

Thermochemical Investigations of Associated Solutions

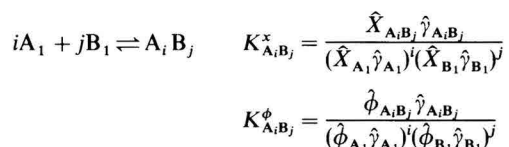
Part 14.—Calculation of Anthracene–Butyl Acetate Association Parameters from Measured Solubility Data

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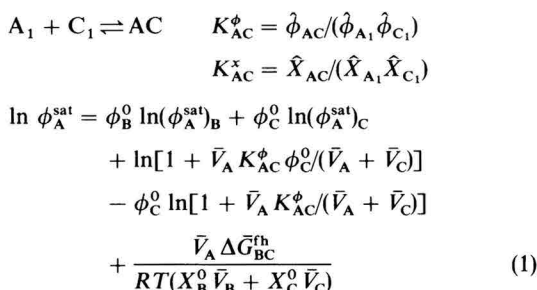
Experimental solubilities are reported for anthracene dissolved in binary solvent mixtures containing butyl acetate with n-hexane, n-heptane, n-octane, cyclohexane, methylcyclohexane and 2,2,4-trimethylpentane at 25.0 °C. Results of these measurements, combined with estimates for the excess Gibbs free energies of the binary solvents, are used to evaluate the equilibrium constant for a presumed anthracene–butyl acetate molecular complex from the extended nearly ideal binary solvent model. A single association constant was needed to describe the experimental data to within an average deviation of 2%. The numerical value of the calculated constant varied slightly with inert hydrocarbon cosolvent, ranging from $K_{AC}^{\phi} = 4.5$ in 2,2,4-trimethylpentane to an upper value of $K_{AC}^{\phi} = 8.0$ in both cyclohexane and methylcyclohexane cosolvents.

Molecular complexation occurs in many systems having both chemical and engineering significance. Calculation of meaningful association constants is an important first step in understanding solution non-ideality at the molecular level. Interpretation of solution non-ideality follows two dissimilar lines. The physical approach assumes a random distribution of molecules throughout the entire solution, whereas a chemical approach is characterized by a specific orientation of one molecule with respect to an adjacent neighbouring molecule. Strong molecular interactions are generally treated by invoking a dynamic equilibrium between a presumed molecular complex and the uncomplexed monomers



with the equilibrium constant being expressed in either mole fraction ($K_{A_i B_j}^x$) or volume fraction ($K_{A_i B_j}^{\phi}$) concentration units. Chemical effects are contained in the concentration ratio while the much weaker physical interactions are incorporated into the activity coefficients. Neglect of non-specific physical interactions can lead to an appreciable error in the calculated equilibrium constant, particularly in the case of weak molecular complexes.^{1,2}

Earlier papers in this series have been primarily devoted to the development of simple mixing models for describing the thermodynamic excess properties of associated solutions containing AB, AC and/or AC₂ molecular complexes. Expressions were derived for the calculation of volume-fraction-based and mole-fraction-based solute–solvent association constants from experimental solute solubility using the infinite-dilution form of the extended nearly ideal binary solvent (NIBS) model^{1–6}



$$\ln X_A^{\text{sat}} = \phi_B^0 \ln(X_A^{\text{sat}})_B + \phi_C^0 \ln(X_A^{\text{sat}})_C + \ln[1 + K_{AC}^x X_C^0]$$

$$- \phi_C^0 \ln[1 + K_{AC}^x] + \frac{\bar{V}_A \Delta \bar{G}_{BC}^{\text{ex}}}{RT(X_B^0 \bar{V}_B + X_C^0 \bar{V}_C)} \quad (2)$$

and the competitive associated NIBS model^{7,8}



$$\ln \phi_A^{\text{sat}} = \phi_B^0 \ln(\phi_A^{\text{sat}})_B + \phi_C^0 \ln(\phi_A^{\text{sat}})_C$$

