SOLUBILITY DATA SERIES

Editor-in-Chief
A. S. KERTES

Volume 20

HALOGENATED BENZENES, TOLUENES AND PHENOLS WITH WATER

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FOREWORD

If the knowledge is
undigested or simply wrong,
more is not better

How to communicate and disseminate numerical data effectively in chemical science and technology has been a problem of serious and growing concern to IUPAC, the International Union of Pure and Applied Chemistry, for the last two decades. The steadily expanding volume of numerical information, the formulation of new interdisciplinary areas in which chemistry is a partner, and the links between these and existing traditional subdisciplines in chemistry, along with an increasing number of users, have been considered as urgent aspects of the information problem in general, and of the numerical data problem in particular.

Among the several numerical data projects initiated and operated by various IUPAC commissions, the *Solubility Data Project* is probably one of the most ambitious ones. It is concerned with preparing a comprehensive critical compilation of data on solubilities in all physical systems, of gases, liquids and solids. Both the basic and applied branches of almost all scientific disciplines require a knowledge of solubilities as a function of solvent, temperature and pressure. Solubility data are basic to the fundamental understanding of processes relevant to agronomy, biology, chemistry, geology and oceanography, medicine and pharmacology, and metallurgy and materials science. Knowledge of solubility is very frequently of great importance to such diverse practical applications as drug dosage and drug solubility in biological fluids, anesthesiology, corrosion by dissolution of metals, properties of glasses, ceramics, concretes and coatings, phase relations in the formation of minerals and alloys, the deposits of minerals and radioactive fission products from ocean waters, the composition of ground waters, and the requirements of oxygen and other gases in life support systems.

The widespread relevance of solubility data to many branches and disciplines of science, medicine, technology and engineering, and the difficulty of recovering solubility data from the literature, lead to the proliferation of published data in an ever increasing number of scientific and technical primary sources. The sheer volume of data has overcome the capacity of the classical secondary and tertiary services to respond effectively.

While the proportion of secondary services of the review article type is generally increasing due to the rapid growth of all forms of primary literature, the review articles become more limited in scope, more specialized. The disturbing phenomenon is that in some disciplines, certainly in chemistry, authors are reluctant to treat even those limited-in-scope reviews exhaustively. There is a trend to preselect the literature, sometimes under the pretext of reducing it to manageable size. The crucial problem with such preselection - as far as numerical data are concerned - is that there is no indication as to whether the material was excluded by design or by a less than thorough literature search. We are equally concerned that most current secondary sources, critical in character as they may be, give scant attention to numerical data.

On the other hand, tertiary sources - handbooks, reference books and other tabulated and graphical compilations - as they exist today are comprehensive but, as a rule, uncritical. They usually attempt to cover whole disciplines, and thus obviously are superficial in treatment. Since they command a wide market, we believe that their service to the advancement of science is at least questionable. Additionally, the change which is taking place in the generation of new and diversified numerical data, and the rate at which this is done, is not reflected in an increased third-level service. The emergence of new tertiary literature sources does not parallel the shift that has occurred in the primary literature.

With the status of current secondary and tertiary services being as briefly stated above, the innovative approach of the *Solubility Data Project* is that its compilation and critical evaluation work involve consolidation and reprocessing services when both activities are based on intellectual and scholarly reworking of information from primary sources. It comprises compact compilation, rationalization and simplification, and the fitting of isolated numerical data into a critically evaluated general framework.

The *Solubility Data Project* has developed a mechanism which involves a number of innovations in exploiting the literature fully, and which contains new elements of a more imaginative approach for transfer of reliable information from primary to secondary/tertiary sources. *The fundamental trend of the Solubility Data Project is toward integration of secondary and tertiary services with the objective of producing in-depth critical analysis and evaluation which are characteristic to secondary services, in a scope as broad as conventional tertiary services.*

