PREFACE

This volume contains a comprehensive collection and critical evaluation of published solubility data for halogenated benzenes, halogenated toluenes, and halogenated phenols in water prior to 1983. In addition, the solubilities of water in some of the mentioned compounds are also included as well as the mutual solubilities between heavy water (D_2O) and some of the compounds. It should be readily apparent to the reader that there is a great scarcity of data available from the published literature on these systems. This is due primarily to the limited use of the organic compounds in commercial quantities.

All halogenated benzenes, toluenes, and phenols are liquids or solids at room temperature. Consequently, this volume is concerned entirely with the solubility behavior for condensed systems only (solid or liquid solutes in liquid solvents). For several of the compounds considered, only one single measured solubility value is available. It is particularly noteworthy, for example, that only one source (1) has provided the only reported data for solubilities in water of almost the entire series of halogenated, substituted phenols. As the critical evaluators often observe, further experimental investigations are needed for an improvement of the reported solubilities and for an extension of the solubilities over wider temperature ranges. Of course, higher temperature (above the normal boiling point of water) and higher pressure (above atmospheric pressure) solubility data are extremely scarce and available for only a very few systems.

The evaluators for this volume have often been faced with the difficult task of examining and evaluating the reliability of a single solubility with only a limited description of the experimental procedures used for the measurement. In such cases, the evaluator's experience in the techniques of measurement has proved invaluable. Also, some of the reported solubility data are several decades old. However, despite the dated experimental techniques, these published measurements have been found to be no less reliable than those of more recent investigations. Consequently, a recently reported result of a solubility measurement has not automatically become the most reliable or recommended value. In every case, efforts have been made to provide the most reliable and realistic solubility value regardless of the period of origin.

Because of their nature, mixtures of water and halogenated benzenes, halogenated toluenes, and halogenated phenols at room temperature over a wide range of proportions form two distinct phases, one aqueous rich and the other organic rich. However, at higher temperatures and at high pressures, the mutual solubilities usually increase significantly as shown, for example, in Figure 1 for 1,4-difluorobenzene in water system (from the reported work of Jockers and Schneider (2)). With changing temperature and pressure, the two liquid phases generally become identical at a critical, or consolute, point. With changing pressure, the critical solution temperature will change, forming a critical solution line. However, applied pressure exerts only a small effect on the critical temperature.

Systems containing halogen derivatives of benzenes, toluenes, and phenols with water are classified as non-regular type solutions. Consequently, those theories and relationships which were developed by J. H. Hildebrand and his co-workers over several decades for explaining solubility behavior are not generally useful for such systems. However, for the organic rich phase, where the less-well-behaved and more non-ideal water molecules are in very low concentrations, the solubility can be correlated against Absolute temperature by means of the equation:

$$\log x(2) = A - B/T$$

where: $x(2)$ = mole fraction solubility of water in the organic phase
T = Absolute temperature
A,B = Adjustable constants

That is, for water as the solute, the logarithm of its mole fraction composition is a linear (straight line) function of the reciprocal of the Absolute temperature (3-6). This linearity of the solubility behavior indicates that the organic-rich phase may approach the random distribution of molecules in solution which is one of the basic assumptions in the regular solution theory as detailed by Hildebrand and Scott (7). However, the strictly straight line correlation given above is not always followed for a wide temperature interval, e.g., from the triple point to the critical point. Even so, for the solubility of water in the halogenated benzenes, toluenes, and phenols, a good fit can be anticipated in the temperature range between the triple point of the solvent and the normal boiling point of water (373.15 K).

