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THERMODYNAMIC PROPERTIES OF NON-ELECTROLYTE SOLUTIONS.

Part 4. Estimation and mathematical representation of solute activity coefficients and solubilities in binary solvents using the NIBS and Modified Wilson equations

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ABSTRACT

The limitations and applications of the various nearly ideal binary solvent (NIBS) and Modified Wilson models for predicting the thermochemical properties of solutes dissolved in binary solvent mixtures are examined using published solute solubility and infinite dilution activity coefficient data for 72 systems. Expressions derived from the basic NIBS and extended NIBS models provide very reasonable predictions for anthracene, thianthrene and carbazole solubilities in systems containing both specific and non-specific interactions. For many of the systems considered, deviations between experimental and NIBS predictions are of the order of 6% or less. In comparison, the Modified Wilson equation grossly underpredicts the observed solubilities, with deviations for several of the carbazole systems being 40% or more. Both models can serve as a point-of-departure for the mathematical representation of experimental solubility data, and two possible descriptive forms are suggested.

INTRODUCTION

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 the design of better instrumentation, establishment of data bases and development of predictive methods specifically for infinite dilution properties. Several expressions have been suggested for predicting vapor–liquid equilibria in dilute solutions using pure component properties and binary parameters determined from experimental data over the entire binary composition range. The more sophisticated solution models, which assume preferential solvation and/or local compositions,

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require that at least two parameters be calculable for each contributing sub-binary system.

Prediction of solid–liquid equilibria and solute solubilities in mixed solvents is also possible; however, the number of available predictive equations is significantly reduced. The nature of solubility determinations restricts the number of adjustable parameters to no more than one per binary mixture, as there is only one data point associated with the saturated solute solubility in a pure solvent. Hence, local composition models such as the Wilson or UNIQUAC models have been of very limited use when it comes to predicting solubilities of crystalline substances. In the few published examples involving the Wilson equation, McLaughlin and co-workers [1–3], Domanska et al. [4–9] and Acree et al. [10] were able to evaluate both parameters from measured solubility data at several temperatures. Comer and Kopecni [11] recently modified the Wilson model by eliminating two solute–solvent parameters from the infinite dilution form of the predictive ternary expression, thus permitting estimation of infinite dilution activity coefficients (or solid solubilities) in binary solvent mixtures from measured values in the two pure solvents and excess Gibbs free energies for the binary solvent mixture. The limitations and applications of this newly-derived equation have yet to be tested. For this reason we have compared values based on the Modified Wilson equation with experimental activity coefficient and saturation solubility data for anthracene, thianthrene and carbazole dissolved in 72 binary solvent systems. Also included are the corresponding predictions from the nearly ideal binary solvent (NIBS) expressions and suggestions for the mathematical representation of experimental data.

NEARLY IDEAL BINARY SOLVENT MODELS

The basic NIBS approach developed by Bertrand and co-workers [12–14] 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

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

$$f_B^0 = 1 - f_C^0 = X_B^0 \Gamma_B / \left(X_B^0 \Gamma_B + X_C^0 \Gamma_C \right) \qquad (2)$$

in the two pure solvents, $(\Delta \bar{Z}_A^{ex})_B^\infty$ and $(\Delta \bar{Z}_A^{ex})_C^\infty$, 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 of compositions in the binary solvent mixture. Weighting factors Γ_i used in eqns. (1) and (2) represent a rough measure of the skew of the binary $\Delta \bar{Z}_{ij}^{ex}$ 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 [12,15] have been suggested for the evaluation of these weighting factors from the thermodynamic properties of the binary mixtures. To avoid calculating weighting factors, the following three simple approximations are generally made: approximating weighting factors with pure component molar volumes ($\Gamma_i \approx \bar{V}_i$), 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

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

or, in systems where considerable size disparities exist,

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

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

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

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

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 $\Delta \bar{G}^{\text{fh}}$ is the calculated excess free energy relative to the Flory–Huggins model.

Equations (5) and (6) enable 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 ($a_{\text{A}}^{\text{solid}} = X_{\text{A}}^{\text{sat}} \gamma_{\text{A}}^{\text{sat}}$; $\gamma_{\text{A}}^{\text{sat}} \approx \gamma_{\text{A}}^{\infty}$), 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

$$\Delta \bar{G}_{\text{A}}^{\text{ex}} = RT \ln(a_{\text{A}}^{\text{solid}} / X_{\text{A}}^{\text{sat}}) \tag{7}$$

$$\Delta \bar{G}_{\text{A}}^{\text{fh}} = RT \{ \ln(a_{\text{A}}^{\text{solid}} / \phi_{\text{A}}^{\text{sat}}) - [1 - (\bar{V}_{\text{A}} / \bar{V}_{\text{soln}})] \} \tag{8}$$

where $a_{\mathrm{A}}^{\mathrm{solid}}$ 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 $a_{\mathrm{A}}^{\mathrm{solid}}$ can be calculated from

$$\ln a_{\mathrm{A}}^{\mathrm{solid}} = \frac{-\Delta \bar{H}_{\mathrm{A}}^{\mathrm{fus}}(T_{\mathrm{mp}} - T)}{RTT_{\mathrm{mp}}} + \frac{\Delta \bar{C}_p(T_{\mathrm{mp}} - T)}{RT} - \left(\Delta \bar{C}_p/R\right) \ln\left(T_{\mathrm{mp}}/T\right) \quad (9)$$

the molar enthalpy of fusion $\Delta \bar{H}_{\mathrm{A}}^{\mathrm{fus}}$ 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