$$- \phi_B^0 \ln[1 + \bar{V}_A K_{AB}^{\phi} / (\bar{V}_A + \bar{V}_B)]$$

$$+ \ln[1 + \bar{V}_A K_{AB}^{\phi} \phi_B^0 / (\bar{V}_A + \bar{V}_B)]$$

$$+ \bar{V}_A K_{AC}^{\phi} \phi_C^0 / (\bar{V}_A + \bar{V}_C)]$$

$$- \phi_C^0 \ln[1 + \bar{V}_A K_{AC}^{\phi} / (\bar{V}_A + \bar{V}_C)]$$

$$+ \frac{\bar{V}_A \Delta \bar{G}_{BC}^{\text{rh}}}{RT(X_B^0 \bar{V}_B + X_C^0 \bar{V}_C)} \quad (3)$$

In the absence of solute–solvent complexation, eqn. (1) (with $K_{AC}^{\phi} = 0$) and eqn. (3) (with $K_{AC}^{\phi} = K_{AB}^{\phi} = 0$) reduce to the basic NIBS model, which has been shown to provide very reasonable predictions for enthalpies of solution, gas–liquid chromatographic partition coefficients and solid–solute solubilities in binary solvent mixtures. (The NIBS model is reviewed in greater detail in a monograph.⁹) Activity coefficients are absent from the equilibrium constant expressions as the extended NIBS and competitive associated NIBS models require that the $\hat{\gamma}_{AC} / \hat{\gamma}_{A_1} \hat{\gamma}_{C_1}$ and $\hat{\gamma}_{AB} / \hat{\gamma}_{A_1} \hat{\gamma}_{B_1}$ ratios be independent of mixture composition. This constant ratio does not necessarily equal unity, however, and it is incorporated into the calculated K_{AC}^{ϕ} , K_{AC}^x and K_{AB}^{ϕ} values. The superscript (ˆ) indicates the ‘true’ compositions of the various species in the associated solution, rather than the stoichiometric concentrations. Other symbols used in eqn. (1)–(3) are defined in the Glossary.

To date, the extended NIBS model has described experimental solubilities for carbazole dissolved in 10 binary alkane–dibutyl ether mixtures ($K_{AC}^{\phi} = 25.3 \pm 2.7$),^{2,5,6} for pyrene in six binary alkane–1,4-dichlorobutane mixtures ($K_{AC}^{\phi} = 14.2 \pm 2.4$)¹⁰ and for anthracene in six binary alkane–1-chlorobutane mixtures ($K_{AC}^{\phi} = 3.9 \pm 1.3$)¹¹ to within an average absolute deviation of ca. ±2% using a single equilibrium constant. The equilibrium constant did vary slightly from one inert hydrocarbon cosolvent to another. Success of eqn. (1) in describing these three sets of systems suggests that

the extended NIBS model will provide a suitable basis for investigating weak molecular complexes in non-electrolyte solutions. Further studies are needed in order to establish more firmly the applications and limitations of eqn. (1) and (2). For this reason, anthracene solubilities have been experimentally measured in binary solvent mixtures containing butyl acetate with n-hexane, n-heptane, n-octane, cyclohexane, methylcyclohexane and 2,2,4-trimethylpentane. Results of these measurements are used to calculate equilibrium constants for a presumed anthracene-butyl acetate complex and to ascertain the effect of the inert hydrocarbon cosolvents on calculated association parameters.

