

Thermochemical Investigations of Nearly Ideal Binary Solvents. 6. Solubilities of Iodine and Benzil in Systems of Nonspecific Interactions

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Solubilities have been determined at 25°C for iodine in binary mixtures of carbon tetrachloride with cyclohexane, n-hexane, n-heptane, and octamethylcyclotetrasiloxane (OMCTS) and in mixtures of cyclohexane with n-hexane and OMCTS; and for benzil in binary mixtures of carbon tetrachloride with cyclohexane, n-hexane, and n-heptane, mixtures of n-hexane with cyclohexane and n-heptane, and mixtures of benzene with cyclohexane and toluene. With the exception of the benzene + cyclohexane system, the nearly ideal binary solvent model predicts these solubilities with a maximum deviation of 6% and an overall standard deviation of 2.4%. The model correctly predicts minima for solubility (mole fraction) of iodine in the OMCTS systems, and predicts solubilities within 4% for benzil in the carbon tetrachloride + n-hexane system, in which the solubility changes by a factor of 14. The failure of the model for predicting solubilities of benzil in mixtures of benzene and cyclohexane (maximum error of 25% for an 18-fold range of solubilities) is possibly due to specific interactions between benzil and benzene.

KEY WORDS: iodine and benzil solubilities in binary solvent mixtures; solubility predictions; specific interactions; nonspecific interactions; nearly ideal binary solvent model.

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1. INTRODUCTION

In this series of papers,⁽¹⁻⁵⁾ we have investigated the applications and limitations of a simple equation for the excess partial molar properties of a solute $(\Delta Z_3^e)^*$ at infinite dilution in a binary solvent (components 1 and 2), using the properties of the solute in each of the pure solvents and the excess properties of the solvent pair ΔZ_{12}^e

$$\Delta Z_3^e = f_1^0(\Delta Z_3^e)_1^* + f_2^0(\Delta Z_3^e)_2^* - \Gamma_3(X_1^0\Gamma_1 + X_2^0\Gamma_2)^{-1}(\Delta Z_{12}^e) \quad (1)$$

$$f_1^0 = (1 - f_2^0) = X_1^0\Gamma_1/(X_1^0\Gamma_1 + X_2^0\Gamma_2) \quad (2)$$

in which Γ_i are weighting factors, and X_i^0 are mole fractions of the solvents before addition of solute. The partial molar property of the solute is estimated as a weighted average of its properties in the pure solvents, with a contribution from 'unmixing' the solvents. Because of the difficulties involved in estimation of the weighting factor Γ_3 of the solute, we have suggested replacement of the last term of Eq. (1) with an approximation based on molar volumes⁽⁵⁾

$$\Gamma_3(X_1^0\Gamma_1 + X_2^0\Gamma_2)^{-1}(\Delta Z_{12}^e) = V_3^0(X_1^0V_1^0 + X_2^0V_2^0)^{-1}(\Delta Z_{12}^e) \quad (3)$$

and have suggested a method of estimating relative weighting factors for the solvents. This equation leads to quite accurate predictions of solubilities,⁽³⁾ gas-liquid partition coefficients,⁽⁴⁾ and enthalpies of solution^(2,5) in systems of nonspecific interactions when weighting factors are approximated with molar volumes, though predictions of enthalpies of solution are improved considerably with weighting factors estimated from the excess properties of binary solvent. We have suggested^(4,5) that failure of Eq. (1) might be taken as an indication of specific solvent-solute or solvent-solvent interactions in a system, but we have discovered a possible flaw in the evidence leading to this conclusion. It is possible that failure of Eq. (1) is not due directly to the specific nature of solvent-solute interactions, but instead to the large differences between the excess properties of the solute in the pure solvents, which are normally encountered in systems in which only one solvent interacts specifically with the solute. The applicability of Eq. (1) is not very sensitive to errors in the relative magnitude of the weighting factors for systems in which the excess properties of the solute in the pure solvents are similar, but these errors become much more important as the difference between properties in the pure solvents increases. Thus, the success of Eq. (1) for predicting solubilities

of iodine, naphthalene, and stannic iodide in systems of nonspecific interactions may be due to the narrow ranges of solubilities in these systems (standard free energies of transfer are generally less than 2 kJ-mol⁻¹), and the failure to predict solubilities of iodine in systems containing benzene may be due to the large differences in solubility (up to 5 kJ-mol⁻¹ for standard free energies of transfer).

