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Thermochemical investigations of associated solutions. II. Calculation of iodine–benzene equilibrium constants from solute solubility in binary solvent mixtures

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Summary

Solubilities have been determined at 25°C for iodine in binary mixtures of benzene with *n*-hexane, *n*-heptane and isooctane. The results of these measurements are compared to solution models previously developed for solubility in systems containing only non-specific interactions and to models assuming solute–solvent complexation. The Nearly Ideal Binary Solvent Model (NIBS) based entirely on non-specific interactions provides rather poor predictions of the iodine solubilities, with some of deviations greater than 25%. In comparison, a 1 : 1 solute–solvent complexation model describes the experimental solubilities to within a maximum deviation of 6%. An example is presented to illustrate the calculation of association constants from solubility measurements.

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, the basic NIBS model was extended to systems containing association between the solute (component A) and a complexing cosolvent (component C)

$$A_1 + C_1 \rightleftharpoons AC$$

$$K^{\phi}_{AC} = \frac{\phi_{AC}}{\phi_{A_1}\phi_{C_1}}$$

A relatively simple expression was developed (Acree et al., in press) for the determination of solute–solvent equilibrium constants from the measured solubility as a function of solvent composition and the excess Gibbs free energy of the binary solvent mixture

$$RT\left[\ln\left(a_A^{solid}/\phi_{A_1}^{sat}\right) - 1 + \bar{V}_A\left(\frac{\phi_{A_1}}{\bar{V}_A} + \frac{\phi_B}{\bar{V}_B} + \frac{\phi_C}{\bar{V}_C}\right)\right] =$$

$$(1-\phi_A^{sat})^2\left[\phi_B^0\left(\Delta\bar{G}_A^{fh}\right)_B^{\infty} + \phi_C^0\left(\Delta\bar{G}_A^{fh}\right)_C^{\infty} - \bar{V}_A\left(X_B^0\bar{V}_B + X_C^0\bar{V}_C\right)^{-1}\Delta\bar{G}_{BC}^{fh}\right] \quad (1)$$

with the overall volume fraction solubility, ϕ_A^{sat}, being related to the solubility of the *uncomplexed* solute and the equilibrium constant by

$$\phi_A^{sat} = \phi_{A_1}^{sat}\left[1 + \bar{V}_A K^{\phi}_{AC}\phi_{C_1}/\left(\bar{V}_A + \bar{V}_C\right)\right] \quad (2)$$

and the quantities $(\Delta\bar{G}_A^{fh})_B^{\infty}$ and $(\Delta\bar{G}_A^{fh})_C^{\infty}$ being calculated from the appropriate binary reduction of Eqn. 1

$$\left(\Delta\bar{G}_A^{fh}\right)_B^{\infty} = (1-\phi_A^{sat})^{-2}RT\left[\ln\left(a_A^{solid}/\phi_A^{sat}\right) - (1-\phi_A^{sat})\left(1 - \frac{\bar{V}_A}{\bar{V}_B}\right)\right] \quad (3)$$

$$\left(\Delta\bar{G}_A^{fh}\right)_C^{\infty} = (1-\phi_A^{sat})^{-2}RT\left[\ln\left(a_A^{solid}/\phi_{A_1}^{sat}\right) - 1 + \bar{V}_A\left(\frac{\phi_{A_1}}{\bar{V}_A} + \frac{\phi_C}{\bar{V}_C}\right)\right] \quad (4)$$

using the molar volumes of the pure components, $\bar{V}_i$, and the solubilities in the two pure solvents. The superscript (o) denotes that the solvent compositions are calculated as if the solute were not present.

Postulating the formation of a 1 : 1 anthracene–benzene complex, the authors

demonstrated that Eqn. 1 could describe the solubility of anthracene in benzene + *n*-heptane and benzene + isooctane mixtures to within a maximum deviation of 4% using a single value of $K^{\phi}_{AC} = 1.91$. 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 the case of anthracene solubilities' failure to include non-specific interactions led to a calculated value of $K^{\phi}_{AC} = 4.07$ for the anthracene–benzene complex in solvent mixtures containing *n*-heptane.

Since the afore-mentioned study represents the only application of Eqn. 1 to solubility measurements, I thought that it would be worthwhile to provide several additional examples using a fairly well-documented complex, such as the iodine–benzene charge transfer complex. Presented here are the solubilities of iodine in benzene + *n*-hexane, benzene + *n*-heptane and benzene + isooctane mixtures, and the interpretation of the experimental results in accordance with Eqn. 1.