$$RT \ln\left(a_{\mathrm{A}}^{\mathrm{solid}}/X_{\mathrm{A}}^{\mathrm{sat}}\right) = \left(1 - X_{\mathrm{A}}^{\mathrm{sat}}\right)^2\left[X_{\mathrm{B}}^0\left(\Delta \bar{G}_{\mathrm{A}}^{\mathrm{ex}}\right)_{\mathrm{B}}^{\infty} + X_{\mathrm{C}}^0\left(\Delta \bar{G}_{\mathrm{A}}^{\mathrm{ex}}\right)_{\mathrm{C}}^{\infty} - \Delta \bar{G}_{\mathrm{BC}}^{\mathrm{ex}}\right] \quad (10)$$

$$\begin{aligned} RT \ln\left(a_{\mathrm{A}}^{\mathrm{solid}}/X_{\mathrm{A}}^{\mathrm{sat}}\right) = {} & \left(1 - \phi_{\mathrm{A}}^{\mathrm{sat}}\right)^2\Big[\phi_{\mathrm{B}}^0\left(\Delta \bar{G}_{\mathrm{A}}^{\mathrm{ex}}\right)_{\mathrm{B}}^{\infty} + \phi_{\mathrm{C}}^0\left(\Delta \bar{G}_{\mathrm{A}}^{\mathrm{ex}}\right)_{\mathrm{C}}^{\infty} \\ & - \bar{V}_{\mathrm{A}}\left(X_{\mathrm{B}}^0 \bar{V}_{\mathrm{B}} + X_{\mathrm{C}}^0 \bar{V}_{\mathrm{C}}\right)^{-1} \Delta \bar{G}_{\mathrm{BC}}^{\mathrm{ex}}\Big] \end{aligned} \quad (11)$$

and

$$\begin{aligned} & RT\left\{\ln\left(a_{\mathrm{A}}^{\mathrm{solid}}/\phi_{\mathrm{A}}^{\mathrm{sat}}\right) - \left(1 - \phi_{\mathrm{A}}^{\mathrm{sat}}\right)\left(1 - \frac{\bar{V}_{\mathrm{A}}}{X_{\mathrm{B}}^0 \bar{V}_{\mathrm{B}} + X_{\mathrm{C}}^0 \bar{V}_{\mathrm{C}}}\right)\right\} \\ & = \left(1 - \phi_{\mathrm{A}}^{\mathrm{sat}}\right)^2\left[\phi_{\mathrm{B}}^0\left(\Delta \bar{G}_{\mathrm{A}}^{\mathrm{fh}}\right)_{\mathrm{B}}^{\infty} + \phi_{\mathrm{C}}^0\left(\Delta \bar{G}_{\mathrm{A}}^{\mathrm{fh}}\right)_{\mathrm{C}}^{\infty} - \bar{V}_{\mathrm{A}}\left(X_{\mathrm{B}}^0 \bar{V}_{\mathrm{B}} + X_{\mathrm{C}}^0 \bar{V}_{\mathrm{C}}\right)^{-1} \Delta \bar{G}_{\mathrm{BC}}^{\mathrm{fh}}\right] \end{aligned} \quad (12)$$

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 $(\Delta \bar{G}_{\mathrm{A}}^{\mathrm{ex}})_i^{\infty}$ and $(\Delta \bar{G}_{\mathrm{A}}^{\mathrm{fh}})_i^{\infty}$ values. These quantities are then combined with the excess free energy of the binary solvent mixture to estimate solubilities in mixed solvents via a reiterative computational procedure. The quantity $1 - X_{\mathrm{A}}^{\mathrm{sat}}$ or $1 - \phi_{\mathrm{A}}^{\mathrm{sat}}$ 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 physical interactions, and is not expected to describe all non-electrolyte systems encountered. Expressions for systems containing solute complexation with a single solvent [16,17]

$$\mathrm{A}_1 + \mathrm{C}_1 \rightleftharpoons \mathrm{AC} \qquad K_{\mathrm{AC}}^{\phi} = \hat{\phi}_{\mathrm{AC}}/\left(\hat{\phi}_{\mathrm{A}_1}\hat{\phi}_{\mathrm{C}_1}\right)$$

$$\begin{aligned} \ln \phi_{\mathrm{A}}^{\mathrm{sat}} = {} & \phi_{\mathrm{B}}^0 \ln\left(\phi_{\mathrm{A}}^{\mathrm{sat}}\right)_{\mathrm{B}} + \phi_{\mathrm{C}}^0 \ln\left(\phi_{\mathrm{A}}^{\mathrm{sat}}\right)_{\mathrm{C}} + \ln\left[1 + K_{\mathrm{AC}}^{\phi} \bar{V}_{\mathrm{A}} \phi_{\mathrm{C}}^0/\left(\bar{V}_{\mathrm{A}} + \bar{V}_{\mathrm{C}}\right)\right] \\ & - \phi_{\mathrm{C}}^0 \ln\left[1 + \bar{V}_{\mathrm{A}} K_{\mathrm{AC}}^{\phi}/\left(\bar{V}_{\mathrm{A}} + \bar{V}_{\mathrm{C}}\right)\right] + \bar{V}_{\mathrm{A}}\, \Delta \bar{G}_{\mathrm{BC}}^{\mathrm{fh}}/RT\left(X_{\mathrm{B}}^0 \bar{V}_{\mathrm{B}} + X_{\mathrm{C}}^0 \bar{V}_{\mathrm{C}}\right) \end{aligned} \quad (13)$$

and for systems where the solute complexes with both solvent components [18]

$$A_1 + C_1 \rightleftharpoons AC \quad K_{AC}^{\phi} = \hat{\phi}_{AC}/\left(\hat{\phi}_{A_1}\hat{\phi}_{C_1}\right)$$

$$A_1 + B_1 \rightleftharpoons AB \quad K_{AB}^{\phi} = \hat{\phi}_{AB}/\left(\hat{\phi}_{A_1}\hat{\phi}_{B_1}\right)$$

