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Solubility in binary solvent systems. 6. Prediction of naphthalene and biphenyl solubilities based on the Wilson model

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Summary

Solubilities have been determined at 30, 35 and 40 °C for biphenyl in carbon tetrachloride, cyclohexane, *n*-hexane, *n*-heptane and *n*-octane, and for naphthalene in benzene, cyclohexane, toluene, ethylbenzene, carbon tetrachloride and *n*-hexane. Results of these measurements, combined with published data at 25 °C, are used to calculate the Wilson interaction parameters and to predict the solubilities of naphthalene and biphenyl in binary solvent mixtures. The Wilson model predicts the binary solvent solubilities to within an average deviation of 2.2%, using as input data the solubilities in the pure solvents.

Introduction

This work continues a systematic search for mixing models and equations which will provide predictions for the thermochemical properties of a solute at high dilution in binary solvent mixtures. In two earlier papers, Acree and Rytting (1982a and b) reported solubilities for benzil and *p*-benzoquinone in binary solvent mixtures containing carbon tetrachloride, in which the mole fraction solubility of benzil and *p*-benzoquinone cover a 14-fold and 6-fold range, respectively. The experimental data were interpreted with solution models developed previously for solubility in systems containing specific solute–solvent interactions and with models of purely non-specific interactions. A stoichiometric complexation model based entirely on specific interactions (non-specific interactions ignored) required several equilibrium constants to mathematically describe the experimental results, while the Nearly Ideal Binary Solvent (NIBS) model, based on non-specific interactions, described adequately the observed solubilities without introducing a single equilibrium constant.

The success of the NIBS approach in predicting the binary solvent effect on benzil and *p*-benzoquinone solubilities suggested the possibility that this solution model may provide a foundation for approximations of the physical interactions even in a system known to contain chemical interactions. To pursue this idea further, Acree et al. (1983) extended the basic NIBS model to systems containing association between the solute (component A) and a complexing cosolvent (component C)

$$A_1 + C_1 \rightleftharpoons AC$$

$$K_{AC} = \frac{\phi_{AC}}{\phi_{A_1} \cdot \phi_{C_1}}$$

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Postulating the formation of a 1:1 anthracene–benzene complex, the authors demonstrated that the solubility of anthracene in benzene + *n*-heptane and benzene + isooctane could be described to within a maximum deviation of 4% using a single equilibrium constant, $K_{AC} = 1.91$. More importantly, it was noted that the determination of solute–solvent equilibrium constants from solubility measurements does depend on the manner in which non-specific interactions are incorporated into the model.

In a follow-up study comparing iodine solubilities in binary solvent mixtures, Acree (1983) compared the solubility-based association constant for the iodine–benzene complex, $K^{c}_{AC} = 0.393\ M^{-1}$, to the spectroscopic values of Bhowmik (1971) determined in cyclohexane ($K^{c}_{AC} = 0.260\ M^{-1}$), methylcyclohexane ($K^{c}_{AC} = 0.252\ M^{-1}$) and *n*-heptane ($K^{c}_{AC} = 0.246\ M^{-1}$) solvents. Deviations of this magnitude are to be expected in comparing independently determined equilibrium constants, particularly in the case of weak association complexes as both specific and non-specific interactions play an important role in determining the total non-ideality of the solution.

Weak complexes pose an additional problem as it is often difficult to distinguish between complexation and preferential solvation. Thermodynamic models that include preferential solvation, such as the Wilson model, have been very successful in describing liquid–vapor equilibria. To date preferential solvation models have been largely ignored in developing predictive expressions for solubility in binary solvent mixtures. Choi et al. (1985) recently demonstrated that the Wilson model could predict biphenyl, naphthalene, fluorene, phenanthrene and acenaphthene solubilities in binary mixtures containing cyclohexane and benzene. The Wilson solute–benzene and solute–cyclohexane interaction parameters, two parameters for each solute–solvent pair, were calculated from solubilities in the pure solvents at several different temperatures. In this paper we compare the predictions of the Wilson model and the NIBS model to experimental solubilities of naphthalene and biphenyl in a wide range of binary solvent mixtures. The 14 systems considered should provide a better indication of the limitations of the Wilson model.