The present research was designed in part to test this possible flaw in the applicability of Eq. (1) with a solute, benzil, for which solubility changes by a factor of 14 between solvents *n*-hexane and carbon tetrachloride, corresponding to 6.5 kJ-mol⁻¹ for the standard free energy of transfer. Greater ranges of solubility of benzil are found in systems containing benzene, but dipole moment measurements of benzil in benzene and in carbon tetrachloride have been interpreted as evidence for specific interactions of benzil with benzene but not with carbon tetrachloride.⁽⁶⁾ This allows comparison of the applicability of Eq. (1) to systems with and without specific solvent-solute interactions over a comparable range of solubilities. Benzil also provides a better test for the approximation of Eq. (3), since its molar volume (estimated as 183 cm³-mol⁻¹) is considerably larger than that of any other solute for which we have measured solubilities.

In an earlier study,⁽³⁾ we developed three forms of the solubility equation using different approximations for weighting factors and different models of solution ideality in Eq. (1):

$$RT \ln(a_3^{\text{solid}}/X_3^{\text{sat}}) = (1 - X_3^{\text{sat}})^2 [X_1^0(\Delta G_3^c)_1^* + X_2^0(\Delta G_3^c)_2^* - (\Delta G_{12}^c)] \quad (4)$$

$$RT \ln(a_3^{\text{solid}}/X_3^{\text{sat}}) = (1 - \phi_3^{\text{sat}})^2 [\phi_1^0(\Delta G_3^c)_1^* + \phi_2^0(\Delta G_3^c)_2^* - V_3^0(X_1^0V_1^0 + X_2^0V_2^0)^{-1}(\Delta G_{12}^c)] \quad (5)$$

$$RT[\ln(a_3^{\text{solid}}/\phi_3^{\text{sat}}) - (1 - \phi_3^{\text{sat}})(1 - \frac{V_3^0}{X_1^0V_1^0 + X_2^0V_2^0})] = (1 - \phi_3^{\text{sat}})^2 [\phi_1^0(\Delta G_3^{\text{th}})_1^* + \phi_2^0(\Delta G_3^{\text{th}})_2^* - V_3^0(X_1^0V_1^0 + X_2^0V_2^0)^{-1}(\Delta G_{12}^{\text{th}})] \quad (6)$$

in which a_3^{solid} is the activity of the solid solute relative to the pure supercooled liquid (estimated from the melting point and enthalpy of fusion), ϕ_i is volume fraction, V_i^0 is the molar volume of a pure liquid, and

$$\Delta G_{12}^{\text{th}} = \Delta G_{12}^c + RT[\ln(X_1^0V_1^0 + X_2^0V_2^0) - X_1^0 \ln V_1^0 - X_2^0 \ln V_2^0] \quad (7)$$

We have concluded^(2,3) that Eq. (4) is inferior to the other two equations for systems in which the molar volumes of the components differ substantially, and that Eq. (6) appears to be slightly better than Eq. (5) for systems of this type. However, in the systems we have studied to date, the predictions of Eqs. (5) and (6) differ by no more than 3% of the solubility, which is normally determined to $\pm 1\%$. Calculations on the solubility of iodine in systems containing octamethylcyclotetrasiloxane (OMCTS) showed that the predictions of Eqs. (5) and (6) differed by more than 11% in some cases, thus providing a more sensitive test of the relative accuracy of these two equations. The most striking differences between these equations were predicted for the OMCTS + cyclohexane and OMCTS + carbon tetrachloride systems, in which Eq. (6) predicts minima in the solubility curves, and Eq. (5) does not. Therefore, we have determined the solubilities of iodine in these and a few other systems.

