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Mathematical representation of thermodynamic properties Part 2. Derivation of the combined nearly ideal binary solvent (NIBS)/Redlich–Kister mathematical representation from a two-body and three-body interactional mixing model

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Abstract

A relatively simple two-body and three-body interactional mixing model is used to derive expressions for the mathematical representation of experimental solute solubilities and activity coefficients in binary solvent mixtures. The derived expressions are identical with those based upon the combined NIBS/Redlich–Kister model, and enable solute solubility/activity coefficient data to be expressed as a mole fraction average of measured solute properties in both pure solvents plus a term involving a power series expansion in solvent composition.

INTRODUCTION

Knowledge of infinite dilution activity coefficients is required in the 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, 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

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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 a single data point associated with the saturated solute in a pure solvent. The nearly ideal binary solvent (NIBS) model [1–3] developed previously provides a relatively simple method for estimating the excess partial molar properties of a solute Z_A^{ex} at infinite dilution in a binary solvent (components B and C)

$$Z_A^{ex} = f_B^0 (Z_A^{ex})_B + f_C^0 (Z_A^{ex})_C - \Gamma_A (X_B^0 \Gamma_B + X_C^0 \Gamma_C)^{-1} Z_{BC}^{ex} \tag{1}$$

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

in terms of a weighted mole fraction average of solute properties in the two pure solvents $(Z_A^{ex})_B$ and $(Z_A^{ex})_C$, and a contribution owing to the unmixing of the solvent pair by the presence of the solute. Equation (1) (with $Z^{ex} = G^{ex}$) gives accurate predictions for naphthalene, iodine, *p*-benzoquinone, benzil, *p*-dibromobenzene, carbazole, thianthrene, benzoic acid, tolylacetic acid, and phenylacetic acid solubilities in systems of nonspecific interactions when molar volumes are used as weighting factors ($\Gamma_i = V_i$) [3–8]. Approximation of weighting factors with molecular surface areas enables eqn. (1) to provide accurate predictions for anthracene [9] and pyrene [10] solubilities in binary solvent mixtures containing benzene.

More recently, both the NIBS model and a modified version of the Wilson equation [11] have served as the point of departure fo the mathematical representation of solute solubility as a function of solvent composition [12,13]

$$\ln X_A^{sat} = X_B^0 \ln(X_A^{sat})_B + X_C^0 \ln(X_A^{sat})_C + X_B^0 X_C^0 \sum_{i=0}^{n} S_i (X_B^0 - X_C^0)^i \tag{3}$$

and

$$\ln(a_A^{solid}/X_A^{sat}) = 1 - \frac{X_B^0 \{1 - \ln[a_A^{solid}/(X_A^{sat})_B]\}}{X_B^0 + X_C^0 \Lambda_{BC}^{adj}} - \frac{X_C^0 \{1 - \ln[a_A^{solid}/(X_A^{sat})_C]\}}{X_B^0 \Lambda_{CB}^{adj} + X_C^0} \tag{4}$$

with the various S_i and Λ_{ij}^{adj} coefficients computed from measured solubility data via least-squares analysis. The symbols are defined at the end of the manuscript. To date eqn. (3) has been successfully used to describe anthracene solubilities in numerous binary alkane + dibutyl oxalate, alkane + carbon tetrachloride, alkane + dibutyl ether, alkane + aromatic hydrocarbon and alkane + dimethyl adipate mixtures, and carbazole solubilities in binary alkane + dibutyl ether and alkane + tetrahydropyran solvent mixtures covering up to a 300-fold range in mole fraction solubilities [12–14]. I have been unable, though, to derive its basic mathematical form from any of the known two-body interactional solution models.

Hwang and coworkers [15] recently presented a thermodynamic mixing model that includes contributions from both two-body and three-body interactions. The derived expressions were found to correlate exactly binary excess free energy data, and also to predict fairly accurately ternary free energies of several aqueous–organic systems. During the course of extending Hwang and coworkers' two/three-body interactional model to other thermodynamic properties, I noted that through appropriate algebraic manipulations and simplifying assumptions it was possible to transform the model's infinite dilution activity coefficient expression into eqn. (3). In this paper I present the formal derivation of the combined NIBS/Redlich–Kister mathematical representation (eqn. (3)) based upon a two/three-body interactional model. To familiarize readers with the procedure used in the derivation of eqn. (3), I will first briefly review the interaction model of Hwang et al.