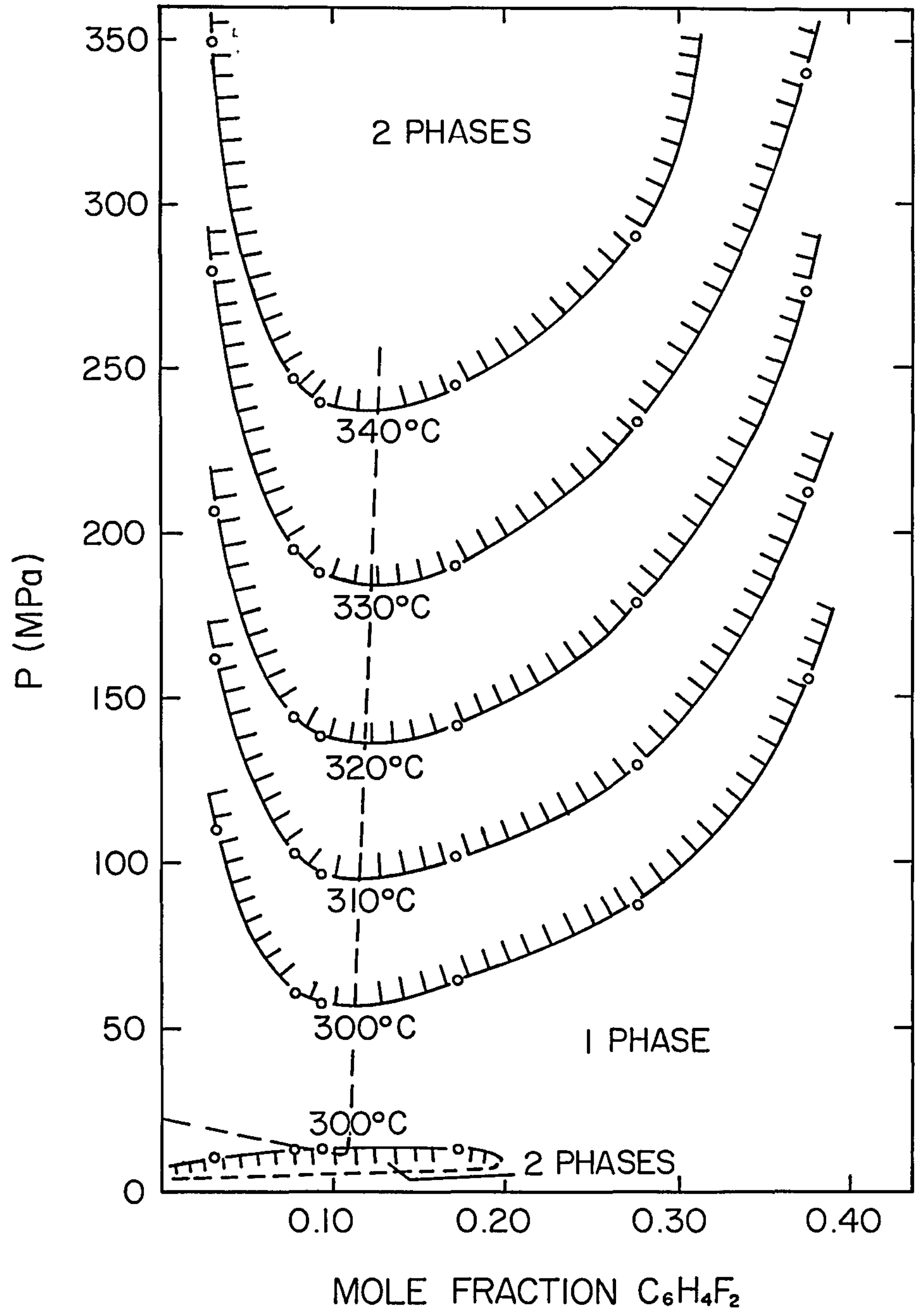

Figure 1. Solubility behavior of 1,4-difluorobenzene and water versus pressure and temperature (2).

Since each system has been treated separately in the evaluation procedure, it is appropriate here in the Introduction to present the general behavior of the evaluated solubilities of water in the various organic constituents as a function of temperature. These relationships are shown in Figure 2 as the logarithm of mole fraction solubility versus the reciprocal of Absolute temperature. It can be seen that, despite the similarity of the organic solvents, the solubility curves do not show any sort of strict regularity. However, according to Horvath (8), some relatively simple pattern of behavior such as parallel straight lines should be expected. It is clear from Figure 2 that, for example, the solubility curve for iodobenzene shows a slope which differs from the remaining system. Indeed, further studies are needed as additional solubility data become available.

