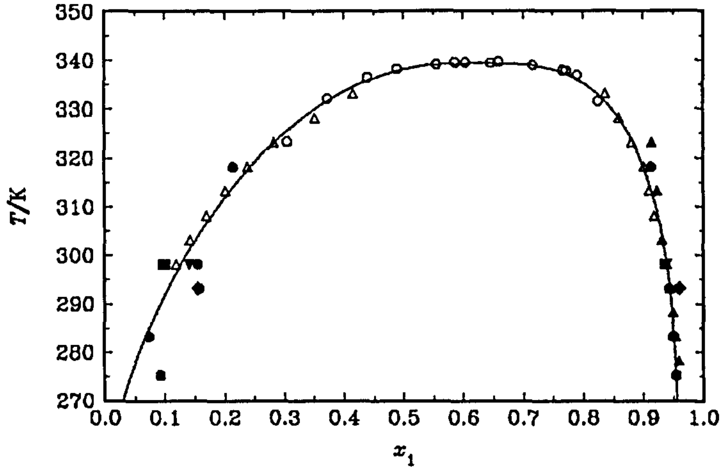

Fig. 1: Solubilities in the system methanol (1) - octane (2). Line: fitting equation (see text). Points and reference: ●, 3; △, 4; ■, 5; ♦, 6; ▼, 7; ○, 8; ▲, 9; □, 10. The plot gives an overall impression of the data.

Table 2. Recommended values of solubility in the system methanol (1) - octane (2)

T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
270.0	0.029	0.956
280.0	0.058	0.953
290.0	0.093	0.947
300.0	0.136	0.937
310.0	0.189	0.921
315.0	0.220	0.910
320.0	0.257	0.895
325.0	0.300	0.876
330.0	0.352	0.848
335.0	0.425	0.804
338.7	0.639	0.639 UCST

REFERENCES:

1. Fischer, R.; Neupauer, E. *Mikrochem. Ver. Mikrochim. Acta* 1949, *34*, 319.
2. Sieg, L. *Chem.-Ing.-Tech.* 1951, *23*, 112.
3. Kogan, V.B.; Deizenrot, I.V.; Kul'byaeva, T.A.; Fridman, V.M. *Zh. Prikl. Khim.* 1956, *29*, 1387.
4. Kiser, R.W.; Johnson, G.D.; Shetlar, M.D. *J. Chem. Eng. Data* 1961, *6*, 338.
5. Sergeeva, V.F.; Ustanova, I.Z. *Zh. Obshch. Khim.* 1973, *43*, 1878.
6. Budantseva, L.S.; Lesteva, T.M.; Nemstov, M.S. *Zh. Fiz. Khim.* 1976, *50*, 1344; *Deposited Doc. VINITI* 1976, 437.
7. Iwai, Y.; Nishimura, Y.; Wanatabe, Y.; Arai, Y. *Fluid Phase Equilib.* 1986, *25*, 107.
8. Ott, J.B.; Hoelscher, I.F.; Schneider, G.M. *J. Chem. Thermodyn.* 1986, *18*, 815.
9. Higashiuchi, H.; Sukuragi, Y.; Iwai, Y.; Arai, Y.; Nagatani, M. *Fluid Phase Equilib.* 1987, *36*, 35.
10. Nagata, I. *Thermochim. Acta* 1987, *114*, 227.a,

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Fischer, R.; Neupauer, E.

Mikrochem. Ver. Mikrochim. Acta 1949, *34*, 319-35.

VARIABLES:

One temperature: 355 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 82.0°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The sample in a sealed glass capillary was placed in a melting point microapparatus and the appearance and disappearance of the meniscus with temperature changes was observed. The mass of the sample was 0.001-0.002 g. The method is described in ref 1.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; purified; $n_D(20°C) = 1.3313$.

(2) source not specified; $n_D(20°C) = 1.3965$.

ESTIMATED ERROR:

temp. ±0.5 K.

REFERENCES:

1. Fischer, R.; Karasek, G. *Mikrochemie* 1947, *33*, 316.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Sieg, L.

Chem.-Ing.-Tech. 1951, *23*, 112-3.

VARIABLES:

One temperature: 340 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 66.7°C.

Mutual solubility was presented on a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A mixture of known composition was sealed in an ampoule and the temperature of appearance or disappearance of turbidity was observed. The ampoules and pipets were filled in a moistureless atmosphere over P_2O_5.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; boiled with Mg, fractionated; physical properties were in agreement with literature values.

(2) source not specified, pure grade; fractionated; physical properties were in agreement with literature values.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Kogan, V.B.; Deizenrot, I.V.;

Kul'byaeva, T.A.; Fridman, V.M.

Zh. Prikl. Khim. 1956, *29*, 1387-92.

VARIABLES:

Temperature: 275 - 318 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and octane

$t/^\circ C$	100 w_1		x_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
2	2.79	85.67	0.0928	0.9552
10	2.20	84.25	0.0744	0.9502
10 a)	2.2	84.4	0.074	0.951
20 a)	5.0	82.3	0.158	0.943
25	4.9	80.60	0.155	0.9368
45	7.13	74.88	0.2149	0.9140

a) from octane - methanol - water ternary equilibrium data.

(1)-rich phase was observed to be the lower layer.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. The two-phase mixture was periodically shaken in a thermostatted burette with water jacket for several hours. The phases were taken out for analysis after separation. Methanol was determined two-times by reaction with phthalic anhydride.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, pure grade; distilled; < 0.01% of water; $n_D(20^\circ C) = 1.3391$.

(2) source not specified; used as received; b.p. 125.4°C, $n_D(20^\circ C) = 1.3976$.

ESTIMATED ERROR:

soly. < ±1% (relative error of methanol concentration);
temp. ±0.05 K.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Octane; C_8H_{18}; [111-65-9]	Kiser, R.W.; Johnson, G.D.; Shetlar, M.D. *J. Chem. Eng. Data* 1961, *6*, 338-41.
VARIABLES:	PREPARED BY:
Temperature: 278 - 339 K	A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of octane in methanol

t/°C	g(2)/100 ml(1)	100 w_1 (compiler)	x_2 (compiler)
5	12.2	13.1	0.0407
10	13.6	14.5	0.0455
15	15.2	16.0	0.0508
20	16.7	17.4	0.0559
25	18.4	19.0	0.0616
30	20.6	20.8	0.0688
35	23.0	22.8	0.0767
40	26.0	25.1	0.0861
65.7	UCST		

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4°C) = 0.80999 - 9.253\ 10^{-4}\ (t/°C) - 4.1\ 10^{-7}\ (t/°C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; $n_D(20°C) = 1.3293$, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Eastman Organic Chemicals, practical grade; passage through short columns of silica gel until the unsaturated compounds were removed, purified; estimated impurities < 0.2 mole%; $n_D(20°C) = 1.3975$.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables* *vol. 3*, New York, 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Budantseva, L.S.; Lesteva, T.M.; Nemtsov, M.S.

Zh. Fiz. Khim. 1976, *50*, 1344; *Russ. J. Phys. Chem. (Engl. Transl.)* 1976, *50*, 814; *Dep. *Doc. VINITI* 1976, 437.

VARIABLES:

One temperature: 293 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities at 20°C:

methanol in octane: $x_1 = 0.1550$, or 100 $w_1 = 4.894$ (compiler).

octane in methanol: $x_2 = 0.0400$, or 100 $w_2 = 12.93$ (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. Hydrocarbon was analyzed by glc as in ref. 1.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified

ESTIMATED ERROR:

REFERENCES:

1. Budantseva, L.S.; Lesteva, T.M.; Nemtsov, M.S. *Zh. Fiz. Khim.* 1976, *50*, 1343; *Dep. *Doc. VINITI* 1976, 437.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Sergeeva, V.F.; Ustanova, I.Z.

Zh. Obshch. Khim. 1973, *43*, 1878-81; *J. Gen. Chem. USSR (Engl. Transl.)* 1973, *43*, 1866-8.

VARIABLES:

One temperature: 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities at 25°C:

methanol in octane: $x_1 = 0.100$, or 100 $w_1 = 3.02$ (compiler)

octane in methanol: $x_2 = 0.063$, or 100 $w_2 = 19.3$ (compiler)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was not specified.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified; purified, dried; physical properties agreed with values in literature.

ESTIMATED ERROR:

not specified

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Iwai, Y.; Nishimura, Y.;
Wanatabe, Y.; Arai, Y.

Fluid Phase Equilib. 1986, *25*, 107-12.

VARIABLES:

One temperature: 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities at 25°C:

methanol in octane: x_1 = 0.1406 or 100 w_1 = 4.39.
octane in metanol: x_2 = 0.0604 or 100 w_2 = 18.6.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. Double-walled glass cells (thermostatically controlled) were used (similar to those in ref 1). Samples of both phases in equilibrium were withdrawn with a precision syringe and compositions were determined by gc with FID. The binary data are given in ref 2. Data on the ternary system octane-methanol-toluene are also given.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified, reagent grade, purity > 99%; without purification; no impurities were detected by glc with FID.

ESTIMATED ERROR:

soly. ±1% (accuracy);
temp. ±0.0.05 K.

REFERENCES:

1. Fabries, J.-F.; Gustin, J.-L.; Renon, H. *J. Chem. Eng. Data* 1977, *22*, 303-8.
2. Higashiuchi, H. *Unpublished.*

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Ott, J.B.; Hoelscher, I.F.; Schneider, G.M.

J. Chem. Thermodyn. 1986, *18*, 815-26.

VARIABLES:

Temperature: 324 - 372 K
Pressure: 0.1 - 151 MPa

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol and octane

T/K	p/MPa	x_1	100 w_1 (compiler)
335.2	0.1	0.8248	56.91
336.4	0.1	0.4491	18.61
339.5	0.1	0.6510	34.35
323.7	1.0	0.304	10.9
326.4	10.0	0.304	10.9
328.4	19.9	0.304	10.9
330.4	30.2	0.304	10.9
332.7	40.1	0.304	10.9
334.3	50.1	0.304	10.9
336.0	60.0	0.304	10.9
338.6	80.2	0.304	10.9
341.4	100.8	0.304	10.9
343.6	120.8	0.304	10.9
344.4	140.9	0.304	10.9
345.4	150.7	0.304	10.9

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A high-pressure optical cell (ref 1) with sapphire windows with Al-to-Au-to-Al sandwich seals and magnetic stirring was used. Pressure was measured with a Heise gauge calibrated against a dead-weight gauge, temperature with a chromel-to-alumel thermocouple calibrated against a certified platinum resistance thermometer. Equilibrium temperatures were obtained from visual observation of phase separation as the sample was cooled. Composition was determined from the volumes added to the cell. A glass cell, volume 30 mL, surrounded by a vacuum jacket was used at atmospheric pressure. The sample was stirred with a PTFE-coated magnetic stirring bar. Visual measurements were made during cooling. Special precautions were taken to exclude moisture.

SOURCE AND PURITY OF MATERIALS:

(1) Fisher, purity 0.999 mole fraction; distilled twice over Na in 2 m column packed with glass helices; purity > 0.9999 mole fraction by glc analysis.

(2) Phillips, pure grade; dist. 2x in a 2-m column packed with glass helices; purity 0.9989 mole fraction by glc.

ESTIMATED ERROR:

temp. ±0.2 K, ±0.1 K at p = 0.1 MPa.
pressure ±0.2 MPa.
composition ±0.005 mole fraction, ±0.0001 mole fraction at 0.1 MPa.

REFERENCES:

1. Liphard, K.G.; Schneider, G.M. *J. Chem. Thermodyn.* 1975, *7*, 805.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Ott, J.B.; Hoelscher, I.F.; Schneider, G.M.

J. Chem. Thermodyn. 1986, *18*, 815-26.

EXPERIMENTAL VALUES: (Continued)

Solubility of methanol and octane

T/K	p/MPa	x_1	100 w_1 (compiler)
332.6	1.0	0.373	14.3
335.3	10.0	0.373	14.3
337.9	20.2	0.373	14.3
340.3	30.0	0.373	14.3
342.5	40.1	0.373	14.3
344.7	50.0	0.373	14.3
346.7	60.0	0.373	14.3
350.1	80.0	0.373	14.3
352.8	100.7	0.373	14.3
355.6	120.6	0.373	14.3
358.1	140.8	0.373	14.3
359.1	150.5	0.373	14.3
336.6	1.0	0.439	18.0
339.6	10.0	0.439	18.0
342.5	19.9	0.439	18.0
345.3	30.1	0.439	18.0
347.5	40.0	0.439	18.0
349.9	50.0	0.439	18.0
352.0	60.0	0.439	18.0
356.1	80.0	0.439	18.0
359.8	100.6	0.439	18.0
362.8	120.5	0.439	18.0
365.8	140.6	0.439	18.0
367.4	150.7	0.439	18.0
338.5	1.0	0.489	21.2
341.6	10.1	0.489	21.2
344.7	20.0	0.489	21.2
347.6	30.1	0.489	21.2
350.1	40.1	0.489	21.2
352.5	50.1	0.489	21.2
354.7	60.1	0.489	21.2
358.8	80.0	0.489	21.2
362.7	100.8	0.489	21.2
366.2	120.8	0.489	21.2
369.2	140.8	0.489	21.2
370.8	151.0	0.489	21.2
339.4	1.0	0.555	25.9
342.5	10.0	0.555	25.9
345.6	19.9	0.555	25.9
348.6	30.1	0.555	25.9
351.3	40.2	0.555	25.9
353.6	50.0	0.555	25.9
355.7	60.2	0.555	25.9
360.0	80.0	0.555	25.9
363.9	100.6	0.555	25.9
367.2	120.7	0.555	25.9
370.5	141.1	0.555	25.9
372.1	151.0	0.555	25.9
339.8	1.0	0.586	28.4
342.9	10.3	0.586	28.4

(continued)

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Ott, J.B.; Hoelscher, I.F.; Schneider, G.M.

J. Chem. Thermodyn. 1986, *18*, 815-26.

EXPERIMENTAL VALUES: (Continued)

Solubility of methanol and octane

T/K	p/MPa	x_1	100 w_1 (compiler)
346.1	20.2	0.586	28.4
348.9	30.0	0.586	28.4
351.4	40.1	0.586	28.4
354.0	50.1	0.586	28.4
356.3	60.3	0.586	28.4
360.4	80.2	0.586	28.4
364.1	100.6	0.586	28.4
367.5	120.4	0.586	28.4
370.6	140.1	0.586	28.4
372.3	150.7	0.586	28.4
339.8	1.0	0.603	29.9
342.9	10.0	0.603	29.9
346.2	20.0	0.603	29.9
349.0	29.8	0.603	29.9
351.7	40.1	0.603	29.9
354.0	50.0	0.603	29.9
356.4	60.0	0.603	29.9
360.7	80.2	0.603	29.9
364.4	100.6	0.603	29.9
368.0	121.1	0.603	29.9
371.2	140.8	0.603	29.9
339.7	1.0	0.646	33.9
342.8	10.0	0.646	33.9
346.1	20.1	0.646	33.9
348.9	30.1	0.646	33.9
351.5	40.1	0.646	33.9
353.9	50.1	0.646	33.9
356.2	60.0	0.646	33.9
360.3	80.0	0.646	33.9
364.2	101.2	0.646	33.9
367.5	121.0	0.646	33.9
370.8	141.0	0.646	33.9
372.1	150.8	0.646	33.9
342.8	9.9	0.659	35.2
346.1	20.1	0.659	35.2
349.0	30.1	0.659	35.2
351.5	40.0	0.659	35.2
353.9	50.0	0.659	35.2
356.2	60.1	0.659	35.2
360.4	80.0	0.659	35.2
364.3	100.8	0.659	35.2
368.0	121.0	0.659	35.2
371.0	140.7	0.659	35.2
339.2	0.9	0.716	41.4
342.4	9.9	0.716	41.4
345.7	20.0	0.716	41.4
348.3	30.1	0.716	41.4
351.0	40.1	0.716	41.4
353.5	50.1	0.716	41.4

(continued)

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Ott, J.B.; Hoelscher, I.F.; Schneider, G.M.

J. Chem. Thermodyn. 1986, *18*, 815-26.

EXPERIMENTAL VALUES: (Continued)

Solubility of methanol and octane

T/K	*p*/MPa	x_1	100 w_1 (compiler)
355.7	60.1	0.716	41.4
359.8	80.1	0.716	41.4
363.4	100.6	0.716	41.4
366.8	120.8	0.716	41.4
369.9	140.5	0.716	41.4
371.2	150.6	0.716	41.4
338.3	1.0	0.766	47.9
341.4	9.9	0.766	47.9
344.7	20.0	0.766	47.9
347.4	29.9	0.766	47.9
350.1	40.1	0.766	47.9
352.4	50.0	0.766	47.9
354.7	60.0	0.766	47.9
358.7	80.1	0.766	47.9
362.2	100.7	0.766	47.9
365.4	121.1	0.766	47.9
368.3	141.3	0.766	47.9
369.3	151.4	0.766	47.9
338.1	1.0	0.771	48.6
341.4	10.0	0.771	48.6
344.5	20.0	0.771	48.6
347.2	30.0	0.771	48.6
349.9	40.1	0.771	48.6
352.1	50.0	0.771	48.6
354.4	60.0	0.771	48.6
358.2	79.9	0.771	48.6
361.7	100.5	0.771	48.6
364.9	120.7	0.771	48.6
367.6	140.7	0.771	48.6
368.9	151.1	0.771	48.6
337.4	1.0	0.790	51.3
340.5	10.0	0.790	51.3
343.5	20.0	0.790	51.3
346.3	30.0	0.790	51.3
348.3	40.0	0.790	51.3
351.0	50.1	0.790	51.3
353.2	60.0	0.790	51.3
357.0	80.0	0.790	51.3
360.4	100.8	0.790	51.3
363.3	120.8	0.790	51.3
365.7	140.8	0.790	51.3
367.0	150.7	0.790	51.3
332.1	1.0	0.825	56.9
336.5	10.0	0.825	56.9
339.5	20.0	0.825	56.9
342.0	30.0	0.825	56.9
344.4	40.0	0.825	56.9
346.3	50.0	0.825	56.9
348.3	60.1	0.825	56.9
351.6	80.1	0.825	56.9
354.5	100.8	0.825	56.9
356.7	121.0	0.825	56.9
358.2	140.8	0.825	56.9
358.6	150.9	0.825	56.9
358.6	150.9	0.825	56.9

(continued)

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Octane; C_8H_{18}; [111-65-9]	Ott, J.B.; Hoelscher, I.F.; Schneider, G.M. *J. Chem. Thermodyn.* 1986, *18*, 815-26.