Experimental

Anthracene (Aldrich Gold Label, 99.9+%) was used as received. Cyclohexane (Aldrich HPLC), n-hexane (Aldrich 99%), n-heptane (Aldrich HPLC), n-octane (Aldrich 99+%, anhydrous), methylcyclohexane (Aldrich 99+%), 2,2,4-trimethylpentane (Aldrich HPLC) and butyl acetate (Aldrich 99+%, anhydrous) were stored over molecular sieves to remove trace water. Gas-chromatographic analysis showed solvent purities to be 99.8% or better. 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 amber glass bottles to equilibrate in a constant temperature bath at $25.0 \pm 0.1^\circ\text{C}$ for several days. Attainment of equilibrium was verified by repetitive measurements after several additional days and by approaching equilibrium from supersaturation after first pre-equilibrating the solution at a slightly higher temperature. Aliquots of saturated anthracene solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample and diluted quantitatively with methanol. Concentrations were determined spectrophotometrically at 356 nm on a Bausch and Lomb Spectronic 2000 UV-VIS spectrophotometer. Undissolved material from several containers was removed and analysed to ensure that the equilibrium solid phase was indeed pure crystalline anthracene. Melting temperatures of the undissolved residues were identical to that of anthracene. Experimental anthracene solubilities in the six binary solvent mixtures studied are listed in Table 1. Numerical values represent the average of between four and eight independent determinations, with the measured values being reproducible to within $\pm 1\%$.

Results and Discussion

The NIBS equations which have been most successful for describing the excess chemical potential of solutes in multi-component mixtures are derived from the following expressions

$$\Delta G_{1,2,\dots,N}^{\text{mix}} = RT \sum_{i=1}^N n_i \ln X_i + \left(\sum_{i=1}^N n_i \Gamma_i \right) \left(\sum_{i=1}^N \sum_{j>i}^N f_i f_j A_{ij} \right) \quad (4)$$

$$\Delta G_{1,2,\dots,N}^{\text{mix}} = RT \sum_{i=1}^N n_i \ln \phi_i + \left(\sum_{i=1}^N n_i \Gamma_i \right) \left(\sum_{i=1}^N \sum_{j>i}^N f_i f_j A_{ij} \right) \quad (5)$$

where X_i and f_i refer to the mole fraction and weighted mole fraction of component i , respectively, n_i is the number of moles of component i and A_{ij} is a binary interaction param-

Table 1 Comparison between predicted and experimental anthracene solubilities in binary alkane-butyl acetate solvent mixtures at 25.0°C

X_C^0	X_A^{sat}	deviations (%) of calculated values ^a		
		eqn. (6)	eqn. (7)	eqn. (8)
n-hexane (B)-butyl acetate (C)				
0.0000	0.00127	—	—	—
0.1076	0.00180	-12.7	-12.0	-12.0
0.2107	0.00239	-20.9	-19.6	-19.6
0.3995	0.00350	-24.5	-22.7	-22.7
0.4878	0.00404	-23.8	-21.9	-21.9
0.5944	0.00467	-21.1	-19.3	-19.3
0.7930	0.00572	-12.2	-11.0	-11.0
0.8808	0.00615	-7.7	-6.9	-6.9
1.0000	0.00661	—	—	—
n-heptane (B)-butyl acetate				
0.0000	0.00157	—	—	—
0.1233	0.00218	-11.6	-13.1	-13.0
0.2259	0.00275	-17.8	-20.2	-20.2
0.4250	0.00387	-20.9	-24.1	-24.0
0.5263	0.00446	-20.2	-23.4	-23.4
0.6255	0.00501	-18.0	-21.0	-20.9
0.8050	0.00586	-10.5	-12.3	-12.3
0.9058	0.00629	-5.5	-6.5	-6.5
1.0000	0.00661	—	—	—
n-octane (B)-butyl acetate (C)				
0.0000	0.00184	—	—	—
0.1238	0.00245	-9.5	-12.4	-12.4
0.2677	0.00322	-15.5	-20.7	-20.7
0.4604	0.00425	-16.6	-23.2	-23.2
0.5555	0.00480	-16.5	-23.0	-23.0
0.6591	0.00532	-14.2	-20.0	-19.9
0.8330	0.00604	-7.3	-10.9	-10.9
0.9145	0.00632	-3.6	-5.6	-5.5
1.0000	0.00661	—	—	—
cyclohexane (B)-butyl acetate (C)				
0.0000	0.00155	—	—	—
0.0948	0.00225	-23.0	-20.1	-20.1
0.1704	0.00277	-32.5	-27.9	-27.8
0.3559	0.00398	-41.4	-34.2	-34.1
0.4493	0.00457	-41.6	-34.0	-33.9
0.5268	0.00494	-38.1	-30.6	-30.5
0.7596	0.00591	-22.6	-17.5	-17.4
0.8694	0.00626	-12.9	-9.7	-9.7
1.0000	0.00661	—	—	—
methylcyclohexane (B)-butyl acetate (C)				
0.0000	0.00165	—	—	—
0.1107	0.00239	-20.0	-19.3	-19.3
0.2020	0.00298	-28.3	-27.2	-27.2
0.3942	0.00416	-33.7	-32.0	-32.0
0.4848	0.00472	-33.6	-31.8	-31.8
0.5969	0.00522	-28.3	-26.6	-26.6
0.7992	0.00607	-16.6	-15.5	-15.5
0.8882	0.00630	-9.0	-8.4	-8.4
1.0000	0.00661	—	—	—
2,2,4-trimethylpentane (B)-butyl acetate (C)				
0.0000	0.00107	—	—	—
0.1336	0.00158	-5.7	-10.7	-10.7
0.2471	0.00211	-8.1	-16.0	-16.0
0.4636	0.00332	-8.0	-18.2	-18.2
0.5532	0.00385	-6.2	-16.1	-16.1
0.6511	0.00447	-4.6	-13.4	-13.4
0.8344	0.00565	-1.9	-6.9	-6.0
0.9165	0.00617	-1.2	-3.9	-3.9
1.0000	0.00661	—	—	—