DEVELOPMENT OF BINARY MIXING MODEL AND CORRELATION EXPRESSIONS

Binary mixtures contain two-body interactions (e.g., A–A, B–B and A–B), and three-body interactions (eq., A–A–A, B–B–B, A–A–B and A–B–B) to a much lesser extent. Higher-order interactions are generally negligible. Random mixing requires that internal energy contributions from all two-body interactions be

$$u_{\mathrm{m}}(2) = X_{\mathrm{A}}^2 u_{\mathrm{AA}} + X_{\mathrm{B}}^2 u_{\mathrm{BB}} + 2X_{\mathrm{A}}X_{\mathrm{B}}u_{\mathrm{AB}} \tag{5}$$

and that those from all three-body interactions be

$$u_{\mathrm{m}}(3) = X_{\mathrm{A}}^3 u_{\mathrm{AAA}} + X_{\mathrm{B}}^3 u_{\mathrm{BBB}} + 3X_{\mathrm{A}}X_{\mathrm{B}}(X_{\mathrm{A}}u_{\mathrm{AAB}}^* + X_{\mathrm{B}}u_{\mathrm{ABB}}^*) \tag{6}$$

given as a simple summation over all possible interactions, and that the number of each type of interaction must be proportional to a weighted mole fraction product. Molecular interactions between molecules A and B are counted twice as either A–B or B–A, whereas ternary interactions are triply degenerate. For simplicity the present model is restricted to molecules of comparable size so that Raoult's law will represent a good approximation of the entropic contribution to the overall free energy of mixing.

The apparent three-body interactional parameters u_{AAB}^* and u_{ABB}^* are not purely cross-parameters except in infinitely dilute solutions. In a non-random mixture, some AAA and BBB clustering may occur along with mixed collisions. Hence the apparent interactions are concentration dependent. The empirical forms for the apparent interactions at infinite dilution are assumed to be

$$u_{\mathrm{AAB}}^* = u_{\mathrm{AAB}}(1 - c_1 X_{\mathrm{A}}^2) \tag{7}$$

$$u_{\mathrm{ABB}}^* = u_{\mathrm{ABB}}(1 - c_2 X_{\mathrm{B}}^2) \tag{8}$$

where c_1 and c_2 denote constants. Through suitable mathematical manipulation, eqns. (6)–(8) can be combined

$$\begin{aligned} u_{\mathrm{m}}(3) &= X_{\mathrm{A}}^2 u_{\mathrm{AAA}} + X_{\mathrm{B}}^2 u_{\mathrm{BBB}} + X_{\mathrm{A}} X_{\mathrm{B}} \\ &\quad \times \left[3(X_{\mathrm{A}} u_{\mathrm{AAB}}^* + X_{\mathrm{B}} u_{\mathrm{ABB}}^*) - X_{\mathrm{A}} u_{\mathrm{AAA}} - X_{\mathrm{B}} u_{\mathrm{BBB}}\right] \\ &= X_{\mathrm{A}}^2 u_{\mathrm{AAA}} + X_{\mathrm{B}}^2 u_{\mathrm{BBB}} + X_{\mathrm{A}} X_{\mathrm{B}} \left[X_{\mathrm{A}}(3u_{\mathrm{AAB}} - u_{\mathrm{AAA}}) \right. \\ &\quad \left. + X_{\mathrm{B}}(3u_{\mathrm{ABB}} - u_{\mathrm{BBB}}) - 3u_{\mathrm{AAB}} c_1 X_{\mathrm{A}}^3 - 3u_{\mathrm{ABB}} c_2 X_{\mathrm{B}}^3 \right] \end{aligned} \tag{9}$$