EXPERIMENTAL VALUES: (Continued)

COMMENTS AND ADDITIONAL DATA:

Data for isopleths at high pressures were fitted to the Simon equation

$$p(x,T)/\text{MPa} = a[(T/T_0)^c-1]$$

From these equations, the corresponding (T, x) isobars were calculated and were fitted to the equation

$$T/\text{K} = T_c/\text{K}+k|y-y_c|^\nu$$

where

$$y = \alpha x_1/[1+x_1(\alpha-1)]$$
$$y_c = \alpha x_{c1}/[1+x_{c1}(\alpha-1)]$$

The coefficients found are (s = std. error of estimate):

x_1	T_0/K	a	c	s/K
0.304	323.3	48.62	21.08	0.33
0.373	332.2	69.16	14.82	0.13
0.439	336.4	90.58	11.15	0.10
0.489	338.2	89.49	10.77	0.07
0.555	339.1	86.91	10.88	0.09
0.586	339.5	86.10	11.00	0.08
0.603	339.5	84.83	10.98	0.07
0.646	339.4	83.11	11.25	0.08
0.659	339.6	91.44	10.52	0.08
0.716	338.9	77.86	11.84	0.09
0.766	337.9	65.43	13.40	0.09
0.771	337.8	66.70	13.43	0.05
0.790	336.9	61.51	14.48	0.09
0.825	331.6	28.08	23.31	0.31

p/MPa	T_c/K	k	α	x_{c1}	ν	s
0.1	339.3	-32.95	0.460	0.639	4.208	0.22
25	347.4	-1966	0.518	0.641	3.878	0.16
50	353.9	-2114	0.514	0.642	3.849	0.16
75	359.4	-2249	0.516	0.639	3.797	0.18
100	364.1	-2427	0.516	0.637	3.770	0.22
125	368.4	-2615	0.518	0.635	3.749	0.26
150	372.2	-2683	0.524	0.633	3.708	0.32

Equations are also given for (p, x) pairs, which are of the same form as those for the (T, x) pairs.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Octane; C_8H_{18}; [111-65-9]	Higashiuchi, H.; Sukuragi, Y.; Iwai, Y.; Arai, Y.; Nagatani, M. *Fluid Phase Equilib.* 1987, *36*, 35-47.
VARIABLES:	PREPARED BY:
Temperature: 298 - 333 K	A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and octane

$t/°C$	x_1		$100\ w_1$ (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
25.00	0.1182	0.9396	3.62	81.36
30.00	0.1411	0.9314	4.41	79.20
35.00	0.1687	0.9181	5.39	75.87
40.00	0.2012	0.9098	6.60	73.89
45.00	0.2390	0.9020	8.10	72.08
50.00	0.2823	0.8808	9.94	67.46
55.00	0.3513	0.8600	13.19	63.28
60.00	0.4158	0.8374	16.64	59.09

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. Thermostatically controlled double-walled glass cells similar to those of ref 1 were used.
Samples of both phases in equilibrium were withdrawn carefully with a precision syringe and compositions were determined by gas chromatography with FID. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, guaranteed reagent grade, purity > 99%; used as received.

(2) source not specified, guaranteed reagent grade, purity 98.0%; used as received.

ESTIMATED ERROR:

soly. ±1% (accuracy);
temp. ±0.05°C (thermostating).

REFERENCES:

1. Fabries, J.-F.; Gustin, J.-L.; Renon, H.
J. Chem. Eng. Data 1977, *22*, 303

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Nagata, I.

Thermochim. Acta 1987, *114*, 227-38

VARIABLES:

One temperature: 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities at 25°C:

methanol in octane: $x_1 = 0.0968$, 100 $w_1 = 2.92$ (compiler)

octane in methanol: $x_2 = 0.0632$, 100 $w_2 = 19.39$ (complier).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. A two-phase mixture in an equilibrium cell of volume 70 mL was stirred intensely for 2 h and then allowed to settle for 2 h in a thermostatted water bath. Samples of both phases were withdrawn with Hamilton syringes and analyzed by glc (Shimadzu GC-8C and integrator Shimadzu C-E1B). Four analyses were made for each phase.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, C.P.grade; dried over CaO, distilled; no impurities by glc; density at 25°C was in agreement with literature value.

(2) source not specified; no impurities by glc; density at 25°C was in agreement with literature values; used as received.

ESTIMATED ERROR:

soly. ±0.002 mole fraction (reproducibility);
temp. ±0.01 K.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) 2,2,4-Trimethylpentane; C_8H_{18}; [540-84-1]

EVALUATOR:

A. Skrzecz and A. Maczynski
Institute of Physical Chemistry
Polish Academy of Sciences
Warsaw, Poland

J.W. Lorimer
Department of Chemistry
The University of Western Ontario
London, Ont., Canada

July, 1989

CRITICAL EVALUATION:

Table 1 summarizes reported solubilities, upper critical solution temperatures (UCST) and compositions for the system methanol (1) - 2,2,4-trimethylpentane (2).

Table 1. Solubilities, upper critical solution temperatures and compositions for the system methanol (1) - 2,2,4-trimethylpentane (2)

Author(s)	T/K	Range x_1 (2)-rich phase	x_1 (1)-rich phase
1. Cornish 1934	315.7 UCST	-	-
2. Francis 1944	316 UCST	-	-
3. Sieg 1951	315.7 UCST	-	-
4. Francis 1954	273-315.8 UCST	0.144-0.643	0.643-0.923
5. Buchowski 1959	291 and 293	0.177	0.875-0.879
6. Kiser 1961	278-316.2 UCST	-	0.784-0.920
7. Budantseva 1976	293	0.246	0.922

Critical Solution Temperature and Composition

The five reported values of the UCST, ref. 1-4 and 6, are in good agreement; their average is (omitting the less precise value of ref. 2) $T_c = 315.8 \pm 0.2$ K (± 1 std. dev). The critical composition was reported to be $x_{c1} = 0.643$ in ref. 4; this value is *tentative*.

Mutual Solubility

Solubilities for 2,2,4-trimethylpentane in methanol, at four common temperatures reported in refs. 4 and 6, agree within 0.002 mole fraction. By comparison, the value at 293.2 K of Buchowski and Teperek, ref 5, is low by 0.004 mole fraction. The values of Budantseva et al., ref 7, at 293.2 K for the mole fraction of methanol are 0.2460 (2,2,4-TMP-rich phase) and 0.9220 (methanol-rich phase), compared to Francis' values of 0.224 and 0.8909, i.e., both values are high by about mole fraction 0.02. Therefore the combined data of Francis, ref 4, and Kiser, ref. 6, for the alcohol-rich phase are *recommended*, while the remaining data of Francis, ref. 4, are considered as *tentative*.

(continued)

CRITICAL EVALUATION: (continued)

The figure shows these recommended data together with the fitting equation:

$$x_1 = x_{1c} \pm B_1\theta^{\beta} \pm B_2\theta^{\beta+w} + A_1\theta \pm B_3\theta^{\beta+2w} + A_2\theta^{1-\alpha+w}$$

where $\theta = |1 - T/T_c|$, + and - refer to the branches below and above the critical composition, and the indices have their theoretical values $\beta = 0.325$, $\alpha = 0.11$, $w = 0.5$. The constants (with standard deviations in parentheses) are:

$x_c = 0.656$ (0.015) $T_c/K = 315.8$ (0.1)
$B_1 = 0.9671$ (0.46) $B_2 = -0.8218$ (3.1) $B_3 = -0.6296$ (5.1)
$A_1 = -3.298$ (0.74) $A_2 = 5.2455$ (1.5) $s = 0.014$

s is the total standard error of estimate in temperature and composition, assuming equal weights for each; the equation is valid over the temperature range 270-316 K.

Table 2. Values of solubility in the system
methanol (1) - 2,2,4-trimethylpentane (2)
t - tentative value; r - recommended value
(All values for the 2,2,4-TMP- rich phase are tentative)

T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
273.2	0.144	0.923
278.2	-	0.920
283.2	0.158	0.911
288.2	0.212	0.901
293.2	0.224	0.890
298.2	0.237	0.876
303.2	-	0.858
308.2	-	0.832
315.8	0.643	0.643 UCST

REFERENCES:

1. Cornish, R.E.; Archibald, R.C.; Murphy, E.A.; Evans, H.M. *Ind. Eng. Chem.* 1934, *26*, 397.
2. Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 764.
3. Sieg, L. *Chem.-Ing.-Tech.* 1951, *23*, 112.
4. Francis, A.W. *J. Am. Chem. Soc.* 1954, *76*, 393.
5. Buchowski, H.; Teperek, J. *Rocz. Chem.* 1959, *33*, 1093.
6. Kiser, R.W.; Johnson, G.D.; Shetlar, M.D. *J. Chem. Eng. Data* 1961, *6*, 338.
7. Budantseva, L.S.; Lesteva, T.M.; Nemstov, M.S. *Zh. Fiz. Khim.* 1976, *50*, 1344; *Deposited Doc. VINITI* 1976, 437.

(continued)

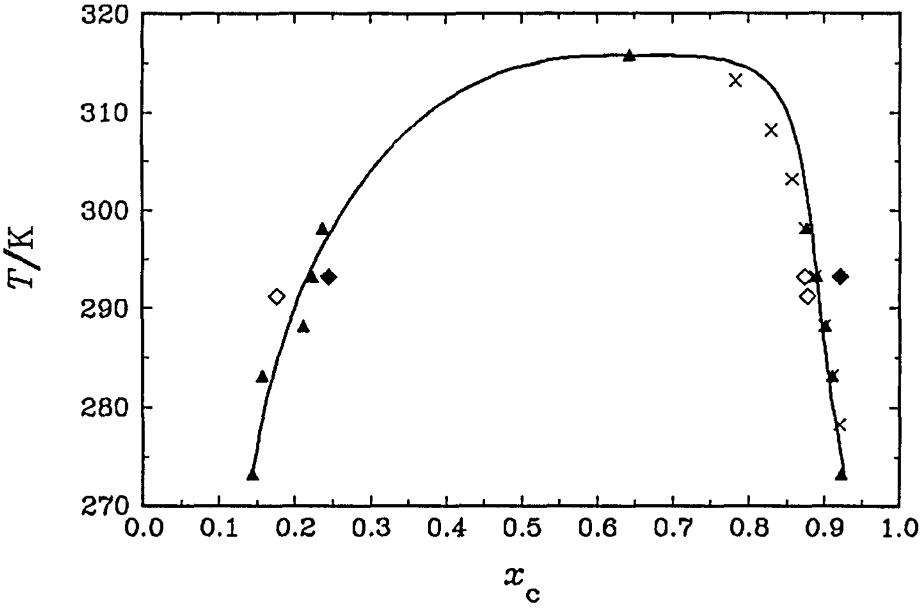

Fig. 1. Phase diagram of the system methanol-2,2,4-trimethylpentane; line, fitting equation; points: Francis, ref. 2, ●; Buchowski and Teperek, ref. 5, ◇; Kiser et al., ref. 6 ×; Budantseva et al., ref. 7 ◆.

COMPONENTS: (1) Methanol; CH_4O; [67-56-1] (2) 2,2,4-Trimethylpentane; C_8H_{18}; [540-84-1]	ORIGINAL MEASUREMENTS: Cornish, R.E.; Archibald, R.C.; Murphy, E.A.; Evans, H.M. *Ind. Eng. Chem.* <u>1934</u>, *26*, 397-406.
VARIABLES: One temperature: 316 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 42.5°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: The method was not specified.	SOURCE AND PURITY OF MATERIALS: (1) source not specified; distilled; $\rho(20°C)/\rho(20°C) = 0.78656$, (corr. for buoyancy), anhydrous. (2) source not specified; purified; boiling range <0.1°C, b.p. 99.3 ±0.05 K, f.p. -107.5 ±0.5°C, $n_D(20°C) = 1.39162 \pm 0.00012$, $\rho(20°C)/\rho(20°C) = 30.69314 \pm 0.00001$.
	ESTIMATED ERROR: not specified.
	REFERENCES:

COMPONENTS: (1) Methanol; CH_4O; [67-56-1] (2) 2,2,4-Trimethylpentane; C_8H_{18}; [540-84-1]	ORIGINAL MEASUREMENTS: Francis, A.W. *Ind. Eng. Chem.* <u>1944</u>, *36*, 764-71.
VARIABLES: One temperature: 316 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 43°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temperature of disappearance or reappearance of the cloudiness was read two or three times in each direction.	SOURCE AND PURITY OF MATERIALS: (1) source not specified, "substantially pure"; used as received. (2) source not specified.
	ESTIMATED ERROR: not specified.
	REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) 2,2,4-Trimethylpentane; C_8H_{18}; [540-84-1]

ORIGINAL MEASUREMENTS:

Sieg, L.

Chem.-Ing.-Tech. 1951, *23*, 1093-8.

VARIABLES:

Temperature: 316 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 42.5°C.
Mutual solubility was presented on a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A mixture of known composition was sealed in an ampoule and the temp. of appearance or disappearance of turbidity was observed. Ampoules and pipets were filled in a moisture-free atmosphere over P_2O5.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; boiled with Mg, fractionated.

(2) source not specified; pure grade; fractionated. For both (1) and (2), physical properties agreed with values in literature.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) 2,2,4-Trimethylpentane; C_8H_{18}; [540-84-1]	Francis, A.W. *J. Am. Chem. Soc.* 1954, *76*, 393-5.
VARIABLES: Temperature: 273 - 316 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and 2,2,4-trimethylpentane

$t/^\circ C$	$100\ w_1$		x_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
0	4.5	77.0	0.144	0.9227
10	5.0	74.2	0.158	0.9111
15	7.0	72.0	0.212	0.9016
20	7.5	69.6	0.224	0.8909
25	8.0	66.6	0.237	0.8767
42.6 UCST	33.6	33.6	0.643	0.643

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The observations were made in narrow graduated glass-stoppered tubes immersed in a water bath in a large silvered Dewar. Compositions were made up by volume from graduated pipets until cloudiness just disappeared or reappeared. The bath temperature was adjusted by addition of small quantities of cooler or warmer water and stirred several minutes.

SOURCE AND PURITY OF MATERIALS:

(1) J.T. Baker, anhydrous, chemical pure grade; used as received.

(2) source not specified, reagent grads.

ESTIMATED ERROR:

temp. ±0.2 K.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) 2,2,4-Trimethylpentane; C_8H_{18}; [540-84-1]	Buchowski, H.; Teperek, J. *Rocz. Chem.* 1959, *33*, 1093-8.
VARIABLES:	PREPARED BY:
Temperature: 291 and 293 K	A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and 2,2,4-trimethylpentane

$t/^{\circ}C$	$100\ w_1$		x_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
18.	5.7	67.0	0.177	0.879
20.	-	66.2	-	0.875

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The titration method was used. A known amount of methanol was titrated with isooctane until turbidity was turbidity was obtained. Composition was calc. from weight and mass balance. Data for the ternary system isooctane-methanol-water are also given.

SOURCE AND PURITY OF MATERIALS:

(1) F.O.Ch. (Poland) pure grade; heated with I_2 and Mg; distilled; $\rho(20^{\circ}C)$ = 0.7915 g/mL, $n(20^{\circ}C)$ = 1.3288.

(2) high purity reagent from Warsaw Univ.; $\rho(20^{\circ}C)$ = 0.6920 g/mL, $n(20^{\circ}C)$ = 1.3914, agreed with values from literature; used as received.

ESTIMATED ERROR:

temp. ±0.5°C.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) 2,2,4-Trimethylpentane; C_8H_{18}; [540-84-1]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.;
Shetlar, M.D.
J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 278 - 316 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of 2,2,4-trimethylpentane in methanol

$t/^\circ C$	g(2)/100 ml(1)	100 w_1 (compiler)	x_2 (compiler)
5	24.9	23.6	0.0798
10	27.9	25.8	0.0890
15	31.4	28.3	0.0996
20	35.3	30.8	0.1112
25	40.2	33.8	0.1254
30	46.0	37.0	0.1417
35	56.0	41.9	0.1681
40	76.	49.6	0.2163
43.0	UCST		

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4^\circ C) = 0.80999 - 9.253\ 10^{-4}\ (t/^\circ C) - 4.1\ 10^{-7}\ (t/^\circ C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; $n_D(20^\circ C)$ = 1.3293, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Eastman Organic Chemicals; purified; without unsaturated material by u.v. analysis, less than 0.04 mole % of impurity by glc; $n_D(20^\circ C)$ = 1.39145.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables vol. 3*, New York, 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) 2,2,4-Trimethylpentane; C_8H_{18}; [540-84-1]

ORIGINAL MEASUREMENTS:

Budantseva, L.S.; Lesteva, T.M.; Nemtsov, M.S.

Zh. Fiz. Khim. 1976, *50*, 1344; *Russ. J. Phys. Chem. (Engl. Transl.)* 1976, *50*, 814; **Dep. Doc. VINITI* 1976, 437.

VARIABLES:

One temperature: 293 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities at 20°C:

methanol in 2,2,4-trimethylpentane: $x_1 = 0.2460$ or $100\ w_1 = 8.384$.

2,2,4-trimethylpentane in methanol: $x_2 = 0.0780$ or $100\ w_2 = 23.17$.

COMMENTS: The papers in *Zh. Phys. Khim.* consist of a short abstract only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. Hydrocarbon was analysed by glc method by ref 1.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Budantseva, L.S.; Lesteva, T.M.; Nemtsov, M.S. *Zh. Fiz. Khim.* 1976, *50*, 1343; *Dep. Doc. VINITI* 1976, 438.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) 1,2,4-Trimethylbenzene (pseudocumene); C_9H_{12}; [95-63-6]	Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 1096-1104.
VARIABLES:	PREPARED BY:
One temperature: 247 K	A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be -26°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents, about 1 mL of each, were introduced into a small tube and stirred with a thermometer while the tube was warmed gradually in a bath of water or glycerol or was cooled with ice or a bath of acetone and dry ice. The temperature of disappearance or reappearance of the cloud was read 3 or 4 times in each direction. The proportion of components was varied to obtain the UCST.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; dried.

(2) source not specified; properties agreed with literature values; b.p. 169°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Nonane; C_9H_{20}; [111-84-2]

EVALUATOR:

A. Skrzecz
Institute of Physical Chemistry
Polish Academy of Sciences
Warsaw, Poland

J.W. Lorimer
Department of Chemistry
The University of Western Ontario
London, Ont., Canada

July, 1989

CRITICAL EVALUATION:

Table 1 lists solubilities and upper critical solution temperatures (UCST) and compositions for the system methanol (1) - nonane (2) which have been reported in the literature.

Table 1. solubilities, upper critical solution temperatures and compositions for the system methanol (1) - nonane (2)

Author(s)	T/K	Range x_1 (2)-rich phase	x_1 (1)-rich phase
1. Fischer 1949	367.3 UCST	-	-
2. Kogan 1956	275-333	0.072-0.279	0.936-0.961
3. Zieborak 1958	351.2 UCST	-	-
4. Kiser 1961	278-313	-	0.948-0.974
5. Hoelscher 1986	349-387 [a]	0.481-0.681	0.709-0.832
	352.6 UCST	0.662	0.662
6. Higashiuchi 1987	298-333	0.100-0.311	0.909-0.966

[a] At elevated pressures, p = 0.1-150.4 MPa.

Critical Solution Temperature and Composition

The UCST of Fischer and Neupauer, ref 1, was rejected since all values of the UCST reported in ref 1 for different alcohol-hydrocarbon systems are higher by about 10-20 K than recommended or tentative values, suggesting a significant amount of impurities, probably mainly water. Zieborak and Maczynska, ref. 3, and Hoelscher et al., ref. 5, took great care to prevent contamination by moisture. Their values are both considered to be reliable, and average T_c = 351.9 ± 0.7 K (std. dev.); this value is *recommended.*

Only one value of the critical solution composition has been reported: x_{c1} = 0.662 by Hoelscher et al. ref. 5. This value is considered to be *tentative.*

(continued)

CRITICAL EVALUATION:

Mutual Solubility

Forty-six values of mutual solubility, in addition to points designated specifically as critical solution points, have been reported. These are shown in the figure, from which it is seen that there are two regions of overlap. For the solubility of nonane in ethanol (ethanol-rich phase), the data of Kogan et al., ref 2, Kiser et al., ref. 4, and Higashiuchi et al., ref. 6, overlap. In general, the data of Kogan et al. show more scatter in this region, especially when compared to the fitting curve for all data (see below), and are rejected. The data of Kogan et al., ref. 2, and of Higsshiuichi et al., ref. 6, overlap in the region of the solubility of ethanol in nonane (nonane-rich region), and the former show considerable scatter. However, if the data of kogan et al. are removed, the resulting calculated fitting equation approaches zero mole fraction of ethanol at ablut 270 K, in contradiction to the behavior of the neighboring systems ethanol-dacane and ethanol-octane. Thus, the Kogan et al.'s data appear to show the correct trend at lower temperatures, and are included in the tentative fitting equation. The data of Hoelscher et al., ref. 5, appear to be slightly high near the shoulder on the ethanol-rich side of the coexistence curve.