^a Deviations (%) = $100 \ln(X_A^{\text{calc}}/X_A^{\text{exp}})$.

eter which is independent of composition. The weighting factors (Γ_i) represent a rough measure of the skew of the binary excess property from a symmetric curve with an extremum at the equimolar composition. For simplicity, weighting

factors are assumed to be independent of temperature and pressure. Therefore, molar volumes and other experimentally determined weighting factors must be regarded as approximations of these 'true' weighting factors. Replacement of weighting factors with molar volumes requires that the values be referred to a specified condition, such as 25 °C and 1 atm, or to an extrapolated state such as 'close-packed' volume.

Based on the two mixing models and different weighting factor approximations Acree and Bertrand¹² derived the following three NIBS expressions for predicting solute solubilities in binary solvent mixtures containing only non-specific interactions:

$$RT \ln(a_A^{\text{solid}}/X_A^{\text{sat}}) = (1 - X_A^{\text{sat}})^2 [X_B^0 (\Delta \bar{G}_{AB}^{\text{ex}})^* + X_C^0 (\Delta \bar{G}_{AC}^{\text{ex}})^* - \Delta \bar{G}_{BC}^{\text{ex}}] \quad (6)$$

$$RT \ln(a_A^{\text{solid}}/X_A^{\text{sat}}) = (1 - \phi_A^{\text{sat}})^2 [\phi_B^0 (\Delta \bar{G}_{AB}^{\text{ex}})^* + \phi_C^0 (\Delta \bar{G}_{AC}^{\text{ex}})^* - \bar{V}_A (X_B^0 \bar{V}_B + X_C^0 \bar{V}_C)^{-1} \Delta \bar{G}_{BC}^{\text{ex}}] \quad (7)$$

$$RT \left[\ln(a_A^{\text{solid}}/\phi_A^{\text{sat}}) - (1 - \phi_A^{\text{sat}}) \left(1 - \frac{\bar{V}_A}{X_B^0 \bar{V}_B + X_C^0 \bar{V}_C} \right) \right] = (1 - \phi_A^{\text{sat}})^2 [\phi_B^0 (\Delta \bar{G}_{AB}^{\text{rh}})^* + \phi_C^0 (\Delta \bar{G}_{AC}^{\text{rh}})^* - \bar{V}_A (X_B^0 \bar{V}_B + X_C^0 \bar{V}_C)^{-1} \Delta \bar{G}_{BC}^{\text{rh}}] \quad (8)$$