The compositional dependence can be further simplified by assuming that

$$3u_{\mathrm{AAB}} - u_{\mathrm{AAA}} = 3u_{\mathrm{ABB}} - u_{\mathrm{BBB}} = \delta u_{(3,\mathrm{AB})} \tag{10}$$

where $\delta u_{(3,ij)}$ eliminates the effect of pure three-body interactions u_{AAA} and u_{BBB} from mixed interactions. The molar internal energy u_{m} involves the sum of all molecular interactions in solution

$$\begin{aligned} u_{\mathrm{m}} &= u_{\mathrm{m}}(2) + u_{\mathrm{m}}(3) \\ &= X_A^2(u_{AA} + u_{AAA}) + X_B^2(u_{BB} + u_{BBB}) + X_A X_B \\ &\quad \times \left[2u_{AB} + \delta u_{(3,AB)} - 3u_{AAB} c_1 X_A^3 - 3u_{ABB} c_2 X_B^3\right] \\ &= X_A(u_{AA} + u_{AAA}) + X_B(u_{BB} + u_{BBB}) + X_A X_B \\ &\quad \times \left[2u_{AB} + \delta u_{(3,AB)} - (u_{AA} + u_{AAA}) - (u_{BB} + u_{BBB}) \right. \\ &\quad \left. - 3u_{AAB} c_1 X_A^3 - 3u_{ABB} c_2 X_B^3\right] \\ &= X_A \epsilon_{AA} + X_B \epsilon_{BB} + X_A X_B \\ &\quad \times \left(\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB} - 3u_{AAB} c_1 X_A^3 - 3u_{ABB} c_2 X_B^3\right) \end{aligned} \tag{11}$$

where $\epsilon_{\mathrm{AA}} \equiv u_{\mathrm{AA}} + u_{\mathrm{AAA}}$, $\epsilon_{\mathrm{BB}} \equiv u_{\mathrm{BB}} + u_{\mathrm{BBB}}$, and $\epsilon_{\mathrm{AB}} \equiv 2u_{\mathrm{AB}} + \delta u_{(3,\mathrm{AB})}$

Recalling that the model assumes that the entropic contribution is described by Raoult's law, u_{m} is converted to the excess Helmholtz energy

$$A^{\mathrm{ex}} = X_{\mathrm{A}} X_{\mathrm{B}} (a_0 + a_1 X_{\mathrm{A}}^3 + a_2 X_{\mathrm{B}}^3) \tag{12}$$

by subtracting $(X_{\mathrm{A}} \epsilon_{\mathrm{AA}} + X_{\mathrm{B}} \epsilon_{\mathrm{BB}})$ from u_{m}; with $a_0 = -(\epsilon_{\mathrm{AA}} + \epsilon_{\mathrm{BB}} - \epsilon_{\mathrm{AB}})$, $a_1 = -3u_{\mathrm{AAB}} c_1$, and $a_2 = -3u_{\mathrm{ABB}} c_2$. A more rigorous treatment involving chemical lattice theory and coordination numbers is presented elsewhere [15]. Similarly, the model yields the relation between excess Helmholtz and Gibbs functions

$$G^{\mathrm{ex}} = A^{\mathrm{ex}} - (\Delta V)^2 / 2\beta V + \ldots \tag{13}$$

where ΔV denotes volume change on mixing, β is the compressibility and G^{ex} is the excess Gibbs free energy. If $(\Delta V)^2/2\beta V$ and higher-order terms are negligible, as will often be the case for pressures not too far removed from 1.0 atm, then the Gibbs and Helmholtz free energies are identical.

$$A^{\mathrm{ex}} = G^{\mathrm{ex}} = X_{\mathrm{A}} X_{\mathrm{B}} (a_0 + a_1 X_{\mathrm{A}}^3 + a_2 X_{\mathrm{B}}^3) \tag{14}$$

DEVELOPMENT OF TERNARY MIXING MODEL AND PREDICTIVE EXPRESSIONS

The basic model presented in the preceeding section can be easily extended to ternary and higher-order multicomponent systems. In the case of ternary mixtures, the internal energy is described in terms of six binary interactions

$$\begin{aligned} u_{\mathrm{m}}(2) = {} & X_{\mathrm{A}}^2 u_{\mathrm{AA}} + X_{\mathrm{B}}^2 u_{\mathrm{BB}} + X_{\mathrm{C}}^2 u_{\mathrm{CC}} + 2X_{\mathrm{A}} X_{\mathrm{B}} u_{\mathrm{AB}} \\ & + 2X_{\mathrm{A}} X_{\mathrm{C}} u_{\mathrm{AC}} + 2X_{\mathrm{B}} X_{\mathrm{C}} u_{\mathrm{BC}} \end{aligned} \tag{15}$$

