

LIQUID-LIQUID SOLUBILITY: INTRODUCTORY INFORMATION

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The Solubility Data Series is made up of volumes of comprehensive and critically evaluated solubility data on chemical systems in clearly defined areas. Data of suitable precision are presented on data sheets in a uniform format, preceded for each system by a critical evaluation if more than one set of data are available. In those systems where data from different sources agree sufficiently, recommended values are proposed. In other cases, values may be described as "tentative" or "rejected".

This volume is primarily concerned with liquid-liquid systems, but a limited number of related solid-liquid and multicomponent (organic-water-salt) systems have been included where it was 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. Such data have not been found for systems in this volume. Generally, however, data on reported miscibility gap regions and upper and lower critical solution temperatures are included where appropriate and when available.

TERMINOLOGY

In this volume, a mixture (1,2) or a solution (1,2) refers to a single liquid phase containing components 1 and 2. In a mixture, no distinction is made between solvent and solute.

The solubility of a substance is the relative proportion of 1 in a mixture which is saturated with respect to component 1 at a specified temperature and pressure. (The term "saturated" implies the existence of equilibrium with respect to the processes of mass transfer between phases.)

QUANTITIES USED AS MEASURES OF SOLUBILITY

Mole fraction of component 1, x_1 or $x(1)$:

$$x_1 = \frac{n_1}{\sum_i n_i} = \frac{m_1/M_1}{\sum (m_i/M_i)}$$

where n_i is the amount of substance (number of moles) of component i , m_i is the mass of substance i and M_i is its molar mass.

Mole per cent of component 1 is $100x_1$

Mass fraction of component 1, w_1

$$w_1 = \frac{m_1}{\sum m_i}$$

where m_i is the mass of component i .

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Mass per cent of component 1 is $100w_1$, and may be described as g(1)/100g in which the 100g without a subscript means that it is mass of solute relative to solution and not to solvent. The equivalent terms "weight fraction" and "weight per cent" are not used. The mole fraction solubility is related to the mass fraction solubility in a binary system by

$$x_1 = \frac{w_1/M_1}{w_1/M_1 + (1 - w_1)/M_2}$$

Amount of substance concentration of component i in a solution of volume V ,

$$c_i = n_i/V$$

is expressed in units of mol L^{-1} . The terms "molarity" and "molar" and the unit symbol M are not used. However, the unit mol(1)/dm^3 is used frequently rather than "molarity" (where the dm^3 without a subscript means solution and not solvent volume). Within the range of experimental errors usually encountered in reported solubility measurements, this unit may be taken as equal to "molarity".

Mass ratio is frequently used for a two-component solution in the form g(1)/g(2), mg(1)/g(2), etc. The term "parts per million" (ppm) is not used, but may be expressed as mg(1)/kg or g(1)/10⁶g, etc.

Molality of component 1 in component 2 is often used in solid-liquid systems defined as $m_1 = n_1/n_2M_2$, but is not used in liquid-liquid systems where the distinction between "solute" 1 and "solvent" 2 is inappropriate. The term molality alone is inadequate, and the units (mol kg(2)^{-1}) , (mmol kg(2)^{-1}) must be stated.

Mole fractions 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.

ORDERING OF SYSTEMS

It is necessary to establish a method of ordering chemical compounds, to be used for the lists of saturating components which define each chemical system. This order is also used for ordering systems within volumes.

The systems are ordered first on the basis of empirical formula according to the Hill system (ref. 2). The organic compounds, within each Hill formula are ordered as follows:

- (i) by degree of unsaturation, then
- (ii) by order of increasing chain length in the parent hydrocarbon, then
- (iii) by order of increasing chain length of hydrocarbon branches, then
- (iv) numerically by position of unsaturation, then
- (v) numerically by position by substitution, then
- (vi) alphabetically by IUPAC name.

For example,

C_5H_8	cyclopentane
	2-methyl-1,3-butadiene
	1,4-pentadiene
	1-pentyne

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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
$C_6H_{12}O$	3-pentanol
	cyclohexanol
	4-methyl-1-penten-3-ol
	1-hexen-3-ol
	4-hexen-3-ol

Deuterated (2H) compounds immediately follow the corresponding 1H compounds.

GUIDE TO THE COMPILATIONS AND EVALUATIONS

The format used for the compilations and evaluations has been discussed in the Forward. Additional information on the individual sections of each sheet is now provided in the following.

"Components". Each component is listed by its IUPAC name (ref. 1), chemical formula according to the Hill system, and Chemical Abstracts Registry Number. Also included are the "Chemical Abstracts" name if this differs from the IUPAC name, and trivial name or names if appropriate. IUPAC and common names are cross-referenced to "Chemical Abstracts" names in the System Index.