The data of Hoelscher et al., ref. 5, require further comment. these authors extrapolated their data measured at high pressures to 0.1 MPa, and gave the results at p = 0.1 MPa in terms of fitting equations and tables of constants which, with values calculated therefrom, are given on the compilation sheets. The basic experimental data were obtained through a carefully-conducted study with precautions to avoid cintamination with water, ad are considered as *tentative.* In conclusion, all solubilities for this system must be considered as *tentative.*

See the compilation sheets for the data of Hoelscher et al. at high pressures, where the methods of fitting and extrapolation are described. These data can also be considered as *tentative.*

The mutual solubilities given in the table below were obtained by fitting all data to the equation:

$$x_1 = x_{c1} \pm B_1\theta^{\beta} \pm B_2\theta^{\beta+w} + A_1\theta \pm B_3\theta^{\beta+2w} + A_2\theta^{1-\alpha+w}$$

where $\theta = |1 - T/T_c|$, + and - refer to the branches below and above the critical composition, and the constants have their theoretical values β = 0.325, α = 0.11, w = 0.5. The constants (with standard deviations in parentheses) are:

x_{c1} = 0.6690 (0.0046) T_c/K = 352.7 K (0.1 K)
B_1 = 0.6424 (0.044) B_2 = 1.2233 (0.27) B_3 = -2.2157 (0.42)
A_1 = -2.1493 (0.21) A_2 = 2.6624 (0.39) s = 0.014

s is the standard error of estimate in composition. The values of x_{c1} and T_c are within the 95 % confidence limits calculated for the recommended and tentative values given above.

Pressure Coefficient of Critical Solution Temperature

This quantity can be calculated from the fitting equations of Hoelscher et al., ref. 5:

$$(\partial T/\partial p)_{xc} = T_0/ac = 3.59\times10^{-7} \text{ K Pa}^{-1}$$

where T_0, a and c are constants given on the compilation sheet.

(continued)

CRITICAL EVALUATION:

Tentative values of mutual solubility in the
system methanol (1) - nonane (2)

T/K	x_1 (2)-rich phase	x_1 (1)-rich phase	T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
270	0.0732	0.9660	315	0.1688	0.9477
275	0.0751	0.9662	320	0.1937	0.9411
280	0.0788	0.9660	325	0.2229	0.9326
285	0.0845	0.9653	330	0.2573	0.9216
290	0.0923	0.9642	335	0.2982	0.9073
295	0.1022	0.9625	340	0.3480	0.8876
300	0.1146	0.9602	345	0.4116	0.8587
305	0.1296	0.9570	350	0.5053	0.8059
310	0.1476	0.9529	352.70	0.669 UCST	

REFERENCES:

1. Fischer, R.; Neupauer, E. *Mikrochem. Ver. Mikrochim. Acta* 1949, *34*, 319.
2. Kogan, V.B.; Deizenrot, I.V.; Kul'byaeva, T.A.; Fridman, V.M. *Zh. Prikl. Khim.* 1956, *29*, 1387.
3. Zieborak, K.; Maczynska, Z. *Rocz. Chem.* 1958, *32*, 295.
4. Kiser, R.W.; Johnson, G.D.; Shetlar, M.D. *J. Chem. Eng. Data* 1961, *6*, 338.
5. Hoelscher, I.F.; Schneider, G.M.; Ott, J.B. *Fluid Phase Equilib.* 1986, *27*, 153.
6. Higashiuchi, H.; Sukuragi, Y.; Iwai, Y.; Arai, Y.; Nagatani, M. *Fluid Phase Equilib.* 1987, *36*, 35.

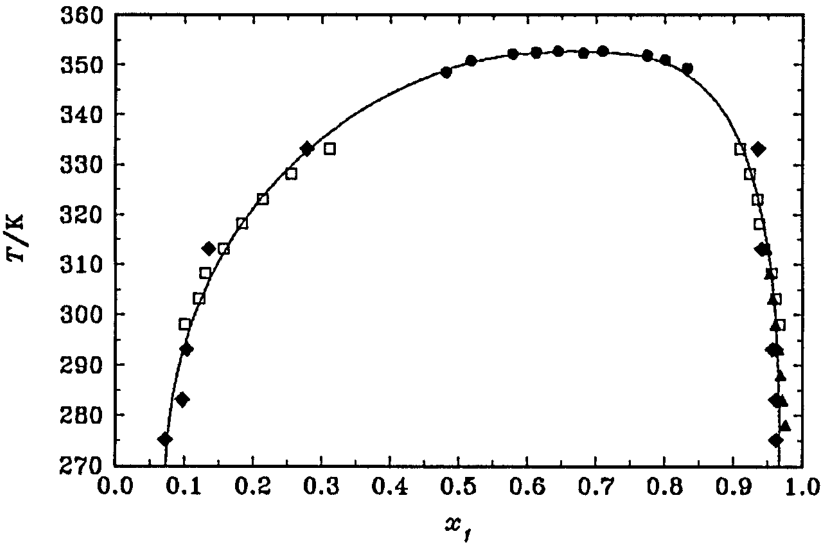

Fig. 1: Mutual solubilities in the system methanol-nonane; ◆, ref. 2; ▲, ref. 4; ●, ref. 5; □, ref. 6; solid curve, fitting equation.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Nonane; C_9H_{20}; [111-84-2]

ORIGINAL MEASUREMENTS:

Fischer, R.; Neupauer, E.

Mikrochem. Ver. Mikrochim. Acta 1949, *34*, 319-35.

VARIABLES:

One temperature: 367 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 94.0°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The sample in a sealed glass capillary was placed in a melting point microapparatus and the appearance and disappearance of the meniscus with temperature changes was observed. The mass of the sample was 0.001 - 0.002 g. For method see ref 1.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; purified; $n_D(20°C) = 1.3313$.

(2) source not specified; $n_D(20°C) = 1.4047$.

ESTIMATED ERROR:

temp. ±0.5 K.

REFERENCES:

1. Fischer, R.; Karasek, G. *Mikrochemie* 1947, *33*, 316.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Nonane; C_9H_{20}; [111-84-2]

ORIGINAL MEASUREMENTS:

Zieborak, K.; Maczynska, Z.

Rocz. Chem. 1958, *32*, 295-302.

VARIABLES:

One temperature: 351 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 78.0°C.

Solubility data were presented on a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A mixture of constant composition was sealed in a glass tube and the temperature of turbidity and clearness was observed visually. The mean of several results was reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; distilled in the presence of Na; b.p. 64.7°C, $n_D(25°C) = 1.3265$.

(2) obtained from Synthin; unsaturated hydrocarbons removed by repeated shaking with H_2SO_4 in presence of butanol, washed with a base and H_2O, distilled; b.p. 150.7°C, $n_D(25°C) = 1.4046$.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Nonane; C_9H_{20}; [111-84-2]

ORIGINAL MEASUREMENTS:

Kogan, V.B.; Deizenrot, I.V.;

Kul'byaeva, T.A.; Fridman, V.M.
Zh. Prikl. Khim. 1956, *29*, 1387-92.

VARIABLES:

Temperature: 275 - 333 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and nonane

$t/^\circ C$	100 w_1		x_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
2	1.91	86.17	0.0723	0.9614
10 a)	2.6	86.2	0.096	0.962
20	2.80	86.17	0.1034	0.9614
20 a)	2.8	84.5	0.103	0.956
40	3.77	79.93	0.1356	0.9410
60	8.80	78.48	0.2786	0.9359

a) from nonane - methanol - water ternary equilibrium data.

(1)-rich phase was observed to be the lower layer.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. The two-phase mixture was periodically shaken in a thermostatted burette with water jacket for several hours. The phases were taken out for analysis after separation. Methanol was determined two-times by reaction with phthalic anhydride.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, pure grade; distilled; < 0.01% of water; $n_D(20^\circ C) = 1.3391$.

(2) source not specified; used as received; b.p. 150.5°C, $n_D(20^\circ C) = 1.4035$.

ESTIMATED ERROR:

soly. < ±1% (relative error of methanol concentration);
temp. ±0.05 K.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Nonane; C_9H_{20}; [111-84-2]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.;

Shetlar, M.D.

J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 278 - 313 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of nonane in methanol

$t/^{\circ}C$	g(2)/100 ml(1)	100 w_1 (compiler)	x_2 (compiler)
5	8.4	9.4	0.0254
10	9.5	10.6	0.0288
15	10.5	11.6	0.0319
20	11.6	12.8	0.0353
25	12.9	14.1	0.0394
30	14.2	15.4	0.0434
35	15.5	16.6	0.0475
40	17.0	18.0	0.0520

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4^{\circ}C) = 0.80999 - 9.253\ 10^{-4}\ (t/^{\circ}C) - 4.1\ 10^{-7}\ (t/^{\circ}C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; $n_D(20^{\circ}C) = 1.3293$, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Matheson, Coleman and Bell; used as received; contained small amounts of unsaturated impurities; $n_D(20^{\circ}C) = 1.40545$.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables* *vol. 3*, New York, 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Nonane; C_9H_{20}; [111-84-2]

ORIGINAL MEASUREMENTS:

Hoelscher, I.F.; Schneider, G.M.: Ott, J.B.

Fluid Phase Equilib. 1986, *27*, 153-69.

VARIABLES:

Temperature: 349 - 387 K
Pressure: 0.1 - 150 MPa

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol and nonane

T/K	p/MPa	x_1	100 w_1 (compiler)	
352.6	0.1	0.66	32.7	UCST extrapolated
348.8	1.0	0.481	18.8	
351.5	10.0	0.481	18.8	
354.4	20.0	0.481	18.8	
357.0	30.0	0.481	18.8	
359.5	40.0	0.481	18.8	
361.6	50.0	0.481	18.8	
363.6	60.0	0.481	18.8	
367.5	80.0	0.481	18.8	
370.9	100.5	0.481	18.8	
374.1	120.3	0.481	18.8	
377.2	140.3	0.481	18.8	
378.6	150.4	0.481	18.8	
351.0	1.0	0.517	21.1	
354.0	10.0	0.517	21.1	
357.4	20.0	0.517	21.1	
360.0	30.0	0.517	21.1	
362.5	40.0	0.517	21.1	
364.8	50.0	0.517	21.1	
367.1	60.0	0.517	21.1	

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A high-pressure optical cell (ref 1) with sapphire windows with Al-to-Au-to-Al sandwich seals and magnetic stirring was used. Pressure was measured with a Heise gauge calibrated against a dead-weight gauge, temperature with a chromel-to-alumel thermocouple calibrated against a certified platinum resistance thermometer. Equilibrium temperatures were obtained from visual observation of phase separation as the sample was cooled. Composition was determined from the volumes added to the cell. Special precautions were taken to exclude moisture. Data for 0.1 MPa were extrapolated.

SOURCE AND PURITY OF MATERIALS:

(1) Fisher, purity 0.999 mole fraction; distilled twice over Na in 2 m column packed with glass helices; purity > 0.9999 mole fraction by glc analysis.

(2) Fluka, purissimum grade, purity > 99.5 %; purity 0.9955 mole fraction by glc analysis; used as received.

ESTIMATED ERROR:

temp. ±0.2 K, ±0.1 K at p = 0.1 MPa.
pressure ±0.2 MPa.
composition ±0.005 mole fraction.

REFERENCES:

1. Liphard, K.G.; Schneider, G.M. *J. Chem. Thermodyn.* 1975, *7*, 805.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Nonane; C_9H_{20}; [111-84-2]

ORIGINAL MEASUREMENTS:

Hoelscher, I.F.;
Schneider, G.M.: Ott, J.B.

Fluid Phase Equilib. 1986, *27*, 153-69.

EXPERIMENTAL VALUES: (Continued)

Solubility of methanol and nonane

T/K	p/MPa	x_1	100 w_1 (compiler)
371.3	80.0	0.517	21.1
374.9	100.6	0.517	21.1
378.3	120.3	0.517	21.1
381.7	140.0	0.517	21.1
383.2	150.4	0.517	21.1
352.4	1.0	0.578	25.5
355.6	10.0	0.578	25.5
358.9	20.0	0.578	25.5
361.8	30.0	0.578	25.5
364.5	40.0	0.578	25.5
366.8	50.0	0.578	25.5
369.1	60.0	0.578	25.5
373.3	80.0	0.578	25.5
377.3	100.3	0.578	25.5
381.1	120.0	0.578	25.5
384.4	140.4	0.578	25.5
386.1	150.4	0.578	25.5
352.8	1.0	0.612	28.3
356.1	10.0	0.612	28.3
359.2	20.0	0.612	28.3
362.2	30.0	0.612	28.3
365.0	40.0	0.612	28.3
367.4	50.0	0.612	28.3
369.7	60.0	0.612	28.3
374.0	80.0	0.612	28.3
377.9	100.3	0.612	28.3
381.3	120.3	0.612	28.3
384.6	140.3	0.612	28.3
386.1	150.0	0.612	28.3
352.9	1.0	0.644	31.1
356.0	10.0	0.644	31.1
359.4	20.0	0.644	31.1
362.3	30.0	0.644	31.1
364.9	40.0	0.644	31.1
346.1	20.2	0.586	28.4
348.9	30.0	0.586	28.4
351.4	40.1	0.586	28.4
354.0	50.1	0.586	28.4
356.3	60.3	0.586	28.4
360.4	80.2	0.586	28.4
364.1	100.6	0.586	28.4
367.5	120.4	0.586	28.4
370.6	140.1	0.586	28.4
372.3	150.7	0.586	28.4
339.8	1.0	0.603	29.9
342.9	10.0	0.603	29.9
346.2	20.0	0.603	29.9
349.0	29.8	0.603	29.9
351.7	40.1	0.603	29.9
354.0	50.0	0.603	29.9

(continued)

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Nonane; C_9H_{20}; [111-84-2]

ORIGINAL MEASUREMENTS:

Hoelscher, I.F.; Schneider, G.M.: Ott, J.B.

Fluid Phase Equilib. 1986, *27*, 153-69.

EXPERIMENTAL VALUES: (Continued)

Solubility of methanol and nonane

T/K	*p*/MPa	x_1	100 w_1 (compiler)
356.4	60.0	0.603	29.9
360.7	80.2	0.603	29.9
364.4	100.6	0.603	29.9
368.0	121.1	0.603	29.9
371.2	140.8	0.603	29.9
339.7	1.0	0.646	33.9
342.8	10.0	0.646	33.9
346.1	20.1	0.646	33.9
348.9	30.1	0.646	33.9
351.5	40.1	0.646	33.9
353.9	50.1	0.646	33.9
356.2	60.0	0.646	33.9
360.3	80.0	0.646	33.9
364.2	101.2	0.646	33.9
367.5	121.0	0.646	33.9
370.8	141.0	0.646	33.9
372.1	150.8	0.646	33.9
342.8	9.9	0.659	35.2
346.1	20.1	0.659	35.2
349.0	30.1	0.659	35.2
351.5	40.0	0.659	35.2
353.9	50.0	0.659	35.2
356.2	60.1	0.659	35.2
360.4	80.0	0.659	35.2
364.3	100.8	0.659	35.2
368.0	121.0	0.659	35.2
371.0	140.7	0.659	35.2
339.2	0.9	0.716	41.4
342.4	9.9	0.716	41.4
345.7	20.0	0.716	41.4
348.3	30.1	0.716	41.4
351.0	40.1	0.716	41.4
353.5	50.1	0.716	41.4
367.4	50.0	0.644	31.1
369.5	60.0	0.644	31.1
373.8	80.0	0.644	31.1
377.8	100.5	0.644	31.1
381.3	119.8	0.644	31.1
384.8	139.8	0.644	31.1
386.4	149.9	0.644	31.1
352.6	1.0	0.681	34.8
355.7	10.0	0.681	34.8
358.8	20.0	0.681	34.8
361.8	30.0	0.681	34.8
364.8	40.1	0.681	34.8
367.1	50.0	0.681	34.8
369.3	60.0	0.681	34.8
373.7	80.0	0.681	34.8
377.7	100.3	0.681	34.8
381.1	120.3	0.681	34.8
384.6	140.3	0.681	34.8
386.3	149.9	0.681	34.8
352.9	1.0	0.709	37.8
356.1	10.0	0.709	37.8
359.4	20.0	0.709	37.8

(continued)

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Nonane; C_9H_{20}; [111-84-2]

ORIGINAL MEASUREMENTS:

Hoelscher, I.F.; Schneider, G.M.: Ott, J.B.

Fluid Phase Equilib. 1986, *27*, 153-69.

EXPERIMENTAL VALUES: (Continued)

Solubility of methanol and nonane

T/K	p/MPa	x_1	100 w_1 (compiler)
362.2	30.0	0.709	37.8
365.0	40.0	0.709	37.8
367.4	50.0	0.709	37.8
369.6	60.0	0.709	37.8
373.8	80.0	0.709	37.8
377.6	100.3	0.709	37.8
381.2	120.3	0.709	37.8
384.7	140.1	0.709	37.8
386.5	149.9	0.709	37.8
352.2	1.0	0.774	46.1
355.3	10.0	0.774	46.1
358.8	20.0	0.774	46.1
361.7	30.0	0.774	46.1
364.5	40.0	0.774	46.1
366.9	50.0	0.774	46.1
369.1	60.0	0.774	46.1
373.2	80.0	0.774	46.1
377.1	99.8	0.774	46.1
380.8	120.2	0.774	46.1
384.2	140.2	0.774	46.1
385.7	149.9	0.774	46.1
351.4	1.0	0.800	50.0
354.4	10.0	0.800	50.0
357.6	20.0	0.800	50.0
360.8	30.0	0.800	50.0
363.4	40.0	0.800	50.0
365.8	50.0	0.800	50.0
368.0	60.0	0.800	50.0
372.1	80.0	0.800	50.0
375.9	100.4	0.800	50.0
379.3	120.3	0.800	50.0
382.5	140.3	0.800	50.0
384.1	150.2	0.800	50.0
349.6	1.0	0.832	55.3
352.9	10.0	0.832	55.3
356.0	20.0	0.832	55.3
359.0	30.0	0.832	55.3
361.5	40.0	0.832	55.3
363.7	50.0	0.832	55.3
365.8	60.0	0.832	55.3
369.5	80.0	0.832	55.3
372.6	100.3	0.832	55.3
375.7	120.3	0.832	55.3
378.7	140.0	0.832	55.3
380.2	149.9	0.832	55.3
380.2	149.9	0.832	55.3

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Nonane; C_9H_{20}; [111-84-2]	Hoelscher, I.F.; Schneider, G.M.: Ott, J.B. *Fluid Phase Equilib.* 1986, *27*, 153-69.

