Solubility of *p*-Dibromobenzene at 25° C. in Some Mixed Solvents

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The solubility of *p*-dibromobenzene has been determined at 25° C. in seven solvents and in six mixtures of these solvents. The results have been treated by the approaches of Guggenheim and Hildebrand to regular solutions. Results have been compared with previous studies using naphthalene as the solute in the same solvents and solvent mixtures.

THE SOLUBILITY of naphthalene in 21 binary solvent mixtures of combinations of ethylbenzene, toluene, benzene, carbon tetrachloride, cyclohexane, hexadecane, and hexane has been reported previously (*3-5*). In the present work some of the same mixed solvent systems have been restudied using *p*-dibromobenzene as the solute. The purpose is a comparison of the behavior of these two solutes toward these mixed solvent systems: carbon tetrachloride–cyclohexane, hexane-hexadecane, hexadecane–carbon tetrachloride, hexadecane-ethylbenzene, benzene-hexadecane, and toluene-hexane. *p*-Dibromobenzene was chosen for this work because it is similar to naphthalene: For the former, the melting point and ideal solubility at 25° C. are 87.8° C. (*1*) and 0.248 mole fraction (*7*); for the latter, 80.3° C. (*6*) and 0.312 mole fraction (*3*).

EXPERIMENTAL

p-Dibromobenzene was Matheson Coleman and Bell practical grade, recrystallized twice from ethanol. The experimental melting point of the purified solid, 87.4° C., corresponds to an impurity of 0.007 mole fraction, assuming ideal behavior as a first approximation. The solvents were prepared by methods described previously (*3*). Differences in purity between these solvent batches and those used in previous work had no effect on the experimentally determined solubility. Both the equipment and the procedure used in the determination of the solubilities are the same as those used in the previous studies of this type (*3-5*). A detailed description has been given (*3*). The solubility was determined a minimum of twice in each pure solvent and singly in the solvent mixtures. In the former, duplicate determinations agreed to within 0.0005 mole fraction solute at saturation. By estimation, in the latter an uncertainty of less than 0.001 is indicated.

BINARY SYSTEMS

Results. The experimental solubility of *p*-dibromobenzene in mole and volume fractions is given in Columns 2 and 4 of Table I. Literature values, when available, are also given (Column 3).

Solvent-solute molar interchange energies, W_{ij}, defined by the *s*-regular equation of Guggenheim (*2*)

$$\Delta G_{ij}^{E} = x_i x_j W_{ij}$$

were obtained through

$$\ln \gamma_2 = \frac{x_1^2 W}{RT} \qquad (1)$$

Table I. Binary *p*-Dibromobenzene–Solvent Systems at 25° C.

	p-Dibromobenzene Solubility						
	Mole Fraction		Volume Fract.	*W* by Eq. 1, Cal. Mole^{-1}	*W'* by Eq. 2 Cal. Ml.$^{-1}$	δ_2 by Eq. 2, 3	$\delta_2$by Eq. 3, 5
Solvent	This work	Lit.					
Toluene	0.2452	0.230 (*9*)	0.264	11.4	0.101	9.22	9.25
Ethylbenzene	0.2393	. . .	0.232	37.2	0.309	9.36	9.35
Benzene	0.2279	0.217 (*6*) 0.238 (*9*)	0.280	83.3	0.818	10.05	10.18
Carbon tetrachloride	0.1917	0.189 (*9*) 0.193 (*6*)	0.224	234	2.15	10.06	10.09
n-Hexadecane	0.1522	. . .	0.0672	402	2.82	9.67	10.07
Cyclohexane	0.1126	. . .	0.121	594	5.13	10.46	10.47
n-Hexane	0.0834	0.086 (*6*)	0.0755	769	6.40	9.80	9.80
Av. all values ± av. dev.						9.80 ± 0.33	9.89 ± 0.36
Av. (cyclohexane omitted) ± av. dev.						9.69 ± 0.28	9.79 ± 0.33

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and are listed in Column 5. While unequal molar volumes of solute and solvent logically preclude strict adherence to the *s*-regular model, these interchange energies frequently give a useful indication of the solvent-solute interaction (*8*).