Fundamental to the philosophy of the project is the recognition that the basic element of strength is the active participation of career scientists in it. Consolidating primary data, producing a truly critically-evaluated set of numerical data, and synthesizing data in a meaningful relationship are demands considered worthy of the efforts of top scientists. Career scientists, who themselves contribute to science by their involvement in active scientific research, are the backbone of the project. The scholarly work is commissioned to recognized authorities, involving a process of careful selection in the best tradition of IUPAC. This selection in turn is the key to the quality of the output. These top experts are expected to view their specific topics dispassionately, paying equal attention to their own contributions and to those of their peers. They digest literature data into a coherent story by weeding out what is wrong from what is believed to be right. To fulfill this task, the evaluator must cover *all* relevant open literature. No reference is excluded by design and every effort is made to detect every bit of relevant primary source. Poor quality or wrong data are mentioned and explicitly disqualified as such. In fact, it is only when the reliable data are presented alongside the unreliable data that proper justice can be done. The user is bound to have incomparably more confidence in a succinct evaluative commentary and a comprehensive review with a complete bibliography to both good and poor data.

It is the standard practice that the treatment of any given solute-solvent system consists of two essential parts: I. Critical Evaluation and Recommended Values, and II. Compiled Data Sheets.

The Critical Evaluation part gives the following information:

(i)   a verbal text of evaluation which discusses the numerical solubility information appearing in the primary sources located in the literature. The evaluation text concerns primarily the quality of data after consideration of the purity of the materials and their characterization, the experimental method employed and the uncertainties in control of physical parameters, the reproducibility of the data, the agreement of the worker's results on accepted test systems with standard values, and finally, the fitting of data, with suitable statistical tests, to mathematical functions;

(ii) a set of recommended numerical data. Whenever possible, the set of recommended data includes weighted average and standard deviations, and a set of smoothing equations derived from the experimental data endorsed by the evaluator;

(iii) a graphical plot of recommended data.

The Compilation part consists of data sheets of the best experimental data in the primary literature. Generally speaking, such independent data sheets are given only to the best and endorsed data covering the known range of experimental parameters. Data sheets based on primary sources where the data are of a lower precision are given only when no better data are available. Experimental data with a precision poorer than considered acceptable are reproduced in the form of data sheets when they are the only known data for a particular system. Such data are considered to be still suitable for some applications, and their presence in the compilation should alert researchers to areas that need more work.

The typical data sheet carries the following information:

(i)   components – definition of the system – their names, formulas and Chemical Abstracts registry numbers;

(ii)   reference to the primary source where the numerical information is reported. In cases when the primary source is a less common periodical or a report document, published though of limited availability, abstract references are also given;

(iii)   experimental variables;

(iv)   identification of the compiler;

(v)   experimental values as they appear in the primary source. Whenever available, the data may be given both in tabular and graphical form. If auxiliary information is available, the experimental data are converted also to SI units by the compiler.

Under the general heading of Auxiliary Information, the essential experimental details are summarized:

(vi)   experimental method used for the generation of data;

(vii)   type of apparatus and procedure employed;

(viii) source and purity of materials;

(ix)   estimated error;

(x)   references relevant to the generation of experimental data as cited in the primary source.

This new approach to numerical data presentation, formulated at the initiation of the project and perfected as experience has accumulated, has been strongly influenced by the diversity of background of those whom we are supposed to serve. We thus deemed it right to preface the evaluation/compilation sheets in each volume with a detailed discussion of the principles of the accurate determination of relevant solubility data and related thermodynamic information.

Finally, the role of education is more than corollary to the efforts we are seeking. The scientific standards advocated here are necessary to strengthen science and technology, and should be regarded as a major effort in the training and formation of the next generation of scientists and engineers. Specifically, we believe that there is going to be an impact of our project on scientific-communication practices. The quality of consolidation adopted by this program offers down-to-earth guidelines, concrete examples which are bound to make primary publication services more responsive than ever before to the needs of users. The self-regulatory message to scientists of the early 1970s to refrain from unnecessary publication has not achieved much. A good fraction of the literature is still cluttered with poor-quality articles. The Weinberg report (in 'Reader in Science Information', ed. J. Sherrod and A. Hodina, Microcard Editions Books, Indian Head, Inc., 1973, p. 292) states that 'admonition to authors to restrain themselves from premature, unnecessary publication can have little effect unless the climate of the entire technical and scholarly community encourages restraint...' We think that projects of this kind translate the climate into operational terms by exerting pressure on authors to avoid submitting low-grade material. The type of our output, we hope, will encourage attention to quality as authors will increasingly realize that their work will not be suited for permanent retrievability unless it meets the standards adopted in this project. It should help to dispel confusion in the minds of many authors of what represents a permanently useful bit of information of an archival value, and what does not.