One very simple and practical relationship has been found to be quite useful for solubility data correlation. A plot of the logarithm of solubility in water expressed as molarity against the solute molar volume at 25°C follows a simple linear behavior and such plots may be used to check reported solubility data (9-11). The great advantage of this procedure is that the only information required is the density of the solute at 25°C which is relatively easy to measure when not available in standard references. Such a relation, which was reported by Horvath (8), has been used in this volume and is shown in Figure 3 for eight halogenated benzenes. However, the values shown in the figure do not include the recently reported measurements by Yalkowsky et al. (12).

The utility of the logarithm of molar saturation versus molar volume correlation was recognized in its application to the evaluation of the solubility of 1,3-dibromobenzene in water where the two independently determined measurements were in conflict. The solubility data for eighteen of the substances reported by Yalkowsky et al., including the 1,3-dibromobenzene, were correlated as shown in Figure 4. This graph suggests that the errors for the measured solubilities may, in fact, not agree well with the ± 10 percent which was reported by Yalkowsky (13) for the measurements. The graph suggests also that the reported solubility of 1,3-dibromobenzene in water may be too high in relation to the other solubilities reported by Yalkowsky et al.

It is, of course, relevant to consider the existence of trends and regularities observed in the behavior of physical parameters and properties, such as their thermodynamic constants and hydrophobic interactions, as determined from solubility measurements involving groups of compounds. In the case of solution enthalpies, for example, Gill et al. (14) have investigated their positive linear dependence with temperature for slightly soluble aromatic compounds. The calorimetric enthalpy of solution determinations for slightly soluble aromatic compounds over a temperature interval provide a very useful relationship for the temperature dependence of the solubility in water. The heat capacity change derived from the enthalpy of solution varies slightly with temperature (over limited, but reasonable, ranges of temperature). Consequently, thermodynamic expressions can provide useful descriptions of the temperature dependence of solubilities.

The curve for solubility versus temperature for all liquid aromatic hydrocarbons shows a minimum for zero heat of solution. This temperature minimum is calculated from the equation:

$$\Delta H^{\infty}_{soln}(T) = \Delta H^{\infty}_{soln}(T_o) + \Delta C^{\infty}_{p,soln}(T - T_o)$$

by use of the condition: $\Delta H^{\infty}_{soln}(T) = 0$ at $T = T_{min}$

so that: $T_{min} = T_o - \Delta H^{\infty}_{soln}(T_o)/\Delta C^{\infty}_{p,soln}$

In other words, the minimum solubility temperatures, T_{min}, for liquid aromatic hydrocarbons in water are calculated from the measured solution enthalpies at $T_o = 298.15$ K, $\Delta H^{\infty}_{soln}(T_o)$ and the heat capacity change at $T_o = 298.15$ K, $\Delta C^{\infty}_{p,soln}$.

The minimum solubility phenomenon is a characteristic of the solubility versus temperature curves in the 285 through 320 K range for liquid aromatic hydrocarbon in water systems. This minimum is illustrated in the cases of 1,2-dichlorobenzene, 1,3-dichlorobenzene, and chlorobenzene in water where solubilities have been reported over wide ranges of temperature.

The solubility in water behavior for 1,4-dichlorobenzene has been evaluated in two parts, one below and the other above the normal melting point (326.25 K) of the compound. This is necessary because of the distinct break in the solubility versus temperature behavior at the compound melting point. Here it is important to note that the solubility versus