Solute-solvent volume interchange energies, W'_{ij}, are listed in Column 6. These energies were obtained from the less restrictive regular solution model (*7*) through

$$\ln \gamma_2 = -\frac{V_2^0 \phi_1^2 W'}{RT} \tag{2}$$

By definition, for a component pair *i* and *j*, W'_{ij} has the following significance (*7*):

$$\Delta G_{ij}^E = V_{ij}^0 \phi_i \phi_j W'_{ij}$$

The molar volume of supercooled *p*-dibromobenzene, evaluated from density data of Tyrer (*11*) on toluene–*p*-dibromobenzene mixtures, is 118 ± 3 ml. mole^{-1}. This result is considered more reliable than that which may be obtained by the extrapolation through a 65° C. interval of density data for the liquid. Table I shows the experimental solubility, 0.2452, of the solute in toluene is only slightly less than the ideal value, 0.248. Thus, additive volumes appear to be quite probable. The density data of Tyrer show no dependence of the apparent molal volume of the solute upon concentration. Thus solute apparent molal volume and true molal volume appear to be identical in this system, within the stated uncertainty.

Column 7 lists the solubility parameter (δ_2) of *p*-dibromobenzene obtained from the following relationship and Equation 2.

$$W'_{ij} = (\delta_i - \delta_j)^2 \tag{3}$$

By definition (*7*)

$$\delta_i = (\Delta E_i^{\text{ideal}} / V_i^0)^{1/2} \tag{4}$$

Column 8 lists δ_2 obtained from Equation 3 with solvent-solute interchange energies calculated with (*7*)

$$\ln \frac{\gamma_2 x_2}{\phi_2} = \frac{V_2^0 \phi_1^2 W'}{RT} + \left(1 - \frac{V_2^0}{V_1^0}\right)\phi_1 \tag{5}$$

instead of with Equation 2. Equation 5 includes a Flory-Huggins entropy factor to account for effects arising from dissimilar molecular size of the solution components. The solubility parameters of the solvents used in Equation 3 were obtained from energies of vaporization through Equation 4.

Discussion. The solubilities of *p*-dibromobenzene agree well with previously reported values in three of four instances. As a small standard deviation is found in all the binary systems, including that involving toluene, the solubility of *p*-dibromobenzene in that solvent appears to be significantly greater than previously reported (*9*). It was noted visually in this work that no solid phase is present in a synthesized system with a *p*-dibromobenzene mole fraction of 0.236. This concentration is greater by 0.006 than the previously reported saturation value. The rate of solution of the solid solute was rather slow in this system.

The mean value of the solubility parameter of *p*-dibromobenzene is 9.80 ± 0.33 by Equation 2 and 9.89 ± 0.36 by Equation 5. Hence, inclusion of the Flory-Huggins entropy factor does not produce significant improvement in the constancy of the solubility parameter. This was also true when naphthalene was used as the solute (*3*). There, also, the solubility parameter of naphthalene determined in cyclohexane was significantly different from the values obtained with the other solvents (*3*). Here, however, the relative difference between the cyclohexane-solute system and the other binary systems is less pronounced.

The similarity of the extent of naphthalene-solvent and the *p*-dibromobenzene–solvent interactions is evident in several ways: γ_2 for saturated solutions in a given solvent, molar solvent-solute interchange energies and solubility parameters.

TERNARY SYSTEMS

Results. Columns 2 and 3 of Table II list the composition of the solvent mixtures in mole and volume fractions, respectively. The solubility of *p*-dibromobenzene in solvent mixtures is listed as mole and volume fractions in Columns 4 and 5.