If we succeed in that aim, even partially, we have then done our share in protecting the scientific community from unwanted and irrelevant, wrong numerical information.

A. S. Kertes

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$_2$O) 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).
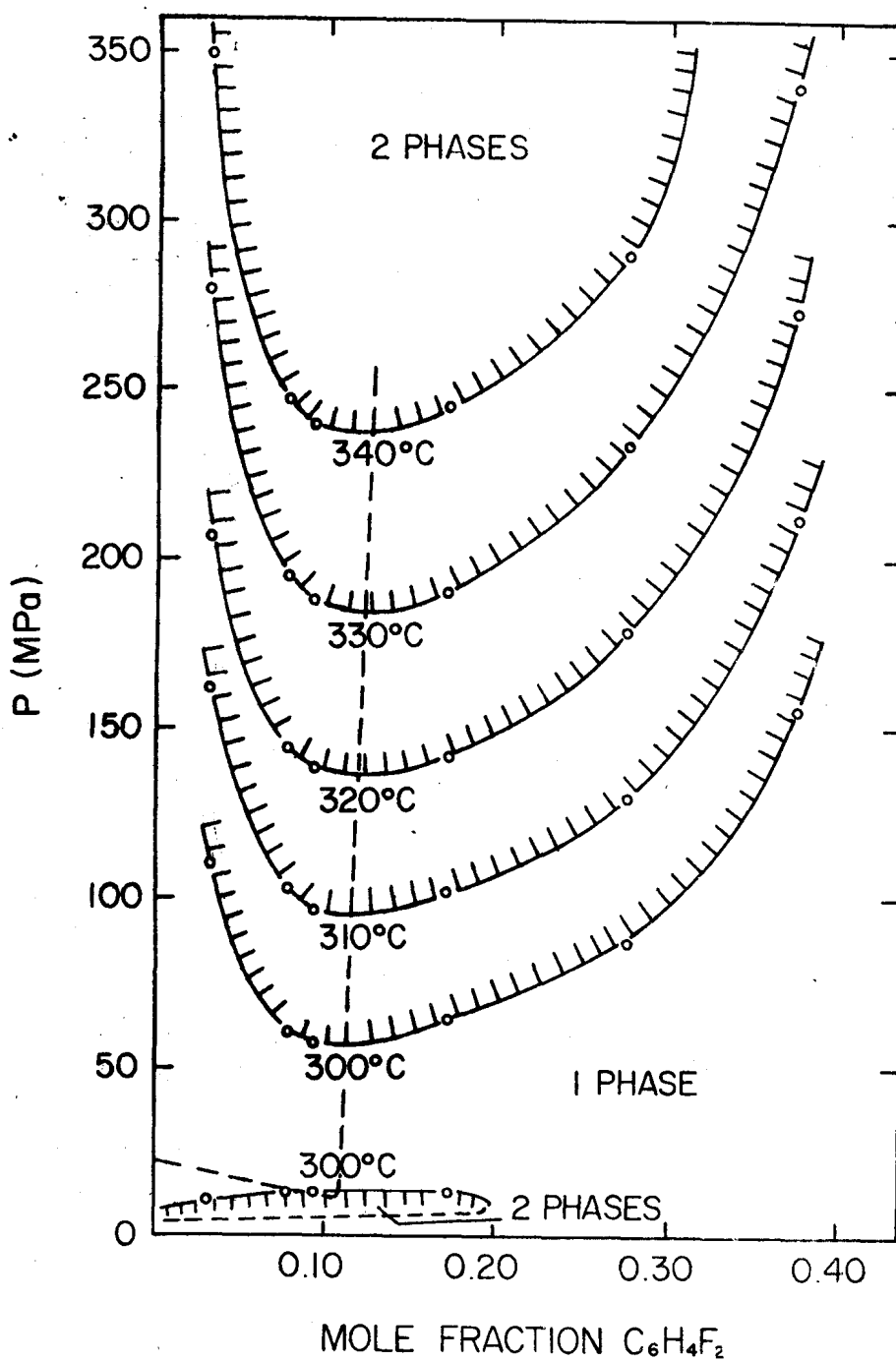
Figure 1.   Solubility behavior of 1,4-difluorobenzene and water versus pressure
and temperature (2).

