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THERMODYNAMIC PROPERTIES OF TERNARY NON-ELECTROLYTE SOLUTIONS. PART 2. PREDICTION OF INFINITE DILUTION ACTIVITY COEFFICIENTS AND SOLUBILITIES BASED ON THE VARIOUS NIBS AND MICROSCOPIC PARTITION MODELS

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ABSTRACT

The limitations and applications of the various nearly ideal binary solvent (NIBS) and microscopic partition (MP) models for predicting the thermochemical properties of solutes dissolved in binary solvent mixtures are re-examined using published solute solubility and infinite dilution activity coefficient data for 48 systems. Expressions derived from the basic NIBS and extended NIBS models provide very reasonable predictions for anthracene and carbazole solubilities in systems containing both non-specific and specific interactions. For many of the systems considered, deviations between experimental values and NIBS predictions are of the order of 6% or less. In comparison, the two expressions derived from the MP model grossly overpredict the observed solubilities, with the average absolute deviations for several of the carbazole systems being 30% or more.

INTRODUCTION

For many years the chemical industry has recognized the importance of thermodynamic and physical properties in design calculations involving chemical separations, fluid flow and heat transfer. Development of flow calorimeters, continuous dilution dilatometers and vibrating-tube densimeters has enabled the experimental determination of excess enthalpies, heat capacities and volumes of non-electrolyte liquid mixtures with convenience and accuracy. The use of continuous dilution methods, combined with chromatographic head-space sampling techniques, has reduced the experimental time needed for the determination of excess Gibbs free energies and activity coefficients through conventional vapor pressure measurements. However, even with today's instrumentation, experimental measurements of

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thermodynamic properties become progressively more difficult and time-consuming with each additional component beyond binary mixtures.

In the chemical literature, properties for binary mixtures are relatively abundant, properties for ternary systems are scarce and properties for higher-order multicomponent systems are virtually non-existent. To address this problem, researchers have turned to predictive methods as a way to generate desired quantities from pure component physical properties, measured binary data and/or structural information. Derived expressions generally will provide very reasonable estimates of integral excess Gibbs free energies, excess enthalpies and excess volumes for non-electrolyte multicomponent systems containing only non-specific interactions (non-complexing systems) and at concentrations far removed from infinite dilution [1–4]. Near infinite dilution, many of the solution models begin to fail, particularly in systems which have strong solute–solvent complexation or solute self-association.

Knowledge of infinite dilution activity coefficients is required in qualitative and quantitative analysis of separation processes such as liquid–liquid extraction, extractive distillation and azeotropic distillation. In recent years considerable effort has been devoted to design of better instrumentation, establishment of data bases and development of predictive methods specifically for infinite dilution properties. The various nearly ideal binary solvent (NIBS) [5–13] and microscopic partition (MP) [14–20] models were originally derived to describe solute thermochemical properties in mixed solvents, and to date have shown great success in predicting infinite dilution activity coefficients, gas–liquid chromatographic partition coefficients and saturation solubilities of solid solutes in well over 300 non-electrolyte systems. Although the number of specific systems studied by the various models is large, there has never been a comparison of predictive abilities using a common set of experimental data. For this reason, the authors have compared calculated values based on the various NIBS and MP equations with experimental saturation solubility and activity coefficient data for anthracene and carbazole dissolved in 48 binary solvent mixtures.

