Method for Predicting Solubilities of Solids in Mixed Solvents

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A method is presented for predicting solubilities of solid solutes in mixed solvents, based on excess Henry's law constants. The basis is statistical mechanical fluctuation solution theory for composition derivatives of solute/solvent infinite dilution activity coefficients. Suitable approximations are made for a single parameter characterizing solute/solvent interactions. Comparisons with available data show that the method is successful in describing a variety of observed mixed solvent solubility behavior, including nearly ideal systems with small excess solubilities, systems with solute-independent excess solubilities, and systems deviating from these simple rules. Successful predictions for new solvent mixtures can be made using limited data from other mixtures. © 2009 American Institute of Chemical Engineers *AIChE J*, 55: 1256–1264, 2009*
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Introduction

The solubility of solids in mixtures with one or more liquid solvents plays an important role in the design and production of traditional chemical and pharmaceutical products. While solubilities of solids in single solvents have been reported extensively,[1–3] the literature has fewer data on solubilities in mixed solvents. The dependence of these solubilities on solvent composition can be quite complex, ranging from linear to having extrema. Previously we have presented a method for predicting the solubility of a single solute in pure and mixed solvents.[4,5] That method was based on a "reference solvent," in which the solubility is known and used to predict the solubility of the same solid species in other solvents. The method used differences between infinite dilution activity coefficients of the solute in different solvents, which might be calculated from group contribution methods such as UNIFAC. However, the selection of reference solvent is mostly empirical and substantial numbers of parameters may need to be determined from fitting to experimental data.

There are several other cosolvency models employed in the literature.[6] Such models express the solubility of the solute as a power series of the solute-free composition of the solvent using molecular descriptors. A method based more directly on fundamental theory may provide a more generalizable application especially as measurements of solid solubility data are now appearing frequently in the literature.

Here we provide an approach for correlating and estimating the "excess" solubility or "excess" Henry's law constant of a single solute in mixed solvents based on a solution theory arising from statistical mechanics.[7,8] Previously,[9] a similar approach was taken to gas solubilities in mixed solvents. First, we give some basic definitions and expressions. Second, we present results of correlation and prediction of solubilities in mixed solvents.

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Thermodynamic Framework

The "excess" solubility is defined

$$\ln x_i^E \equiv \ln x_{i,m} - \sum_{j \neq 1} x_j' \ln x_{i,j} \qquad (1)$$

where x' denotes a mole fraction on a solute-free basis. $x_{i,j}$ is the mole fraction solubility of species i in pure solvent j, and $x_{i,m}$ is the solubility of solute i in a mixed solvent. Using Lewis/Randall normalized solute liquid-phase activity coefficients (γ_i), the solubility of a species, i, in a pure and mixed solvent can be written[10]

$$\ln x_i \gamma_i (T, x) \approx \frac{\Delta H_{m,i}}{RT_{m,i}} \left(1 - \frac{T_{m,i}}{T} \right). \qquad (2)$$

The right-hand side of Eq. 2 does not depend on the nature of the solvent(s). It is a function only of the pure solute's melting properties. If the solubility in mole fraction is smaller than 0.01, the activity coefficient of Eq. 2 can usually be approximated as the infinite dilution value, γ_i^∞, and Eq. 1 may be written in terms of the infinite dilution Lewis/Randall normalized activity coefficients. With this approximation, inserting Eq. 2 into Eq. 1 gives

$$\ln x_{i,m} - \sum_{j \neq i} x_j' \ln x_{i,j} \approx -\ln \gamma_{i,m}^\infty + \sum_{j \neq i} x_j' \ln \gamma_{i,j}^\infty. \qquad (3)$$

The "excess" Henry's law constant[10,11] is defined by an equation similar to Eq. 1

$$\ln H_i^E \equiv \ln H_{i,m} - \sum_{j \neq i} x_j' \ln H_{i,j} = \ln \gamma_{i,m}^\infty - \sum_{j \neq i} x_j' \ln \gamma_{i,j}^\infty. \qquad (4)$$

Thus,

$$\ln H_i^E \equiv \ln H_{i,m} - \sum_{j \neq i} x_j' \ln H_{i,j}$$
$$\approx -\ln x_{i,m} + \sum_{j \neq i} x_j' \ln x_{i,j} = -\ln x_i^E. \qquad (5)$$