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

have additional equilibrium constant terms to represent the chemical interactions. To date, the extended NIBS (eqn. (13)) and competitive associated NIBS (eqn. (14)) models have been used to evaluate association parameters for presumed carbazole–dibutyl ether ($K_{AC}^{\phi} = 25.3 \pm 2.7$ [17,19,20]), anthracene–chlorobutane ($K_{AC}^{\phi} = 3.9 \pm 1.3$ [21]), anthracene–butyl acetate ($K_{AC}^{\phi} = 6.2 \pm 1.4$ [22]), pyrene–dichlorobutane ($K_{AC}^{\phi} = 14.2 \pm 2.4$ [23]) and various carbazole–chloroalkane ($K_{AB}^{\phi} = 2$–3 [18,24]) complexes from measured solute solubilities in binary solvent mixtures. The models are not perfect, however, as the calculated K_{AC}^{ϕ} (and K_{AB}^{ϕ}) values did vary slightly with the inert hydrocarbon co-solvent. In the case of carbazole–dibutyl ether, the constant ranged from a low value of $K_{AC}^{\phi} = 22$ for *n*-heptane to an upper limit of $K_{AC}^{\phi} = 30$ for both isooctane and *t*-butylcyclohexane co-solvents. This limitation does not detract from the model's predictive applications, and if an a priori value of about $K_{AC}^{\phi} = 26$ is assumed for the carbazole–dibutyl ether, the estimated solubilities fall within 6–10% of the observed data for the 10 systems studied.

THE MODIFIED WILSON MODEL

Interpretation of solution non-ideality can take several different forms, particularly in the case of very weak specific solute–solvent interactions as it is often difficult (if not impossible) to distinguish between complexation and preferential solvation of the solute by a solvent component. Thermodynamic models, such as the Wilson model, have been quite successful in describing liquid–vapor equilibria. The Wilson model expresses the excess molar Gibbs free energy $\Delta\bar{G}^{ex}$ and activity coefficients of a ternary mixture

$$\begin{aligned}\Delta\bar{G}^{ex} = {} & -RT\left[X_A \ln(X_A + X_B\Lambda_{AB} + X_C\Lambda_{AC}) + X_B \ln(X_A\Lambda_{BA} + X_B \right. \\ & \left. + X_C\Lambda_{BC}) + X_C \ln(X_A\Lambda_{CA} + X_B\Lambda_{CB} + X_C)\right]\end{aligned} \tag{15}$$

$$\begin{aligned}\ln \gamma_A = {} & 1 - \ln(X_A + X_B\Lambda_{AB} + X_C\Lambda_{AC}) - X_A/(X_A + X_B\Lambda_{AB} + X_C\Lambda_{AC}) \\ & - X_B\Lambda_{BA}/(X_A\Lambda_{BA} + X_B + X_C\Lambda_{BC}) \\ & - X_C\Lambda_{CA}/(X_A\Lambda_{CA} + X_B\Lambda_{CB} + X_C)\end{aligned} \tag{16}$$

where

$$\Lambda_{ij} = \left(\bar{V}_j/\bar{V}_i\right) \exp\left[-\left(\lambda_{ij} - \lambda_{ii}\right)/RT\right] \tag{17}$$

in terms of six adjustable Λ_{ij}-parameters, two from each of the three contributing sub-binary systems. A prior knowledge of six parameters is required to predict solute activity coefficients in binary solvent mixtures. The nature of solubility determinations has for the most part excluded the use of the Wilson equation from predictions involving isothermal solid–liquid equilibria. It is impossible to evaluate the two sets of required solute–solvent parameters (Λ_{AB} and Λ_{BA}; Λ_{AC} and Λ_{CA}) from only the single data point associated with the saturated mole fraction solubility of the solute in the two pure solvents.

To overcome this limitation, Comer and Kopecni [11] suggested eliminating two of the solute–solvent parameters

$$\ln \gamma_A^\infty = 1 - \frac{X_B^0 \Lambda_{BA}}{X_B^0 + X_C^0 \Lambda_{BC}} - \frac{X_C^0 \Lambda_{CA}}{X_C^0 + X_B^0 \Lambda_{CB}} \tag{18}$$

on the basis that at infinite dilution the local volume fraction composition around the solute would be approximately equal to zero. The remaining solute–solvent parameters can be determined conveniently from either solute activity coefficients.

$$\ln(\gamma_A^\infty)_i = 1 - \Lambda_{iA} \qquad (i = \text{B, C}) \tag{19}$$

or solute solubilities (under the condition that $\gamma_A^\infty = \gamma_A^{sat}$)

$$\ln\left(a_A^{solid}/X_A^{sat}\right) = 1 - \Lambda_{iA} \qquad (i = \text{B, C}) \tag{20}$$

measured in the two pure solvents, whereas Λ_{BC} and Λ_{CB} values are obtained from

$$\Delta\bar{G}_{BC}^{ex} = -RT\left[X_B^0 \ln\left(X_B^0 + X_C^0 \Lambda_{BC}\right) + X_C^0 \ln\left(X_B^0 \Lambda_{CB} + X_C^0\right)\right] \tag{21}$$

by a least squares analysis of binary $\Delta\bar{G}_{BC}^{ex}$ data in accordance with eqn. (21). Combination of eqns. (18) and (20) gives the following expression

$$\ln\left(a_A^{solid}/X_A^{sat}\right) = 1 - \left(\frac{X_B^0\left\{1 - \ln\left[a_A^{solid}/\left(X_A^{sat}\right)_B\right]\right\}}{X_B^0 + X_C^0 \Lambda_{BC}}\right) - \left(\frac{X_C^0\left\{1 - \ln\left[a_A^{solid}/\left(X_A^{sat}\right)_C\right]\right\}}{X_B^0 \Lambda_{CB} + X_C^0}\right) \tag{22}$$

for predicting solid–liquid equilibria and solute solubilities in binary solvent systems. The Modified Wilson equation is a relatively new expression and its predictive limitations have not yet been properly assessed.