TABLE I

MOLE FRACTION SOLUBILITIES OF IODINE IN SEVERAL BINARY SOLVENT MIXTURES CONTAINING BENZENE AT 25°C

Solvent (B) + Solvent (C)	X^{0}_{B}	X^{sat}_{A}
n-Hexane + Benzene	0.0000	0.04852
	0.1404	0.03811
	0.2538	0.03199
	0.4005	0.02423
	0.5723	0.01739
	0.7354	0.01210
	1.0000	0.00614
n-Heptane + Benzene	0.0000	0.04852
	0.3115	0.02868
	0.3898	0.02478
	0.4796	0.02108
	0.5451	0.01849
	0.6700	0.01456
	0.7673	0.01188
	0.8695	0.00938
	0.9470	0.00801
	1.0000	0.00691
Isooctane + Benzene	0.0000	0.04852
	0.2815	0.02731
	0.4772	0.01840
	0.5816	0.01528
	0.6645	0.01268
	0.7292	0.01107
	0.8082	0.00922
	0.9004	0.00753
	1.0000	0.00592

Materials and methods

Iodine was Matheson Coleman and Bell Certified ACS Reagent Grade. Aldrich benzene, *n*-heptane, *n*-hexane and isooctane were stored over molecular sieves and were distilled shortly before use. Binary solvent mixtures were prepared by weight so that mole fraction compositions could be calculated to 0.0001.

Excess solute and solvent were placed in amber glass bottles and allowed to equilibrate in a constant temperature bath at 25.0°C for several days. Attainment of equilibrium was verified by repetitive measurements after several additional days. Iodine concentrations were determined by transferring a weighed aliquot of the saturated solution to a flask containing a known excess of aqueous arsenic trioxide, and then back-titrating the solution with freshly standardized iodine solution to the starch endpoint. Experimental solubilities of iodine in several binary solvent mixtures are given in Table 1. The experimental results at each composition represent the average of at least 8 determinations with a maximum deviation of about 1.5%.

Results and Discussion

Despite the complex appearance of Eqn. 1, its predictive application to solubilities in mixed solvents is relatively straightforward, and is similar in concept to the numerical example presented in an earlier paper (Acree and Rytting, 1983) for systems containing only non-specific interactions. The quantities $(\Delta\bar{G}_A^{fh})_B^{\infty}$ and $(\Delta\bar{G}_A^{fh})_C^{\infty}$ are calculated from the volume fraction solubility of the solid in the pure solvents using an *assumed* value for the equilibrium constant. These quantities, along with the excess Gibbs free energy of the binary solvent mixture (usually obtained from the literature), are then used in Eqn. 1 to calculate ϕ_A^{sat} via a reiterative approach. The entire procedure can be repeated until one obtains the numerical value of K_{AC}^{ϕ} which best describes the experimental solubility in a particular binary solvent mixture.

When the solubility is sufficiently small, $\phi_A^{sat} \approx 0$ and $1 - \phi_A^{sat} \approx 1$, very reasonable estimates of K_{AC}^{ϕ} are often obtainable from a simplified form of Eqn. 1 relating the overall solute solubility in the binary solvent mixture to the solubility in the two pure solvents, $(\phi_A^{sat})_B$ and $(\phi_A^{sat})_C$:

$$\ln \phi_A^{sat} = \phi_B^0 \ln(\phi_A^{sat})_B + \phi_C^0 \ln(\phi_A^{sat})_C + \ln\left[1 + \bar{V}_A K_{AC}^{\phi} \phi_C^0/(\bar{V}_A + \bar{V}_C)\right]$$

$$- \phi_C^0 \ln\left[1 + \bar{V}_A K_{AC}^{\phi}/(\bar{V}_A + \bar{V}_C)\right] + \frac{\bar{V}_A \Delta\bar{G}_{BC}^{fh}}{RT(X_B^0 \bar{V}_B + X_C^0 \bar{V}_C)} \qquad (5)$$

To calculate the equilibrium constant, one substitutes the solute solubility at a particular solvent composition (e.g. $\phi_C \approx 0.5$) into Eqn. 5 and solves the resulting mathematical expression for K_{AC}^{ϕ}. For example, if one wished to evaluate the iodine–benzene association constant from the iodine solubility in the benzene + isooctane system at $X_C^0 = 0.5228$ ($\phi_C^0 = 0.3710$), one solves Eqn. 5 using the ap-