If only pairwise interaction is assumed, equations corresponding to Equations 1 and 2 for binary systems can be written for ternary systems (*3*):

$$RT \ln \gamma_2 = x_1^2 W_{12} + x_3^2 W_{23} + x_1 x_3 \, (W_{12} + W_{23} - W_{13}) \tag{6}$$

$$RT \ln \gamma_2 = V_2^0 [\phi_1^2 W'_{12} + \phi_3^2 W'_{23} + \phi_1 \phi_3 (W'_{12} + W'_{23} - W'_{13})] \tag{7}$$

For the three ternary systems for which the solvent-solvent interchange energies are known, experimental solubilities are compared with those predicted by Equations 6 and 7 in Columns 6 and 7. The solvent-solvent interchange energies used in calculations relating to Table II have been listed previously (*3–5*).

A volume interchange energy of the solute-mixed solvent, W'_{02}, may be defined as (*3*, *7*)

$$W'^{1/2}_{02} = \phi_1^0 W'^{1/2}_{12} \pm \phi_3^0 W'^{1/2}_{23} \tag{8}$$

where W'_{12} and W'_{23} are the corresponding quantities for the individual solute-solvent pairs. Assuming a Raoult entropy of mixing, W'_{02} obtained from Equation 8 can be incorporated into an equation (*3*, *7*),

$$RT \ln \gamma_2 = V_2^0 (1 - \phi_2)^2 W'_{02} \tag{9}$$

for the calculation of γ_2 and hence solute solubility. Column 8 compares experimental solubility data with values obtained using Equation 9 and solute-mixed solvent volume interchange energies from Equation 8.

A suitable means of comparing results by Equations 8 and 9 for the two different solutes is through the use of a deviation function. By this method, disagreement arising from systematic errors in the various solute-solvent interchange energies are eliminated. Such errors result from relatively uncertain values in the properties of the supercooled liquid solutes. Thus, both molal volumes and heats of fusion of the solutes are involved in the present calculations. As noted previously (*3*), the ideal solubility of naphthalene reported in the literature varies from 0.298 to 0.322 mole fraction. For *p*-dibromobenzene, fewer literature values are available, but it is likely that similar uncertainty exists. As an illustration of the effect of such uncertainty in the ideal solubility of the solute, ±0.01 mole fraction of the solute at saturation is equivalent to ±0.4 cal. ml.$^{-1}$ in solute-solvent W' or ±40 cal. mole^{-1} in solute-solvent W.

Figure 1 compares experimental and calculated values of $(W'_{02})^{1/2}$ for each solute. The experimental values are obtained by treatment of the experimentally determined solubility with Equation 9, and calculated values are directly from Equation 8. By this device Equation 9 is applied in a manner the opposite of that used in comparisons in the last column of Table II. A difference of zero for a solute in Figure 1 indicates that the experimental data adhere to the linear dependence of $(W'_{02})^{1/2}$ on solvent composition predicted by Equation 8. The size of the data points in Figure 1 correspond to an uncertainty of ±0.0005 mole fraction in measured solubility—that is, about ±0.15 in $(W'_{02})^{1/2}$.

Discussion. For all except the hexadecane–carbon tetrachloride system, the *p*-dibromobenzene solubility (mole fraction) decreases monotonically from the solvent of greater to the solvent of lesser solvent action toward the solute. In the hexadecane–carbon tetrachloride solvent