PREDICTIVE ABILITIES OF THE NIBS AND MODIFIED WILSON MODELS

The chemical literature contains thermodynamic data for a number of solutes dissolved in both non-complexing and complexing binary solvent mixtures. Published experimental data can be used to compare the predictive abilities of the various NIBS (eqn. (10)–(14)) and Modified Wilson (eqn. (22)) expressions. For systems exhibiting only modest deviations from ideality it should be difficult, if not impossible, to distinguish statistically between the predictive expressions. All solution models should adequately describe these simple systems. In fact, careful examination reveals that eqns. (10) and (22) are mathematically equivalent in the very special case of an ideal binary solvent mixture for which both Λ_{BC} and Λ_{CB} equal unity. Differences between these two equations, however, do become more pronounced with increasing skew in the binary $\Delta\bar{G}_{BC}^{ex}$ curve, which suggests the possibilities of using cosolvents having considerable molecular size disparity. A more demanding and definite test is to describe the thermochemical behavior of a solute in highly skewed, non-ideal binary solvents and systems for which the measured solute properties in the two pure solvents are quite dissimilar. With these ideas in mind, we have estimated anthracene, thianthrene and carbazole solubilities in the 72 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. The three 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, and the binary solvent mixtures exhibit varying degrees of solution non-ideality.

Table 1 presents a summarized comparison between the basic NIBS and Modified Wilson equations for predicting anthracene, thianthrene and carbazole solubilities in 50 systems believed to contain only non-specific interactions. Solute and solvent properties used in the NIBS predictions (see Table 3), or the method used to estimate $\Delta\bar{G}_{BC}^{ex}$ if experimental values were not available, were given in the earlier publications [17–31] from which the actual solubility data were taken. Wilson parameters (see Table 4) for the various binary solvent mixtures were obtained from experimental Gibbs free energy data whenever possible. For a few select systems, vapor pressure and $\Delta\bar{G}_{BC}^{ex}$ data have been reported by several research groups, and we were thus able to examine the effect that experimental uncertainties in $\Delta\bar{G}_{BC}^{ex}$ values have on the Modified Wilson solubility predictions. Surprisingly, a small ±5 cal mol^{-1} error in the binary $\Delta\bar{G}_{BC}^{ex}$ data can affect the predicted solubilities by more than 10%, particularly if the error significantly changes the relative skew in the $\Delta\bar{G}_{BC}^{ex}$ versus mole fraction composition curve as would be the case for a nearly ideal binary solution.

TABLE 1

Summarized comparison between experimental anthracene, thianthrene and carbazole solubilities and calculated values based on the NIBS and Modified Wilson equations

Binary solvent system	Ref.	Dev. (%) [a], NIBS eqns.			Dev. (%) [a]	$\Delta\bar{G}^{ex}_{BC}$
		(10)	(11)	(12)	(22)	data
Anthracene						
Carbon tetrachloride + *n*-hexane	28	+7.0	0.9	1.2	−11.1	Yes
Carbon tetrachloride + cyclohexane	28	0.2	−1.5	−1.4	−6.3	Yes
Carbon tetrachloride + *n*-heptane	28	+10.5	+2.4	+2.8	−5.4	Yes
Carbon tetrachloride + methylcyclohexane	28	+4.3	−1.1	0.9	−3.9	No
Carbon tetrachloride + *n*-octane	28	+11.2	+2.3	+2.9	1.2	Yes
Carbon tetrachloride + iso-octane	28	+12.4	−2.2	−1.8	−9.2	Yes
Toluene + *n*-hexane	27	−1.1	−5.7	−5.6	−27.5	No
Toluene + cyclohexane	27	−12.7	−13.6	−13.4	−18.0	Yes
Toluene + *n*-heptane	27	+4.6	−4.3	−4.0	−13.5	Yes
Toluene + methylcyclohexane	27	−7.4	−10.9	−10.7	−18.5	Yes
Toluene + *n*-octane	27	+8.0	−3.6	−3.3	−14.6	No
Toluene + iso-octane	27	+14.6	1.7	1.6	−35.0	No
Toluene + cyclooctane	27	−2.5	−5.8	−5.6	−11.4	Yes
Cyclohexane + *n*-hexane	25	−1.2	−1.2	−1.1	−11.9	Yes
Cyclohexane + *n*-heptane	25	1.0	0.6	0.6	−4.5	Yes
Cyclohexane + iso-octane	25	+1.9	−1.2	−1.0	−4.7	Yes
Cyclohexane + *n*-octane	25	−1.3	+0.6	+0.7	−7.4	Yes
Cyclohexane + cyclooctane	25	−1.4	0.9	0.9	−2.7	Yes
Benzene + *n*-hexane	25	+2.7	−6.0	−5.4	−35.0	Yes
Benzene + *n*-heptane	25	+7.9	−4.6	−3.8	−25.3	Yes
Benzene + cyclohexane	25	−6.9	−7.7	−7.5	−22.2	Yes
Benzene + cyclooctane	25	1.8	−8.3	−7.7	−23.1	Yes
Benzene + iso-octane	25	+10.5	−11.6	−10.7	−24.3	Yes
Dibutyl ether + *n*-hexane	29	−5.9	0.3	0.3	−4.0	No
Dibutyl ether + *n*-heptane	29	−4.3	−1.8	−1.8	−3.4	No
Dibutyl ether + cyclohexane	29	−9.4	−1.3	−1.0	−4.8	No
Dibutyl ether + methylcyclohexane	29	−6.9	−2.1	−2.1	−5.5	No
Dibutyl ether + *n*-octane	29	−2.6	−2.1	−2.1	−3.0	No
Dibutyl ether + iso-octane	29	−2.6	−2.5	−2.5	−11.1	No
Dibutyl ether + cyclooctane	29	−6.9	−4.6	−4.6	−8.8	No
p-Xylene + *n*-hexane	26	−7.9	−8.2	−8.2	−22.8	No
p-Xylene + cyclohexane	26	−12.7	−5.3	−5.3	−10.7	Yes
p-Xylene + methylcyclohexane	26	−10.0	−9.9	−9.9	−15.8	No
p-Xylene + *n*-octane	26	+2.0	−5.9	−5.9	−16.3	No
p-Xylene + *n*-heptane	26	+0.7	−4.0	−3.9	−15.4	No
p-Xylene + iso-octane	26	+10.6	0.6	0.6	4.9	No
Benzene + *n*-octane	26	+12.7	2.2	1.4	−13.0	Yes
Benzene + methylcyclohexane	26	+2.7	−4.7	−4.2	−26.6	Yes