NEARLY IDEAL BINARY SOLVENT MODELS

The basic NIBS approach developed by Bertrand and coworkers [5–7] provides a relatively simple method for estimating the excess partial molar properties of a solute $(\Delta\bar{Z}_A^{ex})^\infty$, at infinite dilution in a binary solvent

$$(\Delta\bar{Z}_A^{ex})^\infty = f_B^0(\Delta\bar{Z}_A^{ex})_B^\infty + f_C^0(\Delta\bar{Z}_A^{ex})_C^\infty - \Gamma_A(X_B^0\Gamma_B + X_C^0\Gamma_C)^{-1}\,\Delta\bar{Z}_{BC}^{ex} \tag{1}$$

$$f_B^0 = 1 - f_C^0 = X_B^0\Gamma_B/(X_B^0\Gamma_B + X_C^0\Gamma_C) \tag{2}$$

in terms of a weighted mole fraction average of the properties of the solute in the two pure solvents, $(\Delta \overline{Z}_{\mathrm{A}}^{\mathrm{ex}})_{\mathrm{B}}^{\infty}$ and $(\Delta \overline{Z}_{\mathrm{A}}^{\mathrm{ex}})_{\mathrm{C}}^{\infty}$, and a contribution from the 'unmixing' of the solvent pair caused by the presence of the solute. In eqns. (1) and (2) f_{B}^{0} and f_{C}^{0} refer to the weighted mole fraction compositions of the initial binary solvent mixture. Weighting factors Γ_i used in eqns. (1) and (2) represent a rough measure of the skew of the binary $\Delta \overline{Z}_{ij}^{\mathrm{ex}}$ mixing property from a symmetric curve with an extremum at the equimolar composition, and can be evaluated only in a relative sense as the ratio of two weighting factors, Γ_i/Γ_j. Several methods [2,5] have been suggested for the evaluation of these weighting factors from the thermodynamic properties of binary mixtures. To avoid calculating weighting factors, the following three simple approximations are generally made: approximating weighting factors with pure component molar volumes $(\Gamma_i \approx \overline{V}_i)$, equating the weighting factors of all components $(\Gamma_i \approx \Gamma_j)$, or approximating weighting factors by molecular surface areas $(\Gamma_i \approx A_i)$.

Excess properties are relatively straightforward in the case of enthalpy and volume, which are measured directly. For Gibbs free energy, however, the total free energy of mixing ΔG^{mix} is observed and the excess Gibbs free energy ΔG^{ex} is calculated as the difference between the observed value and the value for an ideal solution with the same composition

$$\Delta G^{\mathrm{mix}} = RT \sum_{i=1}^{N} n_i \ln X_i + \Delta G^{\mathrm{ex}} \tag{3}$$

or, in systems where considerable size disparities exist,

$$\Delta G^{\mathrm{mix}} = RT \sum_{i=1}^{N} n_i \ln \phi_i + \Delta G^{\mathrm{fh}} \tag{4}$$

the ideal solution is based on the Flory–Huggins model with volume fractions ϕ_i replacing mole fractions X_i inside of the logarithm term. The basic NIBS model has two expressions for partial molar excess Gibbs free energies

$$\Delta \overline{G}_{\mathrm{A}}^{\mathrm{ex}} = (1 - f_{\mathrm{A}})^2 \left[f_{\mathrm{B}}^{0} (\Delta \overline{G}_{\mathrm{A}}^{\mathrm{ex}})_{\mathrm{B}} + f_{\mathrm{C}}^{0} (\Delta \overline{G}_{\mathrm{A}}^{\mathrm{ex}})_{\mathrm{B}} - \Gamma_{\mathrm{A}} (X_{\mathrm{B}}^{0} \Gamma_{\mathrm{B}} + X_{\mathrm{C}}^{0} \Gamma_{\mathrm{C}})^{-1} \Delta \overline{G}_{\mathrm{BC}}^{\mathrm{ex}} \right] \tag{5}$$

$$\Delta \overline{G}_{\mathrm{A}}^{\mathrm{fh}} = (1 - f_{\mathrm{A}})^2 \left[f_{\mathrm{B}}^{0} (\Delta \overline{G}_{\mathrm{A}}^{\mathrm{fh}})_{\mathrm{B}}^{\infty} + f_{\mathrm{C}}^{0} (\Delta \overline{G}_{\mathrm{A}}^{\mathrm{fh}})_{\mathrm{C}}^{\infty} - \Gamma_{\mathrm{A}} (X_{\mathrm{B}}^{0} \Gamma_{\mathrm{B}} + X_{\mathrm{C}}^{0} \Gamma_{\mathrm{C}})^{-1} \Delta \overline{G}_{\mathrm{BC}}^{\mathrm{fh}} \right] \tag{6}$$