Table I. Mole Fraction in Pure Solvents at 25.0°C

Solute (3)	Solvent	$10^3 X_3^{\text{sat}}$ (This Work)	$10^3 X_3^{\text{sat}}$ (Literature)
Iodine	<i>n</i> -Hexane	6.14	6.23, ^a 6.37 ^b
Iodine	<i>n</i> -Heptane	6.91	6.93, ^a 6.92, ^c 6.79 ^d
Iodine	OMCTS	8.26	8.16 ^e
Iodine	Cyclohexane	9.15	9.01, ^d 9.03, ^f 8.74, ^g 9.18 ^h
Iodine	CCl ₄	11.26	11.47, ^d 11.24 ^h
Benzil	Benzene	180.4	179 ⁱ

^a Ref. 17. ^b J. H. Hildebrand and J. Dymond, *Proc. Natl. Acad. Sci. N.Y.* **54**, 1001 (1965). ^c G. Kortum and V. M. Vogel, *Z. Elektrochem.* **59**, 16 (1955). ^d J. H. Hildebrand and C. A. Jenks, *J. Am. Chem. Soc.* **42**, 2180 (1920). ^e K. Shinoda and J. H. Hildebrand, *J. Phys. Chem.* **61**, 789 (1957). ^f Ref. 16. ^g J. H. Hildebrand, H. A. Benesi, and L. M. Mower, *J. Am. Chem. Soc.* **72**, 1017 (1950). ^h S. E. Wood, B. D. Fine, and L. M. Isaacs, *J. Phys. Chem.* **61**, 1605 (1957). ⁱ B. H. Carroll, G. K. Rollefson, and J. H. Mathews, *J. Am. Chem. Soc.* **47**, 1785 (1925).

2. EXPERIMENTAL

2.1. Materials for the Iodine Study

Fisher Certified ACS Resublimed iodine was used as received. Cyclohexane (Fisher Certified ACS), *n*-hexane (Fisher Certified 99%), and *n*-heptane (Aldrich 99+% Gold Label) were stored over KOH pellets and distilled shortly before use. Carbon tetrachloride (Fisher Spectranalyzed) was further purified by the method of Scatchard, Wood, and Mochel,⁽⁷⁾ then distilled from molecular sieves (Type 4A) shortly before use. OMCTS (Silar) was used as received.

2.2. Materials for the Benzil Study

Benzil (Eastman) was recrystallized several times from methanol, giving a melting point of 95 ± 0.5 °C (literature value 95.2 °C⁽⁸⁾). Cyclohexane (Aldrich, Gold Label), *n*-heptane (Aldrich Gold Label), *n*-hexane (Fisher, Certified 99%), benzene (Aldrich, Gold Label), and toluene (Fisher, Certified 99%) were stored over molecular sieves (Type 4A) and distilled shortly before use. Carbon tetrachloride (Aldrich, Gold Label) was further purified by the method described above.

2.3. Solubility Measurements

Binary solvent mixtures were prepared by weight so that compositions could be calculated to 0.0001 mole fraction. Excess solute and solvent were placed in brown glass bottles and allowed to equilibrate for several days in a constant temperature bath at 25.00 ± 0.01 °C. The attainment of equilibrium was verified by repetitive measurements after several additional days, and in some cases by approaching equilibrium from supersaturation by pre-equilibrating the solution at a higher temperature. Iodine solutions were analyzed by the method described previously.⁽³⁾ Aliquots of benzil solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample. The solvent was then allowed to evaporate at room temperature, and the sample was diluted quantitatively with ethanol. Concentrations were determined spectrophotometrically at 390 nm on a Beckmann Model DU spectrophotometer. All solubilities were reproducible to within $\pm 1\%$. Our solubility measurements in pure solvents show good agreement with data available in the literature (Table I), as are our measurements in binary mixtures of *n*-hexane with cyclohexane

Table II. Properties of Pure Components at 25 °C

Component	V^d	Component	V^d	$a_R(\text{solid})$
Benzene	89.40	Iodine	59.59 ^b	0.258 ^c
CCl ₄	97.08	Benzil	183 ^d	0.224 ^e
Toluene	106.84			
Cyclohexane	108.76			
<i>n</i> -Hexane	131.59			
<i>n</i> -Heptane	147.48			
OMCTS	314			