and ten ternary interactions

$$\begin{aligned} u_{\mathrm{m}}(3) = {} & X_{\mathrm{A}}^3 u_{\mathrm{AAA}} + X_{\mathrm{B}}^3 u_{\mathrm{BBB}} + X_{\mathrm{C}}^3 u_{\mathrm{CCC}} + 3X_{\mathrm{A}} X_{\mathrm{B}} (X_{\mathrm{A}} u_{\mathrm{AAB}}^* + X_{\mathrm{B}} u_{\mathrm{ABB}}^*) \\ & + 3X_{\mathrm{A}} X_{\mathrm{C}} (X_{\mathrm{A}} u_{\mathrm{AAC}}^* + X_{\mathrm{C}} u_{\mathrm{ACC}}^*) + 3X_{\mathrm{B}} X_{\mathrm{C}} (X_{\mathrm{B}} u_{\mathrm{BBC}}^* + X_{\mathrm{C}} u_{\mathrm{BCC}}^*) \\ & + 6X_{\mathrm{A}} X_{\mathrm{B}} X_{\mathrm{C}} u_{\mathrm{ABC}}^* \end{aligned} \tag{16}$$

which result from molecular interactions between similar (u_{ii}) and dissimilar (u_{iij} and u_{ijk}) mixture components. Using steps analogous to those employed in the case of binary mixtures, and remembering that in the ternary mixture the mole fraction compositions are interrelated via $X_{\mathrm{A}} = 1 - X_{\mathrm{B}} - X_{\mathrm{C}}$, we rewrite eqn. (14) as

$$\begin{aligned} u_{\mathrm{m}}(3) = {} & X_{\mathrm{A}}^2 u_{\mathrm{AAA}} + X_{\mathrm{B}}^2 u_{\mathrm{BBB}} + X_{\mathrm{C}}^2 u_{\mathrm{CCC}} + X_{\mathrm{A}} X_{\mathrm{B}} \\ & \times \left[(X_{\mathrm{A}} + X_{\mathrm{B}}) \delta u_{(3,\mathrm{AB})} - 3u_{\mathrm{AAB}} c_1^{(\mathrm{AB})} X_{\mathrm{A}}^3 \right. \\ & \left. - 3u_{\mathrm{ABB}} c_2^{(\mathrm{AB})} X_{\mathrm{B}}^3 \right] + X_{\mathrm{A}} X_{\mathrm{C}} \\ & \times \left[(X_{\mathrm{A}} + X_{\mathrm{C}}) \delta u_{(3,\mathrm{AC})} - 3u_{\mathrm{AAC}} c_1^{(\mathrm{AC})} x_{\mathrm{A}}^3 - 3u_{\mathrm{ACC}} c_3^{(\mathrm{AC})} x_{\mathrm{C}}^3 \right] + X_{\mathrm{B}} X_{\mathrm{C}} \\ & \times \left[(X_{\mathrm{B}} + X_{\mathrm{C}}) \delta u_{(3,\mathrm{BC})} - 3u_{\mathrm{BBC}} c_2^{(\mathrm{BC})} X_{\mathrm{B}}^3 - 3u_{\mathrm{BBC}} c_3^{(\mathrm{BC})} X_{\mathrm{C}}^3 \right] \\ & + 6X_{\mathrm{A}} X_{\mathrm{B}} X_{\mathrm{C}} u_{\mathrm{ABC}}^* \end{aligned} \tag{17}$$

In order to reduce the compositional dependence of the terms in the parentheses, one first assumes that

$$3u_{\mathrm{ABC}}^* = u_{\mathrm{AAA}} + u_{\mathrm{BBB}} + u_{\mathrm{CCC}} + 1/2(\delta u_{\mathrm{AB}} + \delta u_{\mathrm{AC}} + \delta u_{\mathrm{BC}}) \tag{18}$$

and then uses the resulting approximation to expand eqn. (10) to

$$\begin{aligned} \delta u_{ij} & = (3u_{iij} - u_{iii}) - u_{iii} - u_{jjj} \\ & = (3u_{ijj} - u_{jjj}) - u_{iii} - u_{jjj} \\ & = \delta u_{3,ij} - u_{iii} - u_{jjj} \end{aligned} \tag{19}$$