EXPERIMENTAL VALUES: (Continued)

COMMENTS AND ADDITIONAL DATA:

Data for isopleths at high pressures were fitted to the Simon equation

$$p(x,T)/\text{MPa} = a[(T/T_0)^c - 1]$$

From these equations, the corresponding (T, x) isobars were calculated and were fitted to the equation

$$T/\text{K} = T_c/\text{K} + k|y - y_c|^{\nu}$$

where

$$y = \alpha x_1/[1 + x_1(\alpha - 1)]$$
$$y_c = \alpha x_{c1}/[1 + x_{c1}(\alpha - 1)]$$

The coefficients found are (s = std. error of estimate):

x_1	T_0/K	a	c	s/K
0.481	348.5	93.56	11.61	0.11
0.517	350.8	93.14	10.90	0.15
0.578	352.2	97.13	10.22	0.15
0.612	352.5	85.82	11.13	0.06
0.644	352.7	95.21	10.41	0.15
0.681	352.3	92.63	10.51	0.13
0.709	352.7	94.31	10.49	0.17
0.774	351.9	85.98	11.04	0.14
0.800	351.0	81.03	11.71	0.12
0.832	349.3	63.50	14.46	0.19

p/MPa	T_c/K	k	α	x_{c1}	ν	s
0.1	352.6	-1946	0.985	0.662	3.622	0.11
25	360.6	-2986	0.991	0.667	3.812	0.11
50	367.2	-5137	0.902	0.669	4.111	0.10
75	372.9	-7292	0.838	0.670	4.290	0.09
100	377.8	-8701	0.793	0.670	4.359	0.08
125	382.2	-1187	0.767	0.670	4.502	0.07
150	386.2	-1410	0.751	0.670	4.565	0.08

Equations are also given for (p, x) pairs, which are of the same form as those for the (T, x) pairs.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Nonane; C_9H_{20}; [111-84-2]

ORIGINAL MEASUREMENTS:

Higashiuchi, H.; Sukuragi, Y.;

Iwai, Y.; Arai, Y.; Nagatani, M.

Fluid Phase Equilib. 1987, *36*, 35-47.

VARIABLES:

Temperature: 298 - 333 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and nonane

$t/°C$	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
25.00	0.0999	0.9664	2.70	87.78
30.00	0.1209	0.9608	3.32	85.96
35.00	0.1298	0.9557	3.59	84.35
40.00	0.1575	0.9454	4.46	81.22
45.00	0.1846	0.9377	5.35	78.99
50.00	0.2138	0.9348	6.36	78.17
55.00	0.2554	0.9234	7.89	75.07
60.00	0.3109	0.9091	10.13	71.42

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. Thermostatically controlled double-walled glass cells which were similar to that of ref 1 were used. Samples of both phases in equilibrium were carefully withdrawn with a precision syringe and the compositions were determined by gas chromatogrphy with FID. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, guaranteed reagent grade, purity > 99%; used as received.

(2) source not specified, guaranteed reagent grade, purity 98.0%; used as received.

ESTIMATED ERROR:

soly. ±1% (accurancy);
temp. ±0.05°C (thermostating).

REFERENCES:

1. Fabries, J.-F.; Gustin, J.-L.; Renon, H. *J. Chem. Eng. Data* 1977, *22*, 303

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) 2,2,5-Trimethylhexane; C_9H_{20}; [3522-94-9]	Kiser, R.W.; Johnson, G.D.; Shetlar, M.D. *J. Chem. Eng. Data* 1961, *6*, 338-41.
VARIABLES: Temperature: 278 - 331 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of 2,2,5-trimethylhexane in methanol

t/°C	g(2)/100 ml(1)	100 w_1 (compiler)	x_2 (compiler)
5	16.2	16.7	0.0478
10	17.9	18.3	0.0529
15	20.0	20.1	0.0591
20	22.1	21.8	0.0652
25	24.7	23.9	0.0727
30	28.0	26.4	0.0821
35	31.6	28.9	0.0922
40	36.0	31.8	0.1043
57.5	UCST		

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4°C) = 0.80999 - 9.253\ 10^{-4}\ (t/°C) - 4.1\ 10^{-7}\ (t/°C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; n_D(20°C) = 1.3293, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Matheson, Coleman and Bell; used as received; 0.2 mole % of impurities of unsaturated nature by u.v. analysis; n_D(20°C) = 1.3997.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables vol. 3*, New York, 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) 1,2,3,4-Tetrahydronaphthalene (tetralin); $C_{10}H_{12}$; [119-64-2]

ORIGINAL MEASUREMENTS:

Herz, W.; Schutan, P.

Z. Phys. Chem. 1922, *101*, 269-85.

VARIABLES:

One temperature: 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The solubility of methanol in 1,2,3,4-tetrahydronaphthalene at 25°C was reported to be 49.4% (type of % was not reported).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The saturated mixture was kept at 25°C for 24 h and its density was measured. The concentration was calculated from density as a fn. of concentration obtained from four experimental points.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; purified with Ag_2O to remove aldehyde, distilled over CaO to remove H_2O: b.p. 64.1°C at 747 Torr, $\rho(25^\circ C)/\rho 4^\circ C)$ = 0.7867.

(2) GmbH in Rodleben; dist. in vacuum over Na, dist. several times; b.p. 207.3°C, $\rho(15.1^\circ C)$ = 0.9731, $\rho(15.1^\circ C)$ = 0.9658.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Cymene (methyl(1-methylethyl)-benzene); $C_{10}H_{14}$; [25155-15-1] (3) Diethylbenzene; $C_{10}H_{14}$; [25340-17-4] (4) Bicyclo[4.4.0]decane (decalin, decahydronaphthalene); $C_{10}H_{18}$; [91-17-8]	Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 1096-1104.
VARIABLES:	PREPARED BY:
Temperatures: 240, 255, 374 K	A. Skrzecz

EXPERIMENTAL VALUES:

Methanol + Cymene: UCST = -33°C.
Methanol + Diethylbenzene: UCST = -18°C.
Methanol + Bicyclo[4.4.0]decane: UCST = 101°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents, about 1 mL of each, were introduced into a small tube and stirred with a thermometer while the tube was warmed gradually in a bath of water or glycerol or was cooled with ice or a bath of acetone and dry ice. The temp. of disappearance or reappearance of the cloud was read three or four times in each direction. The proportion of components was varied to obtain the critical solution temperature.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; dried.
(2) presumably synthesized by alkylation and distilled in the laboratory; the isomers were not separated, structure was not investigated; properties agreed with those recorded for meta and para isomers; b.p. 176°C.
(3) As for (2); b.p. 187°C.
(4) Source not specified; b.p. 194.6°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) trans-Bicyclo[4.4.0]decane (trans-decalin, trans-decahydronaphthalene); $C_{10}H_{18}$; [493-02-7]

ORIGINAL MEASUREMENTS:

Antosik, M.; Stafiej, A.

Fluid Phase Equilib. 1990, *58*, 325-33.

VARIABLES:

Temperature: 319 - 370 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and trans-decalin

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
319.43	-	0.9515	-	81.97
326.00	-	0.9455	-	80.08
337.07	-	0.9352	-	76.98
345.28	0.2584	-	7.472	-
353.03	0.3133	-	9.563	-
355.23	0.3388	-	10.615	-
360.59	-	0.9060	-	69.08
364.32	0.4576	-	16.355	-
364.86	-	0.8694	-	60.67
365.54	-	0.8510	-	56.97
365.83	0.4918	-	18.32	-
365.97	-	0.8478	-	56.35
368.00	0.5255	-	20.42	-
368.83	0.5912	-	25.10	-
369.17	0.6120	-	26.77	-
369.84	-	0.7822	-	45.43

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. About 4 g mixture of known composition was sealed in glass ampoules and immersed in thermostat (stability within 0.005 K) with a platinum resistance thermometer. Sample was mixed by a glass ball which rolled in the mechaniclly-agitated ampoule. Visual observations of appearance and disappearance of turbidity were made during heating/cooling.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; distilled; purity 99.9 wt% by glc with FID; water < 0.03 wt% (Karl Fischer).

(2) source not specified; distilled; purity 99.8 wt% by glc with FID.

ESTIMATED ERROR:

soly. < ±0.0005 mole fraction (estimated);

temp. ±0.01 K in the vicinity of UCST,
±0.2 K temp. much lower than UCST (reproducibility).

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) trans-Bicyclo[4.4.0]decane (trans-decalin, trans -decahydro-naphthalene); $C_{10}H_{18}$; [493-02-7]	Antosik, M.; Stafiej, A. *Fluid Phase Equilib.* 1990, *58*, 325-33.

EXPERIMENTAL VALUES: (continued)

Mutual solubility of methanol and trans-decalin

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
369.87	0.6785	-	32.85	-
369.96	0.6948	-	34.54	-
370.04	-	0.7556	-	41.74
370.07	0.7357	-	39.21	-
370.08	0.7275	0.7275	38.22	38.22 UCST a)

a) Upper critical solution temperature and composition were extrapolated by the authors from experimental data.

Authors' correlation equation:

$$x = 0.7313 - 23.8596\ t + 17.7653\ t^{0.9} + 7.5694\ t^{1.4} + 1.6184\ b\ t^{0.4564} + - 1.8048\ b\ t^{0.9564}$$

where

$t = 1 - T/T_c$

$b = 1$ for $x > x_c$, -1 for $x < x_c$

T_c, x_c - upper critical solution temperature, composition.

COMPONENTS:	EVALUATOR:
(1) Methanol; CH_4O; [67-56-1] (2) Decane; $C_{10}H_{22}$; [124-18-5]	A. Skrzecz Institute of Physical Chemistry Polish Academy of Sciences Warsaw, Poland J.W. Lorimer Department of Chemistry The University of Western Ontario London, Ont., Canada July, 1989

CRITICAL EVALUATION:

Table 1 lists solubilities and upper critical solution temperatures (UCST) and compositions for the system methanol (1) - decane (2) which have been reported in the literature.

Table 1. Solubilities, upper critical solution temperatures and compositions for the system methanol (1) - decane (2)

Author(s)	Range		
	T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Bingham 1907	349 UCST	-	-
2. Fischer 1949	374.7 UCST	-	-
3. Zieborak 1956	364 UCST	-	-
4. Zieborak 1958	364.1 UCST	-	-
5. Kiser 1961	278-313	-	0.966-0.983
6. Hoelscher 1986	359-390 [a]	0.512-0.689	0.718-0.831
	363.9 or 364.0		0.703
7. Higashiuchi 1987	298-333	0.083-0.238	0.938-0.976

[a] At elevated pressures, p = 0.1-100.6 MPa critical values at 0.1 MPa.

Critical Solution Temperature and Composition

The UCST of Bingham, ref. 1, and of Fischer and Neupauer, ref. 2, are rejected. The value of ref. 1 is in poor agreement with others and all values of UCST reported in ref. 2 for different alcohol-hydrocarbon systems are higher by about 10-20 K than recommended or tentative values, indicating a significant amount of impurities, probably water. Values of the UCST by Zieborak et al., refs. 3 and 4, and by Hoelscher et al., ref. 6, are in good agreement, and the average T_c = 364.0 ± 0.2 K (std. dev.) is *recommended*; both sets of workers took great care to prevent contamination with moisture. (The paper of Hoelscher et al. actually gives two separate values, but their difference is well within experimental error.)

(continued)

CRITICAL EVALUATION: (continued)

The only value of the critical composition is that of Hoelscher et al., ref. 6: $x_{c1} = 0.703$. This value is considered to be *tentative.*

Mutual Solubility

Thirty-three values of mutual solubility, in addition to points designated specifically as critical solution points, have been reported. These are shown in the figure, from which it is seen that the only region of overlap is between the values of Kiser et al., ref. 5, and Higashiuchi et al., ref. 7 for the solubility of methanol in decane. At a general level of error of about 0.005 mole fraction, points in this region can be *recommended.* The remaining points appear to lie on a smooth curve, and are considered as *tentative.*

The data of Hoelscher et al., ref. 6, require comment. These authors extrapolated their data measured at high pressures to 0.1 MPa, and gave the results for $p = 0.1$ MPa in terms of fitting equations and tables of constants, which, with values calculated therefrom, are given on the compilation sheets. The basic experimental data were obtained through a carefully-conducted study with precautions to avoid contamination with water, and are considered to be *tentative.*

See the compilation sheets for the data of Hoelscher et al. at higher pressures, where the methods of fitting and extrapolation are described. These data can also be considered as *tentative.*

The mutual solubilities given in the table below were obtained by fitting all data to the equation:

$$x_1 = x_{c1} \pm B_1\theta^{\beta} \pm B_2\theta^{\beta+w} + A_1\theta \pm B_3\theta^{\beta+2w} + A_2\theta^{1-\alpha+w}$$

where $\theta = |1 - T/T_c|$, + and - refer to the branches below and above the critical composition, and the constants have their theoretical values $\beta = 0.325$, $\alpha = 0.11$, $w = 0.5$. The constants (with standard deviations in parentheses) are:

$x_{c1} = 0.7047$ (0.0012) $T_c/\mathrm{K} = 363.9$ (0.1)
$B_1 = 0.5522$ (0.012) $B_2 = 1.2526$ (0.078) $B_3 = -1.9516$ (0.13)
$A_1 = -2.5764$ (0.070) $A_2 = 3.1246$ (0.14) $s = 0.0033$
s is the total standard error of estimate in composition.

Pressure Coefficient of Critical Solution Temperature

This quantity can be calculated from the fitting equations of Hoelscher et al.:

$$(\partial T/\partial p)_{x_c} = T_0/ac = 3.60\times10^{-7}\ \mathrm{K\ Pa^{-1}}$$

where T_0, a and c are constants given on the compilation sheet.

(continued)

CRITICAL EVALUATION: (continued)

Table 2. Recommended values of mutual solubility in the system methanol (1) - decane (2).

T/K	x_1 (2)-rich phase	x_1 (1)-rich phase	T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
270	0.0413	0.9893	320	0.1636	0.9548
275	0.0450	0.9867	330	0.2180	0.9423
280	0.0503	0.9841	340	0.2886	0.9245
285	0.0573	0.9813	350	0.3834	0.8964
290	0.0661	0.9784	355	0.4459	0.8738
300	0.0895	0.9720	360	0.5301	0.8360
310	0.1215	0.9643	363.5	0.6405	0.7644
			364.0	0.703	UCST

REFERENCES:

1. Bingham, E.C. *Am. Chem. J.* 1907, *37*, 549.
2. Fischer, R.; Neupauer, E. *Mikrochem. Ver. Mikrochim. Acta* 1949, *34*, 319.
3. Zieborak, K.; Maczynska, Z.; Maczynski, A. *Bull. Acad. Pol. Sci., Cl.3* 1956, *4*, 153.
4. Zieborak, K.; Maczynska, Z. *Rocz. Chem.* 1958, *32*, 295.
5. Kiser, R.W.; Johnson, G.D.; Shetlar, M.D. *J. Chem. Eng. Data* 1961, *6*, 338.
6. Hoelscher, I.F.; Schneider, G.M.; Ott, J.B. *Fluid Phase Equilib.* 1986, *27*, 153.
7. Higashiuchi, H.; Sukuragi, Y.; Iwai, Y.; Arai, Y.; Nagatani, M. *Fluid Phase Equilib.* 1987, *36*, 35.

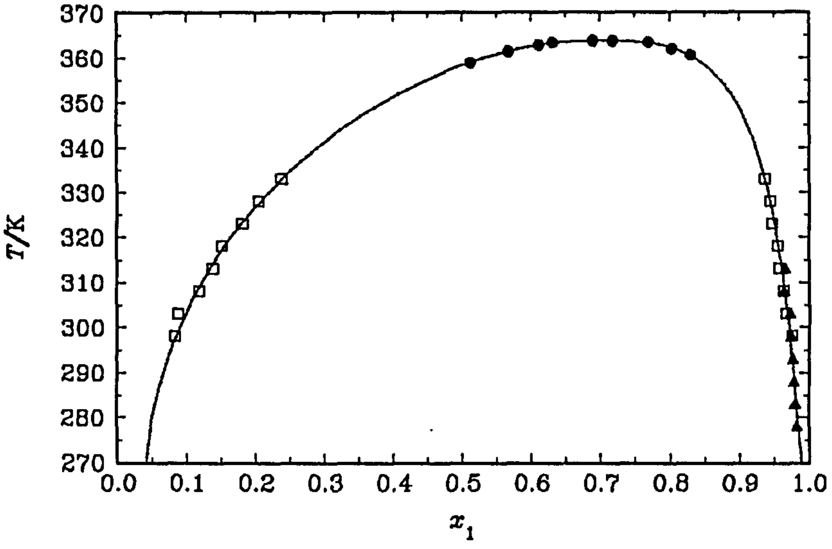

Fig. 1: Mutual solubilities in the system methanol-decane; ▲, ref. 5; ●, ref. 6; □, ref. 7; solid curve, fitting equation.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Decane; $C_{10}H_{22}$; [124-18-5]

ORIGINAL MEASUREMENTS:

Bingham, E.C.

Am. Chem. J. 1907, *37*, 549-57.

VARIABLES:

One temperature: 349 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 76°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The components were added from burettes to thick-walled glass tubes of about 2 mm internal diameter and 6-7 mm long which were sealed. The tubes and the components during the adding procedure were protected from moisture. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) Kahlbaum, the best provided; used as received.

(2) Kahlbaum, the best provided; used as received.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Decane; $C_{10}H_{22}$; [124-18-5]

ORIGINAL MEASUREMENTS:

Fischer, R.; Neupauer, E.

Mikrochem. Ver. Mikrochim. Acta 1949, *34*, 319-35.

VARIABLES:

One temperature: 375 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 101.5°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The sample in a sealed glass capillary was placed in a melting point microapparatus and the appearance and disappearance of the meniscus with temperature changes was observed. The mass of the sample was 0.001-0.002 g. The method is described in ref 1.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; purified; $n_D(20^\circ C) = 1.3313$.

(2) source not specified; $n_D(20^\circ C) = 1.4157$.

ESTIMATED ERROR:

temp. ±0.5 K.

REFERENCES:

1. Fischer, R.; Karasek, G. *Mikrochemie* 1947, *33*, 316.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Decane; $C_{10}H_{22}$; [124-18-5]

ORIGINAL MEASUREMENTS:

Zieborak, K.; Maczynska, Z.;
Maczynski, A.

Bull. Acad. Pol. Sci. C13 1956, *4*, 153-7.

VARIABLES:

One temperature: 364 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 91°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The critical solution temperature was determined by the conventional method. Special care was taken to prevent contamination with moisture. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; dehydrated distilled in the presence of Na; b.p. 64.7°C.

(2) obtained from Fischer-Tropsch synthesis; unsaturated hydrocarbons removed by repeated shaking with H_2SO_4; b.p. 174.2°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Decane; $C_{10}H_{22}$; [124-18-5]

ORIGINAL MEASUREMENTS:

Zieborak, K.; Maczynska, Z.

Rocz. Chem. 1958, *32*, 295-302.

VARIABLES:

One temperature: 364 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 90.9°C.

Solubility data were presented on a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A mixture of constant composition was sealed in a glass tube and the temperatures of turbidity and clarity were observed visually. The mean of several results was reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; distilled in the presence of Na; b.p. 64.7°C, $n_D(25°C) = 1.3265$.

(2) obtained from Synthin; unsaturated hydrocarbons removed by repeated shaking with H_2SO_4 in presence of butanol, washed with a base and H_2O, distilled; b.p. 174.2°C, $n_D(25°C) = 1.4157$.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Decane; $C_{10}H_{22}$; [124-18-5]

ORIGINAL MEASUREMENTS:

Kiser, R.W.; Johnson, G.D.; Shetlar, M.D.

J. Chem. Eng. Data 1961, *6*, 338-41.

VARIABLES:

Temperature: 278 - 313 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of decane in methanol

$t/^{\circ}C$	g(2)/100 ml(1)	100 w_1 (compiler)	x_2 (compiler)
5	6.2	7.1	0.0170
10	6.8	7.8	0.0188
15	7.4	8.5	0.0205
20	8.1	9.3	0.0225
25	8.9	10.2	0.0248
30	9.8	11.1	0.0275
35	10.9	12.3	0.0306
40	12.0	13.4	0.0337

Concentrations were recalculated using the density equation for methanol by ref 1 :

$$\rho/\rho(4^{\circ}C) = 0.80999 - 9.253\ 10^{-4}\ (t/^{\circ}C) - 4.1\ 10^{-7}\ (t/^{\circ}C)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The isoplethal or cloud point method was used. Samples of known composition were heated and/or cooled and the temperature of phase transition was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible.