^aUnits: cm³-mol⁻¹. ^bS. E. Wood, B. D. Fine, and L. M. Isaacson, *J. Phys. Chem.* **61**, 1605 (1957). ^cJ. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, 'Regular and Related Solutions', (Van Nostrand-Reinhold, New York, N.Y., 1970) p 142. ^dEstimated from the density of the liquid at 102 °C (Ref. 8) and the coefficient of thermal expansion for benzophenone calculated over the range 50-95 °C (Ref. 10). This is in reasonable agreement with limiting partial molar volumes of benzil in benzene (179 cm³-mol⁻¹), toluene (179 cm³-mol⁻¹), and nitrobenzene (183 cm³-mol⁻¹) calculated from data in Ref. 11. ^eBased on the enthalpy of fusion (22.15 cal-gm⁻¹) at the melting point (368.3 K) from Ref. 8.

and with carbon tetrachloride.⁽⁹⁾

3. RESULTS AND DISCUSSION

The properties of the pure components used in subsequent calculations can be found in Table II. Solubilities of iodine and percentage deviations between observed values and the predictions of Eqs. (4), (5), and (6) are given in Table III. The predictions of Eq. (4) are slightly better in the cyclohexane + *n*-hexane system, though the differences are not really significant, but this equation is the poorest approximation for most of the systems studied. Eq. (6) correctly predicts minimum solubility in both systems containing OMCTS, but these systems do not distinguish between Eqs. (5) and (6) on the basis of deviations from experimental data. The best approximation for these systems, and for all of the systems of nonspecific interactions we have considered, appears to be an average of the predictions of Eqs. (5) and (6). However, of the two equations, we still prefer Eq. (6) on the basis of its correct prediction of the minimum solubility of iodine in these two systems containing OMCTS, and of *p*-dibromobenzene⁽¹²⁾ and naphthalene⁽¹³⁾ in the carbon tetrachloride + *n*-hexadecane system.

Solubilities of benzil and comparisons of the predictions of Eqs.

Table III. Comparison of Observed and Predicted Solubilities of Iodine (3) in Some Binary Solvents at 25°C

X_1^0	X_3^{sat}	$100 \ln (X_3^{\text{sat}})_{\text{calc}} / (X_3^{\text{sat}})_{\text{obsd}}$		
		Eq. (4)	Eq. (5)	Eq. (6)
<i>CCl₄(1) + n-Heptane(2) ΔG_{12}^{c} (Ref. 22)</i>				
0.0000	0.00691	-	-	-
0.2451	0.00767	4.8	-0.5	-1.1
0.2966	0.00784	5.7	-0.4	-1.1
0.5667	0.00891	7.4	-0.4	-1.4
0.7806	0.00997	5.4	-0.4	-1.1
0.7814	0.01000	5.2	-0.7	-1.5
0.8599	0.01047	3.3	-0.9	-1.5
1.0000	0.01126	-	-	-
<i>CCl₄(1) + OMCTS(2) ΔG_{12}^{c} (Ref. 20)</i>				
0.0000	0.00826	-	-	-
0.2885	0.00803	7.7	5.3	-1.1
0.3610	0.00806	8.9	7.4	-1.8
0.6095	0.00848	10.8	5.7	-5.3
0.6924	0.00874	10.8	5.6	-5.9
0.7686	0.00900	10.8	5.7	-5.2
0.8772	0.00984	7.3	2.6	-5.1
0.9119	0.01008	6.5	2.7	-3.5
0.9529	0.01064	3.2	0.8	-3.0
1.0000	0.01126	-	-	-
<i>n-Hexane(1) + CCl₄(2) ΔG_{12}^{c} (Ref. 23)</i>				
0.0000	0.01126	-	-	-
0.2798	0.00945	5.9	0.6	-1.1
0.4289	0.00862	6.8	-0.8	-1.4
0.5538	0.00800	6.6	-0.9	-1.5
0.5840	0.00784	6.6	-0.8	-1.3
0.7428	0.00715	4.6	-1.0	-1.5
0.8392	0.00670	3.8	0.0	-0.2
1.0000	0.00614	-	-	-
<i>Cyclohexane(1) + n-Hexane(2) ΔG_{12}^{c} (Ref. 25)</i>				
0.0000	0.00614	-	-	-
0.1937	0.00670	1.0	-1.2	-1.3
0.4188	0.00738	1.9	-1.8	-1.9
0.5687	0.00788	1.6	-2.3	-2.4
0.6221	0.00803	1.8	-2.0	-2.1
0.7199	0.00836	1.4	-2.0	-2.0
1.0000	0.00915	-	-	-