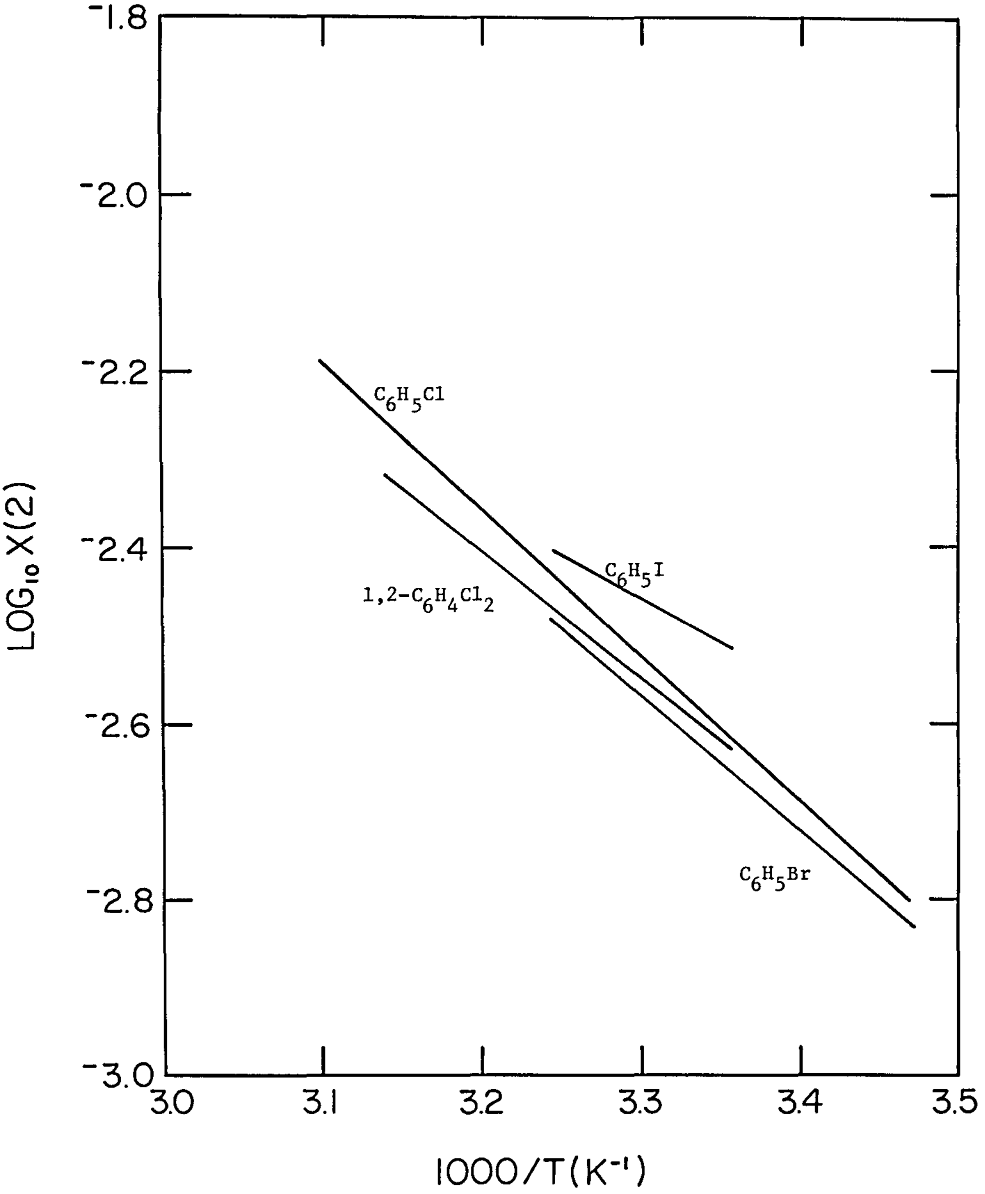

Figure 2. Logarithm of mole fraction water versus the reciprocal of Absolute temperature for the solubility of water in selected halogenated aromatic solvents.