TABLE 1 (continued)

Binary solvent system	Ref.	Dev. (%) [a], NIBS eqns. (10)	(11)	(12)	Dev. (%) [a] (22)	$\Delta\overline{G}_{BC}^{ex}$ data
Thianthrene						
Cyclohexane + *n*-hexane	30	0.3	−1.6	−1.3	−15.3	Yes
Cyclohexane + methylcyclohexane	30	0.4	0.5	0.7	0.7	Yes
Cyclohexane + *n*-heptane	30	0.6	−2.8	−2.5	−5.2	Yes
Cyclohexane + *n*-octane	30	+2.2	−0.9	−0.6	1.1	Yes
Cyclohexane + cyclooctane	30	−4.9	−1.5	−1.3	−6.4	Yes
Cyclohexane + iso-octane	30	+4.0	−2.5	−2.1	−5.4	Yes
Carbazole						
Cyclohexane + *n*-hexane	31	0.5	−0.7	−0.7	−21.6	Yes
Cyclohexane + *n*-heptane	31	0.5	0.5	0.4	−9.4	Yes
Cyclohexane + *n*-octane	31	−0.8	0.6	0.8	−13.3	Yes
Cyclohexane + methylcyclohexane	31	0.2	0.2	0.3	−1.4	Yes
Cyclohexane + iso-octane	31	+1.6	−1.4	−1.2	−8.9	Yes
Cyclohexane + cyclooctane	31	−2.7	0.5	0.5	−5.7	Yes

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

Wilson parameters are extremely sensitive to skew. Every effort was made to compute Λ_{BC} and Λ_{CB} parameters which minimized deviations between observed and back-calculated $\Delta\overline{G}_{BC}^{ex}$ values, while simultaneously retaining the shape of the free energy curve. Inherent in this parameterization is the underlying assumption that the Wilson model does adequately describe the binary properties. In the few instances where large discrepancies existed in published $\Delta\overline{G}_{BC}^{ex}$ values, i.e. benzene + *n*-heptane and benzene + *n*-hexane systems, Wilson parameters were computed from each different data set. To conserve journal space, only one set of parameters and predictions per binary system are tabulated. Experimental $\Delta\overline{G}_{BC}^{ex}$ data could not be found in the chemical literature for dibutyl ether + alkane, *p*-xylene + alkane and several other select mixtures, and numerical values used in the Wilson equation parameterization were thus estimated via the Scatchard–Hildebrand solubility approach, as was also done in the case of the NIBS predictions. Understandably, estimation of binary $\Delta\overline{G}_{BC}^{ex}$ data becomes incorporated into the overall predictive method whenever experimental free energy data is not available, and comparison of the predictive abilities of the various NIBS and Modified Wilson expressions must reflect this fact. While one may always argue that failure of either model could conceivably result from poor $\Delta\overline{G}_{BC}^{ex}$ predictions, there are 34 systems marked in Table 1 for which experimental free energy data could be found. Our discussions include all systems studied.

TABLE 2

Summarized comparison between experimental carbazole and anthracene solubilities and calculated values based on the Extended NIBS and Modified Wilson equations [a]

Binary solvent system	Ref.	Dev. (%) [b], NIBS eqn.		Dev. (%) [b]
		K^{ϕ}_{AC}	(13)	(22)
Carbazole				
Dibutyl ether + *n*-hexane	17	24.0	2.0	−58.1
Dibutyl ether + *n*-heptane	17	22.0	1.8	−53.8
Dibutyl ether + *n*-octane	17	25.0	1.7	−57.5
Dibutyl ether + cyclohexane	17	24.0	2.2	−59.3
Dibutyl ether + methylcyclohexane	17	26.0	1.8	−65.0
Dibutyl ether + iso-octane	17	30.0	1.7	−71.6
Dibutyl ether + cyclooctane	17	25.0	2.1	−83.7
Dibutyl ether + *n*-hexadecane	19	24.0	1.4	−21.0
Dibutyl ether + squalane	19	23.0	1.7	−18.6
Dibutyl ether + *t*-butylcyclohexane	20	30.0	1.5	−60.4
Anthracene				
1-Chlorobutane + *n*-hexane	21	3.5	0.6	−17.5
1-Chlorobutane + *n*-heptane	21	3.5	0.6	−13.8
1-Chlorobutane + *n*-octane	21	3.0	0.6	−11.5
1-Chlorobutane + cyclohexane	21	6.0	1.3	−18.5
1-Chlorobutane + methylcyclohexane	21	5.0	0.3	−16.2
1-Chlorobutane + iso-octane	21	2.5	1.0	−23.4
Butyl acetate + *n*-hexane	22	5.5	0.3	−28.3
Butyl acetate + *n*-heptane	22	5.8	0.4	−25.2
Butyl acetate + *n*-octane	22	5.5	0.6	−23.8
Butyl acetate + cyclohexane	22	8.0	1.5	−23.7
Butyl acetate + methylcyclohexane	22	8.0	0.9	−27.7
Butyl acetate + iso-octane	22	4.5	1.3	−36.2