the first being based on Raoult's Law and the second on the Flory–Huggins model for the combinatorial entropic term. In the above expressions n_i refers to the number of moles of component i, f_{A} is the weighted mole fraction of the solute and $\Delta \overline{G}^{\mathrm{fh}}$ is the calculated excess free energy relative to the Flory–Huggins model.

Equations (5) and (6) enable the prediction of infinite dilution activity coefficients, or any measurable quantity such as saturation solubilities of sparingly soluble solutes which are directly related to activity coefficients ($a_A^{solid} = X_A^{sat} \gamma_A^{sat}$; $\gamma_A^{sat} \approx \gamma_A^{\infty}$), as a function of binary solvent composition. Through basic thermodynamic relationships, the saturation solubility of a solid is related to the excess partial molar Gibbs free energies as follows

$$\Delta \bar{G}_A^{ex} = RT \ln\left(a_A^{solid}/X_A^{sat}\right) \tag{7}$$

$$\Delta \bar{G}_A^{fh} = RT\left\{\ln\left(a_A^{solid}/\phi_A^{sat}\right) - \left[1 - \left(\bar{V}_A/\bar{V}_{soln}\right)\right]\right\} \tag{8}$$

where a_A^{solid} is the activity of the solid solute. It is defined as the ratio of the fugacity of the solid to the fugacity of the pure hypothetical subcooled liquid. The numerical value of a_A^{solid} can be calculated from

$$\ln a_A^{solid} = -\left[\Delta \bar{H}_A^{fus}\left(T_{mp} - T\right)\right]/\left(RTT_{mp}\right) + \left[\Delta \bar{C}_p\left(T_{mp} - T\right)\right]/(RT)$$
$$-\left(\Delta \bar{C}_p/R\right) \ln\left(T_{mp}/T\right) \tag{9}$$

the molar enthalpy of fusion $\Delta \bar{H}_A^{fus}$ at the normal melting point temperature T_{mp} and the differences between the molar heat capacities of the liquid and solid solute $\Delta \bar{C}_p$.

Expressed in terms of solubility, the basic NIBS equations take the following form

$$RT \ln\left(a_A^{solid}/X_A^{sat}\right) = \left(1 - X_A^{sat}\right)^2\left[X_B^0\left(\Delta \bar{G}_A^{ex}\right)_B^{\infty} + X_C^0\left(\Delta \bar{G}_A^{ex}\right)_C^{\infty} - \Delta \bar{G}_{BC}^{ex}\right] \tag{10}$$

$$RT \ln\left(a_A^{solid}/X_A^{sat}\right) = \left(1 - \phi_A^{sat}\right)^2\left[\phi_B^0\left(\Delta \bar{G}_A^{ex}\right)_B^{\infty} + \phi_C^0\left(\Delta \bar{G}_A^{ex}\right)_C^{\infty}\right.$$
$$\left. - \bar{V}_A\left(X_B^0 \bar{V}_B + X_C^0 \bar{V}_C\right)^{-1} \Delta \bar{G}_{BC}^{ex}\right] \tag{11}$$

and

$$RT\left[\ln\left(a_A^{solid}/\phi_A^{sat}\right) - \left(1 - \phi_A^{sat}\right)\left\{1 - \left[\bar{V}_A/\left(X_B^0 \bar{V}_B + X_C^0 \bar{V}_C\right)\right]\right\}\right]$$
$$= \left(1 - \phi_A^{sat}\right)^2\left[\phi_B^0\left(\Delta \bar{G}_A^{fh}\right)_B^{\infty} + \phi_C^0\left(\Delta \bar{G}_A^{fh}\right)_C^{\infty} - \bar{V}_A\left(X_B^0 \bar{V}_B + X_C^0 \bar{V}_C\right)^{-1} \Delta \bar{G}_{BC}^{fh}\right] \tag{12}$$

