Thermochemical Investigations of Associated Solutions: Calculation of Solute-Solvent Equilibrium Constants from Solubility Measurements

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Abstract □ A simple solution model that has lead to successful predictive equations for the partial molar excess properties of a solute in simple binary solvent mixtures containing only nonspecific interactions is extended to include association between the solute and one of the solvent components. An expression is derived and tested for its ability to describe anthracene solubilities in binary solvent mixtures containing benzene. The best description of the experimental solubilities requires the formation of a 1:1 anthracene-benzene complex, with a molarity-based equilibrium constant of $K_{AC}^{\circ} \approx 0.107 M^{-1}$. In comparison, a stoichiometric complexation model which attributes all solubility enhancement to the formation of anthracene-benzene complexes requires a somewhat larger equilibrium constant ($K_{AC}^{\circ} \approx 0.228 M^{-1}$) to describe the solubility behavior of anthracene in the benzene-*n*-heptane system. The results of these calculations illustrate that the determination of solute-solvent equilibrium constants from solubility data depends on the theoretical model used and the manner in which nonspecific interactions are incorporated into the model.

Keyphrases □ Solute-solvent interactions—determination of equilibrium constants from solubility measurements, comparison of the stoichiometric and nearly ideal binary solvent models □ Solvent systems—binary, anthracene solubility determinations in benzene mixtures using the nearly ideal binary solvent model □ Solubility—binary solvent systems, extension of the nearly ideal binary solvent model to include solute-solvent complexation

Current approaches for predicting solubility often overlook the role of specific interactions in determining the solubilities of organic solids in organic solvents. As part of a continuing study on the thermochemical properties of a solute at high dilution in binary solvent mixtures (1-8), this paper considers the calculation of solute-solvent equilibrium constants from solubility measurements.

Historically, the interpretation of solution nonideality has followed two dissimilar lines of reasoning: the physical approach originated by van Laar (9) and the chemical approach proposed by Dolezalek (10). The physical approach may be described by a random distribution of molecules throughout the entire solution, while the chemical approach may be characterized by a specific geometric orientation of one molecule with respect to an adjacent molecule. Even in systems known to contain specific interactions, the need to properly account for nonspecific interactions is recognized.

Arnett *et al.* (11, 12) attempted a classical separation of specific and nonspecific interactions with their "pure" base calorimetric method for determining enthalpies of hydrogen bond formation. The sensitivity of the numerical results to the selection of the model compound and inert solvent (13) points out the difficulty in separating the physical and chemical contributions of solution nonideality. Christian *et al.* (14, 15) proposed a model for relating the thermodynamic properties of polar solutes involved in complex equilibria to those of analogous nonpolar so-

lutes in the same solvent media. In the nonpolar analogue method, the polar solute is replaced by a hypothetical nonpolar molecule which has the same molecular volume and the same total energy of interaction with a nonpolar solvent as does the polar solute. Saluja *et al.* (16) used a somewhat similar rationale in their comparison of enthalpies of transfer of alkenes and the corresponding alkanes from the vapor state to methanol, dimethylformamide, benzene, and cyclohexane, with the more exothermic values for the alkenes in methanol and dimethylformamide attributed to dipole-induced dipole interactions between the solvent and the polarizable π -bond.

Many of the remaining methods for studying association phenomena can be classified as solubility methods. That is, the increase in solubility of a solute at constant fugacity in a complexing-inert solvent mixture, relative to the solubility in pure inert solvent, is generally attributed to the formation of molecular complexes. This primary assumption is common to several thermodynamic methods, such as the partition of solutes between two immiscible liquid phases, the measurement of infinite dilution GC partition coefficients, and the increased solubility of solids. The techniques for calculating formation constants are essentially identical for all solubility methods, as are the difficulties in properly assessing what portion of the observed solubility enhancement is due to nonspecific interactions.