[a] No $\Delta \bar{G}^{ex}_{BC}$ data are available for any of these systems.

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

Readers can focus their attention on the smaller 34 system subset if they so desire.

Inspection of Table 1 reveals that the NIBS solubility (and activity coefficient) predictions are in fairly good agreement with the observed values. In general, eqns. (11) and (12) are comparable with overall average absolute deviations of 3.4 and 3.2%, respectively, and are superior to eqn. (10), which has an average deviation of 5.0%. 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 weighting factors with molecular surface

TABLE 3

Solute and solvent properties used in the calculations

Component (i)	$\bar{V}_i$ (cm^3 mol^{-1})	δ_i (cal cm^{-3})$^{1/2}$
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
iso-Octane	166.09	6.86
Cyclooctane	134.88	8.51
Benzene	89.41	9.16
Toluene	106.84	8.93
p-Xylene	123.93	8.83
Dibutyl ether	170.41	7.76
Carbon tetrachloride	97.08	8.55
Squalane	525.30	7.90
n-Hexadecane	294.12	7.99
t-Butylcyclohexane	173.93	7.82
1-Chlorobutane	105.10	8.37
Butyl acetate	132.61	8.69
Anthracene	150.00	$a_A^{\text{solid}} = 0.01049$
Carbazole	150.00	$a_A^{\text{solid}} = 0.009354$
Thianthrene	156.00	$a_A^{\text{solid}} = 0.04411$

areas [25–27], 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 and molecular geometries. In comparison, the Modified Wilson equation grossly underpredicts the experimental solubilities, especially in the systems which cover a large mole fraction solubility range or which have highly skewed $\Delta\bar{G}_{BC}^{ex}$ binary data. Particularly surprising is the failure of eqn. (22) to predict carbazole solubilities in the six cyclohexane + alkane solvent mixtures, for which experimental $\Delta\bar{G}_{BC}^{ex}$ data is known. These six systems cover an extremely narrow mole fraction range, from $X_A^{sat} = 0.000139$ to $X_A^{sat} = 0.000183$ in the case of the n-hexane + cyclohexane, yet eqn. (22) underpredicts the observed values by as much as 10–20% (or more). Careful examination of Table 1 further reveals that the NIBS expressions are superior to the Modified Wilson equation, irrespective of whether the $\Delta\bar{G}_{BC}^{ex}$ values are known (e.g., anthracene in benzene + alkanes) or estimated (e.g., anthracene in dibutyl ether + alkanes).

The abilities of the extended NIBS and Modified Wilson models to describe non-electrolyte systems are compared in Table 2 for carbazole dissolved in ten dibutyl ether + alkane mixtures and for anthracene dissolved in six binary chlorobutane + alkane and butyl acetate + alkane solvent mixtures. Based on spectroscopic studies on similar mixtures [32–34], carbazole is expected to interact specifically with dibutyl ether to form a 1 : 1

TABLE 4

Binary interaction parameters used in the Modified Wilson predictions

Component (i) + Component (j)	Λ_{ij}	Λ_{ji}
Cyclohexane + *n*-hexane	1.394	0.552
Benzene + cyclohexane	0.830	0.697
Cyclohexane + carbon tetrachloride	0.827	1.068
Carbon tetrachloride + *n*-hexane	1.254	0.575
Cyclohexane + *n*-heptane	0.944	0.944
Cyclohexane + *n*-octane	0.602	1.377
Carbon tetrachloride + *n*-heptane	1.338	0.553
Benzene + *n*-hexane	1.090	0.380
Dibutyl ether + *t*-butylcyclohexane	1.000	1.000
Dibutyl ether + *n*-octane	0.993	0.993
Dibutyl ether + *n*-hexane	0.780	1.180
Dibutyl ether + *n*-heptane	0.900	1.086
Dibutyl ether + iso-octane	0.889	0.888
Dibutyl ether + cyclooctane	0.730	1.152
Cyclohexane + methylcyclohexane	0.993	0.994
Cyclooctane + cyclohexane	0.980	0.979
Benzene + iso-octane	1.010	0.460
Methylcyclohexane + *p*-xylene	0.872	0.921
Cyclohexane + *p*-xylene	1.136	0.484
n-Octane + *p*-xylene	0.588	1.066
n-Heptane + *p*-xylene	0.665	0.965
Benzene + *n*-octane	1.164	0.410
p-Xylene + iso-octane	0.397	0.800
Methylcyclohexane + carbon tetrachloride	0.730	1.203
Cyclohexane + toluene	0.896	0.896
Methylcyclohexane + toluene	0.770	0.870
Toluene + cyclooctane	0.755	0.795
n-Heptane + toluene	0.639	0.925
Dibutyl ether + cyclohexane [a]	0.650	1.375
Dibutyl ether + methylcyclohexane	0.838	1.141
n-Octane + carbon tetrachloride	0.660	1.212
iso-Octane + cyclohexane	0.708	1.251
Cyclooctane + benzene	0.455	1.193
Benzene + *n*-heptane	1.191	0.376
n-Octane + toluene	0.500	1.160
n-Hexane + toluene	0.540	0.980
n-Hexane + *p*-xylene	0.740	0.770
Methylcyclohexane + benzene	0.418	1.190
iso-Octane + toluene	0.323	0.890
Dibutyl ether + squalane [a]	1.317	0.717
Dibutyl ether + *n*-hexadecane [a]	1.200	0.800