Eqn. (6) and (7) are based on Raoult's law for the configurational contribution to the free energy, and eqn. (8) is based on the Flory–Huggins model. In the above expressions a_A^{solid} is the activity of the solid solute relative to the hypothetical pure subcooled liquid and ϕ_i is an ideal volume fraction. Binary solvent properties $\Delta \bar{G}_{BC}^{\text{ex}}$ and $\Delta \bar{G}_{BC}^{\text{rh}}$ refer to the excess Gibbs free energies relative to Raoult's law and the Flory–Huggins model, respectively. Solubility data measured in each pure solvent can be used to calculate the excess partial molar Gibbs free energy of the solute ($\Delta \bar{G}_{AB}^{\text{ex}})^*$ and ($\Delta \bar{G}_{AC}^{\text{ex}})^*$. The quantities are then combined with the free energy of the binary solvent mixture to predict solubility in mixed solvents. Note that all equations give identical predictions whenever $\bar{V}_A = \bar{V}_B = \bar{V}_C$, and it is only in systems having considerable molecular size disparity that one can distinguish between the three expressions.

Comparison between experimental and predicted anthracene solubilities are tabulated in the last three columns of Table 1 for the six binary solvent systems studied. Properties used in the calculations include $\bar{V}_A = 150 \text{ cm}^3 \text{ mol}^{-1}$ and the activity of the solute, $a_A^{\text{solid}} = 0.01049$,¹³ which is calculated from

$$\ln a_A^{\text{solid}} = \frac{-\Delta \bar{H}_A^{\text{fus}}(T_{\text{mp}} - T)}{RT T_{\text{mp}}} \quad (9)$$

the molar enthalpy of fusion data, $\Delta \bar{H}_A^{\text{fus}}$, at the normal melting temperature, T_{mp} . Eqn. (9) assumes that $\Delta \bar{H}_A^{\text{fus}}$ is independent of temperature. This assumption, while perhaps not valid, introduces only a negligible error into the solubility predictions. For solutes of very limited solubility, the activity of the solid solute can be eliminated mathematically from the NIBS predictions as a_A^{solid} is contained in the ($\Delta \bar{G}_{AB}^{\text{ex}})^*$ and ($\Delta \bar{G}_{AC}^{\text{ex}})^*$ values.¹⁴ Experimental excess molar Gibbs free energies of the binary solvent mixtures were not available in the chemical literature, and numerical values used in the NIBS predictions were estimated *via* the Scatchard–Hildebrand approach:⁹

$$\Delta \bar{G}_{BC}^{\text{ex}} = \phi_B^0 \phi_C^0 (X_B^0 \bar{V}_B + X_C^0 \bar{V}_C) (\delta_B - \delta_C)^2 \quad (10)$$

$$\Delta \bar{G}_{BC}^{\text{rh}} = \Delta \bar{G}_{BC}^{\text{ex}} + RT [\ln(X_B^0 \bar{V}_B + X_C^0 \bar{V}_C) - X_B^0 \ln \bar{V}_B - X_C^0 \ln \bar{V}_C] \quad (11)$$

where δ_i is the solubility parameter of component i . Solvent molar volumes and solubility parameters are listed in Table 2.