ternary systems. Direct substitution of eqn. (19) into eqn. (18) yields

$$\begin{aligned} u_{\mathrm{ABC}} & = 1/6[(3u_{\mathrm{AAB}} - u_{\mathrm{AAA}}) + (3u_{\mathrm{ACC}} - u_{\mathrm{CCC}}) + (3u_{\mathrm{BBC}} - u_{\mathrm{BBB}})] \\ & = 1/6[\delta u_{(3,\mathrm{AB})} + \delta u_{(3,\mathrm{AC})} + \delta u_{(3,\mathrm{BC})}] \end{aligned} \tag{20}$$

a mathematical relationship between the three-body ABC interactional term and the various binary combinations, which should be applicable in the case of small, dissimilar three-body interactions.

After suitable algebraic manipulation of eqns. (15)–(20), the internal energy and excess molar Gibbs free energy of the ternary mixture can be expressed by the equations

$$\begin{aligned} u_{\mathrm{m}} = {} & X_{\mathrm{A}}\epsilon_{\mathrm{AA}} + X_{\mathrm{B}}\epsilon_{\mathrm{BB}} + X_{\mathrm{C}}\epsilon_{\mathrm{CC}} \\ & + X_{\mathrm{A}}X_{\mathrm{B}}\left(\epsilon_{\mathrm{AB}} - \epsilon_{\mathrm{AA}} - \epsilon_{\mathrm{BB}} - 3u_{\mathrm{AAB}}c_1^{(\mathrm{AB})}X_{\mathrm{A}}^3 - 3u_{\mathrm{ABB}}c_2^{(\mathrm{AB})}X_{\mathrm{B}}^3\right) \\ & + X_{\mathrm{A}}X_{\mathrm{C}}\left(\epsilon_{\mathrm{AC}} - \epsilon_{\mathrm{AA}} - \epsilon_{\mathrm{CC}} - 3u_{\mathrm{AAC}}c_1^{(\mathrm{AC})}X_{\mathrm{A}}^3 - 3u_{\mathrm{ACC}}c_3^{(\mathrm{AC})}X_{\mathrm{C}}^3\right) \\ & + X_{\mathrm{B}}X_{\mathrm{C}}\left(\epsilon_{\mathrm{BC}} - \epsilon_{\mathrm{BB}} - \epsilon_{\mathrm{CC}} - 3u_{\mathrm{BBC}}c_2^{(\mathrm{BC})}X_{\mathrm{B}}^3 - 3u_{\mathrm{BCC}}c_3^{(\mathrm{BC})}X_{\mathrm{C}}^3\right) \end{aligned} \tag{21}$$

$$\begin{aligned} G^{\mathrm{ex(ABC)}} = {} & X_{\mathrm{A}}X_{\mathrm{B}}\left(a_0^{(\mathrm{AB})} + a_1^{(\mathrm{AB})}X_{\mathrm{A}}^3 + a_2^{(\mathrm{AB})}X_{\mathrm{B}}^3\right) \\ & + X_{\mathrm{A}}X_{\mathrm{C}}\left(a_0^{(\mathrm{AC})} + a_1^{(\mathrm{AC})}X_{\mathrm{A}}^3 + a_2^{(\mathrm{AC})}X_{\mathrm{C}}^3\right) \\ & + X_{\mathrm{B}}X_{\mathrm{C}}\left(a_0^{(\mathrm{BC})} + a_1^{(\mathrm{BC})}X_{\mathrm{B}}^3 + a_2^{(\mathrm{BC})}X_{\mathrm{C}}^3\right) \end{aligned} \tag{22}$$

Again the entropic contribution to the configurational entropy has been described in terms of Raoult's law, and the various ϵ_{ii} and ϵ_{ij} are defined in accordance with the binary reduction. The nine a coefficients can be obtained by either curve-fitting binary excess free energy data or by parameterizing experimental ternary data. From an operational standpoint, the former method is preferred in that experimental ternary data are relatively scarce, and more importantly it is far less time-consuming to compute three sets of three parameters each than one large set of nine parameters. Our preliminary observations [16], along with unpublished calculations on over 75 ternary systems [17], indicate that eqn. (22) will be applicable to other thermodynamic properties such as excess volumes and enthalpies.