Table III. (Continued)

X_1^o	X_3^{sat}	$100 \ln (X_3^{sat})_{calc} / (X_3^{sat})_{obsd}$		
		Eq. (4)	Eq. (5)	Eq. (6)
Cyclohexane(1) + OMCTS(2) ΔG_{12}^E (Ref. 21)				
0.0000	0.00826	-	-	-
0.2658	0.00798	4.3	4.1	-1.0
0.3443	0.00797	4.8	4.5	-1.9
0.3560	0.00798	4.8	4.4	-2.1
0.5324	0.00804	5.3	4.6	-4.1
0.5981	0.00805	5.8	4.8	-4.3
0.8009	0.00835	5.4	4.1	-3.9
0.9272	0.00875	3.0	2.2	-1.9
1.0000	0.00915	-	-	-
Cyclohexane(1) + CCl ₄ (2) ΔG_{12}^E (Ref. 24)				
0.0000	0.01126	-	-	-
0.2244	0.01091	0.7	-0.7	-0.6
0.3039	0.01076	0.9	-0.7	-0.7
0.3711	0.01054	1.3	-0.5	-0.4
0.5443	0.01024	1.1	-0.8	-0.7
0.5999	0.01014	0.8	-1.0	-0.9
0.8084	0.00962	0.8	-0.4	-0.2
0.8145	0.00961	0.9	-0.4	-0.3
1.0000	0.00915	-	-	-

(4), (5), and (6) are given in Table IV. Comparison of the deviations for the predictions of these three equations for systems of varying ranges of solubility illustrates the dependence of these predictions on the choice of weighting factors. Similarity of the deviations for Eq. (5) and Eq. (6) shows that these predictions are not really very dependent on the choice of a regular solution model [Eq. (5)] or a Flory-Huggins solution model (Eq. (6)), since both of these equations use molar volumes as the weighting factors of Eq. (1). The predictions of Eq. (4) are not substantially different from the other equations in systems of 2-fold or smaller ranges of solubility, but these differences increase with increasing ranges of solubility. The predictions of Eqs. (5) and (6) are within 4.5% for the *n*-hexane + carbon tetrachloride system with a 14-fold range of solubilities. Since this range is much greater than the ranges of solubility of iodine in benzene systems for which Eqs. (5) and

(6) fail by as much as 30%,⁽¹⁴⁾ we conclude that these failures are due to specific solvent-solute interactions, rather than simply due to the range of solubilities covered.

All three equations fail badly for the solubility of benzil in the cyclohexane + benzene system. Deviations between observed solubilities and the predictions of Eqs. (5) and (6) are qualitatively very similar to those for iodine in systems containing benzene. These failures for both solutes in systems containing benzene suggest that the situation could be corrected simply by changing the weighting factor for benzene, but this is not compatible with the observation that Eqs. (5) and (6) give good predictions for solubilities of naphthalene and *p*-dibromobenzene in several systems containing benzene. The failure of the Nearly Ideal Binary Solvent (NIBS) method for iodine + benzene and benzil + benzene systems is more likely related to the existence of specific solvent-solute interactions. Charge-transfer complexes between iodine and benzene are well-documented⁽¹⁵⁾ and there is evidence that some specific interaction between benzil and benzene affects the apparent (or effective) dipole moment of benzil in benzene.⁽⁶⁾ Irrespective of these specific solvent - solute interactions, the NIBS model gives excellent predictions for the solubility of benzil in benzene + toluene mixtures. This success may be taken as an indication that the specific interactions of benzil with toluene are very similar to those with benzene, but is more likely an indication that failure of the NIBS model for systems with specific solvent-solute interactions arises from the approximation of weighting factors. The failure of Eq. (1) for the enthalpy of solution of squalane in the benzene + chloroform system, in which the enthalpies of solution in the pure solvents are quite similar, indicates that the inapplicability of this model to systems of specific solvent-solvent interactions probably arises from the 'unmixing' term of Eq. (1), particularly for very large solute molecules. Therefore, we conclude that Eq. (1) is quite sensitive to specific solvent-solute interactions, provided that the excess partial molar property of the solute differs appreciably in the pure solvents, and to specific solvent-solvent interactions if the molar volume of the solute is sufficiently large relative to the solvents so as to affect the last term of the equation.