Materials and Methods

Biphenyl (Aldrich) and naphthalene (Aldrich Gold Label) were recrystallized several times from methanol, giving melting points of 69.5 ± 0.5°C and 80.3 ± 0.5°C, respectively. Cyclohexane (Aldrich Gold Label), *n*-heptane (Fisher Spectroanalyzed), *n*-octane (Aldrich Gold Label), *n*-hexane (Aldrich 99%), carbon tetrachloride (Fisher Spectroanalyzed), toluene (Aldrich Gold Label), benzene (Aldrich Gold Label) and ethylbenzene (Aldrich 99%) were stored over molecular sieves (Type 4A) to remove trace amounts of water.

Excess solute and solvent were placed in amber glass bottles and allowed to equilibrate in a constant temperature bath for several days. Random duplicate samples were allowed to equilibrate for a longer period of time, but no significant difference in saturation solubility was observed. Aliquots of saturated biphenyl and naphthalene solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample, and diluted quantitatively with cyclohexane. Biphenyl concentrations were determined spectrophotometrically at 250 nm on a Cary 118 spectrophotometer. Naphthalene con-

TABLE 1

EXPERIMENTAL MOLE FRACTION SOLUBILITIES OF NAPHTHALENE AND BIPHENYL IN SELECTED ORGANIC SOLVENTS AT 30, 35 AND 40°C

Solvent	Temperature (°C)		
	30	35	40
Naphthalene			
Benzene	0.3318	0.3789	0.4243
Carbon Tetrachloride	0.3012	0.3462	0.3981
Cyclohexane	0.1825	0.2251	0.2767
Ethylbenzene	0.3288	0.3705	0.4233
n-Hexane	0.1415	0.1763	0.2216
Toluene	0.3291	0.3711	0.4216
Biphenyl			
Carbon Tetrachloride	0.3956	0.4574	0.5198
Cyclohexane	0.2471	0.3175	0.3948
n-Hexane	0.1608	0.2066	0.2631
n-Heptane	0.1750	0.2214	0.2773
n-Octane	0.1836	0.2293	0.2891

centrations were determined chromatographically on a Varian 3700 gas chromatograph. Experimental biphenyl and naphthalene solubilities at 30, 35, 40 °C are given in Table 1. Experimental results in each solvent represent the average of six determinations with a maximum deviation of about 1%. Experimental naphthalene solubilities are within 3% of literature values (Ward, 1926).

Results and Discussion

The mole fraction solubility of a solute in a liquid mixture, X_3^{sat}, is related to the activity coefficient, γ_3^{sat}, through the basic thermodynamic relationship

$$-\ln X_3^{sat} = \frac{\Delta \bar{H}_3^{fus}(T_{mp} - T)}{R \cdot T \cdot T_{mp}} - \frac{\Delta \bar{C}_p (T_{mp} - T)}{R \cdot T} + \frac{\Delta \bar{C}_p}{R} \cdot \ln(T_{mp}/T) + \ln \gamma_3^{sat} \quad (1)$$

where $\Delta \bar{H}_3^{fus}$ refers to the solute's molar enthalpy of fusion and $\Delta \bar{C}_p$ is the difference in molar specific heat between the liquid and crystalline solute. Eq. 1 is valid if no phase transition occurs in the solid phase between the system temperature T and the solute's melting point temperature, T_{mp}. Additional term(s) must be included when a phase transition does occur (see Weimer and Prausnitz, 1965; Choi and McLaughlin, 1983).

Predictive methods for solubility in binary solvent mixtures can be developed by combining equation 1 with a solution model that relates the activity coefficient to mole fraction composition. The Wilson model (Wilson, 1964) expresses the excess Gibbs free energy $\Delta \bar{G}^{ex}$ and activity coefficients of a ternary mixture

$$\Delta \bar{G}^{ex}/RT = -\sum_{i=1}^{3} X_i \cdot \ln\left\{\sum_{i=1}^{3} X_j \Lambda_{ij}\right\} \quad (2)$$

and

$$\ln \gamma_i = 1 - \ln\left\{\sum_{j=1}^{3} X_j \Lambda_{ij}\right\} - \sum_{k=1}^{3} \left\{\frac{X_k \Lambda_{ki}}{\sum_{j=1}^{3} X_j \Lambda_{kj}}\right\} \quad (3)$$

where

$$\Lambda_{ij} = (\bar{V}_j/\bar{V}_i) \exp\{-(\lambda_{ij} - \lambda_{ii})/RT\} \quad (4)$$

in terms of six adjustable Λ_{ij}-parameters, two from each of the three binary mixtures. A priori knowledge of the six parameters enables the estimation of solubility in binary solvent mixtures.