depending upon the particular weighting factor approximation and definition of solution ideality assumed. With eqns. (10)–(12), solubility data measured in the two pure solvents enable calculation of the various $(\Delta \bar{G}_A^{ex})_i^{\infty}$ and $(\Delta \bar{G}_A^{fh})_i^{\infty}$ values. These quantities are then combined with the excess free energy of the binary solvent to estimate solubilities in mixed solvents via a reiterative computational procedure. The quantity $1 - X_A^{sat}$ or $1 - \phi_A^{sat}$ is taken as unity in the first approximation, and the convergence is rapid unless the solubility is large.

From a predictive standpoint, the basic NIBS model is limited in application to systems which contain only non-specific interactions, and is not expected to describe all non-electrolyte systems encountered. Expressions for systems containing solute complexation with a single solvent [8,9]

$$A_1 + C_1 \rightleftharpoons AC \qquad K_{AC}^{\phi} = \hat{\phi}_{AC}/(\hat{\phi}_{A_1}\hat{\phi}_{C_1}) \tag{13}$$

$$\begin{aligned}\ln \phi_A^{sat} = {} & \phi_B^0 \ln(\phi_A^{sat})_B + \phi_C^0 \ln(\phi_A^{sat})_C + \ln[1 + K_{AC}^{\phi}\bar{V}_A\phi_C^0/(\bar{V}_A + \bar{V}_C)] \\ & - \phi_C^0 \ln[1 + K_{AC}^{\phi}\bar{V}_A/(\bar{V}_A + \bar{V}_C)] + \bar{V}_A\, \Delta\bar{G}_{BC}^{fh}/RT(X_B^0\bar{V}_B + X_C^0\bar{V}_C)\end{aligned} \tag{14}$$

and for systems where the solute complexes with both solvent components [13]

$$A_1 + C_1 \rightleftharpoons AC \qquad K_{AC}^{\phi} = \hat{\phi}_{AC}/(\hat{\phi}_{A_1}\hat{\phi}_{C_1}) \tag{15}$$

$$A_1 + B_1 \rightleftharpoons AB \qquad K_{AB}^{\phi} = \hat{\phi}_{AB}/(\hat{\phi}_{A_1}\hat{\phi}_{B_1}) \tag{16}$$

$$\begin{aligned}\ln \phi_A^{sat} = {} & \phi_B^0 \ln(\phi_A^{sat})_B + \phi_C^0 \ln(\phi_A^{sat})_C - \phi_B^0 \ln[1 + \bar{V}_A K_{AB}^{\phi}/(\bar{V}_A + \bar{V}_B)] \\ & - \phi_C^0 \ln[1 + \bar{V}_A K_{AC}^{\phi}/(\bar{V}_A + \bar{V}_C)] \\ & + \ln[1 + \bar{V}_A K_{AB}^{\phi}\phi_B^0/(\bar{V}_A + \bar{V}_B) + \bar{V}_A K_{AC}^{\phi}\phi_C^0/(\bar{V}_A + \bar{V}_C)] \\ & + \bar{V}_A\, \Delta\bar{G}_{BC}^{fh}/RT(X_B^0\bar{V}_B + X_C^0\bar{V}_C)\end{aligned} \tag{17}$$