Various models of selective solvation have been proposed to modify equations similar to Eq. (1) for iodine-benzene systems. Walkley,⁽¹⁶⁾ and more recently Nakanishi and Asakura,⁽¹⁷⁾ have suggested modification of the weighting factors. Walkley's modification is based on the solubility parameters of the solute and solvents, while

Table IV. Comparison of Observed and Predicted Solubilities of Benzil (3) in Binary Solvents at 25 °C

X_1^o	X_3^{sat}	$100 \ln(X_3^{sat})_{calc}/(X_3^{sat})_{obsd}$		
		Eq. (4)	Eq. (5)	Eq. (6)
<i>n</i> -Hexane(1) + <i>n</i> -Heptane(2) ΔG_{12}^e (Ref. 26)				
0.0000	0.00654	-	-	-
0.1893	0.00641	-0.7	-0.5	-0.4
0.3186	0.00631	-0.8	-0.4	-0.3
0.4943	0.00616	-0.9	-0.4	-0.3
0.5168	0.00611	-0.4	0.0	0.1
0.6432	0.00599	-0.4	0.3	0.4
0.8112	0.00587	-0.5	-0.1	0.0
1.0000	0.00570	-	-	-
Cyclohexane(1) + <i>n</i> -Hexane(2) ΔG_{12}^e (Ref. 25)				
0.0000	0.00570	-	-	-
0.2719	0.00699	-0.7	-1.8	-1.8
0.3586	0.00743	-0.5	-1.9	-1.9
0.6190	0.00874	0.0	-0.8	-0.7
0.6773	0.00907	-0.2	-0.9	-0.8
0.7257	0.00934	-0.2	-0.8	-0.7
0.8531	0.01005	-0.4	-0.5	-0.5
1.0000	0.01072	-	-	-
Cyclohexane(1) + CCl ₄ (2) ΔG_{12}^e (Ref. 24)				
0.0000	0.0804	-	-	-
0.2363	0.0507	1.1	-1.6	-1.9
0.2741	0.0462	2.7	-0.4	-0.7
0.3206	0.0424	2.1	-1.4	-1.7
0.6834	0.0206	0.6	-3.2	-3.4
0.6850	0.0204	0.9	-3.1	-3.2
0.6918	0.0200	1.9	-2.0	-2.2
0.7816	0.01661	1.7	-1.6	-1.7
1.0000	0.01072	-	-	-
Benzene(1) + Toluene(2) ΔG_{12}^e (Ref. 26)				
0.0000	0.1504	-	-	-
0.1296	0.1548	-0.5	-0.6	-0.6
0.2971	0.1588	0.1	-0.1	-0.1
0.4540	0.1638	-0.1	-0.3	-0.3
0.5453	0.1663	0.0	-0.3	-0.3
0.7397	0.1719	0.1	0.0	0.0
1.0000	0.1804	-	-	-