In earlier papers, the experimental solubilities for benzil (5) and *p*-benzoquinone (6) in binary solvent mixtures containing carbon tetrachloride were reported, in which the mole fraction solubility of benzil and *p*-benzoquinone cover a 14- 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 nonspecific interactions. A stoichiometric complexation model based entirely on specific interactions (nonspecific interactions ignored) required several equilibrium constants to mathematically describe the experimental results, while the simple nearly ideal binary solvent (NIBS) model based on nonspecific interactions adequately described 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 suggests the possibility that this model may provide a foundation for approximations of the physical interactions even in a system containing chemical interactions such as association between the solute and a complexing solvent. To pursue this idea further, the basic NIBS model

is extended to complexing systems and an expression is derived for the calculation of solute-solvent equilibrium constants from solubility measurements. Equilibrium constants for presumed benzene-anthracene complexes are calculated from the newly derived expression and are compared with values calculated from a stoichiometric complexation model based entirely on specific interactions. Although the magnitude of the calculated equilibrium constants are relatively small, and perhaps meaningless, the calculations do illustrate the importance of including nonspecific interactions, particularly in the case of weak association complexes.

THEORETICAL

Stoichiometric Complexation Model—Stoichiometric complexation models have been used frequently to quantitatively explain enhanced solubilities of a polar organic solute in binary mixtures containing an inert hydrocarbon and a polar cosolvent. The basic model assumes complexation between the solute, A, and an interacting cosolvent, C (17-21):

Each reaction is described by an appropriate equilibrium constant with concentrations expressed in molarities:

$$K_{AC}^s = \frac{C_{AC}}{C_{A_1}^s C_{C_1}} \quad (\text{Eq. 1})$$

$$K_{AC_n}^s = \frac{C_{AC_n}}{C_{AC_{n-1}} C_{C_1}} \quad (\text{Eq. 2})$$

where $C_{A_1}^s$ is the saturation solubility of solute in pure inert hydrocarbon (assumed to represent the free solute concentration in binary mixtures as well) and C_{C_1} is the free (uncomplexed) ligand concentration. This particular model assumes only a single solute molecule is present in each complex, but the mathematical form of the resulting equations is not significantly altered by additional solute molecules per complex.

The total solubility of solute in any system, C_A^{tot} , can be expressed as:

$$C_A^{\text{tot}} = C_{A_1}^s + K_{AC}^s C_{A_1}^s C_{C_1} + K_{AC_2}^s K_{AC}^s C_{A_1}^s C_{C_1}^2 + \dots \quad (\text{Eq. 3})$$

and the total concentration of complexing agent, C_C , as:

$$C_C = C_{C_1} + K_{AC}^s C_{A_1}^s C_{C_1} + 2K_{AC_2}^s K_{AC}^s C_{A_1}^s C_{C_1} + \dots \quad (\text{Eq. 4})$$

If only 1:1 solute-solvent complexes are present, Eqs. 3 and 4 can be combined to give:

$$\text{Fractional change in solubility} = \frac{C_A^{\text{tot}} - C_{A_1}^s}{C_{A_1}^s} = \frac{K_{AC}^s C_C}{1 + K_{AC}^s C_{A_1}^s} \quad (\text{Eq. 5})$$

and a plot of the fractional change in solubility *versus* added ligand gives a straight line, with the equilibrium constant calculated from the slope.

Direct graphical evaluation of equilibrium constants is also possible for systems having both 1:1 and 1:2 solute-solvent complexes. Suitable mathematical manipulations of Eqs. 3 and 4 result in:

$$\frac{C_A^{\text{tot}} - C_{A_1}^s}{C_C - 2(C_A^{\text{tot}} - C_{A_1}^s)} = \alpha + \beta[C_C - 2(C_A^{\text{tot}} - C_{A_1}^s)] \quad (\text{Eq. 6})$$

where $\alpha = K_{AC}^s C_{A_1}^s / (1 - K_{AC}^s C_{A_1}^s)$ and $\beta = K_{AC_2}^s C_{A_1}^s / (1 - K_{AC}^s C_{A_1}^s)^2$. Plots of the left-hand side of Eq. 6 *versus* $C_C - 2(C_A^{\text{tot}} - C_{A_1}^s)$ gives a straight line. The two equilibrium constants, K_{AC}^s and $K_{AC_2}^s$, are easily calculated from the slope and intercept.