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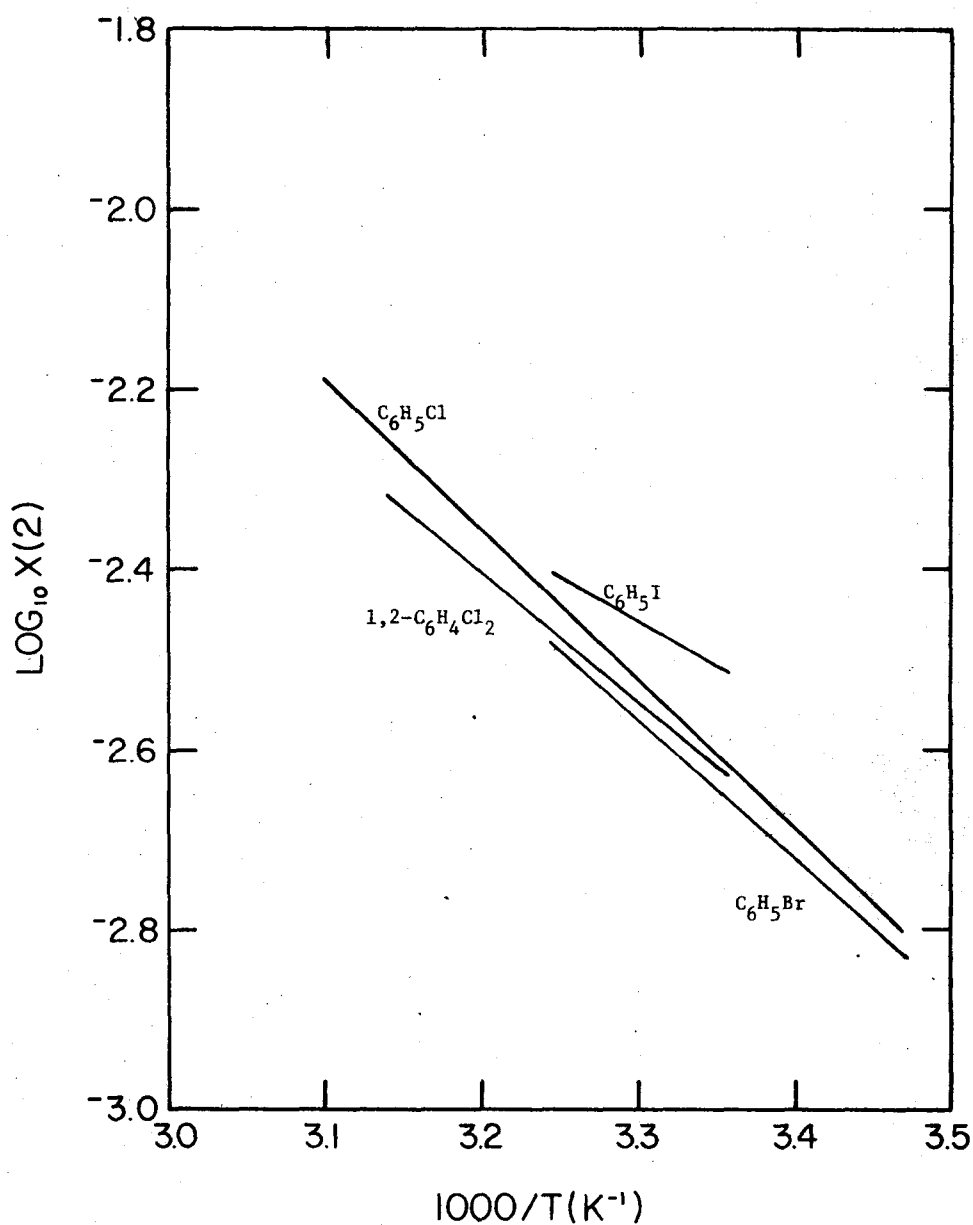
Figure 2.   Logarithm of mole fraction water versus the reciprocal of Absolute