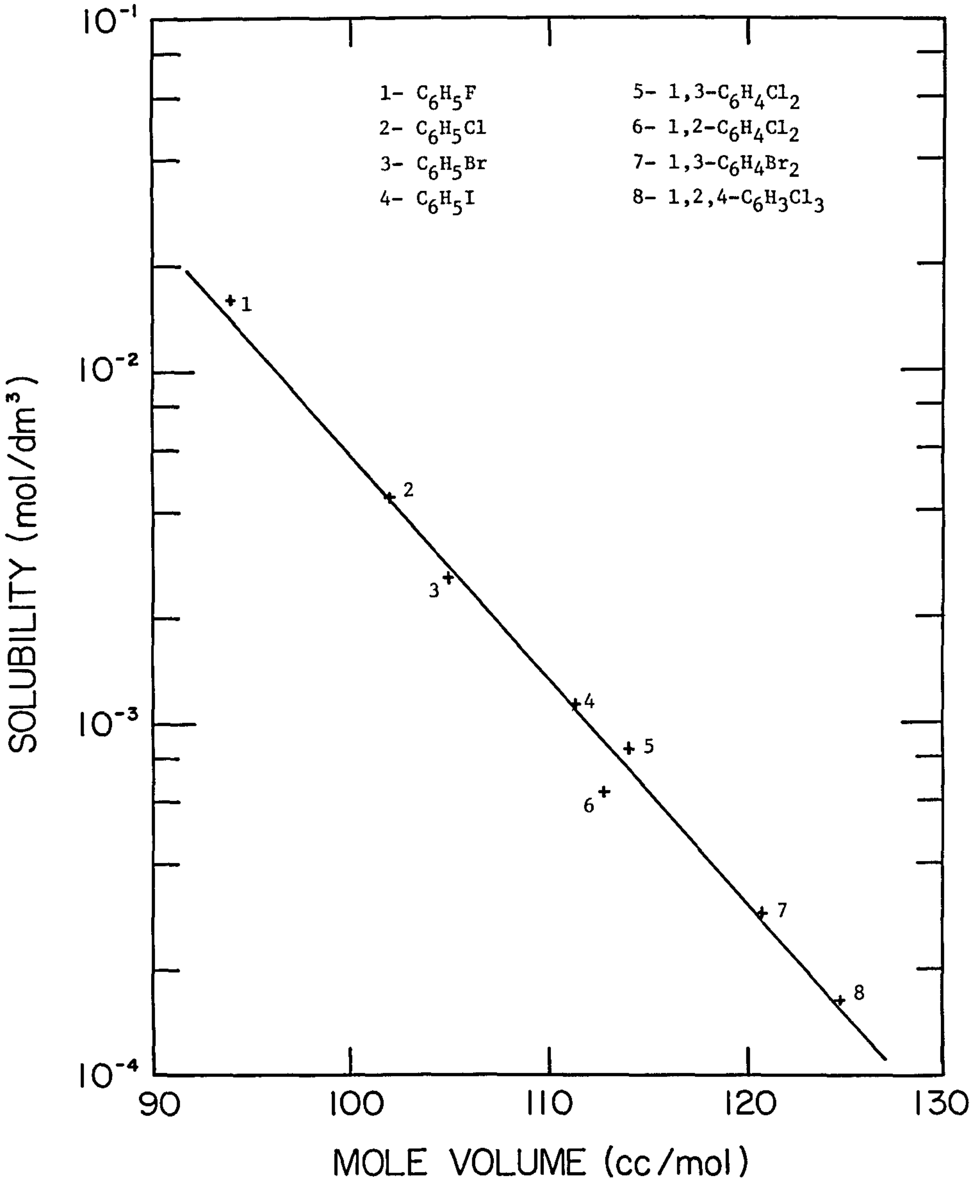

Figure 3. Logarithm of saturation molarity versus solute molar volume at 25°C for selected halogenated benzenes in water.