Table IV. Continued

X_1^0	X_3^{sat}	Eq. (4)	$100 \ln (Y_3^{\text{sat}})_{\text{calc}} / (Y_3^{\text{sat}})_{\text{obsd}}$ Eq. (5)	Eq. (6)
<i>n</i> -Heptane(1) + CCl ₄ (2) ΔG_{12}^{c} (Ref. 22)				
0.0000	0.0804	-	-	-
0.1861	0.0445	15.8	-2.5	-2.1
0.3080	0.0313	21.2	-3.6	-2.9
0.4761	0.0204	22.2	-4.7	-3.9
0.6457	0.01355	19.6	-3.3	-2.5
0.7132	0.01169	16.7	-3.3	-2.6
0.8436	0.00885	10.6	-1.7	-1.7
0.8616	0.00853	9.6	-1.5	-1.3
1.0000	0.00654	-	-	-
<i>n</i> -Hexane(1) + CCl ₄ (2) ΔG_{12}^{c} (Ref. 23)				
0.0000	0.0804	-	-	-
0.2230	0.0415	12.0	-1.7	-1.6
0.2669	0.0365	13.4	-2.1	-2.0
0.5420	0.01739	14.6	-4.4	-4.1
0.5635	0.01629	15.2	-3.5	-3.2
0.5684	0.01616	14.7	-4.0	-3.7
0.7618	0.01002	9.8	-3.3	-3.2
0.7685	0.00982	9.9	-3.0	-2.8
1.0000	0.00570	-	-	-
Cyclohexane(1) + Benzene(2) ΔG_{12}^{c} (Ref. 27)				
0.0000	0.1804	-	-	-
0.1997	0.1453	-18.1	-11.9	-12.4
0.3536	0.1068	-26.1	-19.5	-20.4
0.4748	0.0779	-29.0	-24.4	-25.4
0.4754	0.0775	-28.6	-24.1	-25.0
0.7325	0.0318	-19.3	-19.4	-19.9
1.0000	0.01072	-	-	-

that of Nakanishi and Asakura is based on the enthalpy of formation of the specific interaction. Nitta and Katayama⁽¹⁸⁾ have used molar volumes as weighting factors, but have incorporated the equilibrium constant for complex formation into the solubility relationships. We have suggested similar applications of equilibrium constants for correlations of gas-liquid partition coefficients in complexing systems.⁽⁴⁾ With

the exception of Walkley's approach, however, these methods involve empirical parameters and the assumption that equilibrium constants for complex formation are independent of co-solvent and solvent composition, an assumption that is not necessarily valid.⁽¹⁹⁾ The approaches of both Walkley and Nakanishi are limited by their complete dependence on solubility parameter theory, and cannot be expected to apply to systems with negative deviations from Raoult's law, such as the OMCTS systems we have studied.^(20, 21)

Sytilin⁽⁹⁾ has developed an equation for the solubility of iodine in mixed solvents, which we have shown⁽⁴⁾ to be equivalent (with the ideal solution approximation for the molar volume of the binary solvent) to

$$X_3^{\text{sat}} = X_1^0(X_3^{\text{sat}})_1 + X_2^0(X_3^{\text{sat}})_2 \quad (8)$$

For solutes of limited solubility, we have also shown this equation to be thermodynamically equivalent to an equation which has been used to describe gas-liquid partition coefficients in mixed solvents.⁽²⁷⁾ Sytilin's equation is based on the assumption of solvational complexes with all solvents, and the equation for gas-liquid partition coefficients is usually interpreted in terms of solvational complexes with one of the solvents. While Eq. (8) gives reasonable predictions for some of the systems we have studied, these predictions are off by as much as 17% for iodine in the carbon tetrachloride + OMCTS system, and off by a factor of two for benzil in the *n*-hexane + carbon tetrachloride system. These discrepancies could possibly be explained in terms of multiple equilibria, but the good predictions of the NIBS model for these systems indicates an absence of specific solvent-solute interactions.

Unfortunately, this research has not yet resolved the questions of superiority between Eqs. (5) and (6), on the basis of goodness of fit. For simplicity of calculation, Eq. (5) is the preferred form, and some support for this form can be found in its adaptability to solubility parameter theory and the regular solution model. However, Eq. (6) appears to be more general, especially for its applicability to polymer solutions, and more directly related to gas-liquid partition coefficients and molarity-based equilibrium constants as are normally derived from spectrophotometric data.

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