SOURCE AND PURITY OF MATERIALS:

(1) E.I. du Pont de Nemours and Co.; distilled; $n_D(20^{\circ}C) = 1.3293$, b.p. 64.6°C (corrected), f.p. -99°C.

(2) Matheson, Coleman and Bell; used as received; contained some unidentified unsaturated material, estimated impurities <0.5 mole %; $n_D(20^{\circ}C) = 1.4116$.

ESTIMATED ERROR:

soly. ±2% (relative error);
temp. ±0.2 K.

REFERENCES:

1. *International Critical Tables vol. 3*, New York, 1933.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Decane; $C_{10}H_{22}$; [111-84-2]

ORIGINAL MEASUREMENTS:

Hoelscher, I.F.;
Schneider, G.M.: Ott, J.B.

Fluid Phase Equilib. 1986, *27*, 153-69.

VARIABLES:

Temperature: 359 - 390 K
Pressure: 0.1 - 100 MPa

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of methanol and decane

T/K	p/MPa	x_1	100 w_1 (compiler)	
364.0	0.1	0.70	34.4	UCST extrapolated
359.4	1.0	0.512	19.1	
362.3	10.0	0.512	19.1	
365.4	20.0	0.512	19.1	
368.2	30.0	0.512	19.1	
370.9	40.0	0.512	19.1	
373.4	50.0	0.512	19.1	
375.8	60.0	0.512	19.1	
380.1	80.0	0.512	19.1	
383.3	100.3	0.512	19.1	
361.9	1.0	0.567	22.8	
364.9	10.0	0.567	22.8	
368.0	20.0	0.567	22.8	
371.0	30.0	0.567	22.8	
374.1	40.0	0.567	22.8	

(continued)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A high-pressure optical cell (ref 1) with sapphire windows with Al-to-Au -to-Al sandwich seals and magnetic stirring was used. Pressure was measured with a Heise gauge calibrated against a dead-weight gauge, temperature with a chromel-to-alumel thermocouple calibrated against a certified platinum resistance thermometer. Equilibrium temperatures were obtained from visual observation of phase separation as the sample was cooled. Composition was determined from the volumes added to the cell. Special precautions were taken to exclude moisture. Data for 0.1 MPa were extrapolated.

SOURCE AND PURITY OF MATERIALS:

(1) Fisher, purity 0.999 mole fraction; distilled twice over Na in 2 m column packed with glass helices; purity > 0.9999 mole fraction by glc analysis.

(2) Phillips, purity 99 %; dist. in a 2-m glass column packed with glass beads; purity 0.9988 mole fraction by glc analysis.

ESTIMATED ERROR:

temp. ±0.2 K, ±0.1 K at p = 0.1 MPa.
pressure ±0.2 MPa.
composition ±0.005 mole fraction.

REFERENCES:

1. Liphard, K.G.; Schneider, G.M. *J. Chem. Thermodyn.* 1975, *7*, 805.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Decane; $C_{10}H_{22}$; [111-84-2]

ORIGINAL MEASUREMENTS:

Hoelscher, I.F.;
Schneider, G.M.: Ott, J.B.

Fluid Phase Equilib. 1986, *27*, 153-69.

EXPERIMENTAL VALUES: (Continued)

Solubility of methanol and decane

T/K	p/MPa	x_1	100 w_1 (compiler)
376.9	50.0	0.567	22.8
379.5	60.0	0.567	22.8
384.2	80.0	0.567	22.8
388.6	100.3	0.567	22.8
363.4	1.0	0.611	26.1
366.5	10.0	0.611	26.1
369.9	20.0	0.611	26.1
372.7	30.0	0.611	26.1
375.5	40.0	0.611	26.1
378.5	50.0	0.611	26.1
381.1	60.0	0.611	26.1
385.6	80.0	0.611	26.1
389.6	100.3	0.611	26.1
363.9	1.0	0.631	27.8
366.9	10.0	0.631	27.8
370.2	20.0	0.631	27.8
373.4	30.0	0.631	27.8
376.1	40.0	0.631	27.8
378.8	50.0	0.631	27.8
381.3	60.0	0.631	27.8
386.0	80.0	0.631	27.8
389.9	100.3	0.631	27.8
364.0	1.0	0.689	33.3
367.3	10.0	0.689	33.3
370.5	20.0	0.689	33.3
373.4	30.0	0.689	33.3
376.0	40.0	0.689	33.3
378.6	50.0	0.689	33.3
381.1	60.0	0.689	33.3
385.7	80.0	0.689	33.3
389.8	99.9	0.689	33.3
364.1	1.0	0.718	36.4
367.5	10.0	0.718	36.4
370.3	20.0	0.718	36.4
373.5	30.0	0.718	36.4
376.3	40.0	0.718	36.4
378.6	50.0	0.718	36.4
381.0	60.0	0.718	36.4
385.4	80.0	0.718	36.4
389.7	100.3	0.718	36.4
363.9	1.0	0.769	42.8
367.0	10.0	0.769	42.8
370.4	20.0	0.769	42.8
373.2	30.0	0.769	42.8
375.8	40.0	0.769	42.8
378.3	50.0	0.769	42.8
380.7	60.0	0.769	42.8
384.9	80.0	0.769	42.8
388.7	100.6	0.769	42.8
362.3	1.0	0.803	47.9

(continued)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) Decane; $C_{10}H_{22}$; [111-84-2]	Hoelscher, I.F.; Schneider, G.M.: Ott, J.B. *Fluid Phase Equilib.* 1986, *27*, 153-69.

EXPERIMENTAL VALUES: (Continued)

Solubility of methanol and decane

T/K	p/MPa	x_1	100 w_1 (compiler)
365.8	10.0	0.803	47.9
368.9	20.0	0.803	47.9
371.9	30.0	0.803	47.9
374.6	40.0	0.803	47.9
377.0	50.0	0.803	47.9
379.3	60.0	0.803	47.9
383.6	80.0	0.803	47.9
387.3	100.3	0.803	47.9
360.9	1.0	0.831	52.5
363.9	10.0	0.831	52.5
366.8	20.0	0.831	52.5
369.5	30.0	0.831	52.5
372.0	40.0	0.831	52.5
374.6	50.0	0.831	52.5
376.9	60.0	0.831	52.5
380.9	80.0	0.831	52.5
384.9	100.3	0.831	52.5

COMMENTS AND ADDITIONAL DATA:

Data for isopleths at high pressures were fitted to the Simon equation

$$p(x,T)/\mathrm{MPa} = a[(T/T_0)^c-1]$$

From these equations, the corresponding (T, x) isobars were calculated and were fitted to the equation

$$T/\mathrm{K} = T_c/\mathrm{K}+k|y-y_c|^{\nu}$$

where

$$y = \alpha x_1/[1+x_1(\alpha-1)]$$
$$y_c = \alpha x_{c1}/[1+x_{c1}(\alpha-1)]$$

The coefficients found are (s = std. error of estimate):

x_1	T_0/K	a	c	s/K
0.512	359.0	84.54	11.82	0.15
0.567	361.4	125.27	8.10	0.11
0.611	362.9	101.12	9.64	0.15
0.631	363.4	95.31	10.18	0.08
0.689	363.8	104.89	9.71	0.08
0.718	363.8	95.76	10.49	0.14
0.769	363.5	78.65	12.28	0.04
0.803	362.0	72.60	12.87	0.07
0.831	360.6	104.86	10.30	0.08

(continued)

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Decane; $C_{10}H_{22}$; [111-84-2]

ORIGINAL MEASUREMENTS:

Hoelscher, I.F.;
Schneider, G.M.: Ott, J.B.

Fluid Phase Equilib. 1986, *27*,
153-69.

EXPERIMENTAL VALUES: (Continued)

p/MPa	T_c/K	k	α	x_{c1}	ν	s
0.1	363.9	-2739	0.494	0.703	2.479	0.10
25	372.0	-8994	0.361	0.707	3.115	0.12
50	378.8	-1572	0.482	0.697	3.410	0.11
75	384.6	-2744	0.844	0.682	3.513	0.10
100	389.8	-8565	1.814	0.663	3.453	0.11
125	394.5	-8866	5.453	0.649	3.336	0.12
150	398.8	-4096	1.086	0.644	3.181	0.24

Equations are also given for (p, x) pairs, which are of the same form as those for the (T, x) pairs.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Decane; $C_{10}H_{22}$; [124-18-5]

ORIGINAL MEASUREMENTS:

Higashiuchi, H.; Sukuragi, Y.;
Iwai, Y.; Arai, Y.; Nagatani, M.
Fluid Phase Equilib. 1987, *36*,
35-47.

VARIABLES:

Temperature: 298 - 333 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and decane

$t/^\circ C$	x_1		$100\ w_1$ (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
25.00	0.0830	0.9763	2.00	90.27
30.00	0.0970	0.9674	2.36	86.98
35.00	0.1184	0.9648	2.94	86.06
40.00	0.1378	0.9583	3.47	83.81
45.00	0.1509	0.9563	3.85	83.13
50.00	0.1805	0.9480	4.73	80.41
55.00	0.2041	0.9443	5.46	79.24
60.00	0.2377	0.9376	6.56	77.19

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. Thermostatically controlled double-walled glass cells which were similar to that of ref 1 were used. Samples of both phases in equilibrium were carefully withdrawn with a precision syringe and the compositions were determined by gas chromatogrphy with FID. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, guaranteed reagent grade, purity > 99%; used as received.

(2) source not specified, guaranteed reagent grade, purity > 99%; used as received.

ESTIMATED ERROR:

soly. ±1% (accurancy);
temp. ±0.05 K (thermostating).

REFERENCES:

1. Fabries, J.-F.; Gustin, J.-L.; Renon, H.
J. Chem. Eng. Data 1977, *22*, 303

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Diethylmethylbenzene; $C_{11}H_{16}$; [25550-13-4]

(3) Ethylisopropylbenzene (ethyl (1-methylethyl)benzene); $C_{11}H_{16}$; [26573-16-0]

(4) sec-Pentylbenzene; $C_{11}H_{16}$; [3968-85-2]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*, 1096-1104.

VARIABLES:

Temperature: 283, 268, 267 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Methanol-Diethylmethylbenzene: UCST = 10°C.
Methanol-Ethylisopropylbenzene: UCST = -5°C.
Methanol-sec-Pentylbenzene: UCST = -6°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents, about 1 mL of each, were introduced into a small tube and stirred with a thermometer while the tube was warmed gradually in a bath of water or glycerol or was cooled with ice or a bath of acetone and dry ice. The temp. of disappearance or reappearance of the cloud was read three or four times in each direction. The proportions of components were varied to obtain the UCST.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; dried.
(2) presumably synthesized by alkylation and distilled in the laboratory; the isomers were not separated, structure was not investigated; properties agreed with those recorded for meta and para isomers; b.p. range 204-5°C.
(3) As for (2); b.p. 194.8°C, $\rho(20°C)/\rho(4°C) = 0.8616$.
(4) source not specified; properties agreed with values in literature; b.p. 192°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Methanol; CH_4O; [67-56-1] (2) Undecane; $C_{11}H_{24}$; [1120-21-4]	A. Skrzecz and A. Maczynski Institute of Physical Chemistry Polish Academy of Sciences Warsaw, Poland July, 1989

CRITICAL EVALUATION:

Table 1 gives reported solubilities and upper critical solution temperatures (UCST) for the system methanol (1) - undecane.

Table 1. Solubilities and upper critical solution temperatures (UCST) for the system methanol (1) - undecane (2)

Author(s)	T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Fischer 1949	386.7 UCST	-	-
2. Zieborak 1956	376 UCST	-	-
3. Zieborak 1958	375.2 UCST	-	-

The UCST of Fischer and Neupauer, ref. 1, is rejected because all UCST values reported in ref 1 for different alcohol-hydrocarbon systems are higher by about 10-20 K than Recommended values, which suggests a significant presence of impurities, probably water. This paper, ref. 1, is not compiled. The data of Zieborak et al., refs. 2 and 3, are considered reliable since great care was taken to prevent contamination with moisture. The UCST data of Zieborak et al., refs 2 and 3, are accepted as *tentative*.

TENTATIVE DATA:

UCST = 376 K

REFERENCES:

1. Fischer, R.; Neupauer, E. *Mikrochem. Ver. Mikrochim. Acta* 1949, *34*, 319.
2. Zieborak, K.; Maczynska, Z.; Maczynski, A. *Bull. Acad. Pol. Sci., Cl.3* 1956, *4*, 153.
3. Zieborak, K.; Maczynska, Z. *Rocz. Chem.* 1958, *32*, 295.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Undecane; $C_{11}H_{24}$; [1120-21-4]

ORIGINAL MEASUREMENTS:

Zieborak, K.; Maczynska, Z.;
Maczynski, A.
Bull. Acad. Pol. Sci. Cl3 1956,
4, 153-7.

VARIABLES: One temperature: 376 K

PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 103°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The critical solution temperature was determined by the conventional method. Special care was taken to prevent contamination with moisture. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; dist. in presence of Na; b.p. 64.7°C.

(2) Obtained from Fischer-Tropsch synthesis; unsatd. hydrocarbons removed by repeated shaking with H_2SO_4; b.p. 195.8°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Undecane; $C_{11}H_{24}$; [1120-21-4]

ORIGINAL MEASUREMENTS:

Zieborak, K.; Maczynska, Z.
Rocz. Chem. 1958, *32*, 295-302.

VARIABLES: One temperature: 375 K

PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 102.0°C.

Solubility data were presented on a graph only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A mixture of constant composition was sealed in a glass tube and the temps. of turbidity and clarity were observed visually. The mean of several results was reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; dist. in presence of Na; b.p. 64.7°C, $n_D(25°C) = 1.4202$.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Diisopropylbenzene (bis(1-methyl ethyl)benzene); $C_{12}H_{18}$; [25321-09-9]

(3) Triethylbenzene; $C_{12}H_{18}$; [25340-18-5]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*, 1096-1104.

VARIABLES:

Temperature: 282, 292 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Methanol-Diisopropylbenzene: UCST = 9°C.
Methanol-Triethylbenzene: UCST = 19°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents, about 1 mL of each, were introduced into a small tube and stirred with a thermometer while the tube was warmed gradually in a bath of water or glycerol or was cooled with ice or a bath of acetone and dry ice. The temperature of disappearance or reappearance of the cloud was read three or four times in each direction. The proportion of components was varied to obtain the UCST.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; dried.
(2) presumably synthesized by alkylation and distilled; the isomers were not separated, structure was not investigated; properties agreed with those recorded for meta and para isomers; b.p. 205°C.
(3) as for (2) (no m- or p-isomers); b.p. range 217-8°C, $\rho(20^\circ C)/\rho(4^\circ C) = 0.8737$.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methanol; CH_4O; [67-56-1] (2) 1-Dodecene; $C_{12}H_{24}$; [112-41-4]	Vojtko, J.; Hrusovsky, M.; Fancovic, K.; Rattay, V.; Hargas, R. *Chem. Zvesti* 1973, *27*, 477-81.
VARIABLES:	PREPARED BY:
One temperature: 274 K	A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities at 0.5°C:

methanol in 1-dodecene: 100 w_1 = 1.6 or x_1 = 0.079 (compiler).

1-dodecene in methanol: 100 w_2 = 6.6 or x_2 = 0.013 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The analytical method was used. The mixtures, prepared by weighing the pure components, were stirred thoroughly several times. Equilibrium was reached after 10 h at the desired temp. Samples were taken by a syringe with a long needle. Composition was determined by glc using the internal standard method. Data are also given for the ternary system 1-dodecene-methanol-1,2-dodecene oxide. The mutual solubility was also determined by isothermal titration as in ref 1.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; rectified; b.p. 65°C, $n_D(20^\circ C)$ = 1.3285, $\rho(20^\circ C)/\rho(4^\circ C)$ = 0.7918.

(2) obtained from a technical mixture of C_{11} - C_{15} alkanes by rectification; b.p. 88.9°C at 10 Torr, $n_D(20^\circ C)$ = 1.4300, $\rho(20^\circ C)/\rho(4^\circ C)$ = 0.7600.

ESTIMATED ERROR:

temp. ±0.1 K.

REFERENCES:

1. Othmer, D.F.; White, R.E.; Trueger, E. *Ind. Eng. Chem.* 1941, *33*, 1240.

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Isopropylnaphthalene ((1-methylethyl)naphthalene); $C_{13}H_{14}$; [29253-36-9]

(3) 1,2,3,4-Tetrahydroisopropylnaphthalene (isopropyltetralin); $C_{13}H_{18}$; [26916-60-9]

(4) Diisopropylmethylbenzene; $C_{13}H_{20}$; [26444-54-2]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*, 1096-1104.

VARIABLES:

Temperatures: 284, 330 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Methanol-Isopropylnaphthalene: UCST = 11°C.
Methanol-1,2,3,4-Tetrahydroisopropyl-naphthalene: UCST = 57°C.
Methanol-Diisopropylmethylbenzene: UCST = 32°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents, about 1 mL of each, were introduced into a small tube and stirred with a thermometer while the tube was warmed gradually in a bath of water or glycerol or was cooled with ice or a bath of acetone and dry ice. The temperature of disappearance or reappearance of the cloud was read 3 or 4 four times in each direction. The proportion of components was varied to obtain the UCST.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; dried.
(2) source not specified; properties agreed with values in literature; b.p. 264°C.
(3) as for (2); b.p. 256-66°C, $\rho(20°C)/\rho(4°C) = 0.9536$.
(4) as for (2); b.p. 217°C.

ESTIMATED ERROR:

not specified

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Tetradecane; $C_{14}H_{30}$; [629-59-4]

ORIGINAL MEASUREMENTS:

Pliskin, I.; Treybal, R.E.

J. Chem. Eng. Data 1966, *11*, 49-52.

VARIABLES:

One temperature: 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities at 25.0°C:

methanol in tetradecane: 100 w_1 = 1.00 or x_1 = 0.058.

tetradecane in methanol: 100 w_2 = 3.48 or x_2 = 0.00579.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubilities were determined by titration to a cloud point. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified; distilled.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) sec-Pentylnaphthalene; $C_{15}H_{18}$; (structure not specified)

(3) Diisopropylnaphthalene; (bis(1-methylethyl)naphthalene); $C_{16}H_{20}$; [38640-62-9]

(4) Dipentylbenzene; $C_{16}H_{26}$; (mixture of isomers)

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*, 1096-1104.

VARIABLES:

Temperatures: 322, 331, 349 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Methanol-sec-Pentylnaphthalene: UCST = 49°C.
Methanol-Diisopropylnaphthalene: UCST = 58°C.
Methanol-Dipentylbenzene: UCST = 76°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents, about 1 mL of each, were introduced into a small tube and stirred with a thermometer while the tube was warmed gradually in a bath of water or glycerol or was cooled with ice or a bath of acetone and dry ice. The temperature of disappearance or reappearance of the cloud was read 3 or 4 four times in each direction. The proportion of components was varied to obtain the UCST.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; dried.
(2) source not specified; b.p. 300°C in agreement with values in literature.
(3) source not specified; b.p. 305-15°C, $\rho(20°C)/\rho(4°C) = 0.9541$.
(4) presumably synthesized by alkylation and dist.; isomers were not separated, structure was not investigated; properties agreed with those for m- and p-isomers; b.p. 265°C.

ESTIMATED ERROR:

not specified

REFERENCES:

COMPONENTS:

(1) Methanol; CH_4O; [67-56-1]

(2) Hexadecane; $C_{16}H_{34}$; [544-76-3]

ORIGINAL MEASUREMENTS:

Rogalski, M.; Stryjek, R.