Correlation equation:

$$\log_{10}S_1(\text{mole/dm}^3) = 4.17442 - 6.40668 \times 10^{-2}\ \bar{V}_{25^\circ C}(\text{cc/mol})$$

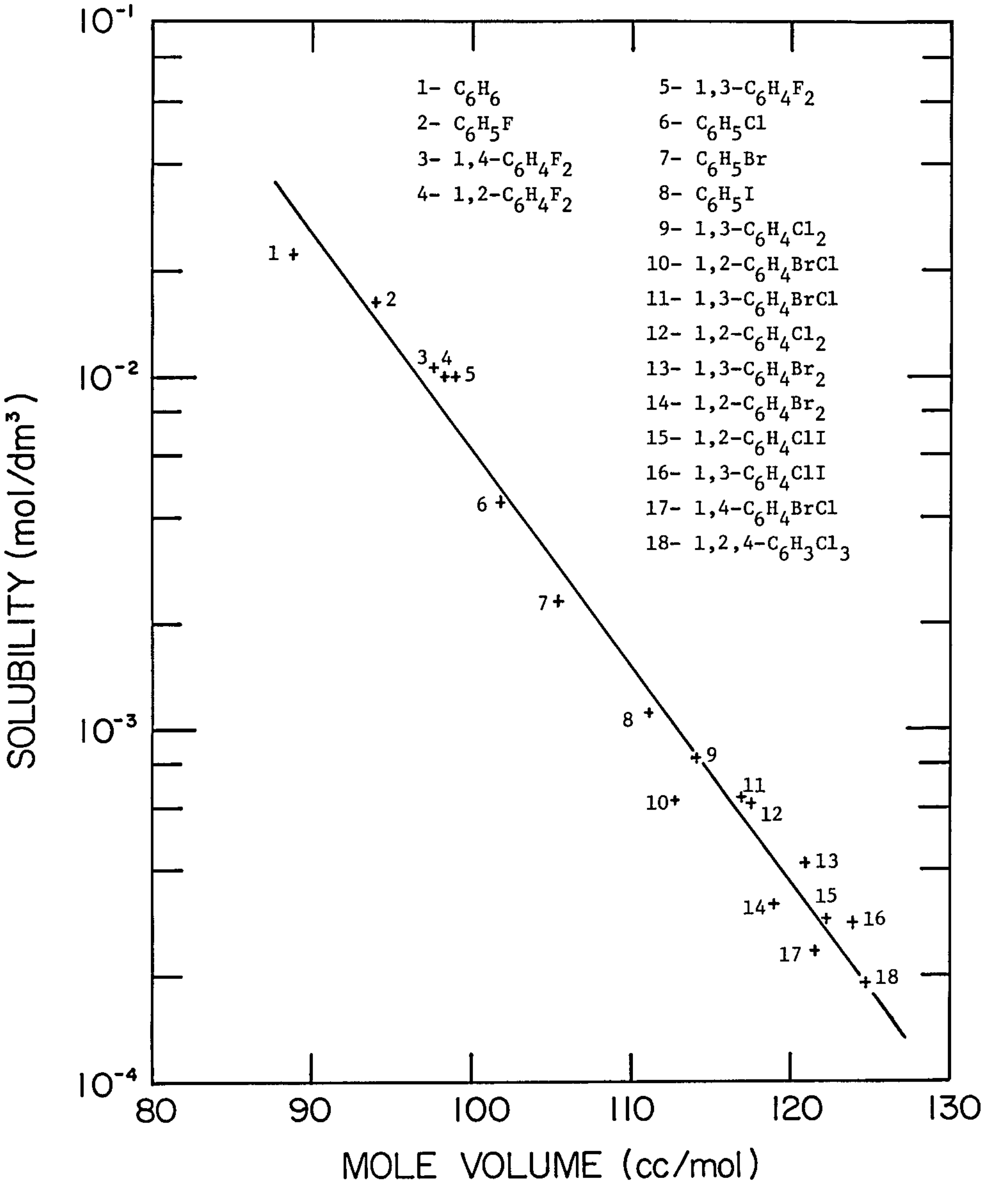

Figure 4. Logarithm of saturation molarity versus solute molar volume at 25°C for selected aromatics in water as reported by Yalkowsky et al. (13).