            temperature for the solubility of water in selected halogenated
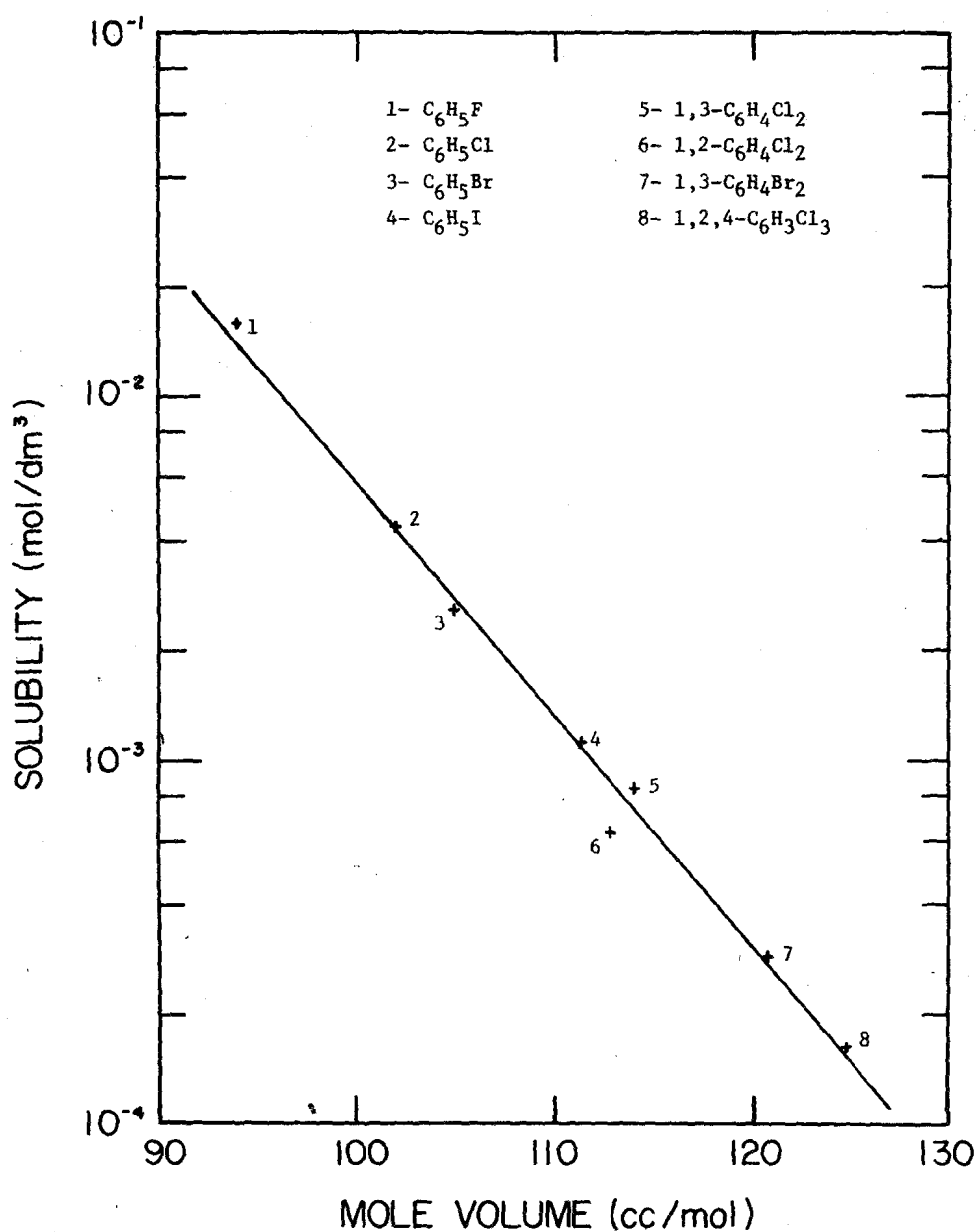   aromatic solvents.