Table II. Solubility of *p*-Dibromobenzene in Binary Solvent Mixtures

Solvent Pair	Initial Solvent Composition		Expt. *p*-Dibromobenzene Solubility		Solubility 10^3 (Exptl. − Calculated)		
	Mole fract. solvent 1	Vol. fract. solvent 1	Mole fract.	Vol. fract.	Eq. 6	Eq. 7	Eq. 8, 9
Carbon tetrachloride–cyclohexane	0.1975	0.1802	0.1297	0.142	1	2	2
	0.3977	0.3709	0.1465	0.165	1	2	2
	0.5999	0.5724	0.1632	0.184	2	2	2
	0.8005	0.7818	0.1786	0.205	1	2	2
Hexadecane-hexane	0.1987	0.3553	0.1013	0.0751	7	−1	−5
	0.3989	0.5973	0.1165	0.0734	10	−1	−7
	0.5954	0.7668	0.1288	0.0710	9	−2	−6
	0.8024	0.9007	0.1399	0.0682	5	−2	−5
Hexadecane–carbon tetrachloride	0.1966	0.4256	0.1693	0.150			−6
	0.4024	0.6710	0.1574	0.111			−8
	0.6008	0.8201	0.1531	0.0901			−6
	0.8030	0.9251	0.1514	0.0762			−4
Hexadecane-ethylbenzene	0.1896	0.3586	0.2184	0.174			0
	0.3939	0.6083	0.1973	0.132			0
	0.5943	0.7778	0.1796	0.103			1
	0.8033	0.9071	0.1644	0.0815			1
Hexadecane-benzene	0.1959	0.4449	0.2099	0.195			7
	0.3927	0.6802	0.1888	0.139			6
	0.5895	0.8253	0.1726	0.105			2
	0.7925	0.9263	0.1601	0.0821			1
Toluene-hexane	0.1945	0.1639	0.1174	0.110	0	4	−1
	0.3985	0.3498	0.1557	0.152	0	7	−4
	0.5982	0.5473	0.1908	0.192	0	6	−7
	0.8014	0.7662	0.2230	0.232	1	4	−6
Average deviation					3	3	4

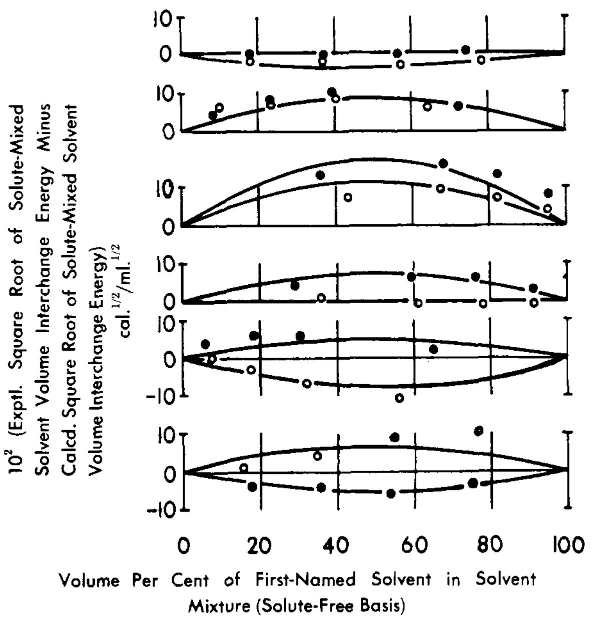

Figure 1. Solute-mixed solvent volume interchange energy

Solvent systems
1 Carbon tetrachloride–cyclohexane
2 Hexane-hexadecane
3 Hexadecane–carbon tetrachloride
4 Hexadecane-ethylbenzene
5 Benzene-hexadecane
6 Toluene-hexane

Solutes
○ *p*-Dibromobenzene
● Naphthalene

system, a minimum occurs at about 0.8 mole fraction of hexadecane in the mixed solvent. This behavior was also encountered when naphthalene was the solute in that same mixed solvent system (*5*), and the minimum was more pronounced there.

The use of Equations 6 and 7 in predicting departures from ideality could not be fully evaluated owing to the sparse literature values of solvent-solvent interaction. For the three systems in which a comparison is possible, the results are comparable. The use of Equations 8 and 9 in the last column of Table II results in errors rather comparable to those in Columns 6 and 7.

In Figure 1, smoothed curves have been arbitrarily drawn to a symmetrical form as an aid in noting the actual trend of the deviations from zero ordinate. Figure 1 and Table II show that as a first approximation the validity of Equation 8 in the present mixed solvent systems is not strongly dependent upon the identity of the solute. For practical usage Equation 8 is a useful approximation in predicting behavior in nonelectrolyte systems of mixed solvents.