have additional equilibrium constant terms to represent the chemical interactions. To date, the extended NIBS (eqn. (14)) and competitive associated NIBS (eqn. (17)) models have been used primarily as a means to evaluate K_{AC}^{ϕ} and K_{AB}^{ϕ} constants from measured solubility data in binary solvent mixtures. McCargar and Acree [9–12] compared values for the carbazole–dibutyl ether association constant evaluated from experimental carbazole solubilities in 10 binary dibutyl ether–alkane solvent mixtures. Equation (14) described the carbazole solubilities to within an average deviation of 2% using a single association constant which varied slightly with cosolvent; from a low value of $K_{AC}^{\phi} = 22$ for *n*-heptane to an upper limit of $K_{AC}^{\phi} = 30$ for iso-octane. If an a priori value of about $K_{AC}^{\phi} \approx 26$ is assumed, the estimated values fall within 6–10% of the observed data for the 10 systems studied. The success of the extended NIBS model is even more remarkable when one realizes that the mole fraction solubilities cover up to a 25-fold range, and that the inert cosolvents included both small (cyclohexane, *n*-hexane) and large (*n*-hexadecane, squalane) saturated hydrocarbon molecules.

MICROSCOPIC PARTITION MODELS

Gas–liquid chromatography (GLC) provides a second experimental method for accurately determining infinite dilution thermodynamic properties. The MP theory, developed by Purnell, Laub and coworkers [14–20] evolved as a consequence of attempts to explain theoretically the observed linear relationship

$$K_R = \phi_B^0 (K_R)_B + \phi_C^0 (K_R)_C \tag{18}$$

between solute partition coefficient (K_R) and volume fraction composition of the binary stationary phase liquid (ϕ_B^0 and ϕ_C^0). To derive eqn. (18), the two miscible solvent components are assumed to be microscopically immiscible in all proportions. For this hypothetical situation, the fugacity of the solute in the binary solvent will equal its fugacity in each of the 'microscopically immiscible' solvent components

$$X_A \gamma_A^\infty f_A^\ominus = (X_A)_B (\gamma_A^\infty)_B f_A^\ominus = (X_A)_C (\gamma_A^\infty)_C f_A^\ominus \tag{19}$$

where $f_A^\ominus$ is the fugacity of the pure solute in its standard state and

$$X_A \approx [(n_A)_B + (n_A)_C]/(n_B + n_C) \tag{20}$$

$$(X_A)_i \approx (n_A)_i / n_i \qquad (i = B \text{ and } C) \tag{21}$$

defines the solute mole fraction compositions in the mixed and pure solvents, respectively. Through mathematical manipulations, eqn. (19) can be rearranged to its more familiar reciprocal activity coefficient form

$$1/\gamma_A^\infty = (X_B^0/(\gamma_A^\infty)_B) + (X_C^0/(\gamma_A^\infty)_C) \tag{22}$$

Recalling that saturation solubilities of solid solutes are related to activity coefficients, the predictive accuracy of the MP model can be tested using

$$X_A^{sat} = X_B^0 (X_A^{sat})_B + X_C^0 (X_A^{sat})_C \tag{23}$$

measured solubility data in binary solvent systems.

A major criticism of eqn. (22) has been its failure both to describe non-linear partition coefficient behavior (eqn. (18)) and to predict maximum mole fraction solubilities, such as has been observed for benzoic acid in cyclohexane–*n*-hexane and cyclohexane–*n*-heptane mixtures [21], and for anthracene in benzene–iodobenzene, benzene–iodoethane, cyclohexane–iodoethane and cyclohexene–iodoethane mixtures [22]. To address this concern, Laub [20] recently incorporated a strictly empirical correction

$$K_R^0 = [\phi_B^0 (K_R)_B + \phi_C^0 (K_R)_C] \bar{\gamma}_{mix} \tag{24}$$

$$\ln \bar{\gamma}_{mix} = \Delta \bar{G}_{BC}^{ex} / 2RT \tag{25}$$

which presumably accounts for binary solvent non-ideality. Equation (24) is a relatively new expression and its limitations have not yet been determined.