TABLE 4 (continued)

Component (i) + Component (j)	Λ_{ij}	Λ_{ji}
1-Chlorobutane + cyclohexane	0.997	0.997
1-Chlorobutane + *n*-hexane	1.106	0.686
1-Chlorobutane + iso-octane	1.155	0.451
1-Chlorobutane + *n*-octane	1.277	0.631
1-Chlorobutane + methylcyclohexane	1.090	0.860
1-Chlorobutane + *n*-heptane	1.206	0.676
Butyl acetate + cyclohexane	0.700	1.295
Butyl acetate + *n*-hexane	0.787	0.787
Butyl acetate + methylcyclohexane	0.920	0.920
Butyl acetate + *n*-heptane	0.942	0.743
Butyl acetate + *n*-octane	1.049	0.658
Butyl acetate + iso-octane	0.820	0.453
iso-Octane + carbon tetrachloride	0.540	1.283

[a] Dissimilar Wilson parameters are needed to imitate the skew in the free energy curve. The estimated $\Delta \bar{G}^{ex}_{BC}$ values are small.

carbazole–dibutyl ether association complex. Specific interactions between aromatic hydrocarbons and esters have also been suggested in past studies [35,36]. Examination of Table 2 reveals that the extended NIBS model can describe the experimental solubilities to within an average absolute deviation of about 2% using a single K^{ϕ}_{AC} value. In the case of the presumed carbazole–dibutyl ether complex, the calculated equilibrium constant varied from a low value of $K^{\phi}_{AC} = 22$ for *n*-heptane to an upper value of $K^{\phi}_{AC} = 30$ for both the iso-octane and *t*-butylcyclohexane cosolvents. In comparison, the Modified Wilson equation again grossly underpredicted the experimental values, this time by as much as 80–100%. Complexation between the solutes and one of the solvent components is not a viable explanation for the failure of eqn. (22) as the original Wilson model assumes preferential solvation, which should be indistinguishable from complexation in the case of very weak molecular complex.

The large negative deviations, noted in many of the complexing and non-complexing systems, appear to result from the manner in which the binary solvent non-ideality is incorporated into the Modified Wilson expression. Positive $\Delta \bar{G}^{ex}_{BC}$ values for all of the solvent systems studied necessitated that at least one of the Λ parameters must be less than unity. Assuming an exaggerated hypothetical situation in which the mole fraction solubility of anthracene is $(X^{sat}_A)_B = 0.00155$ and $(X^{sat}_A)_C = 0.00157$ in the two pure solvents and Wilson parameters of $\Lambda_{BC} = \Lambda_{CB} = 0.850$, one predicts an anthracene solubility of $X^{sat}_A = 0.00145$ at $X^0_B = 0.500$. The predicted value is less than the simple geometric mole fraction solubility average of $X^{sat}_A = 0.00156$ (i.e., from $\ln X^{sat}_A = X^0_B \ln(X^{sat}_A)_B + X^0_C \ln(X^{sat}_A)_C$) or measured values in either pure solvent, and suggests that positive $\Delta \bar{G}^{ex}_{BC}$ values tend to decrease solute solubility. Unfortunately, this observation is contrary to actual experimental data. Positive $\Delta \bar{G}^{ex}_{BC}$ values generally increase solubility and in the case of anthracene dissolved in cyclohexane + n-heptane [25] and thianthrene in cyclohexane + methylcyclohexane [30] binary solvent mixtures led to small maxima in X_A^{sat} versus X_B^0 curves. Results of the present study clearly show that the various NIBS models are far superior to the Modified Wilson model in predicting solubilities (and infinite dilution activity coefficients) of anthracene, thianthrene and carbazole in the 72 systems considered. Large deviations between calculated and observed values suggest that this particular modification of the Wilson equation is not applicable to predicting solid–liquid equilibria and solute solubilities in binary solvent mixtures.

MATHEMATICAL REPRESENTATION OF EXPERIMENTAL SOLUBILITY DATA

Expressions for predicting the thermodynamic properties of ternary systems have served as the point-of-departure for mathematical representation of experimental excess enthalpy and excess volume data. Differences between predicted and observed values are expressed as

$$\left(\Delta \bar{Z}^{ex}_{ABC}\right)^{exp} - \left(\Delta \bar{Z}^{ex}_{ABC}\right)^{calc} = X_A X_B X_C Q_{ABC} \tag{23}$$

with Q-functions of varying complexity. For most systems commonly encountered, the experimental data can be adequately represented by a power series expansion

$$Q_{ABC} = A_{ABC} + \sum_{i=1}^{r} B^i_{AB}(X_A - X_B)^i + \sum_{j=1}^{s} B^j_{AC}(X_A - X_C)^j + \sum_{k=1}^{t} B^k_{BC}(X_B - X_C)^k \tag{24}$$

though rarely are experimental data determined with sufficient precision to justify more than a few parameters.