The significance of both the difference in behavior of a mixed solvent toward each solute and the departure of each individual curve from a zero value of the deviation function is not uniform among the various systems. Thus, in both the first and last systems in Figure 1, the behavior approaches *s*-regularity. This can be shown by combining for a given solute, solubility data from both single solvent and mixed solvent systems and calculating apparent values of the solvent-solvent interaction, W_{13} or W'_{13} via Equations 6 and 7. For *p*-dibromobenzene in, respectively, the first and last systems, the solvent-solvent W values, which are constant within about ±10 cal. mole^{-1}, are 100 and 330 cal. mole^{-1} when determined in this manner. For naphthalene the corresponding quantities are 70 and 300 cal. mole^{-1} (*4, 5*). These results are comparable to the literature values of 67 cal. mole^{-1} for the carbon tetrachloride-cyclohexane mixture and 330 cal. mole^{-1} (*10*) for the toluene-hexane mixture, both obtained from binary data. The agreement between the two solutes and the literature values thus is within the uncertainty in the ideal solubility of the solutes. The remaining systems fail to follow even the less restrictive regular model (*7*).

NOMENCLATURE

ΔE^{ideal} = ideal molar energy of vaporization
ΔG^E = molar excess Gibbs free energy of mixing
R = gas constant
T = absolute temperature
V^0 = molar volume
W = interchange energy, cal. mole^{-1}
W' = interchange energy, cal. ml.$^{-1}$
x = mole fraction
δ = solubility parameter
γ = activity coefficient
ϕ = volume fraction
ϕ^0 = volume fraction in solute-free mixed solvent

Subscripts

i, j = components i, j
1, 3 = solvents
2 = solute
02 = mixed solvent-solute

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RECEIVED for review May 19, 1966. Accepted January 3, 1967. Southeastern Regional Meeting, ACS, Louisville, Ky., October 1966.

Derivatives of 4,4′-Isopropylidenebis(2,6-dichlorophenol)

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Nine bis esters, six bis ethers, three bis amides, and one bis acid of 4,4′-isopropylidenebis(2,6-dichlorophenol) are described along with their significant infrared spectral data.

THE COMPOUND 4,4′-isopropylidenebis(2,6-dichlorophenol), commonly known as tetrachlorobisphenol A, is easily prepared by chlorination of the parent diphenol (*1*). Although this chlorinated product (m.p. 133–134° C.) is well known to the literature as a flame-retardant epoxy and polycarbonate resin intermediate (*2*, *3*), few monomolecular derivatives have been reported.

Nineteen derivatives of tetrachlorobisphenol A have now been prepared and are described in Table I. These include five aromatic and aliphatic carboxylic acid bis esters (I-V), two bis sulfonates (VI and VII), one known bis phosphonate (VIII), one bis thionocarbamate (IX), six aliphatic and arylaliphatic bis ethers (X-XV), three bis amides (XVI-XVIII), and one bis acid (XIX). Pertinent infrared spectral data are recorded in Table II.

EXPERIMENTAL

All products were prepared by well established organic chemical processes. The infrared spectral data were obtained on a Beckman Model IR-5, sodium chloride prism, infrared spectrophotometer. Nujol mulls, containing approximately 40% of the compound, were prepared in the usual manner. The spectra were obtained through a film of the mulls (about 10 microns) between sodium chloride salt plates.

Method A. Tetrachlorobisphenol A (0.1 mole) was dissolved in 125 ml. of dry pyridine. The acyl chloride (0.21 mole) was added slowly with stirring while maintaining the temperature at 35° C. over a 15-minute period. The reaction mixture was then heated at 50° to 80° C. for 2 hours, cooled to room temperature, and poured into 500 ml. of ice water with stirring. When the precipitated gummy mass had broken up and become solid, the solid was filtered and washed with 100 ml. of 3% sodium hydroxide solution, then 100 ml. of 3% hydrochloric acid and finally with water. The product was dried and recrystallized from an appropriate solvent.

Method A1. After the reaction mixture was poured into ice water, the pyridine was removed by azeotropic distillation. The gummy mass or solid was removed by decantation and recrystallized from an appropriate solvent.

Method A2. After the reaction mixture was poured into