RESULTS AND DISCUSSION

The chemical literature contains thermodynamic data for a number of solutes dissolved in both non-complexing and complexing binary solvent

TABLE 1

Summarized comparison between experimental anthracene solubilities and calculated values based on the NIBS and MP equations

Binary solvent system	Data ref.	Dev. (%) [a], NIBS eqns.			Dev. (%) [a], MP eqns.	
		(10)	(11)	(12)	(23)	(24) [b]
Carbon tetrachloride–*n*-hexane	26	+7.0	0.9	1.2	+18.2	+20.5
Carbon tetrachloride–cyclohexane	26	0.2	−1.5	−1.4	+9.7	+10.9
Carbon tetrachloride–*n*-heptane	26	+10.5	+2.4	+2.8	+17.7	+19.7
Carbon tetrachloride–methylcyclohexane	26	+4.3	−1.1	0.9	+12.7	+13.7
Carbon tetrachloride–*n*-octane	26	+11.2	+2.3	+2.9	+15.9	+17.6
Carbon tetrachloride–iso-octane	26	+12.4	−2.2	−1.8	+27.0	+29.5
Toluene–*n*-hexane	25	−1.1	−5.7	−5.6	+17.5	+23.2
Toluene–cyclohexane	25	−12.7	−13.6	−13.4	+7.5	+9.7
Toluene–*n*-heptane	25	+4.6	−4.3	−4.0	+17.8	+22.7
Toluene–methylcyclohexane	25	−7.4	−10.9	−10.7	+7.3	+11.0
Toluene–*n*-octane	25	+8.0	−3.6	−3.3	+17.3	+21.7
Toluene–iso-octane	25	+14.6	1.7	1.6	+27.9	+37.7
Toluene–cyclo-octane	25	−2.5	−5.8	−5.6	2.2	+6.7
Cyclohexane–*n*-hexane	23	−1.2	−1.2	−1.1	−4.0	−2.4
Cyclohexane–*n*-heptane	23	1.0	0.6	0.6	−3.3	−2.1
Cyclohexane–iso-octane	23	+1.9	−1.2	−1.0	+1.7	+2.4
Cyclohexane–*n*-octane	23	−1.3	+0.6	+0.7	−2.9	−1.9
Cyclohexane–cyclo-octane	23	−1.4	0.9	0.9	−0.8	0.5
Benzene–*n*-hexane	23	+2.7	−6.0	−5.4	+17.5	+24.0
Benzene–*n*-heptane	23	+7.9	−4.6	−3.8	+19.1	+24.9
Benzene–cyclohexane	23	−6.9	−7.7	−7.5	7.2	+11.9
Benzene–cyclo-octane	23	1.8	−8.3	−7.7	+3.3	+7.7
Benzene–iso-octane	23	+10.5	−11.6	−10.7	+30.3	+36.6
Dibutyl ether–*n*-hexane	27	−5.9	0.3	0.3	+4.3	+5.0
Dibutyl ether–cyclohexane	27	−9.4	−1.3	−1.0	−2.7	−2.3
Dibutyl ether–*n*-heptane	27	−4.3	−1.8	−1.8	+2.7	+2.9
Dibutyl ether–methylcyclohexane	27	−6.9	−2.1	−2.1	−1.1	−0.8
Dibutyl ether–*n*-octane	27	−2.6	−2.1	−2.1	+2.0	+2.2
Dibutyl ether–iso-octane	27	−2.6	−2.5	−2.5	+8.0	+10.4
Dibutyl ether–cyclo-octane	27	−6.9	−4.6	−4.6	−7.7	−6.1
p-Xylene–*n*-hexane	24	−7.9	−8.2	−8.2	+11.6	+17.0
p-Xylene–cyclohexane	24	−12.7	−5.3	−5.3	2.7	+7.2
p-Xylene–methylcyclohexane	24	−10.0	−9.9	−9.9	+8.2	+10.4
p-Xylene–*n*-octane	24	+2.0	−5.9	−5.9	+12.6	+16.7
p-Xylene–*n*-heptane	24	+0.7	−4.0	−3.9	+15.6	+19.8
p-Xylene–iso-octane	24	+10.6	0.6	0.6	+25.9	+35.5
Benzene–*n*-octane	24	+12.7	2.2	1.4	+19.9	+25.2
Benzene–methylcyclohexane	24	+2.7	−4.7	−4.2	+13.5	+18.8

[a] Deviation (%) $= (100/N^{1/2})\{\Sigma[\ln(X_A^{calc}/X_A^{exp})]^2\}^{1/2}$; an algebraic sign indicates that all devi tions were of the same sign.