Fluctuation Solution Theory Method

The fluctuation solution theory (FST) of Kirkwood and Buff[7] relates integrals of the statistical mechanical radial distribution function to solution isothermal compressibility, partial molar volumes, and composition derivatives of chemical potentials. O'Connell[8] wrote the results in a more general and convenient matrix form, including formal expressions for multicomponent systems. The total correlation function integral (TCFI) between components i and j is

$$H_{ij} = H_{ji} = \rho \int [g(r_{ij}) - 1] dv = \rho \int h_{ij} dv \qquad (6)$$

where g is the radial (pair) distribution function between molecular centers of i and j, ρ is the bulk molecular solution density, and v is the volume. The quantity $h_{ij} = g(r_{ij}) - 1$ is called the total correlation function, and describes the overall correlation between i and j minus the bulk solution average of unity. Using this, exact expressions for composition derivatives may be written in terms of the TCFI. For a binary, one useful result is[9]

$$\left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P,N_2} = -\frac{x_2 f_{12}}{1 + x_1 x_2 f_{12}} \qquad (7)$$

where the f-matrix is defined as

$$f_{ij} \equiv H_{ii} + H_{jj} - 2H_{ij}. \qquad (8)$$

The composition dependence of H_{ij} is generally not known, so integrating Eq. 7 to obtain the activity coefficient is not possible. Alternatively, the activity coefficient may be expanded about a reference state of infinite dilution

$$\ln \gamma_i = (\ln \gamma_i)_{x_i=0} + x_i \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{T,P,N_{j \neq i,x_i=0}}$$
$$+ \frac{x_i^2}{2!} \left(\frac{\partial^2 \ln \gamma_i}{\partial x_i^2} \right)_{T,P,N_{j \neq i,x_i=0}} + \cdots \qquad (9)$$

If Eq. 9 is assumed valid over the entire solvent composition range, the excess Henry's law constant of a single solute (1) in a mixed binary solvent (species 2 and 3) can be expressed as[9]

$$\ln H_1^E = \frac{x_3}{2} \left(\frac{\partial \ln \gamma_3}{\partial x_3} \right)_{T,P,N_2}^+ + \frac{x_2}{2} \left(\frac{f_{12}^+}{1 + x_2 x_3 f_{23}^+} - f_{12}^0 \right)$$
$$+ \frac{x_3}{2} \left(\frac{f_{12}^+}{1 + x_2 x_3 f_{23}^+} - f_{13}^0 \right). \qquad (10)$$

Here $^+$ denotes infinite dilution of the solute in the mixed solvent and ^{0} indicates infinite dilution in the single, pure solvent. The first term on the right-hand side of Eq. 10 is correct to all orders of Eq. 9. Thus, its contribution is not empirical. It may be calculated from any G^E-model. Similarly, f_{23}^+ may be found from a rearranged form of Eq. 7, i.e.

$$f_{23}^+ = -\frac{\frac{1}{x_2} \left(\frac{\partial \ln \gamma_3}{\partial x_3} \right)_{T,P,N_2}^+}{1 + x_3 \left(\frac{\partial \ln \gamma_3}{\partial x_3} \right)_{T,P,N_2}^+}. \qquad (11)$$

While f_{23}^+ in Eq. 10 can be found independently (usually from binary vapor/liquid equilibrium data forming the basis of a G^E-model) several other parameters may be involved; the solute/pure-solvent parameters f_{12}^0 and f_{13}^0, as well as one pair of mixture parameters (f_{12}^+ and f_{13}^+) for each solvent composition. We assume that the "mixture" terms f_{12}^+ and f_{13}^+ are equal to the corresponding "pure solvent" terms, i.e.

$$f_{ij}^+ \overset{\Delta}{=} f_{ij}^0. \qquad (12)$$

The radial distribution function between components i and j is a measure of their total correlations, including indirect effects. The fact that f_{12}^+ and f_{13}^+ are differences, suggests that this approximation is reasonable except when solution density varies strongly with solute-free composition. This is rarely the case with solvent mixtures. The result is that the expression of the excess solubility in Eq. 1 simplifies to

$$\ln x_1^E = -\frac{x_3}{2} \left(\frac{\partial \ln \gamma_3}{\partial x_3} \right)_{T,P,N_2}^+ \left[1 + x_2 f_{12}^0 + x_3 f_{13}^0 \right]. \qquad (13)$$

Table 1. Experimental Data Used; SLE for Solubilities, VLE for Solvent Mixture Nonideality