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

Correlation equation:

$$\log_{10}S_1 (\text{mole/dm}^3) = 4.17442 - 6.40668 \times 10^{-2} \, \bar{V}_{25°C}(\text{cc/mol})$$
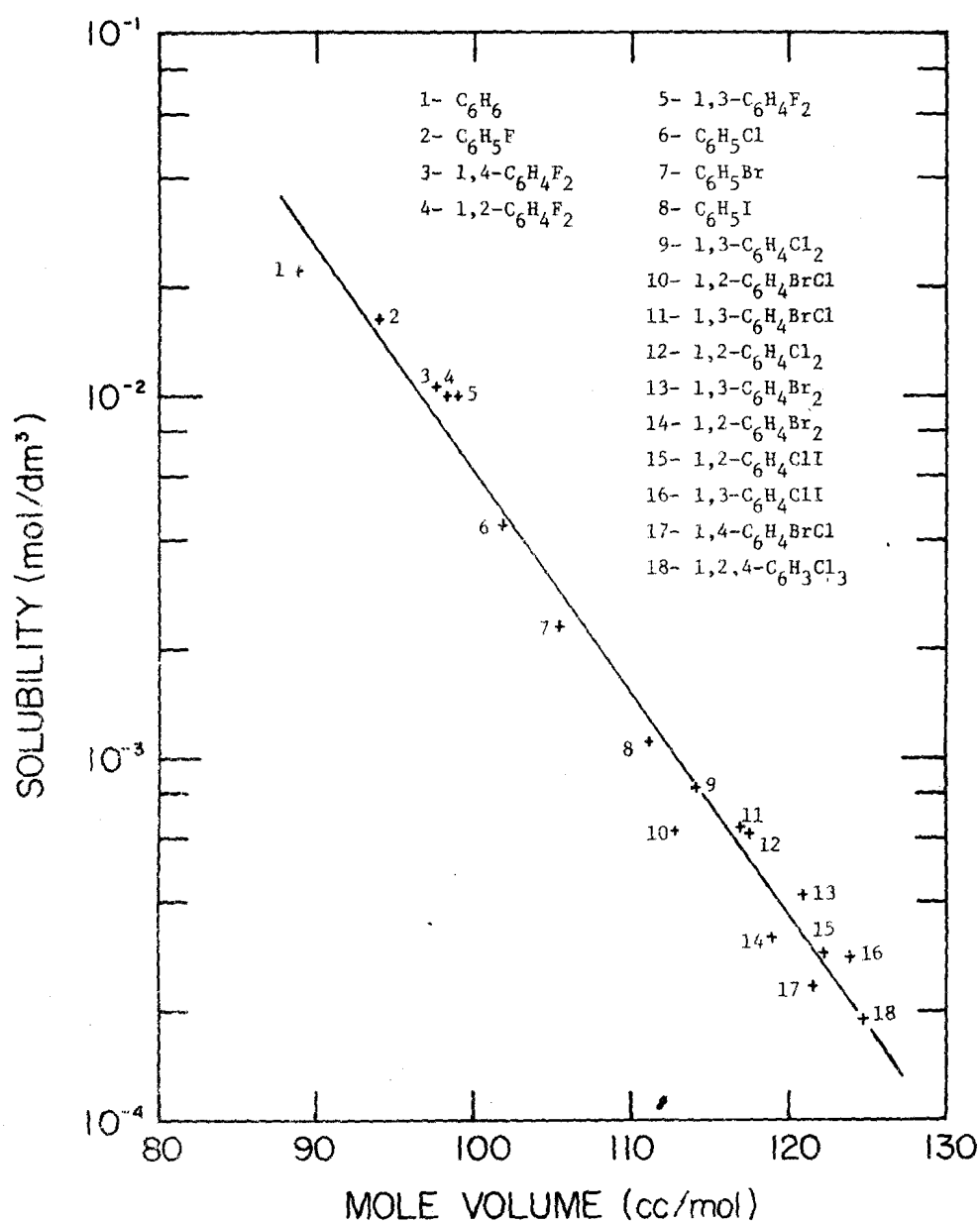
Figure 4. Logarithm of saturation molarity versus solute molar volume at 25°C for selected aromatics in water as reported by Yalkowsky et al. (13).

Correlation equation:

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

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

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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 or 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 artifical 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 $x(1)$:

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

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

$$w_1 = m_1/\sum_i m_i$$

where m_i is the mass of component i.

(continued next page)

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)/10^{6}g, 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 in 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) alphabetcially by IUPAC name.

For 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 (^{2}H) compounds immediately follow the corresponding ^{1}H compounds.

<u>GUIDE TO THE COMPILATIONS AND EVALUATIONS</u>

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 folowing.

"*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/°C or t/°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.