Graphical determination of the association constants is depicted in Figs. 1 and 2 for anthracene solubilities in binary solvent mixtures containing benzene, as reported previously (8). Inspection of the two figures reveal that the solubility data can be described adequately throughout most of the concentration region. The model, however, does not describe the solubility in pure benzene. Equilibrium constants calculated from the various slopes and intercepts are small in magnitude, *e.g.*, linear least-squares analysis of the anthracene solubilities in benzene-*n*-heptane mixtures *via* Eq. 6 gives $K_{AC}^s = 0.228 \text{ M}^{-1}$ and $K_{AC_2}^s = 0.034 \text{ M}^{-1}$. By reporting these numerical values, we do not intend to imply that anthracene-benzene complexes actually exist in solution. Rather, the experimental solubilities are being used to illustrate the calculation of solute-

solvent equilibrium constants from solubility data and to show that the numerical values of these constants depend on how nonspecific interactions are incorporated into the theoretical model. This is particularly true for weak association complexes.

Although the stoichiometric complexation model mathematically describes the experimental solubilities, one is naturally suspicious of whether the calculated values of K_{AC}^s truly represent specific solute-solvent interactions or the failure of the model to properly describe nonspecific interactions. As demonstrated in an earlier paper (5), experimental solubilities of benzil in simple hydrocarbon mixtures do vary with solvent composition, and there is no reason to expect the free solute concentration to be independent of solvent composition in more complex systems. The failure of Eqs. 5 and 6 to allow for variation in free solute concentration has been one of the main criticisms of this model.

A second limitation of this particular complexation model becomes apparent on writing the solubility expressions in terms of the solubility in the two pure solvents: $(C_{A_1}^s)_B$ and $(C_{A_1}^s)_C$. The complete description of experimental solubility in the pure complexing solvent through Eq. 5 requires:

$$\frac{(C_A^{\text{tot}})_C - (C_A^{\text{tot}})_B}{(C_A^{\text{tot}})_B} = \frac{K_{AC}^s C_C^*}{1 + K_{AC}^s (C_A^{\text{tot}})_B} \quad (\text{Eq. 7})$$

where C_C^* refers to the concentration of pure complexing solvent in the saturated solution. Within limitations of the approximate relationships:

$$C_i = 10^3 X_i^0 / (X_B^0 V_B + X_C^0 V_C) \quad (\text{Eq. 8})$$

and

$$(C_A^{\text{tot}})_i = 10^3 (X_A^{\text{tot}})_i / V_i \quad (\text{Eq. 9})$$

combination of Eq. 5 and 7-9 enables the solubility in binary solvent mixtures to be expressed as a mole fraction average of the values in the two pure solvents:

$$X_A^{\text{tot}} = X_B^0 (X_A^{\text{tot}})_B + X_C^0 (X_A^{\text{tot}})_C \quad (\text{Eq. 10})$$

$$X_B^0 = 1 - X_C^0 = X_B / (X_B + X_C)$$

Predictions using Eq. 10 are off by as much as 50% for *p*-benzoquinone in *n*-heptane-carbon tetrachloride mixtures (6) and are off by a factor of two for benzil in the isooctane-carbon tetrachloride system (5). It is difficult to attribute the failure of Eq. 10 to specific solute-solvent interactions between the solutes and carbon tetrachloride or to the departure from infinite dilution, as the nearly ideal binary solvent approach describes these experimental solubilities to within a maximum deviation of 6% without introducing a single equilibrium constant.