No.	Solute (1)	Solvent (2)	Solvent (3)	Number of Data Points	Reference SLE	Reference VLE	AAD
1	Paracetamol	Ethyl acetate	Ethanol	13	13	14	0.1720
2	Paracetamol	Water	1,4-Dioxane	17	13	14	0.1951
3	Paracetamol	Ethyl acetate	Methanol	14	15	14	0.0165
4	Paracetamol	Methanol	Water	7	15	14	0.0262
5	Paracetamol	Ethanol	Methanol	3	15	14	0.0008
6	Paracetamol	Water	Ethanol	13	13	14	0.0733
7	Benzoic acid	Carbon tetrachloride	n-Heptane	10	16	17	0.0248
8	Benzoic acid	n-Heptane	Cyclohexane	7	16	14	0.0166
9	Benzoic acid	Carbon tetrachloride	n-Hexane	7	16	14	0.0046
10	Benzoic acid	Carbon tetrachloride	Cyclohexane	7	16	14	0.0051
11	Benzoic acid	Carbon tetrachloride	n-Heptane	6	16	17	0.0029
12	Benzoic acid	n-Hexane	Cyclohexane	7	16	14	0.0048
13	Beta carotene	Acetone	Cyclohexane	6	18	14	0.0726
14	Beta carotene	Acetone	n-Hexane	6	18	14	0.0115
15	Beta carotene	Acetone	Toluene	6	18	14	0.0153
16	Beta carotene	MEK	Cyclohexane	8	18	14	0.0127
17	Beta carotene	MEK	n-Hexane	5	18	14	0.0078
18	Beta carotene	MEK	Toluene	5	18	14	0.0209
19	Anthracene	n-Hexane	1-Butanol	9	19	14	0.0326
20	Anthracene	n-Hexane	1-Propanol	9	19	14	0.0129
21	Anthracene	n-Heptane	1-Propanol	9	19	14	0.0056
22	Anthracene	Cyclohexane	1-Propanol	9	19	14	0.0074
23	Anthracene	n-Octane	1-Butanol	9	19	20	0.0034
24	Anthracene	n-Hexane	2-Butanol	9	21	14	0.0024
25	Anthracene	n-Hexane	2-Methyl-1-propanol	9	22	23	0.0020
26	Anthracene	n-Heptane	2-Methyl-1-propanol	9	22	24	0.0052
27	Anthracene	Cyclohexane	Ethyl acetate	9	25	14	0.0061
28	Anthracene	n-Octane	1-Propanol	9	19	26	0.0022
29	Anthracene	n-Heptane	1-Butanol	9	19	14	0.0020
30	Anthracene	1-Propanol	2-Pentanol	9	27	28	0.0011
31	Anthracene	2-Propanol	2-Pentanol	9	27	28	0.0016
32	Anthracene	Cyclohexane	MTBE	9	29	30	0.0015
33	Naphthalene	Water	Methanol	14	31	14	0.0740
34	Naphthalene	Water	Ethanol	15	31	14	0.1745
35	Naphthalene	Water	2-propanol	12	31	14	0.1234
36	Naphthalene	Water	1,2-Propanediol	15	31	32	0.2063
37	Naphthalene	Water	Acetone	15	31	14	0.0777
38	Salicylic acid	1,2-Propanediol	Water	11	33	32	0.3490
39	Salicylic acid	1,2-Propanediol	Ethanol	11	33	*	0.1354
40	Salicylic acid	Ethanol	Water	11	33	14	0.0195

Number of experimentally measured solubilities in each system includes solubilities in pure solvents.

*Parameters for the solute-free binary estimated from UNIFAC.[34]

The factors in Eq. 13, f^0_{12} and f^0_{13}, can be found from linear regression. This technique minimizes a sum of squared residuals,

$$\boldsymbol{\beta} = \arg\min\left\{\sum_i r_i(\beta)^2\right\}. \quad (14)$$

The vector $\boldsymbol{\beta}$ is the f^0_{12} and f^0_{13} values relevant to the problem considered. The elements of the residual vector, $\mathbf{r}$, are

$$r_i = \left[\ln \hat{x}^E_1 - \ln x^E_1\right]. \quad (15)$$

Here circumflex denotes a calculated value using Eq. 13. The linear estimation problem in Eq. 14 has a unique solution which is computationally favorable. Estimated variances of the parameters can be obtained from a variance-covariance matrix.[12]

We have used the diagonal terms of the variance-covariance matrix in a propagation-of-errors expression to calculate the error bars of the figures below. The solute-free parameters for the Wilson equation are assumed to have zero variance.