[b] Predictions based on the solubility analog of eqn. (24): $\ln X_A^{sat} = [X_B^0(X_A^{sat})_B + X_C^0(X_A^{sat})_C]\bar{\gamma}_{mi}$

TABLE 2

Summarized comparison between experimental carbazole solubilities and calculated values based on the extended NIBS and MP equations

Binary solvent system	Data ref.	Dev. (%) [a], NIBS eqn.		Dev. (%) [a], MP eqns.	
		K^0_{AC}	(14)	(23)	(24) [b]
Dibutyl ether–*n*-hexane	9	24.0	2.0	+31.8	+32.6
Dibutyl ether–*n*-heptane	9	22.0	1.8	+31.4	+31.5
Dibutyl ether–*n*-octane	9	25.0	1.7	+25.4	+25.5
Dibutyl ether–cyclohexane	9	24.0	2.2	+11.8	+12.2
Dibutyl ether–methylcyclohexane	9	26.0	1.8	+12.9	+13.2
Dibutyl ether–iso-octane	9	30.0	1.7	+37.4	+39.6
Dibutyl ether–cyclo-octane	9	25.0	2.1	3.7	2.7
Dibutyl ether–*n*-hexadecane	10	24.0	1.4	+22.7	+22.6
Dibutyl ether–squalane	10	23.0	1.7	+23.3	+23.3
Dibutyl ether–*t*-butylcyclohexane	11	30.0	1.5	+12.4	+12.4

[a] Deviation (%) = $(100/N)\Sigma|\ln(X_A^{calc}/X_A^{exp})|$; an algebraic sign indicates that all deviations were of the same sign.

[b] Predictions based on the solubility analog of eqn. (24): $\ln X_A^{sat} = [X_B^0(X_A^{sat})_B + X_C^0(X_A^{sat})_C]\bar{\gamma}_{mix}$.

mixtures. Published experimental data can be used to compare the predictive abilities of the five NIBS (eqns. (10)–(12), (14) and (17)), and two MP (eqns. (18) and (24)) expressions. For systems exhibiting only modest deviations from ideality it will be difficult, if not impossible, to distinguish statistically between the different predictive methods. All of the solution models should adequately describe these simple systems. A more demanding and definitive test is to describe very non-ideal multicomponent mixtures and systems for which the measured solute properties in the two pure solvents are very dissimilar. With these ideas in mind, the authors have estimated anthracene and carbazole solubilities in the 48 binary solvent mixtures listed in Tables 1 and 2. Each system contains solubility data determined in both pure solvents and at 5–11 binary solvent compositions covering the entire mole fraction range. Both solutes have limited solubility, and the infinite dilution approximations should thus apply. These systems should provide valuable insight regarding the limitations of the various models as the anthracene and carbazole systems cover up to a six-fold and 25-fold range in mole fraction solubilities.

Table 1 presents a summarized comparison between the basic NIBS and MP equations for predicting anthracene solubilities in 38 binary solvent mixtures believed to contain only non-specific interactions. Solute and solvent properties used in the calculations (see Table 3), or the method used to estimate $\Delta\bar{G}^{ex}_{BC}$ if experimental values were not available, were given in the earlier publications [23–27] from which the actual solubility data were taken. Inspection of Table 1 reveals that the NIBS solubility (and activity coeffi-