Correlation equation:

$$\log_{10} S_1 (\mathrm{mol/dm^3}) = 3.94385 - 6.15067 \times 10^{-2}\ \bar{V}_{25^\circ C} (\mathrm{cc/mol})$$

Table I. Conversion Factors between Solubility Units

From \ To	Bunsen coeff. B_2	Ostwald coeff. O_2	Technical coeff. T_2	Kuenen coeff. K_2	Weight Percent W_2	Mole Fraction X_2
Bunsen coefficient, B_2	1	$\frac{273.15\ O_2}{T}$	$\frac{d\ T_2}{0.9678}$	$d\ K_2$	$\frac{22415\ z\ d\ W_2}{(100-W_2)\ M\ P}$	$\frac{22415\ z\ d\ X_2}{(1-X_2)\ M_L P}$
Ostwald coefficient, O_2	$\frac{T\ B_2}{273.15}$	1	$\frac{d\,T\,T_2}{264.35}$	$\frac{d\,T\,K_2}{273.15}$	$\frac{22415\ z\,d\,T\,W_2}{273.15(100-W_2)\ M\,P}$	$\frac{22415\ z\,d\,T\,X_2}{273.15(1-X_2)\ M_L P}$
Technical coefficient, T_2	$\frac{0.9678\ B_2}{d}$	$\frac{264.35\ O_2}{d\,T}$	1	$0.9678\ K_2$	$\frac{0.9678 \cdot 22415\ z\,W_2}{(100-W_2)\ M\,P}$	$\frac{0.9678 \cdot 22415\ z\,X_2}{(1-X_2)\ M_L P}$
Kuenen coefficient, K_2	$\frac{B_2}{d}$	$\frac{273.15\ O_2}{d\,T}$	$\frac{T_2}{0.9678}$	1	$\frac{22415\ z\,W_2}{(100-W_2)\ M\,P}$	$\frac{0.9678 \cdot 22415\ z\,X_2}{(1-X_2)\ M_L P}$
Weight percent, W_2	$\frac{100}{1+\frac{22415\ z\,d}{M\,P\,B_2}}$	$\frac{100}{1+\frac{22415\ z\,d\,T}{273.15\ M\,P\,O_2}}$	$\frac{100}{1+\frac{22415\ z\ 0.9678}{M\,P\,T_2}}$	$\frac{100}{1+\frac{22415\ z}{M\,P\,K_2}}$	1	$\frac{100}{1+\frac{(1-X_2)M_L}{M\,X_2}}$
Mole fraction, X_2	$\frac{1}{1+\frac{22415\ z\,d}{M_L P\,B_2}}$	$\frac{1}{1+\frac{22415\ z\,d\,T}{273.15\ M_L P\,O_2}}$	$\frac{1}{1+\frac{22415\ z\ 0.9678}{M_L P\ T_2}}$	$\frac{1}{1+\frac{22415\ z}{M_L P\,K_2}}$	$\frac{W_2/M}{\frac{W_2}{M}+\frac{100-W_2}{M_L}}$	1

d = density of liquid solvent [g/ml], z = compressibility factor of gaseous solute, T = absolute temperature [K], P = partial pressure of solute [atm], M = molecular weight of solute, M_L = molecular weight of solvent.

temperature curves for the solid aromatic hydrocarbons such as 1,4-dichlorobenzene do not pass through minima around ambient temperature. Thus, the heats of solution do not become zero in this temperature range.

While the theory of isotope effects upon physical properties of compounds has developed considerably during the last three decades, some areas of understanding still involve qualitative descriptions despite a large number of investigations. In this connection, a large amount of work on the physicochemical properties of heavy water and its effect upon other properties has been done (15). The objective of various studies has been the establishment of the effects of nuclear masses upon intermolecular bond energies and upon the physical properties of liquids relative to their molecular structure, temperature, pressure, and chemical behavior (16).

The solubilities of ordinary water and heavy water have been determined in 29 organic liquids and in all cases the heavy water was found less soluble than the ordinary water (17). This can be explained simply by the difference in the total molecular surface areas. With increasing temperature, the solubility differences decrease markedly.