DERIVATION OF THE COMBINED NIBS/REDLICH–KISTER EXPRESSION OF SOLUBILITY

Solubility is related to chemical potential (μ_i) rather than to the integral excess Gibbs free energy of mixing. The expression for the solubility of a crystalline nonelectrolyte solute in binary solvent mixture is derived by first adding the ideal contribution of the Gibbs free energy of mixing based upon Raoult's law to eqn. (22), and then differentiating the resulting equation

$$\begin{aligned} G^{\mathrm{mix}} = {} & RT\left[n_{\mathrm{A}} \ln X_{\mathrm{A}} + n_{\mathrm{B}} \ln X_{\mathrm{B}} + n_{\mathrm{C}} \ln X_{\mathrm{C}}\right] + n_{\mathrm{A}}X_{\mathrm{B}} \\ & \times \left[a_0^{(\mathrm{AB})} + a_1^{(\mathrm{AB})}X_{\mathrm{A}}^3 + a_2^{(\mathrm{AB})}X_{\mathrm{B}}^3\right] + n_{\mathrm{A}}X_{\mathrm{C}}\left[a_0^{(\mathrm{AC})} + a_1^{(\mathrm{AC})}X_{\mathrm{A}}^3 + a_2^{(\mathrm{AC})}X_{\mathrm{C}}^3\right] \\ & + n_{\mathrm{B}}X_{\mathrm{C}}\left[a_0^{(\mathrm{BC})} + a_1^{(\mathrm{BC})}X_{\mathrm{B}}^3 + a_2^{(\mathrm{BC})}X_{\mathrm{C}}^3\right] \end{aligned} \tag{23}$$

with respect to the number of moles of solute, $\mu_A - \mu_A^0 = (\partial G^{\text{mix}}/\partial n_A)$, while holding T, P, n_B and n_C constant. Performing this differentiation, one obtains the following expression

$$\begin{aligned}\mu_A - \mu_A^0 = RT \ln a_A^{\text{solid}} = RT \ln X_A^{\text{sat}} &+ X_B^0\left[a_0^{(AB)} + a_2^{(AB)}X_B^{03}\right] \\ &+ X_C^0\left[a_0^{(AC)} + a_2^{(AC)}X_C^{03}\right] - X_B^0 X_C^0 \\ &\times \left[a_0^{(BC)} + 4a_1^{(BC)}X_B^{03} + 4a_2^{(BC)}X_C^{03}\right]\end{aligned} \tag{24}$$

provided that the solute solubility is sufficiently small so that $X_A^{\text{sat}} = 0$ and $X_i^0 = X_i$. Mole fractions refer to the initial composition of the binary solvent mixture calculated as if the solute were not present, and a_A^{solid} denotes the activity of the solid solute. This activity, defined as the ratio of the fugacity of the solid to the fugacity of the pure subcooled liquid, is found by integrating the molar enthalpy of fusion (ΔH_A^{fus}) from the normal melting point T_{mp} to the desired solution temperature.

$$\ln a_A^{\text{solid}} = \int_{T_{\text{mp}}}^{T} \left(\Delta H_A^{\text{fus}}/RT^2\right) \mathrm{d}T \tag{25}$$

Not too much emphasis is placed upon this particular solute standard state. As will be shown in the next few paragraphs, the standard state is common for any given crystalline solute dissolved in binary solvent mixtures and both pure solvents, and can be cancelled mathematically from the final solubility expression.

Inspection of eqn. (24) reveals that, for model systems obeying this expression, the $a_0^{(AB)}$ and $a_0^{(AC)}$ interaction parameters can be eliminated via the saturation solubilities in the two pure solvents $(X_A^{\text{sat}})_B$ and $(X_A^{\text{sat}})_C$.

$$RT \ln\left[a_A^{\text{solid}}/(X_A^{\text{sat}})_B\right] = a_0^{(AB)} + a_2^{(AB)} \tag{26}$$

$$RT \ln\left[a_A^{\text{solid}}/(X_A^{\text{sat}})_C\right] = a_0^{(AC)} + a_2^{(AC)} \tag{27}$$