Equation 10 was derived specifically for binary solvent systems containing both a complexing and inert solvent, but comparable equations have been derived from quite dissimilar models. Sytilin (22) described solubility in mixed solvents as:

$$C_A^{\text{tot}} = K_B C_B + K_C C_C \quad (\text{Eq. 11})$$

$$K_i = (C_A^{\text{tot}})_i / C_i^* \quad i = B, C$$

Equation 11 becomes identical to Eq. 10 when the saturation solubility is sufficiently small. Sytilin's expression is based on the assumption of solvational complexes between the solute and solvent and has been applied to systems in which true association is generally not considered to exist (*i.e.*, iodine-*n*-alkane mixtures). While Eq. 10 does provide reasonable predictions for a rather large number of systems, the expression is obviously incapable of describing systems containing either a maximum or minimum mole fraction solubility. Classic examples are found in studies of phenanthrene (23) and 2-nitro-5-methylphenol (24) in cyclohexane-methylene iodide mixtures where the observed solubilities show maximum values that are almost twice that predicted by Eq. 10. Extension of Eq. 11 to include mixed solvates has been proposed by Sytilin (25) as a means of explaining maximum solubilities, but even this explanation seems unsatisfactory since the existence of maximum solubility in these two systems is predicted by solubility parameter theory.

In a series of papers devoted to infinite dilution solubility of volatile third components in binary mixtures of relatively nonvolatile liquids, Purnell and coworkers (26, 27) have shown that a majority of published

¹ The solubility of the solute in the inert solvent $(C_{A_1}^s)_B$ equals the solubility of the uncomplexed solute in the inert solvent $(C_{A_1}^s)_B$.

Figure 1—Graphical determination of K'_{AC} from plots of the fraction change in solubility versus benzene molarity in several binary solvents consisting of benzene and n-hexane (●), n-heptane (●), cyclohexane (Δ), or isooctane (□). The basic model requires additional solute-solvent complexes to explain the nonlinear behavior (see Eqs. 3 and 4).

data can be described by a simple linear relationship between the volume fraction and partition coefficient:

$$K_R^0 = \phi_B(K_R^0)_B + \phi_C(K_R^0)_C \quad (\text{Eq. 12})$$

irrespective of the complexing nature of the solvents. ϕ_B and ϕ_C are volume fractions of solvents B and C, respectively, K_R^0 is the infinite dilution gas-liquid partition coefficient in the mixed solvent, and $(K_R^0)_B$ and $(K_R^0)_C$ refer to the corresponding values of K_R^0 in the pure liquids. Using standard definitions relating partition and activity coefficients, Purnell and Vargas de Andrade (26) have shown that Eq. 12 is equivalent to:

$$\frac{1}{\gamma_A^*} = \frac{X_B^0}{(\gamma_A^*)_B} + \frac{X_C^0}{(\gamma_A^*)_C} \quad (\text{Eq. 13})$$

where γ_A^* is the infinite dilution activity coefficient of the solute (relative to Raoult's law), with only the ideal molar volume approximation.

The activity coefficient of the solute can be related to the solubility of a solid through the thermodynamic relationship:

$$a_A^{\text{solid}} = X_A^{\text{sat}} \gamma_A^{\text{sat}} \quad (\text{Eq. 14})$$

in which the activity of the solid depends on temperature only and is determined relative to the pure supercooled liquid. If the solubility is sufficiently small, the activity coefficient of the solute at infinite dilution may be approximated directly as the activity coefficient at saturation:

$$\gamma_A^{\text{sat}} = \gamma_A^* \quad (\text{Eq. 15})$$

Combination of Eqs. 13-15 yields an expression which is identical to Eq. 10.

The fact that several dissimilar solution models reduce to a common mathematical expression in the limits of low solute solubility suggests that there is often more than one interpretation of solution nonideality that will describe the observed solubility data. Each solution model, therefore, must be judged not only on its ability to describe a particular set of experimental data, but also on the validity and limitations of its underlying assumptions and simplifying approximations.

Extension of the NIBS Approach to Solubility in Complexing Systems—The NIBS treatment has been shown to be quite dependable for estimating heats of solution (28, 29), gas-liquid partition coefficients (1-3), and solubilities (4-8) in binary solvent systems that are free of

Figure 2—Graphical determination of K'_{AC} and K'_{AC1} for anthracene in several binary solvents at 25°. The binary mixtures contained benzene and n-hexane (●), n-heptane (●), cyclohexane (Δ), or isooctane (□).