TABLE 3

Solute and solvent properties used in the calculations

Component	$\overline{V}_i$ (cm^3 mol^{-1})	
n-Hexane	131.51	
n-Heptane	147.48	
n-Octane	163.46	
Cyclohexane	108.76	
Methylcyclohexane	128.32	
Iso-octane	166.09	
Cyclo-octane	134.88	
Benzene	89.41	
Toluene	106.84	
p-Xylene	123.93	
Dibutyl ether	170.41	
Carbon tetrachloride	97.08	
Squalane	525.30	
n-Hexadecane	294.12	
t-Butylcyclohexane	173.93	
Carbazole	150.00	
Anthracene	150.00	($a_A^{\text{solid}} = 0.01049$ [a])

[a] Numerical value is taken from Acree and Rytting [23].

cient) predictions are in fairly good agreement with the observed values. In general, eqns. (11) and (12) are comparable with overall average absolute deviations of 4.1 and 3.9%, respectively and are superior to eqn. (10), which has an average deviation of 6.1%. Slightly larger deviations are noted in many of the benzene–alkane, toluene–alkane and *p*-xylene–alkane solvent mixtures as eqns. (11) and (12) underpredict the experimental values by as much as 8–15%. Deviations in these systems can be reduced considerably by approximating the NIBS weighting factors with molecular surface areas [23–25], but for the present comparison it has been decided to stay with the simpler molar volume approximation. From the standpoint of calculational simplicity, molar volumes are preferred. Molecular surface areas cannot be experimentally determined, and the numerical values must be obtained via computerized calculations involving van der Waals radii and assumed bond distances. In comparison, the two MP equations grossly overpredict the experimental solubilities, particularly in the systems which cover a large mole fraction solubility range or which have solvent components of dissimilar sizes. Incorporation of the empirical correction to account for binary solvent non-ideality (eqn. (24)) fails to improve the predictions. In fact, for most of the systems considered, the predictions are better if the correctional term is ignored.

The abilities of the extended NIBS and MP models to describe non-electrolyte systems are compared in Table 2 using carbazole solubilities in 10 binary dibutyl ether–alkane solvent mixtures. Based on spectroscopic studies on similar mixtures [28–30], carbazole is expected to interact specifically with dibutyl ether to form a 1 : 1 carbazole–dibutyl ether association complex. As mentioned above, the basic NIBS model is limited in application to non-complexing systems. Examination of Table 2 reveals that the extended NIBS model can describe the experimental solubilities to within an average deviation of about 2%, using a single K_{AC}^{ϕ} carbazole–dibutyl ether equilibrium constant which varies slightly with cosolvent; from a low value of $K_{AC}^{\phi} = 22$ for *n*-heptane to an upper limit of $K_{AC}^{\phi} = 30$ for iso-octane. By assuming an average value of about $K_{AC}^{\phi} = 26$ it is possible to estimate the solubility of carbazole in the 10 binary solvent mixtures to within 6–10%. In comparison, the two MP equations again grossly overpredict the experimental values. Complexation between carbazole and dibutyl ether is not a viable explanation for the failure of the MP equations as the basic model is supposed to be applicable to both complexing and non-complexing systems.

Results of the present study clearly show that the various NIBS models are superior to the MP model in predicting the solubilities (and infinite dilution activity coefficients) of carbazole and anthracene in the 48 systems considered. The predictive abilities of eqns. (10)–(12), (23) and (24) have also been compared with published pyrene [31–33], benzil [34,35] and *p*-benzoquinone [36] solubilities. These last three solutes are more soluble and the infinite dilution activity coefficients in the MP calculations had to be obtained by

$$\ln \gamma_A^{\infty} = \left(1 - X_A^{\text{sat}}\right)^{-2} \ln \gamma_A^{\text{sat}}$$

extrapolating γ values measured at finite concentration to infinite dilution conditions. As the extrapolations often involved a sizeable concentration range, the calculations are not presented in the summarized comparisons given in Tables 1 and 2. These additional calculations, however, again showed that the NIBS equations are superior to the MP equations, in complete agreement with the observations for the anthracene and carbazole systems.

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