"Original Measurements". References are expressed in "Chemical Abstracts" style, journal names being abbreviated, and if necessary transliterated, in the form given by the "Chemical Abstracts Service Source Index" (CASSI). In the case of multiple entries (for example translations) an asterisk indicates the publication used for the data compilation.

"Variables". Ranges of variations of temperature, pressures, etc. are indicated here.

"Prepared by". The compiler is name here.

"Experimental Values". Components are described as (1) and (2), as defined in "Components". The experimental data are presented in the units in the original paper. Thus the temperature is expressed $t/^{\circ}C$ or $t/^{\circ}F$ as in the original, and conversion to T/K is made only in the critical evaluation. However, the author's units are expressed according to IUPAC recommendations (ref. 3,4) as far as possible.

In addition, compiler-calculated values of mole fractions and/or mass per cent are included if the original data do not use these units. 1975 or 1977 atomic weights (ref. 5) are used in such calculations. If densities are reported in the original paper, conversions from concentrations to mole fractions are included in the compilation sheets, but otherwise this is done in the evaluation, with the values and sources of the densities being quoted and referenced.

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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.

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.

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.

"*Methods*". An outline of the method is presented, reference being made to sources of further detail if these are cited in the original paper. "Chemical Abstracts" abbreviations are often used in this text.

"*Source and Purity of Materials*". For each component, referred to as (1) and (2), the following information (in this order and in abbreviated form) is provided if it is available in the original papers:

source and specification

method of preparation

properties

degree of purity

"*Estimated Error*". If this information was omitted by the authors, and if the necessary data are available in the paper, 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, the type of apparatus, and other relevant information. Methods used by the compilers for reporting estimated errors are based on the papers of Ku and Eisenhart (ref. 6).

"*References*". These are the references (usually cited in the original paper) which the compiler considers particularly useful in discussing the method and material.

"*Evaluator*". The information provided here is the name of the evaluator, the evaluator's affiliation, and the date of the evaluation.

"*Critical Evaluation*". The evaluator aims, to the best of his or her ability, to check that the compiled data are correct, to assess their reliability and quality, to estimate errors where necessary, and to recommend numerical values. The summary and critical review of all the data supplied by the compiler include the following information:

(a) *Critical text*. The evaluator produces a text evaluating *all* the published data for the particular system being discussed, reviewing their merits or shortcomings. Only published data (including theses and reports) are considered, and even some of the published data may only be referred to in this text if it is considered that inclusion of a data compilation sheet is unjustified.

(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 in the compilation sheets, stating the limits within which it should be used.

(c) *Graphical summary*. This may be provided in addition to tables and/or fitting equations.

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(d) *Recommended values.* Data are *recommended* if the results of at least two independent experimental groups are available and are in good agreement, and if the evaluator has no doubt as to the adequacy and reliability of the experimental and computational procedures used.

Data are reported as *tentative* if only one set of measurements is available, or if the evaluator is uncertain of the reliability of some aspect of the experimental or computational method but judges that it should cause only minor error, or if the evaluator considers some aspect of the computational or experimental method undesirable but believes the data to have some value in those instances when an approximate value of the solubility is needed.

Data determined by an inadequate method or under ill-defined conditions are *rejected*, the reference being included in the evaluation together with a reason for its rejection by the evaluator.

(e) *References.* All pertinent references are listed here, including all those publications appearing in the accompanying compilation sheets and also those which have been rejected and not compiled.

(f) *Units.* The final recommended values are reported in SI units (ref. 3). It should be noted that in most cases the rounded absolute temperature values (e.g. 298 K) actually refer to 298.15 K, etc., although very few solubilities are known with such precision that the differences are significant.

Continuation Sheets. These are used for both compilations and evaluations, and include sections listing the "Components" and also the "Original measurement" or "Evaluator" as well as the word "continued". Compilation continuation sheets may include a section headed "Comments and/or Additional Data".

REFERENCES

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3. Whiffen, D. H., ed. *Manual of Symbols and Terminology for Physicochemical Quantities and Units (IUPAC)*, ("The Green Book"), Pergamon, Oxford, 1979; *Pure Appl. Chem.* 1979, 51, 1.
4. McGlashan, M. L. *Physicochemical Quantities and Units*, 2nd ed. Royal Institute of Chemistry, London, 1971.
5. IUPAC Commission on Atomic Weights, *Pure Appl. Chem.* 1976, 47, 75; 1979, 51, 405.
6. Ku, H. H. and Eisenhart, C., in Ku, H. H., ed. *Precision Measurement and Calibration*, NBS Special Publication 300, Vol. 1, Washington, D. C., 1969.