Careful examination of Table 1 reveals that all three NIBS expressions fail to predict the observed anthracene solubilities. Deviations between experimental and predicted values are of the order of 20–30% for many of the individual binary solvent compositions, and are considerably larger than would be expected for systems containing only non-specific physical interactions. In past studies eqn. (7) and (8) predicted benzil,^{15,16} *p*-benzoquinone,¹⁷ pyrene,^{18–20} biphenyl,²¹ anthracene,^{13,22,23} thianthrene,²⁴ carbazole,²⁵ benzoic acid²⁶ and iodine^{12,16} solubilities in a wide range of binary organic solvent mixtures to within *ca.* $\pm 5\%$. While one can always argue that the failure of the basic NIBS model to predict anthracene solubilities in the six binary alkane–butyl acetate solvent mixtures results from poor $\Delta \bar{G}_{BC}^{\text{ex}}$ estimates, it is believed that complexation between the dissolved anthracene and butyl acetate cosolvent occurs, in which case the extended NIBS model [eqn. (1) and (2)] should be used. Aromatic solutes are capable of undergoing several types of molecular interactions, depending upon the chemical nature of the surrounding solvent molecules. In hydrogen-bond-donating solvents, the electron-rich aromatic compounds serve as hydrogen-bond acceptor sites. Aromatic compounds also have the ability to form electron donor–acceptor complexes, in which case an aromatic solute may act as either acceptor or donor.²⁷ Specific interactions between aromatic hydrocarbons and esters have been suggested in the past. Stephenson and Fuchs²⁸ reported that the enthalpy of transfer for benzene from the vapour phase to ethyl acetate was considerably more exothermic than the corresponding transfer enthalpy for cyclohexane, which served as an inert model compound of comparable molecular size.

If one assumes the existence of a weak anthracene–butyl acetate complex in solution, then the equilibrium constant can be determined using the extended NIBS model and measured anthracene solubilities as a function of binary solvent composition. Table 3 lists numerical K_{AC}^{ϕ} and K_{AC}^x values, along with the corresponding deviations between observed and calculated anthracene solubilities which are of the order of $\pm 1.5\%$ or less. Inspection of Table 3 reveals that both equations do describe the experimental data, although the optimized constants do vary slightly with the inert hydrocarbon cosolvent. In the case of the volume-fraction-based constant, the numerical values ranged from $K_{AC}^{\phi} = 4.5$ in 2,2,4-trimethylpentane to $K_{AC}^{\phi} = 8.0$ in both cyclohexane and methylcyclohexane. Part of the observed variation in K_{AC}^{ϕ} (and K_{AC}^x) undoubtedly arises from the manner in which experimental uncertainties are propagated in the extended NIBS model and from having to use estimated $\Delta \bar{G}_{BC}^{\text{rh}}$ values rather than actual experimental free-energy data in the computations. It must be remembered that four measured quan-

Table 2 Solvent properties used in the NIBS predictions

component (i)	$\bar{V}_i/\text{cm}^3 \text{ mol}^{-1}$	$\delta_i/\text{cal}^{1/2} \text{ cm}^{-3/2}$ ^a
n-hexane	131.51	7.27
n-heptane	147.48	7.50
n-octane	163.46	7.54
cyclohexane	108.76	8.19
methylcyclohexane	128.32	7.83
2,2,4-trimethylpentane	166.09	6.86
butyl acetate	132.61	8.69

^a Except for butyl acetate, values are taken from tabulations contained in ref. 2 and 5. Solubility parameter for butyl acetate is from a compilation by Hoy.³⁰

Table 3 Volume-fraction-based and mole-fraction-based association constants for presumed anthracene-butyl acetate molecular complex

hydrocarbon cosolvent	eqn. (1)		eqn. (2)	
	K_{AC}^{ϕ} ^a	dev. (%) ^b	K_{AC}^x ^a	dev. (%) ^b
n-hexane	5.5	0.3	3.0	0.5
n-heptane	5.8	0.4	2.7	0.6
n-octane	5.5	0.6	2.4	1.0
cyclohexane	8.0	1.5	5.9	1.3
methylcyclohexane	8.0	0.9	4.1	0.4
2,2,4-trimethylpentane	4.5	1.3	1.7	0.8

^a Numerical values subject to re-evaluation when experimental $\Delta\bar{G}_{BC}^{ex}$ data becomes available. ^b Deviation (%) = $(100/N) \sum |\ln(X_A^{calc}/X_A^{exp})|$.