Figure 3—Comparison between experimental solubilities (●) and the predictions of Eq. 30 (—) for anthracene in binary mixtures of benzene-n-heptane. The free energy of mixing data for the binary solvent (ΔG_{BC}^m) is taken from measurements by Harris and Dunlop (32).

association. The form of the NIBS equation which has been most successful for describing the excess chemical potential of solutes is based on a simple mixing model of a multicomponent system:

$$\Delta G_{1,2,\dots,N}^m = RT \sum_{i=1}^N n_i \ln \phi_i + \left(\sum_{i=1}^N n_i \bar{V}_i \right) \left(\sum_{i=1}^N \sum_{j>i}^N \phi_i \phi_j A_{ij} \right) \quad (\text{Eq. 16})$$

in which n_i is the number of moles of component i , $\bar{V}_i$ is the molar volume of a pure liquid, ϕ_i is the volume fraction, and A_{ij} is a binary interaction parameter that is independent of solvent composition. The application of Eq. 16 to the quaternary system (A_1 , B , C_1 , and AC) takes the form of:

$$\begin{aligned} \Delta G^m = & RT(n_A \ln \phi_A + n_B \ln \phi_B + n_{C_1} \ln \phi_{C_1} + n_{AC} \ln \phi_{AC}) \\ & + (n_A \bar{V}_A + n_B \bar{V}_B + n_{C_1} \bar{V}_{C_1} + n_{AC} \bar{V}_{AC})(\phi_A \phi_B A_{A_1B} \\ & + \phi_A \phi_{C_1} A_{A_1C_1} + \phi_A \phi_{AC} A_{A_1AC} + \phi_B \phi_{C_1} A_{BC_1} \\ & + \phi_B \phi_{AC} A_{BAC} + \phi_{C_1} \phi_{AC} A_{C_1AC}) \quad (\text{Eq. 17}) \end{aligned}$$

The only assumption is that the molar volume of the AC complex equals the sum of the molar volumes of components A and C, i.e., $\bar{V}_{AC} = \bar{V}_A + \bar{V}_C$. The chemical potentials of the individual components relative to the pure liquids (μ_i^*) are obtained through the appropriate differentiation:

$$\begin{aligned} \mu_{A_1} - \mu_A^* = & RT \left(\ln \phi_{A_1} + 1 - \frac{\bar{V}_A}{\bar{V}_{\text{solution}}} \right) \\ & + \bar{V}_A [\phi_B (1 - \phi_{A_1}) A_{A_1B} + \phi_{C_1} (1 - \phi_{A_1}) A_{A_1C_1} + \phi_{AC} (1 - \phi_{A_1}) A_{A_1AC} \\ & - \phi_B \phi_{C_1} A_{BC_1} - \phi_B \phi_{AC} A_{BAC} - \phi_{C_1} \phi_{AC} A_{C_1AC}] \quad (\text{Eq. 18}) \end{aligned}$$

$$\begin{aligned} \mu_B - \mu_B^* = & RT \left(\ln \phi_B + 1 - \frac{\bar{V}_B}{\bar{V}_{\text{solution}}} \right) \\ & + \bar{V}_B [\phi_{A_1} (1 - \phi_B) A_{A_1B} + \phi_{C_1} (1 - \phi_B) A_{BC_1} + \phi_{AC} (1 - \phi_B) A_{BAC} \\ & - \phi_{A_1} \phi_{C_1} A_{A_1C_1} - \phi_{A_1} \phi_{AC} A_{A_1AC} - \phi_{C_1} \phi_{AC} A_{C_1AC}] \quad (\text{Eq. 19}) \end{aligned}$$

and

$$\begin{aligned} \mu_{C_1} - \mu_C^* = & RT \left(\ln \phi_{C_1} + 1 - \frac{\bar{V}_C}{\bar{V}_{\text{solution}}} \right) \\ & + \bar{V}_C [\phi_{A_1} (1 - \phi_{C_1}) A_{A_1C_1} + \phi_B (1 - \phi_{C_1}) A_{BC_1} + \phi_{AC} (1 - \phi_{C_1}) A_{C_1AC} \\ & - \phi_{A_1} \phi_B A_{A_1B} - \phi_{A_1} \phi_{AC} A_{A_1AC} - \phi_B \phi_{AC} A_{BAC}] \quad (\text{Eq. 20}) \end{aligned}$$

where $\bar{V}_{\text{solution}}$ is the molar volume of the true solution and:

$$\frac{1}{\bar{V}_{\text{solution}}} = \frac{\phi_{A_1}}{\bar{V}_A} + \frac{\phi_B}{\bar{V}_B} + \frac{\phi_{C_1}}{\bar{V}_C} + \frac{\phi_{AC}}{\bar{V}_A + \bar{V}_C} \quad (\text{Eq. 21})$$