Conceptually, these ideas can be extended to solute solubilities in binary solvent mixtures, however, there has never been a sufficiently large solubility data base to warrant computerized storage in equational form. Our published solubility data now include over 180 different systems, and, with computerized data storage and retrieval becoming increasing popular, it is now time to consider how experimental solubility data should be reported in the chemical literature. As part of the present study we have also examined possible mathematical representations based upon both the NIBS model

$$\ln X_A^{sat} = X_B^0 \ln(X_A^{sat})_B + X_C^0 \ln(X_A^{sat})_C + X_B^0 X_C^0 \sum_{i=0}^{r} S_i (X_B^0 - X_C^0)^i \tag{25}$$

and the Modified Wilson model

$$\ln\left(a_{\mathrm{A}}^{\mathrm{solid}}/X_{\mathrm{A}}^{\mathrm{sat}}\right)=1-\frac{X_{\mathrm{B}}^{0}\left\{1-\ln\left[a_{\mathrm{A}}^{\mathrm{solid}}/\left(X_{\mathrm{A}}^{\mathrm{sat}}\right)_{\mathrm{B}}\right]\right\}}{X_{\mathrm{B}}^{0}+X_{\mathrm{C}}^{0}\Lambda_{\mathrm{BC}}^{\mathrm{adj}}}-\frac{X_{\mathrm{C}}^{0}\left\{1-\ln\left[a_{\mathrm{A}}^{\mathrm{solid}}/\left(X_{\mathrm{A}}^{\mathrm{sat}}\right)_{\mathrm{C}}\right]\right\}}{X_{\mathrm{B}}^{0}\Lambda_{\mathrm{CB}}^{\mathrm{adj}}+X_{\mathrm{C}}^{0}} \qquad (26)$$

with the corresponding S_i and $\Lambda_{ij}^{\mathrm{adj}}$ parameters being determined from measured solubility data via a least squares analysis. Examination of these two expressions reveals that eqn. (25) is perhaps the more versatile of the two mathematical representations. The Redlich–Kister summation term may contain as many 'curve-fit' S_i parameters as are needed to describe the experimental data. Equation (26) on the other hand is limited to only the two $\Lambda_{ij}^{\mathrm{adj}}$ parameters, and may not be able to describe adequately the larger solubility ranges encountered in systems containing strong solute–solvent complexation.

A set of preliminary mathematical representations involving anthracene dissolved in six binary chlorobutane + alkane systems is summarized in Table 5 in the form of 'curve-fit' parameters and percent deviations in back-calculated solubilities (and activity coefficients) for the two-parameter expressions. During the course of evaluating parameters for the Modified Wilson equation, it was noted that on a $\Lambda_{\mathrm{BC}}^{\mathrm{adj}}$ versus $\Lambda_{\mathrm{CB}}^{\mathrm{adj}}$ versus % Deviation three-dimensional map there existed several parameter pairs which described the solubility to within the quoted experimental uncertainty of ±1.5%. For example, in the case of anthracene solubilities in chlorobutane + cyclohexane mixtures, the percent deviation was approximately 1.4% for $\Lambda_{\mathrm{BC}}^{\mathrm{adj}} = 1.672$ and $\Lambda_{\mathrm{CB}}^{\mathrm{adj}} = 0.264$, 1.2% for $\Lambda_{\mathrm{BC}}^{\mathrm{adj}} = 1.793$ and $\Lambda_{\mathrm{CB}}^{\mathrm{adj}} = 0.300$, and 0.9% for $\Lambda_{\mathrm{BC}}^{\mathrm{adj}} = 2.200$ and $\Lambda_{\mathrm{CB}}^{\mathrm{adj}} = 0.450$. No special attempt was made to optimize calculated $\Lambda_{ij}^{\mathrm{adj}}$ values as we wished only to learn if eqn. (26) could be used to represent

TABLE 5

Mathematical representation of anthracene solubilities in several binary alkane (B) + 1-chlorobutane (c) solvent mixtures

Binary solvent mixture	Eqn. (25)			Eqn. (26)		
	S_0	S_1	% Dev. [a]	$\Lambda_{\mathrm{BC}}^{\mathrm{adj}}$	$\Lambda_{\mathrm{CB}}^{\mathrm{adj}}$	% Dev. [a]
n-Hexane + chlorobutane	0.5696	0.0164	0.5	1.427	0.693	1.1
n-Heptane + chlorobutane	0.3379	−0.0038	0.5	1.303	0.773	0.6
n-Octane + chlorobutane	0.2116	0.0597	0.3	1.047	0.640	0.3
Cyclohexane + chlorobutane	1.0492	0.3215	0.9	2.200	0.450	0.9
Methylcyclohexane + chlorobutane	0.7611	0.1774	0.6	1.835	0.563	0.4
Iso-octane + chlorobutane	0.2500	−0.0577	0.6	1.163	0.921	0.7

[a] Deviation (%) = $(100/N^{1/2})\{\Sigma|\ln(X_{\mathrm{A}}^{\mathrm{calc}}/X_{\mathrm{A}}^{\mathrm{exp}})|^2\}^{1/2}$.

solubility data mathematically. Any parameter set having a ±1% deviation was sufficient for this purpose.

As far as descriptive abilities are concerned, eqns. (25) and (26) are both able to describe the 5-fold range in experimental solubilities to within ±1%, which is less than experimental uncertainty. From a computational standpoint, however, eqn. (25) will likely be preferred because most research groups involved in reporting thermodynamic properties already have computer programs for evaluating Redlich–Kister coefficients. In the case of the 2-parameter Redlich–Kister fit, the computations require only a simple linear least squares analysis. With this idea in mind, we recommend that researchers now begin reporting isothermal solute sobulities in binary solvent mixtures in terms of eqn. (25) as part of their experimental data presentation. Mathematical representation of solubility and activity coefficient data will be discussed further in subsequent papers when we report additional experimental values.

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