The two solvent–solvent interaction parameters, Λ_{12} and Λ_{21}, can be determined by parameterizing the excess Gibbs free energy of the binary solvent system in accordance with Eq. 2 (with $X_3 = 0$). Numerical values of $\Delta \bar{G}^{ex}$ can be found in the chemical literature for many common binary systems. For example, the thermodynamic excess properties of several hundred binary systems have been listed by Gmehling et al. (1977). The solute–solvent interaction parameters are calculated from Eq. 3 using the saturation solubility in each pure solvent at two temperatures. Only one parameter can be determined from each experimental measurement. Inherent in these calculations is the approximation that differences in the characteristic energies, $\lambda_{3i} - \lambda_{33}$ and $\lambda_{i3} - \lambda_{ii}$, are independent of temperature over modest temperature ranges.

Naphthalene and biphenyl solubilities were calculated in several binary solvent systems using Eq. 1 with the activity coefficients calculated from the Wilson model. A summarized comparison between predicted values and experimental solubilities at 25 °C determined by Heric and Posey (1964a and b, 1965) and Acree (1984) appears in Table 2. Each system reports solubility data in both pure solvents and in 4–6 binary mixtures covering the entire range of solvent composition. Deviations expressed in percentages are on the order of 2–4% for most of the binary solvent mixtures. Properties used in the calculations include the calorimetric data of Ward (1934) and Plato and Glasgow (1969) for naphthalene and biphenyl, respectively. Binary interaction parameters used in the Wilson predictions are listed in Table 3. The solute–solvent interaction parameters were evaluated from the experimental solubilities at 25 and 40 °C. These temperatures were selected because they covered a sufficient temperature range to ensure a noticeable difference in the activity coefficients. Further-

TABLE 2

SUMMARIZED COMPARISON BETWEEN THE WILSON PREDICTIONS, NIBS PREDICTIONS AND EXPERIMENTAL SOLUBILITIES FOR NAPHTHALENE AND BIPHENYL IN SEVERAL BINARY SOLVENT MIXTURES AT 25°C

Solvent Systems	RMS Deviations (%)[a]		$\Delta\bar{G}_{12}^{ex}$
	Wilson	NIBS[b]	Ref.
Solute = Naphthalene			
Benzene + Cyclohexane	3.1	−1.1	c
Benzene + Carbon tetrachloride	+3.0	+1.9	c
Benzene + *n*-Hexane	+7.2	1.4	d
Carbon tetrachloride + Cyclohexane	+1.0	−0.6	c
Cyclohexane + *n*-Hexane	0.6	0.6	e
Benzene + Toluene	+0.6	+0.6	f
Carbon tetrachloride + *n*-Hexane	+3.2	0.5	d
Ethylbenzene + Cyclohexane	+3.0	0.3	g
Solute = Biphenyl			
Cyclohexane + Carbon tetrachloride	+1.0	+0.7	c
Cyclohexane + *n*-Heptane	+0.9	0.6	h
Carbon tetrachloride + *n*-Hexane	+2.8	0.7	d
Cyclohexane + *n*-Hexane	−1.4	+0.5	e
Cyclohexane + *n*-Octane	0.4	0.6	i
Carbon tetrachloride + *n*-Heptane	+2.5	+0.6	j

[a] RMS Deviations (%) = $(100/N^{1/2})\{\Sigma^n[\ln(X_{calc}^{sat}/X_{exp}^{sat})]^2\}^{1/2}$. The algebraic sign indicates the deviations were all of the same sign.