As shown in many thermodynamic textbooks [e.g., Prigogine and Defay (30)], the chemical potential of stoichiometric component C (and also A) is equal to the chemical potential of the monomeric (uncomplexed) species in the solution:

$$\mu_C = \mu_{C_1} \quad (\text{Eq. 22})$$

Combining Eqs. 18–22, the Gibbs free energy of mixing can be written as:

$$\begin{aligned} \Delta G^m = & RT \left[n_A \ln \phi_{A_1} + n_B \ln \phi_B + n_{C_1} \ln \phi_{C_1} + n_A + n_B + n_C \right. \\ & - \left. \frac{(n_A \bar{V}_A + n_B \bar{V}_B + n_C \bar{V}_C)}{\bar{V}_{\text{solution}}} \right] + (n_A \bar{V}_A + n_B \bar{V}_B + n_C \bar{V}_C)(\phi_A \phi_B A_{A_1B} \\ & + \phi_A \phi_{C_1} A_{A_1C_1} + \phi_A \phi_{AC} A_{A_1AC} + \phi_C \phi_{A_1} A_{A_1C_1} + \phi_C \phi_B A_{BC_1} \\ & + \phi_C \phi_{AC} A_{C_1AC} - \phi_{A_1} \phi_{C_1} A_{A_1C_1} - \phi_{A_1} \phi_{AC} A_{A_1AC} \\ & - \phi_{C_1} \phi_{AC} A_{C_1AC}) \quad (\text{Eq. 23}) \end{aligned}$$

where $n_A = n_{A_1} + n_{AC}$ and $n_C = n_{C_1} + n_{AC}$. Equation 23 obviously contains far too many parameters for useful applications, but reasonable assumptions enable the number of parameters to be greatly reduced. Treatment of all interaction parameters involving the AC complex in a manner similar to that employed by Bertrand (31) for the chloroform-triethylamine complex leads to:

$$A_{A_1AC} = \bar{V}_C^2 (\bar{V}_A + \bar{V}_C)^{-2} A_{A_1C_1} \quad (\text{Eq. 24})$$

and

$$A_{C_1AC} = \bar{V}_A^2 (\bar{V}_A + \bar{V}_C)^{-2} A_{A_1C_1} \quad (\text{Eq. 25})$$

Substitution of these approximations into Eq. 23, after suitable mathematical manipulations, yields the following expression for the Gibbs free energy:

$$\begin{aligned} \Delta G^m = & RT \left[n_A \ln \phi_{A_1} + n_B \ln \phi_B + n_C \ln \phi_{C_1} + n_A + n_B + n_C \right. \\ & - \left. \frac{(n_A \bar{V}_A + n_B \bar{V}_B + n_C \bar{V}_C)}{\bar{V}_{\text{solution}}} \right] + (n_A \bar{V}_A + n_B \bar{V}_B + n_C \bar{V}_C)(\phi_A \phi_B A_{A_1B} \\ & + \phi_B \phi_{AC} A_{BC_1} + \phi_A \phi_{AC} A_{A_1C_1}) \quad (\text{Eq. 26}) \end{aligned}$$