ties are needed to evaluate the equilibrium constant. Anthracene solubilities in each pure solvent and binary solvent mixture were reproducible to within $\pm 1\%$, and it is hoped that the $\Delta\bar{G}_{BC}^{rh}$ estimates are accurate to within ± 20 cal mol⁻¹. Furthermore, eqn. (1) and (2) are derived from the basic NIBS model^{12,29} and any errors in predicting the non-specific physical interaction contributions, which are perhaps as large as 4–5%, would naturally carry over into the equilibrium constant determination. A calculated anthracene-butyl acetate association parameter of $K_{AC}^{\phi} = 4.5$ in the 2,2,4-trimethylpentane cosolvent may be identical, at least to within the limitations of the extended NIBS model, to a value of $K_{AC}^{\phi} = 8.0$ in cyclohexane. Average volume-fraction-based and mole-fraction-based association constants of $K_{AC}^{\phi} = 6.2$ and $K_{AC}^x = 3.3$, respectively, indicate that ca. 20–25% of the total anthracene solubility in butyl acetate corresponds to the uncomplexed solute. (Note: $X_A^{sat}/\bar{X}_{A_i} \approx 1 + K_{AC}^x X_C^0$). In the absence of specific solute-solvent association, the expected mole fraction solubility in butyl acetate is ca. $X_A^{sat} = 0.00154$ and falls between values in n-hexane ($X_A^{sat} = 0.00127$) and methylcyclohexane ($X_A^{sat} = 0.00165$). n-Hexane is the so-called ‘inert hydrocarbon homomorph’ of comparable molecular size to butyl acetate. Based on these observations it is believed that the extended NIBS model provides a more realistic description of the thermochemical properties of anthracene dissolved in binary alkane-butyl acetate mixtures than did the simpler NIBS model discussed previously. Additional experimental studies are currently underway to measure both anthracene and pyrene solubilities in a wider range of binary alkane-ester solvent mixtures to ascertain what effect the ester alkyl chain lengths have on the calculated association parameters, and to determine whether Raoult’s law [eqn. (2)] or the Flory-Huggins model [eqn. (1)] provides the better description of solution ideality in these systems.

This research was supported by a grant from the National Science Foundation (grant no. CTS-8922485).

Glossary

a_A^{solid}	activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure subcooled liquid
$(\Delta\bar{G}_A^{ex})_i^*$	partial molar Gibbs free energy of the solute (Raoult’s law) in pure solvent <i>i</i> , extrapolated back to infinite dilution
$(\Delta\bar{G}_A^{rh})_i^*$	partial molar Gibbs free energy of the solute (Flory-Huggins model) in pure solvent <i>i</i> , extrapolated back to infinite dilution
$\Delta\bar{G}_{BC}^{ex}$	excess molar Gibbs free energy of the binary solvent mixture based on Raoult’s law

$\Delta\bar{G}_{BC}^{rh}$	excess molar Gibbs free energy of the binary solvent mixture based on the Flory-Huggins model
$\Delta\bar{H}_A^{fus}$	molar enthalpy of fusion of the solute
K_{AC}^{ϕ}	volume-fraction-based equilibrium constant for the formation of the AC molecular complex
\bar{V}_i	molar volume of component <i>i</i>
X_B^0, X_C^0	mole fraction composition of the solvent mixture, calculated as if the solute were not present
X_A^{sat}	saturated mole fraction solubility of the solute
ϕ_B^0, ϕ_C^0	ideal volume fraction compositions of the solvent mixture, calculated as if the solute were not present
ϕ_A^{sat}	ideal volume fraction solubility of solute
\bar{X}_i	true mole fraction of component <i>i</i> in the associated solution
$\hat{\phi}_i$	true volume fraction of component <i>i</i> in associated solution
δ_i	solubility parameter of component <i>i</i>
Γ_i	weighting factor of component <i>i</i>

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