In the case of the solubility of liquid organics in ordinary water and in heavy water, there is good indication that the dissolving power of heavy water is less than that of ordinary water under the same conditions (18). As they do for solubilities of ordinary water and heavy water in organics, the isotopic effects decrease in extent with increasing temperature for organic liquid solubilities in the two solvents. With respect to the mutual solubilities of halogenated benzenes, toluenes, and phenols with ordinary water and heavy water, the available data do not show exceptions or unusual irregularities. In all cases, the usual behavior, as described above, is observed.

The solubility data found in the literature have been reported in various units. While the users of solubility data very often prefer mole fraction or weight percentage concentration units, others have been employed. As a convenience, the appropriate conversion factors between the various concentration units are presented in Table I from Horvath (19). Also, it should be pointed out that some original measurement conversions have been made in order to present the reported data in currently used concentration units. However, no assumed parameters have been involved in these conversions. In addition, the actual reported values have been used to calculate concentrations in two other concentration units. These values are reported routinely to one more significant figure than the measured value to aid the user in further calculations. One should not assume that these calculated concentration values have any greater precision than the originally measured values. Care has been taken to identify the reported concentration values throughout the volume.

Finally, it should be indicated that the halogenated compounds have been organized according to the Hill System. The heavy water follows the ordinary water.

REFERENCES

1. Blackman, G. E.; Parke, M. H.; Garton, G. *Arch. Biochem. Biophys.* 1955, *54(1)*, 55-57.

2. Jockers, R.; Schneider, G. M. *Ber. Bunsenges. Phys. Chem.* 1978, *82*, 576.

3. Black, C.; Joris, G. G.; Taylor, H. S. *J. Chem. Phys.* 1948, *16(5)*, 537-43.

4. Burd, S. C., Ph.D. Dissertation, Pennsylvania State University, University Park, 1968.

5. Guerrant, R. P., M.Sc. Dissertation, Pennsylvania State University, University Park, 1964.

6. Hibbard, R. R.; Schalla, R. L. "The Solubility of Water in Hydrocarbons"; National Advisory Committee for Aeronautics: Washington, July 10, 1952; R. M. E52 D24.

7. Hildebrand, J. H.; Scott, R. L. "The Solubility of Nonelectrolytes", 3rd ed.; Reinhold Publishing Corp.: New York, 1950.

8. Horvath, A. L. "Halogenated Hydrocarbons: Solubility-Miscibility with Water"; Marcell Dekker: New York, 1982.

9. Burgess, J.; Haines, R. I. *J. Chem. Eng. Data* 1978, *23(3)*, 196.

10. Natarajan, G. S.; Venkatachalam, K. A. *J. Chem. Eng. Data* 1972, *17(3)*, 328.

11. Peake, E.; Hodgson, G. W. *J. Am. Oil Chem. Soc.* 1966, *43(4)*, 215.

12. Yalkowsky, S. H.; Orr, R. J.; Valvani, S. C. *Ind. Eng. Chem. Fundam.* 1979, *18(4)*, 351-3.

13. Yalkowsky, S. H., Personal Communication, 1978.

14. Gill, S. J.; Nicholas, N. F.; Wadso, I. *J. Chem. Thermodyn.* 1976, *8(5)*, 445-52.

15. Kirschenbaum, I. "Physical Properties and Analysis of Heavy Water"; McGraw-Hill: New York, 1951.

16. Rabinovich, I. B., Doctoral Dissertation, Inst. Phys. Chem., Academy of Science of the Ukraine SSR., Kiev, 1964.

17. Eidinoff, M. L. In "Production of Heavy Water", National Nuclear Energy Series Division III-Vol. 4F, Murphy, G. M., Urey, H. C., Kirshenbaum, I., Eds.; McGraw-Hill: New York, 1955; Part II, Chapter 7, pp 129-44.

18. Guseva, A. I.; Parnov, E. I. *Radiokhimiya* 1965, *5*, 507.

19. Horvath, A. L. *Chem.-Ing.-Techn.* 1976, *48(2)*, 144.

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