Bull. Acad. Polon. Sci., Ser. Sci. Chim. 1980, *28*, 139-47.

VARIABLES:

Temperature: 298 - 413 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of methanol and hexadecane

T/K	x_1		100 w_1 (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
297.95	-	0.9970	-	97.92
300.75	0.0590	-	0.879	-
324.16	0.1283	-	2.040	-
327.35	-	0.9948	-	96.44
383.55	-	0.9782	-	86.39
395.25	0.5716	-	15.881	-
407.35	-	0.9442	-	70.54
409.35	0.7654	-	31.584	-
412.65	0.8454	-	43.623	-
412.95	-	0.8913	-	53.71
413.35 UCST	0.8760	0.8760	49.990	49.99 a)

a) Composition, UCST estimated by authors from a large-scale graph.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. Samples of 4-5 g of various compositions were sealed in glass ampoules which were placed in a thermostat. The sample was then heated to a temp. somewhat higher than that of complete homogeneity and then cooled at 0.5-1 K/h until turbidity reappeared. The cycle was repeated; average temp. was taken as the equilibrium value. Samples were mixed continuously by rotating the ampoules.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; distilled at atmospheric pressure; purity above 99.9% by glc.

(2) source not specified; purified by crystallization using a Mollinari type crystallizer; purity above 99.9% by glc.

ESTIMATED ERROR:

soly. ±0.001 of mole fraction; temp. ±0.1 K at 297 K; ±0.5 K at 353 K.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Ethanol; C_2H_6O; [64-17-5] (2) Heptane; C_7H_{16}; [142-82-5] (3) 2,2,4-Trimethylpentane; C_8H_{18}; [540-84-1]	Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 764-71.
VARIABLES:	PREPARED BY:
Temperatures: 203, 213 K	A. Skrzecz

EXPERIMENTAL VALUES:

Methanol-Heptane: UCST = -60°C.

Methanol-2,2,4-Trimethylpentane: UCST = -70°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced into a test tube and stirred with a thermometer while the tube was warmed and cooled gradually in a bath. The temperature of disappearance or reappearance of the cloudiness was read 2 or 3 times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; "substantially pure", used as received.
(2) obtained from Jeffrey pine; no other information.
(3) sourca not specified.

ESTIMATED ERROR:

not specified

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Ethanol; C_2H_6O; [64-17-5] (2) Decane; $C_{10}H_{22}$; [124-18-5]	A. Maczynski Institute of Physical Chemistry Polish Academy of Sciences Warsaw, Poland July, 1989

CRITICAL EVALUATION:

Solubilities and upper critical solution temperatures (UCST) for the system ethanol (1)-decane (2) have been reported in the references listed below.

Author(s)	T/K		x_1 (2)-rich phase	x_1 (1)-rich phase
1. Bingham 1907	258	UCST	-	-
2. Sadovnikova 1971	293		0.0347	0.8781
3. Balasubramanian 1979	306.7	UCST	0.31	0.31

The UCST value of Bingham, ref 1, is inconsistent with both other sources, and is rejected. The UCST and solubility data of Sadovnikova and Aleksandrova, ref 2, and Balasubramanian and Mitra, ref 3, are accepted as Tentative.

TENTATIVE DATA:

T/K	x_1 (2)-rich phase	x_1 (1)-rich phase	
293	0.035	0.878	
306.7	0.31	0.31	UCST

REFERENCES:

1. Bingham, E.C. *Am. Chem. J.* 1907, *37*, 549.
2. Sadovnikova, L.V.; Aleksandrova, M.V. *Sb. Nauch. Tr., Vladimir Politekh. Inst.* 1971, 137.
3. Balasubramanian, D.; Mitra, P. *J. Phys. Chem.* 1979, *83*, 2724.

COMPONENTS:

(1) Ethanol; C_2H_6O; [64-17-5]

(2) Decane; $C_{10}H_{22}$; [124-18-5]

ORIGINAL MEASUREMENTS:

Bingham, E.C.

Am. Chem. J. 1907, *37*, 549-57.

VARIABLES:

One temperature: 298 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be -15°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The components were added from burets to thick-walled glass tubes of about 2 mm internal diameter and 6-7 mm long which were sealed. The tubes and the components were protected from moisture during filling. No further details are reported.

SOURCE AND PURITY OF MATERIALS:

(1), (2) Kahlbaum, the best provided; used as received.

ESTIMATED ERROR:

not specified

REFERENCES:

COMPONENTS:

(1) Ethanol; C_2H_6O; [64-17-5]

(2) Decane; $C_{10}H_{22}$; [124-18-5]

ORIGINAL MEASUREMENTS:

Sadovnikova, L.V.; Aleksandrova, M.V.

Sb. Nauch. Tr., Vladimir. Vech. Politekh. Inst. 1971, (12), 137-9.

VARIABLES:

One temperature: 293 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubilities at 20°C:

ethanol in decane: 100 w_1 = 1.15 or x_1 = 0.0347 (compiler).

decane in ethanol: 100 w_2 = 32.00 or x_2 = 0.1219 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The titration method was used. The data for the ternary system decane-ethanol-water are also given.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; dist. on 20 TP column; $n_D(20°C)$ = 1.3627.

(2) as for (1); $n_D(20°C)$ = 1.4119.

ESTIMATED ERROR:

temp. ±0.1°C.

REFERENCES:

COMPONENTS:

(1) Ethanol; C_2H_6O; [64-17-5]

(2) Decane; $C_{10}H_{22}$; [124-18-5]

ORIGINAL MEASUREMENTS:

Balasubramanian, D.; Mitra, P.

J. Phys. Chem. 1979, *83*, 2724-7.

VARIABLES:

One temperature: 307 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 33.5°C at x_1 = 0.31 or 100 w_1 = 12.7 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method is described in ref 1. Experiments were conducted in sealed tubes to avoid moisture contamination. No further details are reported.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified; best analytical grade avaliable; ised as received.

ESTIMATED ERROR:

not specified

REFERENCES:

1. Hales, B.J.; Bertrand, G.L.; Hepler, L.G. *J. Phys. Chem.* 1960, *70*, 3970.

COMPONENTS:

(1) Ethanol; C_2H_6O; [64-17-5]

(2) Hexadecane; $C_{16}H_{34}$; [544-76-3]

ORIGINAL MEASUREMENTS:

French, H.T.; Richards, A.; Stokes, R.H.

J. Chem. Thermodyn. 1979, *11*, 671-86.

VARIABLES:

Temperature: 298 - 325 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of ethanol and hexadecane

$t/^{\circ}C$	x_1		$100\,w_1$ (compiler)	
	(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
298.15 a)	0.315	0.957	8.56	81.91
308.15 a)	0.393	0.939	11.64	75.80
318.15 a)	0.516	0.913	17.82	68.10
324.97 b)	-	0.8197	-	48.05
325.15 b)	0.7518	-	38.13	-

See METHOD for explanation of a), b).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Two methods were used.

a) The compositions of conjugated solutions at given temperatures were found by analysis of the enthalpy of mixing curve obtained in an isothermal displacement calorimeter.

b) Visual determination of the phase separation temperature was made by changing the bath temperature at fixed composition.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; purified as described in ref 1; b.p. 325.25 K at 32.597 kPa.

(2) Fluka AG, high-purity material; passed through a column of activated alumina; b.p. 325.25 K at 7 Pa.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Stokes, R.H.; Burfitt, C.J. *J. Chem. Thermodyn.* 1973, *3*, 623.

COMPONENTS:

(1) Ethanol; C_2H_6O; [64-17-5]

(2) Octadecane; $C_{18}H_{38}$; [593-45-3]

ORIGINAL MEASUREMENTS:

Chang, S.-S.; Maurey, J.R.; Pummer, W.J.

J. Chem. Eng. Data 1983, *28*, 187-9.

VARIABLES:

Temperature: 283 - 338 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of octadecane in ethanol

$t/^\circ C$	$100\ w_2$	x_2 (compiler)
10. (solid)	0.89	0.00162
30.3	13.1	0.0266
41.9	17.0	0.0358
52.2	22.2	0.0491
59.5	28.4	0.0670
64.1	36.1	0.0928
64.4	36.6	0.0946

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud-point method was used.

A mixture of known composition was encased with magnetic stirrer in a 5-mL vial and then submerged in a temperature-controlled bath. The temperature of the bath was lowered and raised at a very slow rate and the appearance and disappearance of turbidity was observed visually.

SOURCE AND PURITY OF MATERIALS:

(1) commercially available, 200-proof, purity better than 99.9%; used as received; 0.039% water (Karl Fischer).

(2) commercially available, purity 97%; used as received; m.p. 301.1 K.

ESTIMATED ERROR:

temp. ±0.1 K.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Ethanol; C_2H_6O; [64-17-5] (2) Dotriacontane; $C_{32}H_{66}$; [544-85-4]	Chang, S.-S.; Maurey, J.R.; Pummer, W.J. *J. Chem. Eng. Data* 1983, *28*, 187-9.
VARIABLES: Temperature: 303 - 338 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of dotriacontane in ethanol

$t/°C$	g(2)/100g sln	x_2 (compiler)
30.	0.0081	0.0000083
60.	0.71	0.00073
65.	2.9	0.00304

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud-point method was used. A mixture of known composition was encased with magnetic stirrer in a 5-mL vial and then submerged in a temperature-controlled bath. The temperature of the bath was lowered and raised at a very slow rate and the appearance and disappearance of turbidity was observed visually.

SOURCE AND PURITY OF MATERIALS:

(1) commercially available, 200-proof, purity better than 99.9%; used as received; 0.039% water (Karl Fischer).

(2) commercially available, purity 97%; used as received; m.p. 342.1 K.

ESTIMATED ERROR:

temp. ±0.1 K.

REFERENCES:

COMPONENTS:

(1) 2-Propanol; C_3H_8O; [67-63-0]

(2) Octane; C_8H_{18}; [111-65-9]

(3) Dodecane; $C_{12}H_{26}$; [112-40-3]

ORIGINAL MEASUREMENTS:

Ralston, A.W.; Hoerr, C.W.;
Crews, L.T.
J. Org. Chem. 1944, *9*, 319-28.

VARIABLES:

Temperature: 198 - 213 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of octane in 2-propanol

t/°C	100 mass ratio 2:1	100 w_2 (compiler)	x_2 (compiler)
-75.0	7.1	6.6	0.036
-70.0	9.9	9.0	0.049
-65.0	15.9	13.7	0.077
-60.0	36.0	26.5	0.159

Soluble at temperature -55.0°C.

Solubility of dodecane in 2-propanol

t/°C	100 mass ratio 2:1	100 w_2 (compiler)	x_2 (compiler)
-50.0	0.1	0.1	0.0004
-40.0	0.7	0.7	0.0025
-30.0	2.7	2.6	0.0094
-20.0	9.0	8.3	0.0308
-15.0	21.1	17.4	0.0693

Soluble at temperature above -9.6°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used (ref 1,2,3). Mixtures of (1) and (2) of known composition were placed in glass tubes and sealed. After heating to homogeneity and cooling to give crystals a sealed tube was placed in a water bath and heated electrically at <0.1 K per minute. Solubility was taken as the temperature at which crystals disappeared. Temperature was read to ±0.1 K with an NBS calibrated thermometer and "considered to be accurate to within ±0.2 °C" (ref 1). Graphically smoothed data were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) obtained by the reaction on butyl bromide with Na; distilled; f.p. -56.84°C.

(3) prepared by catalytic hydrogenation of dodecane; distilled; f.p. -9.64°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Harwood, H.J.; Ralston, A.W.;Selby
J. Am. Chem. Soc. 1941, *63*, 1916.
2. Hoerr, C.W.; Ralston, A.W.
J. Am. Chem. Soc. 1942, *64*, 2824.
3. Hoerr, C.W.; Binkerd, E.F.;
Pool, W.O.; Ralston, A.W.
J. Org. Chem. 1944, *9*, 68.

COMPONENTS:

(1) 2-Propanol; C_3H_8O; [67-63-0]

(2) Hexadecane; $C_{16}H_{34}$; [544-76-3]

(3) Heptadecane; $C_{17}H_{36}$; [629-78-7]

ORIGINAL MEASUREMENTS:

Ralston, A.W.; Hoerr, C.W.;
Crews, L.T.
J. Org. Chem. 1944, *9*, 319-28.

VARIABLES:

Temperature: 253 - 288 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of hexadecane in 2-propanol

t/°C	100 mass ratio 2:1	100 w_2 (compiler)	x_2 (compiler)
-20.0	< 0.1	< 0.1	< 0.0003
-10.0	0.4	0.4	0.0011
0.0	1.7	1.7	0.0045
10.0	7.5	7.0	0.0195
15.0	21.2	17.5	0.0533

Soluble at temperature above 18.2°C.

Solubility of heptadecane in 2-propanol

t/°C	100 mass ratio 2:1	100 w_2 (compiler)	x_2 (compiler)
-10.0	< 0.1	< 0.1	< 0.0002
0.0	0.8	0.8	0.0020
10.0	5.0	4.8	0.0123
15.0	11.7	10.5	0.0284

Soluble at temperature above 21.8°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used (ref 1,2,3). Mixtures of (1) and (2) of known composition were placed in glass tubes and sealed. After heating to homogeneity and cooling to give crystals a sealed tube was placed in a water bath and heated electrically at <0.1 K per minute. Solubility was taken as the temperature at which crystals disappeared. Temperature was read to ±0.1 K with an NBS calibrated thermometer and "considered to be accurate to within ±0.2 °C" (ref 1). Graphically smoothed data were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) obtained by reaction of hexadecyl iodide with Na; distilled, crystallized from acetone, twice vacuum distilled; f.p. 18.18°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Harwood, H.J.; Ralston, A.W.;Selby
J. Am. Chem. Soc. 1941, *63*, 1916.
2. Hoerr, C.W.; Ralston, A.W.
J. Am. Chem. Soc. 1942, *64*, 2824.
3. Hoerr, C.W.; Binkerd, E.F.;
Pool, W.O.; Ralston, A.W.
J. Org. Chem. 1944, *9*, 68.

COMPONENTS:

(1) 2-Propanol; C_3H_8O; [67-63-0]
(2) 1-Butanol; $C_4H_{10}O$; [71-36-3]
(3) Dotriacontane; $C_{32}H_{66}$; [544-85-4]
(4) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Ralston, A.W.; Hoerr, C.W.;
Crews, L.T.
J. Org. Chem. 1944, *9*, 319-28.

VARIABLES:

Temperature: 198 - 355 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of dotriacontane in 2-propanol

t/°C	100 mass ratio 2:1	100 w_2 (compiler)	x_2 (compiler)
50.0	0.2	0.2	0.0003
60.0	2.2	2.2	0.0029
70.1	12.2	10.9	0.0160
82.3	24.4	19.6	0.0315

Solubility of octane in 1-butanol

t/°C	100 mass ratio 2:1	100 w_2 (compiler)	x_2 (compiler)
-75.0	12.2	10.9	0.0734
-70.0	15.4	13.3	0.0908
-65.0	22.1	18.1	0.1254
-60.0	45.1	31.1	0.2264

Soluble at temperature -55.0°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used (ref 1,2,3). Mixtures of (1) and (2) of known composition were placed in glass tubes and sealed. After heating to homogeneity and cooling to give crystals a sealed tube was placed in a water bath and heated electrically at <0.1 K per minute. Solubility was taken as the temperature at which crystals disappeared. Temperature was read to ±0.1 K with an NBS calibrated thermometer and "considered to be accurate to within ±0.2 °C" (ref 1). Graphically smoothed data were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified.

(3) obtained by reaction of hexadecyl iodide with Na; recrystallized 3X from $CHCl_3$ at -30°C; f.p. 70.16°C.

(4) obtained from the reaction of butyl bromide with Na; dist.; f.p. -56.84°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Harwood, H.J.; Ralston, A.W.;Selby
J. Am. Chem. Soc. 1941, *63*, 1916.
2. Hoerr, C.W.; Ralston, A.W.
J. Am. Chem. Soc. 1942, *64*, 2824.
3. Hoerr, C.W.; Binkerd, E.F.;
Pool, W.O.; Ralston, A.W.
J. Org. Chem. 1944, *9*, 68.

COMPONENTS:

(1) 1-Butanol; $C_4H_{10}O$; [71-36-3]
(2) Dodecane; $C_{12}H_{26}$; [112-40-3]
(3) Hexadecane; $C_{16}H_{34}$; [544-76-3]

ORIGINAL MEASUREMENTS:

Ralston, A.W.; Hoerr, C.W.; Crews, L.T.

J. Org. Chem. 1944, *9*, 319-28.

VARIABLES:

Temperature: 213 - 288 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of dodecane in 1-butanol

$t/^\circ C$	100 mass ratio 2:1	100 w_2 (compiler)	x_2 (compiler)
-60.0	0.5	0.5	0.0022
-50.0	1.0	1.0	0.0043
-40.0	2.0	2.0	0.0086
-30.0	4.6	4.4	0.0196
-20.0	13.6	12.0	0.0559
-15.0	31.4	23.9	0.1202

Soluble at temperature above -9.6°C.

Solubility of hexadecane in 1-butanol

$t/^\circ C$	100 mass ratio 2:1	100 w_2 (compiler)	x_2 (compiler)
-20.0	0.3	0.3	0.0010
-10.0	1.2	1.2	0.0039
0.0	4.1	3.9	0.0132
10.0	16.7	14.3	0.0518
15.0	50.	33.	0.141

Soluble at temperature above 18.2°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used (ref 1,2,3). Mixtures of (1) and (2) of known composition were placed in glass tubes and sealed. After heating to homogeneity and cooling to give crystals a sealed tube was placed in a water bath and heated electrically at <0.1 K per minute. Solubility was taken as the temperature at which crystals disappeared. Temperature was read to ±0.1 K with an NBS calibrated thermometer and "considered to be accurate to within ±0.2 °C" (ref 1). Graphically smoothed data were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) prepared by catalytic hydrogenation of dodecene; distilled; f.p. -9.64°C.

(3) obtained be reaction of hexadecyl iodide with Na; dist., recryst. from acetone, 2X vacuum dist.; f.p. 18.18°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Harwood, H.J.; Ralston, A.W.;Selby *J. Am. Chem. Soc.* 1941, *63*, 1916.
2. Hoerr, C.W.; Ralston, A.W. *J. Am. Chem. Soc.* 1942, *64*, 2824.
3. Hoerr, C.W.; Binkerd, E.F.; Pool, W.O.; Ralston, A.W. *J. Org. Chem.* 1944, *9*, 68.

COMPONENTS:

(1) 1-Butanol; $C_4H_{10}O$; [71-36-3]
(2) Heptadecane; $C_{17}H_{36}$; [629-78-7]
(3) Dotriacontane; $C_{32}H_{66}$; [544-85-4]

ORIGINAL MEASUREMENTS:

Ralston, A.W.; Hoerr, C.W.; Crews, L.T.
J. Org. Chem. <u>1944</u>, *9*, 319-28.

VARIABLES:

Temperature: 263 - 288 K; 323, 333 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of heptadecane in 1-butanol

$t/^{\circ}C$	100 mass ratio 2:1	100 w_2 (compiler)	x_2 (compiler)
-10.0	0.4	0.4	0.0012
0.0	2.7	2.6	0.0083
10.0	13.0	11.5	0.0385
15.0	35.6	26.3	0.0989

Soluble at temperature above 21.8°C.