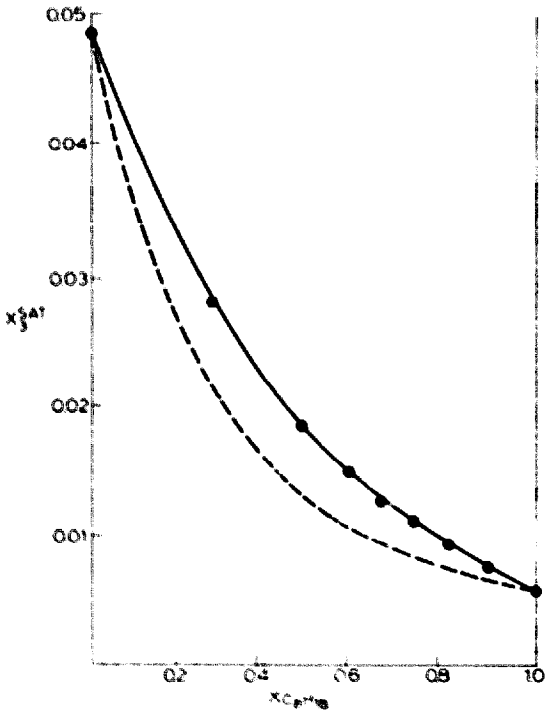

Fig. 1. Comparison between the experimental solubilities (●) and the predictions of Eqn. 1 using $K^{\phi}_{AC} = 0$ (— — —) and $K^{\phi}_{AC} = 11.0$ (———) for iodine in binary mixtures of isooctane and benzene.

propriate available data [1] and obtains $K^{\phi}_{AC} = 11.0$.

Graphical comparison between the experimental solubilities and predictions of Eqn. 1 (with $K^{\phi}_{AC} = 11.0$) is shown in Fig. 1 for iodine in benzene + isooctane mixtures. Included in this comparison are the NIBS predictions based entirely on non-specific interactions ($K^{\phi}_{AC} = 0$). Inspection of the figure reveals that the solubility behavior of iodine cannot be described by expressions derived from purely non-specific interactional models as deviations between experimental and predicted values are on the order of 20–30%. Rather, the 'best' description of experimental data requires the formation of a 1 : 1 iodine–benzene complex. As stated earlier, the existence of a charge transfer complex between iodine and benzene is fairly well-documented in the literature (Benesi and Hildebrand, 1948, 1949; Mulliken 1952a and b). The fact that Eqn. 1 requires a non-zero value of K^{ϕ}_{AC} is particularly gratifying and supports earlier contentions that the magnitude of deviations between

[1] The values of $(\phi_A^{sat})_C = 0.03286$, $(\phi_A^{sat})_B = 0.002137$ and $\phi_A^{sat} = 0.008788$ used in solving Eqn. 5 for $K^{\phi}_{AC} = 11.0$ were obtained using the ideal molar volume approximation together with the experimental solubilities listed in Table 1, and pure component molar volumes previously published (Acree and Bertrand, 1977). The value of $\Delta\bar{G}^{fh}_{BC} = 120.5$ cal/mol was obtained from the work of Weissman and Wood (1960). For calculational simplicity, I have assumed that the volume fraction of the *uncomplexed* solvent, ϕ_{C_f}, equals the stoichiometric volume fraction of component C in the initial binary solvent mixture, ϕ^0_C.

experimental solubilities and predictions based on non-specific interactional models may be useful in identifying systems having specific solute–solvent interactions.

Although Eqn. 1 (with $K^{\phi}_{AC} = 11.0$) predicts the iodine solubilities to within a maximum deviation of 6%, it was noted that the predictions for binary mixtures containing either *n*-hexane or *n*-heptane are always greater than the experimental solubilities. Decreasing the equilibrium constant slightly leads to improved predictions for these two solvent systems, and one can conceivably optimize the value of K^{ϕ}_{AC} by considering all 3 solvent systems at once. Since I am interested in the predictive application of Eqn. 1, I have elected to calculate K^{ϕ}_{AC} from known solubility data in a given solvent system, and then use this value to estimate solubilities in a second solvent system. By doing this, one naturally assumes that the association constant does not vary appreciably from one solvent system to another. There is no reason, however, to expect K^{ϕ}_{AC} to be independent of solvent system, and there have been several studies suggesting that K^{ϕ}_{AC} may indeed vary in going from one solvent system to another (Buchowski et al., 1966; Houng et al., 1969). This subject will certainly merit further study as more experimental solubilities in complexing systems become available.

Spectroscopic studies of Bhowmik (1971) provide an independent determination of the iodine–benzene equilibrium constant in cyclohexane ($K^{c}_{AC} = 0.260\ M^{-1}$), methylcyclohexane ($K^{c}_{AC} = 0.252\ M^{-1}$) and *n*-heptane ($K^{c}_{AC} = 0.246\ M^{-1}$). Although the numerical value of $K^{\phi}_{AC} = 11.0$ is much larger than the 3 molar equilibrium constants, direct comparison requires all constants to be based on an identical concentration scale. Doing this conversion, we find

$$K^{c}_{AC} = K^{\phi}_{AC} \cdot \frac{\bar{V}_A \bar{V}_C}{\bar{V}_A + \bar{V}_C}$$

reasonable agreement between the solubility-based equilibrium constant, $K^{c}_{AC} = 0.393\ M^{-1}$, and the spectroscopic constants. Deviations of this magnitude are to be expected in comparing independently determined equilibrium constants, particularly in the case of weak association complexes.

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