Using the equilibrium condition defined by:

$$\begin{aligned} A_1 + C_1 &= AC \\ K_{AC}^* &= \frac{\phi_{AC}}{\phi_{A_1} \phi_{C_1}} \quad (\text{Eq. 27}) \end{aligned}$$

it can be easily shown that the chemical potential of the solid solute (at saturation) is:

$$\begin{aligned} \mu_A - \mu_A^* = & RT \ln a_A^{\text{solid}} = RT \left(\ln \phi_{A_1}^{\text{sat}} + 1 - \frac{\bar{V}_A}{\bar{V}_{\text{solution}}} \right) \\ & + \bar{V}_A (1 - \phi_{A_1}^{\text{sat}})^2 (\phi_B^{\text{sat}} A_{A_1B} + \phi_{C_1}^{\text{sat}} A_{A_1C_1} - \phi_B^{\text{sat}} \phi_{C_1}^{\text{sat}} A_{BC_1}) \quad (\text{Eq. 28}) \end{aligned}$$

where $\phi_B^{\text{sat}} = 1 - \phi_{A_1}^{\text{sat}} = \phi_B / (\phi_B + \phi_C)$ and a_A^{solid} is the activity of the solid solute. This activity is defined as the ratio of the fugacity of the solid to the fugacity of the pure supercooled liquid and is calculated from:

$$\ln a_A^{\text{solid}} = \int_{T_m}^T (\Delta H_A^{\text{fus}} / RT^2) dT \quad (\text{Eq. 29})$$

with the molar enthalpy of fusion (ΔH_A^{fus}) at the normal melting point (T_m).

Inspection of Eq. 28 reveals that, for model systems obeying this expression, the A_1B and A_1C_1 interaction parameters can be eliminated from the basic model via the saturation solubilities in the pure solvents, and the A_{BC_1} parameter can be eliminated via the excess Gibbs free en-

ergy of the binary solvent mixture calculated according to Eq. 16. Performing these substitutions:

$$RT \left[\ln (a_A^{\text{solid}}/\phi_A^{\text{sat}}) - 1 + \frac{V_A}{V_{\text{solution}}} \right] = (1 - \phi_A^{\text{sat}})^2 [\phi_B^{\text{sat}} (\Delta \bar{G}_B^{\text{h}})^{\text{B}} + \phi_C^{\text{sat}} (\Delta \bar{G}_C^{\text{h}})^{\text{C}} - V_A (X_B \bar{V}_B + X_C \bar{V}_C)^{-1} \Delta \bar{G}_{\text{BC}}^{\text{h}}] \quad (\text{Eq. 30})$$

where:

$$(\Delta \bar{G}_A^{\text{h}})^{\text{B}} = (1 - \phi_A^{\text{sat}})^{-2} RT \left[\ln (a_A^{\text{solid}}/\phi_A^{\text{sat}}) - (1 - \phi_A^{\text{sat}}) \left(1 - \frac{V_A}{V_B} \right) \right] \quad (\text{Eq. 31})$$

and

$$(\Delta \bar{G}_A^{\text{h}})^{\text{C}} = (1 - \phi_A^{\text{sat}})^{-2} RT \left[\ln (a_A^{\text{solid}}/\phi_A^{\text{sat}}) - 1 + V_A \left(\frac{\phi_A^{\text{sat}}}{V_A} + \frac{\phi_C}{V_C} \right) \right] \quad (\text{Eq. 32})$$

The liquid-phase compositions for Eqs. 31 and 32 refer to the saturated pure solvents. In the absence of solute-solvent complexation ($K_{\text{AC}}^{\text{f}} = 0$), the above expression reduces to an equation derived earlier (Eq. VV of Ref. 4) for systems containing only nonspecific interactions.

Despite the complex appearance of Eq. 30, 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 (8) for systems containing only nonspecific interactions. The quantities $(\Delta \bar{G}_A^{\text{h}})^{\text{B}}$ and $(\Delta \bar{G}_A^{\text{h}})^{\text{C}}$ are calculated from the volume fraction solubility of the solid in the pure solvents using an assumed value for the equilibrium constant. These quantities, with the excess Gibbs free energy of the binary solvent mixture (usually obtained from the literature), are then used in Eq. 30 to calculate ϕ_A^{sat} using a reiterative approach. The overall volume fraction solubility, ϕ_A^{sat} , can be calculated from the solubility of the uncomplexed solute and the equilibrium constant:

$$\phi_A^{\text{sat}} = \phi_A^{\text{sat}} [1 + V_A K_{\text{AC}}^{\text{f}} \phi_C / (V_A + V_C)] \quad (\text{Eq. 33})$$

The entire procedure can be repeated until the numerical value of K_{AC}^{f} that best describes the experimental solubility in a particular binary solvent system is obtained.