Solubility of dotriacontane in 1-butanol

$t/^{\circ}C$	100 mass ratio 2:1	100 w_2 (compiler)	x_2 (compiler)
50.0	0.9	0.9	0.0015
60.0	9.2	8.4	0.0149

Soluble at temperature 70.1°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used (ref 1,2,3). Mixtures of (1) and (2) of known composition were placed in glass tubes and sealed. After heating to homogeneity and cooling to give crystals a sealed tube was placed in a water bath and heated electrically at <0.1 K per minute. Solubility was taken as the temperature at which crystals disappeared. Temperature was read to ±0.1 K with an NBS calibrated thermometer and "considered to be accurate to within ±0.2 °C" (ref 1). Graphically smoothed data were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) obtained by heating stearic acid to 350°C in the presence of Raney nickel catalyst; twice vacuum distilled; f.p. 21.72°C.

(3) obtained by reaction of hexacecyl iodide with Na; recryst. 3X from $CHCl_3$ at -30°C; f.p. 70.16°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Harwood, H.J.; Ralston, A.W.;Selby *J. Am. Chem. Soc.* <u>1941</u>, *63*, 1916.
2. Hoerr, C.W.; Ralston, A.W. *J. Am. Chem. Soc.* <u>1942</u>, *64*, 2824.
3. Hoerr, C.W.; Binkerd, E.F.; Pool, W.O.; Ralston, A.W. *J. Org. Chem.* <u>1944</u>, *9*, 68.

COMPONENTS:

(1) Pentane; C_5H_{12}; [109-66-0]

(2) Benzyl alcohol (benzenemethanol); C_7H_8O; [100-51-6]

ORIGINAL MEASUREMENTS:

Durandet, J.; Gladel, Y.L.; Graziani, F.

Rev. Inst. Fr. Petrole 1955, *10*, 585-94.

VARIABLES:

One temperature: 328 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The solution temperature of a mixture of (1) and (2) containing 50 volume % pentane was reported to be 54.8°C.

The corresponding values (compiler) are:

$w_1 = 37$, $x_1 = 0.47$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method of sealed tubes, (ref 1), was used. The volumes of the mixture were assumed to be additive. No further details are reported in the paper.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified, pure grade; distilled; $\rho(20^\circ C)/\rho(4^\circ C) = 1.045$, $n_D(20^\circ C) = 1.5400$.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Gladel, Y.L.; Durandet, J. *Rev. Inst. Franc. Petrole* 1944, *9*, 221.

COMPONENTS:

(1) Cyclohexane; C_6H_{12}; [110-82-7]

(2) Benzyl alcohol (benzenemethanol); C_7H_8O; [100-51-6]

(3) Cinnamyl alcohol (3-phenyl-2-propen-1-ol); $C_9H_{10}O$; [104-54-1]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*, 764-71.

VARIABLES:

Temperature: 275, 312 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Cyclohexane + Benzyl alcohol: UCST = 2°C.

Cyclohexane + Cinnamyl alcohol: UCST = 39°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temp. of disappearance or reappearance of the cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) 2,2-Dimethylbutane; C_6H_{14}; [75-83-2] (2) 2,3-Dimethylbutane; C_6H_{14}; [79-29-8] (3) Benzyl alcohol (benzenemethanol); C_7H_8O; [100-51-6]	Maman, A. *C.R. Hebd. Séances Acad. Sci.* 1934, *198*, 1323-5.
VARIABLES:	PREPARED BY:
Temperatures: 336 K	A. Skrzecz

EXPERIMENTAL VALUES:

2,2-Dimethylbutane + Benzyl alcohol: UCST = 62.9°C.

2,3-Dimethylbutane + Benzyl alcohol: UCST = 54.4°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The method was not specified.	(1) synthesized from pinacoline and phosphorus pentabromide, product hydrogenated; b.p. 52.5°C, $\rho(20°C) = 0.6518$, $n_D(20°C) = 1.37054$. (2) synthesized from anhydrous pinacone and $KHSO_4$, product was hydrogenated; b.p. 58.2°C, $\rho(20°C) = 0.6591$, $n_D(20°C) = 1.37471$. (3) source not specified.
	ESTIMATED ERROR: not specified.
	REFERENCES:

COMPONENTS:

(1) Hexane; C_6H_{14}; [110-54-3]

(2) Benzyl alcohol (benzenemethanol)
C_7H_8O; [100-51-6]

EVALUATOR:

A. Skrzecz

Institute of Physical Chemistry
Polish Academy of Sciences
Warsaw, Poland

July, 1989

CRITICAL EVALUATION:

Table 1 lists reported solubilities and upper critical solution temperatures (UCST) for the system hexane (1)-benzyl alcohol (2).

Table 1. Solubilities and upper critical solution temperatures for the system hexane (1)-benzyl alcohol (2)

Author(s)	*T*/K	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Maman 1934	323.8 UCST	-	-
2. Mulliken 1935	330	(0.50 mL(1)/mL sln)	
3. Francis 1944	322.1 UCST	-	-
4. Durandet 1955	323.6	(0.50 mL(1)/mL sln)	
5. Balasubramanian 1979	323.7 UCST	0.50	0.50

The values of Maman, ref 1, and Balasubramanian and Mitra, ref. 5, are accepted as *tentative*. The solubility values of Mulliken and Wakeman, ref. 2, Francis, ref. 3, and Durandet et al., ref 4, are rejected, since they are in poor agreement with the others or they are expressed only as volumetric ratios with no supporting density data which would enable conversion to other units.

TENTATIVE DATA:

T/K	x_1
323 UCST	0.50

REFERENCES:

1. Maman, A. *C. R. Hebd. Séances Acad. Sci.* 1934, *198*, 1323-5.
2. Mulliken, S.P.; Wakeman, R.L. *Rec. Trav. Chim. Pays-Bas* 1935, *54*, 366.
3. Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 764.
4. Durandet, J.; Gladel, Y.L.; Graziani, F. *Rev. Inst. Fr. Petrole* 1955, *10*, 585.
5. Balasubramanian, D.; Mitra, P. *J. Phys. Chem.* 1979, *83*, 2724.

COMPONENTS:

(1) Hexane; C_6H_{14}; [110-54-3]

(2) Benzyl alcohol (benzenemethanol); C_7H_8O; [100-51-6]

ORIGINAL MEASUREMENTS:

Maman, A.

Compt. Rend. Hebd. Séances Acad. Sci 1934, *198*, 1323-5.

VARIABLES:

One temperature: 324 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 50.6°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was not specified.

SOURCE AND PURITY OF MATERIALS:

(1) synthesized by catalytic hydrogenation of hexanol or by electrolysis of aq. potassium butyrate; b.p. 69.5°C, $\rho(20°) = 0.6583$, $n_D(20°C) = 1.37518$.

(2) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Hexane; C_6H_{14}; [110-54-3]

(2) Benzyl alcohol (benzenemethanol); C_7H_8O; [100-51-6]

ORIGINAL MEASUREMENTS:

Mulliken, S.P.; Wakeman, R.L.

Rec. Trav. Chim. Pays-Bas 1935, *54*, 366-72.

VARIABLES:

One temperature: 330 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of hexane and benzyl alcohol at 57°C: 1 vol(1) in 1 vol(2).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. Miscibility was determined in a glass-stoppered tube of 4 mm inside diameter. One-tenth mL of each component was measured into the tube which was strapped to a thermometer and warmed. The reported solubility temperature was the point at which cloudiness first appeared upon cooling in a homogeneous mixture.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; purest commercial sample available; used as received; b.p. 69 - 70°C.

(2) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Hexane; C_6H_{14}; [110-54-3]

(2) Benzyl alcohol (benzenemethanol); C_7H_8O; [100-51-6]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. <u>1944</u>, *36*, 764-71.

VARIABLES:

One temperature: 322 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 49°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temperature of disappearance or reappearance of the cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) obtained from petroleum.

(2) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Hexane; C_6H_{14}; [110-54-3]

(2) Benzyl alcohol (benzenemethanol); C_7H_8O; [100-51-6]

ORIGINAL MEASUREMENTS:

Durandet, J.; Gladel, Y.L.; Graziani, F.

Rev. Inst. Fr. Petrole <u>1955</u>, *10*, 585-94.

VARIABLES:

One temperature: 324 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The solution temperature of a mixture of (1) and (2) containing 50 volume % hexane was reported to be 50.4°C.

The corresponding mass percentage and mole fraction value, calculated by the compiler, are 39 g(1)/100g sln and $x_1 = 0.44$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method of sealed tubes, ref 1, was used. The volumes of the mixture were assumed to be additive. No further details are reported in the paper.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified, pure grade; distilled; $\rho(20^\circ)/\rho(4^\circ C) = 1.045$, $n_D(20^\circ C) = 1.5400$.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Gladel, Y.L.; Durandet, J. *Rev. Inst. Franc. Petrole* <u>1944</u>, *9*, 221.

COMPONENTS:

(1) Hexane; C_6H_{14}; [110-54-3]

(2) Benzyl alcohol (benzenemethanol);
C_7H_8O; [100-51-6]

ORIGINAL MEASUREMENTS:

Balasubramanian, D.; Mitra, P.

J. Phys. Chem. 1979, *83*, 2724-7.

VARIABLES:

One temperature: 324 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

UCST = 50.5°C at x_1 = 0.50 or 100 w_1 = 7.1 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method is described in ref 1. Experiments were conducted in sealed tubes to avoid contamination with moisture. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified, the best analytical grade available; used as received.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Hales, B.J.; Bertrand, G.L.; Hepler, L.G. *J. Phys. Chem.* 1960, *70*, 3970.

COMPONENTS:

(1) Hexane; C_6H_{14}; [110-54-3]

(2) Phenylethylalcohol
(benzeneethanol); $C_8H_{10}O$;
[60-12-8]

(3) Cinnamyl alcohol
(3-phenyl-2-propen-1-ol);
$C_9H_{10}O$; [104-54-1]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*,
764-71.

VARIABLES:

Temperature: 306, 373 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Hexane + Phenylethyl alcohol: UCST = 33°C.

Hexane + Cinnamyl alcohol: UCST = 100°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temp. of disappearance or reappearance of the cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) obtained from petroleum.
(2) source not specified.
(3) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) 2-Methylpentane; C_6H_{14}; [107-83-5]

(2) 3-Methylpentane; C_6H_{14}; [96-14-0]

(3) Benzyl alcohol (benzenemethanol); C_7H_8O; [100-51-6]

ORIGINAL MEASUREMENTS:

Maman, A.

Compt. Rend. Hebd. Séances Acad. Sci. 1934, *198*, 1323-5.

VARIABLES:

Temperatures: 332, 323 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

2-Methylpentane-Benzyl alcohol: UCST = 58.8°C.

3-Methylpentane-Benzyl alcohol: UCST = 50.1°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was not specified.

SOURCE AND PURITY OF MATERIALS:

(1) synthesized from methylmagnesium iodide and ethyl butyrate, product dehydrated, then catalytically hydrogenated; b.p. 60.5°C, $\rho(20^\circ C)/\rho(4^\circ C) = 0.6519$, $n_D(20^\circ C) = 1.37170$.

(2) synthesized from ethylmagnesium iodide and ethyl acetate, product dehydrated, then catalytically hydrogenated; b.p. 62.7°C, $\rho(20^\circ C)/\rho(4^\circ C) = 0.6614$, $n_D(20^\circ C) = 1.37639$.

(3) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Benzyl alcohol
(benzenemethanol); C_7H_8O;
[100-51-6]

(2) 1-Heptene; C_7H_{14}; [592-76-7]

(3) Methylcyclohexane; C_7H_{14};
[108-87-2]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*,
764-71.

VARIABLES:

Temperature: 265, 287 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Benzyl alcohol + 1-Heptene: UCST = -8°C.

Benzyl alcohol + Methylcyclohexane: UCST = 14°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temp. of disappearance or reappearance of the cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.
(2) obtained by Grignard reacyion; purified; $\rho(20^{\circ}C) = 0.6980$; b.p. range 93-93.5°C.
(3) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Benzyl alcohol (benzenemethanol) C_7H_8O; [100-51-6] (2) 2,2-Dimethylpentane; C_7H_{16}; [590-35-2] (3) 2,3-Dimethylpentane; C_7H_{16}; [565-59-3] (4) 2,4-Dimethylpentane; C_7H_{16}; [108-08-7]	Miller, V.A. *Ind. Eng. Chem., Anal. Ed.* 1945, *17*, 5-12.
VARIABLES: Temperatures: 320, 338 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

Solution temperatures and compositions:

benzyl alcohol + 2,2-Dimethylpentane: 64.7°C. 50 vol. %, or 100 w_1 = 61, x_1 = 0.59 (compiler).

benzyl alcohol + 2,3-Dimethylpentane: 46.4°C. 50 vol. %, or 100 w_1 = 60, x_1 = 0.58 (compiler).

benzyl alcohol + 2,4-Dimethylpentane: 64.9°C. 50 vol. %, or 100 w_1 = 61, x_1 = 0.59 (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The cloud point method was used. A tube containing the sample, stirrer and fitted with a resistance thermometer was placed in an air bath tube in a liquid bath. Temperature was measured with an iron-constantan thermocouple and a Leeds & Northrup Type K potentiometer.	(1) source not specified. (2) source not specified; purified chemically, distilled, stored over P_2O_5, distilled; f.p. -123.7°C, n_D(20°C) = 1.3823. (3) source not specified; purified chemically, distilled, stored over P_2O_5, distilled. (4) source not specified; purified chemically, distilled, stored over P_2O_5, distilled; f.p. -119.3°C, n_D(20°C) = 1.3818.
	ESTIMATED ERROR: temp. ±0.1 K.
	REFERENCES:

COMPONENTS:

(1) Benzyl alcohol (benzenemethanol)
C_7H_8O; [100-51-6]

(2) Heptane; C_7H_{16}; [142-82-5]

EVALUATOR:

A. Maczynski and A. Skrzecz

Institute of Physical Chemistry
Polish Academy of Sciences
Warsaw, Poland

July, 1989.

CRITICAL EVALUATION:

Quantitative solubilities and upper critical solution temperatures (UCST) for the system benzyl alcohol (1)-heptane (2) have been reported in the references listed below.

Author(s)	T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
1. Francis 1944	333 UCST	-	-
2. Miller 1945	324	(50 mL(1)/100 mL sln)	
3. Durandet 1955	273.2 - 324.9 UCST	0.028 - 0.062	0.854 - 0.886

The UCST value of Francis, ref 1, is in poor agreement with the others, and is rejected. The value of Durandet et al., ref 3, is accepted as Tentative with a probable uncertainity of 1 K in temperature.

Durandet et al., ref 3, determined mutual solubility at 273 K by two methods with good agreement; their mean value is adopted as Tentative. The data from the same authors for 288 and 325 K, which were obtained by one method only, are also regarded as Tentative.

TENTATIVE DATA:

T/K	x_1 (2)-rich phase	x_1 (1)-rich phase
273	0.028	0.885
288	0.062	0.854
325 UCST	-	-

REFERENCES:

1. Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 764.
2. Miller, V.A. *Ind. Eng. Chem. Anal. Ed.* 1945, *17*, 5.
3. Durandet, J.; Gladel, Y.L.; Graziani, F. *Rev. Inst. Fr. Petrole* 1955, *10*, 585.

COMPONENTS:

(1) Benzyl alcohol (benzenemethanol)
C_7H_8O; [100-51-6]
(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Francis, A.W.
Ind. Eng. Chem. 1944, *36*, 764-71.

VARIABLES:

One temperature: 333 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 60°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled in a bath gradually. The temperature of disappearance or reappearance of cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) obtained from Jeffrey pine, no more information.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Benzyl alcohol (benzenemethanol)
C_7H_8O; [100-51-6]
(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Miller, V.A.
Ind. Eng. Chem., Anal. Ed. 1945, *17*, 5-12.

VARIABLES:

One temperature: 324 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solution temperature and composition:

benzyl alcohol + heptane: 50.7°C at 50 vol. % or 100 w_1 = 60, x_1 = 0.59

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A tube containing the sample, stirrer and resistance thermometer was placed in an air bath tube in a liquid bath. Temperature was measured with an iron constantan thermocouple and a Leeds & Northrup Type K potentiometer.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified; purified chemically, distilled, stored over P_2O_5, distilled.

ESTIMATED ERROR:

temp. ±0.1 K.

REFERENCES:

COMPONENTS:

(1) Benzyl alcohol (benzenemethanol)
C_7H_8O; [100-51-6]

(2) Heptane; C_7H_{16}; [142-82-5]

ORIGINAL MEASUREMENTS:

Durandet, J.; Gladel, Y.L.; Graziani, F.

Rev. Inst. Fr. Petrole 1955, 10, 585-94.

VARIABLES:

Temperature: 273 - 325 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Mutual solubility of benzyl alcohol and heptane

$t/^\circ C$		100 w_1		x_1 (compiler)	
		(2)-rich phase	(1)-rich phase	(2)-rich phase	(1)-rich phase
0.	a)	3.0	89.3	0.028	0.886
0.	b)	2.7	89.9	0.025	0.892
0.		3.0	89.1	0.028	0.883
15.	a)	6.7	86.3	0.062	0.854
51.7	UCST	-	-	-	-

Mutual solubility of benzyl alcohol and heptane

$t/^\circ C$	100 vol(1)/vol sln	
	(2)-rich phase	(1)-rich phase
18.	-	80.
38.5	10.	-
51.1	-	50.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method a), using sealed tubes, and the titration method b) (ref 1, 2) were used. Solubility data are given on a graph. The volumes of the mixture were assumed to be additive. No further details were reported.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, pure grade; dist.; $\rho(20^\circ C)/\rho(4^\circ C)$ = 1.045, $n_D(20^\circ C)$ = 1.5400.
(2) "motor A.S.T.M."; used as received; $\rho(20^\circ C)/\rho(4^\circ C)$ =0.6828, $n_D(20^\circ C)$ = 1.3880.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Gladel, Y.L.; Durandet, J. *Rev. Inst. Franc. Petrole* 1944, *9*, 221.
2. Graziani, F. *Travail de Recherche E.N.S.P. Determination d'un equilibre liquide-liquide.*

COMPONENTS:

(1) Benzyl alcohol (benzenemethanol) C_7H_8O; [100-51-6]

(2) 2-Methylhexane; C_7H_{16}; [591-76-4]

(3) 2,2,3-Trimethylbutane; C_7H_{16}; [464-06-2]

ORIGINAL MEASUREMENTS:

Miller, V.A.

Ind. Eng. Chem., Anal. Ed. 1945, *17*, 5-12.

VARIABLES:

Temperature: 327, 330 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solution temperatures and compositions:

Benzyl alcohol + 2-Methylhexane: 57.25°C. 50 vol. %, or $100w_1 = 61$, $x_1 = 0.59$ (compiler).

Benzyl alcohol + 2,2,3-Trimethylbutane: 53.5°C. 50 vol. %, or $100w_1 = 61$, $x_1 = 0.59$ (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A tube containing the sample, stirrer and fitted with a resistance thermometer was placed in an air bath tube in a liquid bath. Temperature was measured with an iron-constantan thermocouple and a Leeds & Northrup Type K potentiometer.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified; purified chemically, distilled, stored over P_2O_5, distilled.

(3) source not specified; purified chemically, distilled, stored over P_2O_5, distilled; f.p. -25.1°C, $n_D(20°C) = 1.3897$..