[b] Predictions based on Equation VV from Acree and Bertrand (1977).

[c] Goates, et al. (1959).

[d] Jain et al. (1970).

[e] Li et al. (1973).

[f] Rowlinson (1959).

[g] Jain and Yadav (1974).

[h] Young, et al. (1977).

[i] Jain and Yadav (1971).

[j] Bissell and Williamson (1975).

more, evaluation of the solute–solvent interaction parameters in this manner insured that the Wilson model correctly predicted solute solubility in each pure solvent at 25°C.

Included in the summarized solubility comparison are the corresponding predictions of the Nearly Ideal Binary Solvent model

$$RT\left[\ln\left(a_3^{solid}/\phi_3^{sat}\right) - \left(1-\phi_3^{sat}\right) \times \left(1 - \frac{\bar{V}_3}{X_1^0\bar{V}_1 + X_2^0\bar{V}_2}\right)\right] = \left(1-\phi_3^{sat}\right)^2\left[\phi_1^0\left(\Delta\bar{G}_3^{fh}\right)_{X_1=1}^{*} + \phi_2^0\left(\Delta\bar{G}_3^{fh}\right)_{X_2=1}^{*} - \bar{V}_3\left(X_1^0\bar{V}_1 + X_2^0\bar{V}_2\right)^{-1}\Delta\bar{G}_{12}^{fh}\right] \quad (5)$$

the symbols being defined in an earlier paper (Acree and Bertrand, 1977). Inspection of the last two columns of Table 2 reveals that the NIBS predictions are slightly superior to those of the Wilson model. It must be remembered, however, that the NIBS model was developed for predicting the thermochemical properties of the solute (which

TABLE 3

BINARY INTERACTION PARAMETERS USED IN THE WILSON PREDICTIONS

Component (i) + Component (j)	Λ_{ij}	Λ_{ji}
Cyclohexane + Naphthalene	0.788	0.380
Benzene + Naphthalene	0.598	1.369
Carbon tetrachloride + Naphthalene	1.106	0.600
n-Hexane + Naphthalene	0.611	0.371
Toluene + Naphthalene	0.575	1.382
Ethylbenzene + Naphthalene	0.627	1.311
Cyclohexane + Biphenyl	0.744	0.364
n-Hexane + Biphenyl	0.450	0.348
n-Heptane + Biphenyl	0.411	0.426
n-Octane + Biphenyl	0.398	0.474
Carbon tetrachloride + Biphenyl	1.057	0.689
Benzene + Toluene	1.000	1.000
Benzene + Carbon tetrachloride	0.940	0.930
Benzene + Cyclohexane	0.830	0.697
Cyclohexane + Carbon tetrachloride	0.827	1.068
Cyclohexane + *n*-Hexane	1.394	0.552
Carbon tetrachloride + *n*-Hexane	1.255	0.575
Cyclohexane + *n*-Heptane	0.944	0.944
Cyclohexane + *n*-Octane	1.377	0.602
Carbon tetrachloride + *n*-Heptane	1.338	0.553
Ethylbenzene + Cyclohexane	0.476	1.232
Benzene + *n*-Hexane	0.960	0.500

in this case is the solubility) in binary solvent mixtures containing only non-specific interactions. The Wilson model, on the other hand, incorporates the ideas of local composition and preferential solvation. As a result, the Wilson model is expected to provide better predictions in systems having weak specific interactions where the molecules are not randomly oriented in solution. Preliminary calculations support this idea. The Wilson model predicts the solubility of iodine in benzene + carbon tetrachloride mixtures at 25°C to within an average (RMS) deviation of +6.2% and is superior to Eq. 5 of the NIBS model which has an average (RMS) deviation of −13.2%; the algebraic sign indicating that all deviations were of the same sign.

Readers are reminded that the description of iodine–benzene systems with preferential solvation model does not exclude the possibility that solute–solvent complexation does occur. Rather, the goal of this study is to develop and test predictive expressions for solubility in binary solvent systems based only on a priori knowledge of solute solubility in each pure solvent and the measured thermodynamic properties of the solvent mixture. Prediction of solubilities using a solute–solvent association model does require a priori knowledge of all equilibrium constants.

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