Direct substitution of eqns. (26) and (27) into eqn. (24), followed by algebraic rearrangement, enables one to express solute solubility in binary solvent mixtures as a simple mole fraction average of the measured solute properties in both pure solvents minus a term involving a power series expansion in solvent composition

$$\begin{aligned}RT \ln X_A^{\text{sat}} = X_B^0 RT \ln(X_A^{\text{sat}})_B + X_C^0 RT \ln(X_A^{\text{sat}})_C - X_B^0 X_C^0 \\ \times \left[P_0 + P_1 X_B^0 + P_2 X_B^{02} + P_3 X_B^{03}\right]\end{aligned} \tag{28}$$

where

$$P_0 = a_2^{(AB)} + 3a_2^{(AC)} + a_0^{(BC)} + 4a_2^{(BC)}$$

$$P_1 = a_2^{(AB)} - 3a_2^{(AC)} - 12a_2^{(BC)}$$

$$P_2 = a_2^{(AB)} + a_2^{(AC)} + 12a_2^{(BC)}$$

$$P_3 = a_1^{(BC)} - 4a_2^{(BC)}$$

Readers will note that the activity of the solid solute, a_A^{solid}, appeared on the left- and right-hand sides of eqn. (28) as $-RT \ln a_A^{\text{solid}}$ and $-(X_B^0 + X_C^0) RT \ln a_A^{\text{solid}}$, respectively, and has thus been cancelled mathematically. The power series expansion is third-order in X_B^0, and can be easily transformed into the Redlich–Kister form (see refs. 18–20 for details).

$$RT \ln X_A^{\text{sat}} = X_B^0 RT \ln(X_A^{\text{sat}})_B + X_C^0 RT \ln(X_A^{\text{sat}})_C + X_B^0 X_C^0 \sum_{i=0}^{3} S_i (X_B^0 - X_C^0)^i \qquad (29)$$

Equation (29) is mathematically identical to our combined NIBS/Redlich–Kister expression. Although it is possible to relate the various S_i coefficients back to two- and three-body interactional energies, I prefer to view the actual numerical values as "curve-fit" parameters determined via least-squares analysis of solubility data.

The mathematical derivation of eqn. (3) from a two/three-body interactional mixing model provides some theoretical justification for our combined NIBS/Redlich–Kister approach. Readers will recall that eqn. (3) was first suggested as a mathematical representation for describing how solute solubility varies as a function of binary solvent composition. No theoretical justification was offered in the original article [12], nor in the followup investigation [13] involving the ability of eqn. (3) to describe accurately carbazole solubilities in binary alkane + dibutyl ether and alkane + tetrahydropyran mixtures. I hope that by providing a theoretical basis for the combined NIBS/Redlich–Kister expression I will encourage other research groups to adopt this particular mathematical representation in future data presentations involving either solute solubilities, or infinite dilution solute activity coefficients ($\ln X_A^{\text{sat}}$ replaced by $\ln \gamma_A^{\infty}$), or infinite dilution solute enthalpies of solution ($\ln X_A^{\text{sat}}$ replaced by $\Delta H_A^{\text{soln},\infty}$) in binary solvent mixtures.

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LIST

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
$a_i^{(JK)}$	adjustable "curve-fit" parameter in the two/three-body interactional mixing model for the *JK* binary system
f_B^0, f_C^0	weighted mole fraction composition of the binary solvent mixture, calculated as if the solute were not present

G^{ex}_{BC}	excess molar Gibbs free energy of the binary solvent mixture based upon Raoult's law
ΔH^{fus}_{A}	molar enthalpy of fusion of the solute
$\Delta H^{soln,\infty}_{A}$	molar enthalpy of solution of the solute at infinite dilution
S_i	adjustable "curve-fit" parameter in the combined NIBS/ Redlich–Kister mathematical representation
u_{ij}	two-body interactional energy involving molecules i and j
u_{iij}	three-body interactional energy involving molecules i, i and j
X_i	mole fraction composition of component i
X^{sat}_{A}	saturated mole fraction solubility of the solute
$(X^{sat}_{A})_i$	saturated mole fraction solubility of the solute in pure solvent i
X^0_B, X^0_C	mole fraction composition of the binary solvent mixture, calculated as if the solute were not present
Γ_i	weighting factor of component i used in the NIBS model
μ_A	chemical potential of the solute
γ^{∞}_{A}	infinite dilution activity coefficient of the solute
Λ^{adj}_{ij}	adjustable "curve-fit" parameter in the modified Wilson mathematical representation

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