ESTIMATED ERROR:

temp. ±0.1 K.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Benzyl alcohol (benzenemethanol) C_7H_8O; [100-51-6] (2) 2,5-Dimethyl-1,5-hexadiene (diisobutene); C_8H_{14}; [627-58-7]	Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 764-71.
VARIABLES:	PREPARED BY:
One temperature: 288 K	A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 15°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temperature of disappearance or reappearance of the cloudiness was read two or three times in each direction.	(1) source not specified. (2) source not specified.
	ESTIMATED ERROR:
	not specified.
	REFERENCES:

COMPONENTS:

(1) Benzyl alcohol (benzenemethanol) C_7H_8O; [100-51-6]
(2) 2,3-Dimethylhexane; C_8H_{18}; [584-94-1]
(3) 2,4-Dimethylhexane; C_8H_{18}; [589-43-5]
(4) 2,5-Dimethylhexane; C_8H_{18}; [592-13-2]
(5) 3,4-Dimethylhexane; C_8H_{18}; [583-48-2]
(6) 3-Ethylhexane; C_8H_{18}; [616-99-8]
(7) 3-Ethyl-2-Methylpentane; C_8H_{18}; [609-26-7]
(8) 2-Methylheptane; C_8H_{18}; [592-27-8]
(9) 3-Methylheptane; C_8H_{18}; [589-81-1]
(10) 4-Methylheptane; C_8H_{18}; [589-53-7]

ORIGINAL MEASUREMENTS:

Maman, A.

Compt. Rend. Hebd. Séances Acad. Sci. 1937, *205*, 319-21.

VARIABLES:
Temperature: 320-338 K

PREPARED BY:
A. Skrzecz

EXPERIMENTAL VALUES:

	Component	UCST/°C	n_D(20°C) (pure components)	ρ(20°C)/g cm^{-3}
(1)	Benzyl alcohol +			
(2)	2,3-Dimethylhexane	51.4	1.40069	0.7139
(3)	2,4-Dimethylhexane	57.3	1.39584	0.6993
(4)	2,5-Dimethylhexane	65.3	1.39288	0.6970
(5)	3,4-Dimethylhexane	46.4	1.40470	0.7216
(6)	3-Ethylhexane	49.2	1.40128	0.7124
(7)	3-Ethyl-2-Methylpentane	46.6	1.40353	0.7182
(8)	2-Methylheptane	59.9	1.39531	0.6984
(9)	3-Methylheptane	55.9	1.39829	0.7045
(10)	4-Methylheptane	54.9	1.39814	0.7036

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
The method was not specified.

SOURCE AND PURITY OF MATERIALS:
(1) source not specified.
Other components: source not specified. Measured physical properties given in the table.

ESTIMATED ERROR:
not specified.

REFERENCES:

COMPONENTS:

(1) Benzyl alcohol (benzenemethanol)
C_7H_8O; [100-51-6]

(2) Octane; C_8H_{18}; [111-65-9]

EVALUATOR:

A. Maczynski and A. Skrzecz

Institute of Physical Chemistry
Polish Academy of Sciences
Warsaw, Poland

July, 1989

CRITICAL EVALUATION:

Table 1 lists reported solubilities and upper critical solution temperatures (UCST) for the system benzyl alcohol (1) - octane (2).

Table 1. Solubilities and upper critical solution temperatures for the system benzyl alcohol (1) - octane (2)

Author(s)	*T*/K	composition
1. Mulliken 1935	328	1 mL(1)/1 mL(2)
2. Maman 1937	327.7 UCST	-

The value of Maman, ref 2, is accepted as Tentative with a probable temperature uncertainity of 1 K. The solubility value of Mulliken and Wakeman, ref 1, is rejected since it is expressed only as a volumetric ratio with no supporting data on densities from which mass or mole fractions can be calculated.

TENTATIVE DATA:

UCST = 328 ± 1 K.

REFERENCES:

1. Mulliken, S.P.; Wakeman, R.L. *Rec. Trav. Chim. Pays-Bas* 1935, *54*, 366.

2. Maman, A. *C. R. Hebd. Séances Acad. Sci.* 1937, *205*, 319.

COMPONENTS:

(1) Benzyl alcohol (benzenemethanol)
C_7H_8O; [100-51-6]

(2) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Mulliken, S.P.; Wakeman, R.L.

Rec. Trav. Chim. Pays-Bas 1935, *54*, 366-72.

VARIABLES:

One temperature: 328 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The temperature of mutual solubility of benzyl alcohol and octane was reported to be 55°C at 1 vol(1) in 1 vol(2).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. Miscibility was determined in a glass-stoppered tube of 4 mm inside diameter. One-tenth mL of each component was measured into the tube which was then strapped to a thermometer and warmed. The solubility temperature was the point at which cloudiness first appeared upon cooling in a homogenous mixture.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified; purest commercial sample available; used as received; b.p. about 125°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Benzyl alcohol (benzenemethanol)
C_7H_8O; [100-51-6]

(2) Octane; C_8H_{18}; [111-65-9]

ORIGINAL MEASUREMENTS:

Maman, A.

C. R. Hebd. Séances Acad. Sci. 1937, *205*, 319-21.

VARIABLES:

One temperature: 328 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 54.5°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was not specified.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified; $\rho(20°C) = 0.7023$, $n_D(20°C) = 1.39765$.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Benzyl alcohol (benzenemethanol); C_7H_8O; [100-51-6] (2) 2,2,4-Trimethylpentane; C_8H_{18}; [540-84-1]	A. Maczynski Institute of Physical Chemistry Polish Academy of Sciences Warsaw, Poland July, 1989

CRITICAL EVALUATION:

Solubilities and upper critical solution temperatures (UCST) for the system benzyl alcohol (1)-2,2,4-trimethylpentane (2) were reported in the following two papers:

Author(s)	T/K	composition
1. Mulliken 1935	347	1 mL(1)/1 mL(2)
2. Francis 1944	346 UCST	-

The available data for this system are inadequate for a detailed evluation. Therefore these values are considered as Tentative.

REFERENCES:

1. Mulliken, S.P.; Wakeman, R.L. *Rec. Trav. Chim. Pays-Bas* 1935, *54*, 366.

2. Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 764.

COMPONENTS:

(1) Benzyl alcohol (benzenemethanol)
C_7H_8O; [100-51-6]

(2) 2,2,4-Trimethylpentane; C_8H_{18};
[540-84-1]

ORIGINAL MEASUREMENTS:

Mulliken, S.P.; Wakeman, R.L.

Rec. Trav. Chim. Pays-Bas 1935, *54*,
366-72.

VARIABLES:

One temperature: 347 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The temperature of mutual solubility of benzyl alcohol and 2,2,4-trimethylpentane was reported to be 74°C at 1 vol(1) in 1 vol(2).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. Miscibility was determined in a glass-stoppered tube of 4 mm inside diameter. One-tenth mL of each component was measured into the tube which was then strapped to a thermometer and warmed. The reported solubility temperature was the point at which cloudiness first appeared upon cooling in a homogenous mixture.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified; purest commercial sample available; used as received; b.p. range 98 - 99°C.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Benzyl alcohol (benzenemethanol)
C_7H_8O; [100-51-6]

(2) 2,2,4-Trimethylpentane; C_8H_{18};
[540-84-1]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*, 764-71.

VARIABLES:

One temperature: 346 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 73°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temperature of disappearance or reappearance of the cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS: (1) Benzyl alcohol (benzenemethanol) C_7H_8O; [100-51-6] (2) 2,7-Dimethyloctane; $C_{10}H_{22}$; [1072-16-8]	ORIGINAL MEASUREMENTS: Mulliken, S.P.; Wakeman, R.L. *Rec. Trav. Chim. Pays-Bas* 1935, *54*, 366-72.
VARIABLES: One temperature: 345 K	PREPARED BY: A. Skrzecz

EXPERIMENTAL VALUES:

The temperature of mutual solubility of benzyl alcohol and 2,7-dimethyloctane was reported to be 72°C at 1 vol(1) in 1 vol(2).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: The cloud point method was used. Miscibility was determined in a glass-stoppered tube of 4 mm inside diameter. One-tenth mL of each component was measured into the tube which was then strapped to a thermometer and warmed. The reported solubility temperature was the point at which cloudiness first appeared upon cooling in a homogenous mixture.	SOURCE AND PURITY OF MATERIALS: (1) source not specified. (2) source not specified; purest commercial sample available; used as received; b.p. range 159-160°C. ESTIMATED ERROR: not specified. REFERENCES:

COMPONENTS:

(1) Benzyl alcohol (benzenemethanol)
C_7H_8O; [100-51-6]
(2) Undecane; $C_{11}H_{24}$; [1120-21-4]
(3) Dodecane; $C_{12}H_{26}$; [112-40-3]
(4) Tridecane; $C_{13}H_{28}$; [629-50-5]
(5) Tetradecane; $C_{14}H_{30}$; [629-59-4]
(6) Pentadecane; $C_{15}H_{32}$; [629-62-9]
(7) Hexadecane; $C_{16}H_{34}$; [544-76-3]
(8) Heptadecane; $C_{17}H_{36}$; [629-78-7]

ORIGINAL MEASUREMENTS:

Durandet, J.; Gladel, Y.L.; Graziani, F.

Rev. Inst. Fr. Petrole 1955, *10*, 585-94.

VARIABLES:

Temperature: 339 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Component	UCST/°C	$n_D(20°C)$	$\rho(20°C)/\rho(4°C)$
		(pure components)	
(1) Benzyl alcohol +		1.5400	1.045
(2) Undecane	66.2	-	-
(3) Dodecane	71.9	-	-
(4) Tridecane	77.3	-	-
(5) Tetradecane	81.8	1.4290	0.7612
(6) Pentadecane	86.5	1.4331	0.7676
(7) Hexadecane	89.8	1.4362	0.7738
(8) Heptadecane	92.8	1.4369	0.787

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method of sealed tubes, ref 1, was used. Solubility data, in vol %, were reported in a graph. The volume of the mixture was assumed to be additive. No further details were reported in the paper.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified, pure grade; distilled.

(2) obtained by distillation from petroleum fraction. See table for measured physical properties.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Gladel, Y.L.; Durandet, J.
Rev. Inst. Franc. Petrole 1944, *9*, 221.

COMPONENTS:

(1) Benzyl alcohol (benzenemethanol) C_7H_8O; [100-51-6]

(2) 1-Phenylhexadecane (cetylbenzol); $C_{22}H_{38}$; [1459-09-2]

ORIGINAL MEASUREMENTS:

Tilitschejew, M.D.; Kuryndin, K.S.

Chem. Zentralbl. 1931, *102*, 2559-61.

VARIABLES:

One temperature: 303 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 27.9°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method was not specified. Presumably it is described in ref 1.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified.

(2) synthesized from petroleum fraction, benzene and $AlCl_3$; b.p. 191-4°C at 6 Torr, $\rho(0^{\circ}C) = 0.8805$, $\rho(20.5^{\circ}C) = 0.8640$, $n_D(18.8^{\circ}C) = 1.4839$.

ESTIMATED ERROR:

not specified.

REFERENCES:

1. Tilitschejew, M.D.; Kuryndin, M.D. *Neftjanoe Chosjaistwo* 1930, *19*, 586-98.

COMPONENTS:

(1) 1-Heptene; C_7H_{14}; [592-76-7]
(2) Methylcyclohexane; C_7H_{14}; [108-87-2]
(3) Phenylethyl alcohol (benzeneethanol); $C_8H_{10}O$; [60-12-8]
(4) Cinnamyl alcohol (3-phenyl-2-propen-1-ol); $C_9H_{10}O$; [104-54-1]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. <u>1944</u>, *36*, 764-71.

VARIABLES:

Temperature: 259-324 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

1-Heptene + Phenylethyl alcohol: UCST = -14°C.
1-Heptene + Cinnamyl alcohol: UCST = 47°C.

Methylcyclohexane + Phenylethyl alcohol: UCST = -10°C.
Methylcyclohexane + Cinnamyl alcohol: UCST = 51°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temp. of disappearance or reappearance of the cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) obtained by Grignard reaction; purified; $\rho(20^\circ C) = 0.6980$, b.p. range 93-93.5°C.
(2) source not specified.
(3) source not specified.
(4) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) 2,2-Dimethylpentane; C_7H_{16}; [590-35-2]

(2) 2,3-Dimethylpentane; C_7H_{16}; [565-59-3]

(3) 2,4-Dimethylpentane; C_7H_{16}; [108-08-7]

(4) Phenethyl alcohol (benzeneethanol); $C_8H_{10}O$; [60-12-8]

ORIGINAL MEASUREMENTS:

Miller, V.A.

Ind. Eng. Chem., Anal. Ed. 1945, *17*, 5-12.

VARIABLES:

Temperature: 301-320 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solution temperatures and compositions:

2,2-Dimethylpentane + Phenethyl alcohol: 46.6°C at 50 vol. % or $100\ w_1 = 40$, $x_1 = 0.45$ (compiler).

2,3-Dimethylpentane + Phenethyl alcohol: 28.2°C at 50 vol. % or $100\ w_1 = 40$, $x_1 = 0.45$ (compiler).

2,4-Dimethylpentane + Phenethyl alcohol: 467.05°C at 50 vol. % or $100\ w_1 = 40$, $x_1 = 0.45$ (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A tube containing the sample, stirrer and fitted with a resistance thermometer was placed in an air bath tube in a liquid bath. Temperature was measured with an iron-constantan thermocouple and a Leeds & Northrup Type K potentiometer.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; purified chemically, distilled, stored over P_2O_5, distilled; f.p. -123.7°C, $n_D(20°C) = 1.3823$.

(2) source not specified; purified chemically, distilled, stored over P_2O_5, distilled.

(3) source not specified; purified chemically, distilled, stored over P_2O_5, distilled; f.p. -119.3°C, $n_D(20°C) = 1.3818$.

(4) source not specified.

ESTIMATED ERROR:

temp. ±0.1 K

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Heptane; C_7H_{16}; [142-82-5] (2) Phenethyl alcohol (benzeneethanol); $C_8H_{10}O$; [60-12-8]	A. Maczynski Institute of Physical Chemistry Polish Academy of Sciences Warsaw, Poland July, 1989

CRITICAL EVALUATION:

Solubilities and upper critical solution temperatures (UCST) for the system heptane (1)-phenethyl alcohol (2) were reported in the following two papers:

Author(s)	*T*/K		composition
1. Francis 1944	307	UCST	-
2. Miller 1945	293.9		50 mL(1)/100 mL sln

The available data for this system are inadequate for a detailed evaluation. Therefore these values are considered to be Tentative.

REFERENCES:

1. Francis, A.W. *Ind. Eng. Chem.* 1944, *36*, 764.
2. Miller, V.A. *Ind. Eng. Chem. Anal. Ed.* 1945, *17*, 5.

COMPONENTS:

(1) Heptane; C_7H_{16}; [142-82-5]

(2) Phenethyl alcohol (benzeneethanol); $C_8H_{10}O$; [60-12-8]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*, 764-71.

VARIABLES:

One temperature: 307 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

The UCST was reported to be 34°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled slowly in a bath. The temperature of disappearance or reappearance of cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) obtained from Jeffrey pine, no more information.

(2) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:

(1) Heptane; C_7H_{16}; [142-82-5]

(2) Phenethyl alcohol (benzeneethanol); $C_8H_{10}O$; [60-12-8]

ORIGINAL MEASUREMENTS:

Miller, V.A.

Ind. Eng. Chem., Anal. Ed. 1945, *17*, 5-12.

VARIABLES:

One temperature: 294 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solution temperature of a mixture of (1) and (2) containing 50 volume % heptane: 20.7°C at 100 $w_1 = 40$, $x_1 = 0.45$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A tube containing the sample, stirrer and fitted with a resistance thermometer was placed in an air bath tube in a liquid bath. Temperature was measured with an iron-constantan thermocouple and a Leeds & Northrup Type K potentiometer.

SOURCE AND PURITY OF MATERIALS:

(1) source not specified; purified chemically, distilled, stored over P_2O_5, distilled.

(2) source not specified.

ESTIMATED ERROR:

temp. ±0.1 K.

REFERENCES:

COMPONENTS:

(1) Heptane; C_7H_{16}; [142-82-5]
(2) Phenylethyl alcohol (benzeneethanol); $C_8H_{10}O$; [60-12-8]
(3) 2,5-Dimethyl-1,5-hexadiene (diisobutene); C_8H_{14}; [627-58-7]
(4) 2,2,4-Trimethylpentane; C_8H_{18}; [540-84-1]
(5) Cinnamyl alcohol (3-phenyl-2-propen-1-ol); $C_9H_{10}O$; [104-54-1]

ORIGINAL MEASUREMENTS:

Francis, A.W.

Ind. Eng. Chem. 1944, *36*, 764-71.

VARIABLES:

Temperatures: 259 to 388 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Heptane + Cinnamyl alcohol: UCST = 102°C.

Phenylethyl alcohol + 2,5-Dimethyl-1,5-hexadiene: UCST = -14°C.

Phenylethyl alcohol + 2,2,4-Trimethylpentane: UCST = 49°C.

2,5-Dimethyl-1,5-hexadiene + Cinnamyl alcohol: UCST = 60°C.

2,2,4-Trimethylpentane + Cinnamyl alcohol: UCST = 115°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. The reagents were introduced and stirred with a thermometer in test tubes which were warmed and cooled gradually in a bath. The temp. of disappearance or reappearance of the cloudiness was read two or three times in each direction.

SOURCE AND PURITY OF MATERIALS:

(1) obtained from Jeffrey pine; no more information.
(2)-(5) source not specified.

ESTIMATED ERROR:

not specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) 2-Methylhexane; C_7H_{16}; [591-76-4] (2) 2,2,3-Trimethylbutane; C_7H_{16}; [464-06-2] (3) Phenylethyl alcohol (benzeneethanol) $C_8H_{10}O$; [60-12-8]	Miller, V.A. *Ind. Eng. Chem., Anal. Ed.* 1945, *17*, 5-12.
VARIABLES:	PREPARED BY:
Temperatures: 308, 312 K	A. Skrzecz

EXPERIMENTAL VALUES:

Solution temperatures and compositions:

2-Methylhexane + Phenylethyl alcohol: 39.1°C, 50 vol. %, or $100w_1 = 40$, $x_1 = 0.45$ (compiler).

2,2,3-Trimethylbutane + Phenylethyl alcohol: 34.45°C, 50 vol. %, or $100\ w_1 = 40$, $x_1 = 0.45$ (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud point method was used. A tube containing the sample, stirrer and fitted with a resistance thermometer was placed in an air bath tube in a liquid bath. Temperature was measured with an iron-constantan thermocouple and a Leeds & Northrup Type K potentiometer.

SOURCE AND PURITY OF MATERIALS:

(1), (2) source not specified; purified chemically, distilled, stored over P_2O_5, distilled.

(3) source not specified.

ESTIMATED ERROR:

temp. ±0.1 K.

REFERENCES:

COMPONENTS:

(1) 1-Octanol; $C_8H_{18}O$; [111-87-5]

(2) Dotriacontane; $C_{32}H_{66}$; [544-85-4]

ORIGINAL MEASUREMENTS:

Chang, S.-S.; Maurey, J.R.; Pummer, W.J.

J. Chem. Eng. Data <u>1983</u>, *28*, 187-9.

VARIABLES:

Temperature: 303 - 338 K

PREPARED BY:

A. Skrzecz

EXPERIMENTAL VALUES:

Solubility of dotriacontane in octanol

$t/°C$	$100\ w_2$	x_2 (compiler)
30.	0.27	0.00078
60.	17.	0.056
65.	67.	0.370

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The cloud-point method was used. A mixture of known composition was placed with magnetic stirrer in a 5-mL vial and then submerged in a temperature-controlled bath. The temperature of the bath was lowered and raised at a very slow rate and the appearance and disappearance of turbidity was observed visually.

SOURCE AND PURITY OF MATERIALS:

(1) commercially available; used as received.

(2) commercially available, purity 97%; used as received; m.p. 342.1 K.

ESTIMATED ERROR:

temp. ±0.1 K.

REFERENCES:

SYSTEM INDEX

Pages preceded by E refer to evaluation texts whereas those not preceded by E refer to compiled tables.

REGISTRY NUMBER INDEX

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AUTHOR INDEX

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