Graphical comparison between the experimental solubilities and predictions of Eq. 30 (with $K_{\text{AC}}^{\text{f}} = 1.91$) are shown in Figs. 3 and 4 for anthracene in *n*-heptane-benzene and isooctane-benzene mixtures. Properties of the pure components were taken from a previous tabulation (8). Examination of these two figures indicates Eq. 30 can describe adequately the experimental data using a single equilibrium constant². Readers are reminded that the calculation of association constants for a presumed anthracene-benzene complex does not imply the authors believe such a complex actually exists in solution. As in all cases, the presence of molecular complexes should be supported by independent measurements involving spectroscopy, calorimetry, etc.

Although the numerical value of $K_{\text{AC}}^{\text{f}} = 1.91$ is much larger than the equilibrium constant used in Eq. 6, direct comparison requires both constants to be based on an identical concentration scale. Doing this conversion:

$$K_{\text{AC}}^{\text{c}} = K_{\text{AC}}^{\text{f}} \frac{V_A V_C}{(V_A + V_C)} \quad (\text{Eq. 34})$$

one finds that the molarity-based equilibrium constant of Eq. 6 ($K_{\text{AC}}^{\text{c}} = 0.228 M^{-1}$) is actually two times greater than the molarity-based equilibrium constant of Eq. 30 ($K_{\text{AC}}^{\text{f}} = 0.107 M^{-1}$). These calculations further support our earlier observation (5) that equilibrium constants determined from solution models based entirely on specific interactions may not truly represent specific solute-solvent interactions, but rather, in some cases, the failure of the particular solution model to properly describe nonspecific interactions.

RESULTS AND DISCUSSION

A simple solution model that has led to successful predictive equations for the thermochemical properties of a solute in simple binary solvent

² Improvements in the descriptive ability of Eq. 30 could be obtained by permitting the equilibrium constant to vary from one solvent system to another. For example, the best description of the benzene-isooctane system required a slightly larger value for K_{AC}^{f} . This fact is not too disturbing as many of the prevailing solution theories predict that complex formation constants will not be constant in different solvents, even if a maximum-randomness criterion is met by all the species involved in the formation reaction in each of the solvents (34, 35). The numerical value quoted in the text is for the benzene-*n*-heptane system.

Figure 4—Comparison between experimental solubilities (●) and the predictions of Eq. 30 (—) for anthracene in binary mixtures of benzene-isooctane. The free energy of mixing data for the binary solvent is taken from an article by Weissman and Wood (33).

systems containing only nonspecific interactions has been extended to include association between the solute and one of the solvent components. An expression has been derived and tested for its ability to describe anthracene in binary solvent mixtures containing benzene. The best description of the experimental solubilities required the postulation of a 1:1 anthracene-benzene complex, with a molarity-based equilibrium constant of $K_{\text{AC}}^{\text{f}} = 0.107 M^{-1}$. In comparison, a stoichiometric complexation model that attributes all solubility enhancement to the formation of anthracene-benzene complexes required a larger equilibrium constant ($K_{\text{AC}}^{\text{f}} = 0.228 M^{-1}$) to describe the six-fold mole fraction range of anthracene solubilities in the benzene-*n*-heptane system. That the two equilibrium constants differ by a factor of two demonstrates the importance of including nonspecific interactions in equilibrium constant calculations, particularly in the case of weak association complexes.

Furthermore, it has been shown that several dissimilar solution models, developed previously for predicting solubility in binary solvent mixtures, reduce to a common mathematical expression in the limits of low solute solubility. Based on this observation, we conclude that there may be more than one interpretation of solution nonideality that will describe the observed solubility data. As criteria for selecting the best description of solution nonideality, we suggest that each solution model should be judged on its ability to describe the thermochemical properties of the solute (in this case, solubility) and on the validity of the model's underlying assumptions and simplifying approximations.

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