Results

Combination of Eqs. 5 and 10 allows us to reduce experimental excess solubility data for solid solutes in binary, mixed solvents. We have compiled 40 data sets of five solutes in a variety of solvent mixtures, ranging from almost ideal to strongly nonideal solutions. Table 1 lists the solubility data with references. References are also given for the parameters characterizing the solvent–solvent nonideality from binary vapor/liquid equilibrium data. Neither parameters nor data could be found for the solute-free binary of 1,2-propanediol and ethanol. For this case, the solvent parameters have been estimated from fitting Wilson equation[35] activity coefficients to values calculated with the UNIFAC model.[34]
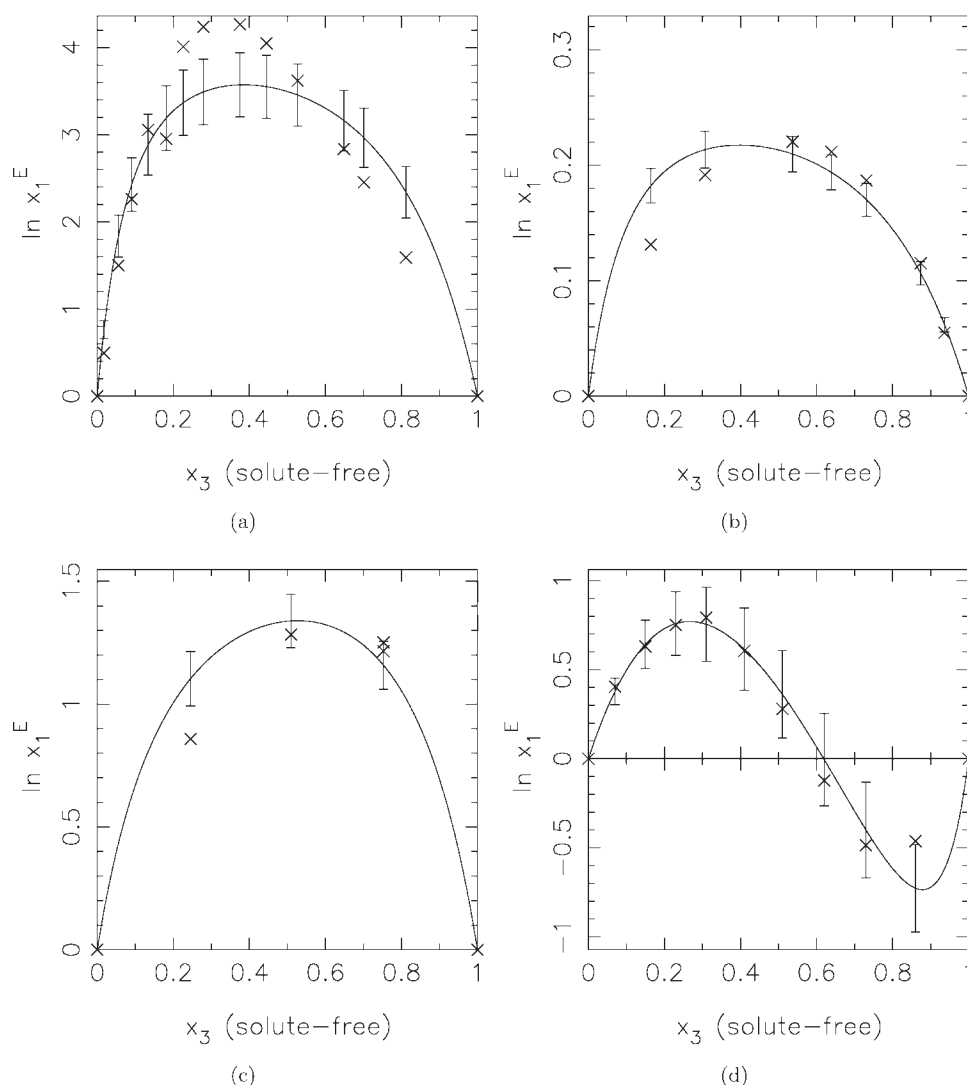
Figure 1. Estimated and experimental excess solubility of solid solutes in binary mixed solvents: (a) Naphthalene(1)/water(2)/acetone, (b) anthracene(1)/*n*-octane(2)/1-butanol(3), (c) beta carotene(1)/acetone(2)/ *n*-hexane(3), and (d) salicylic acid(1)/ethanol(2)/water(3).

The solute-free binary mixture forms a nonideal solution in all of these systems.

Excess solubility in binary mixed solvents—correlation

For parameter estimation all data sets in Table 1 are used. The rightmost column of Table 1 lists the average absolute deviation of the regressed mixtures, computed as

$$AAD = \frac{1}{M-2}\sum_{i}^{M}|r_i| \tag{16}$$

excluding the pure solvent endpoints. Figure 1 shows data/ model agreement in four representative systems where the solute-free binary solution is nonideal. In Figures 1a–c the excess solubility is parabolic and the correlation performs satisfactorily. In Figure 1d the excess solubility is complex and changes sign but this is generally captured with the method. Standard deviations are provided as error bars on the calculated results at the experimental solvent compositions.

Nearly all data points lie within the error bars. Parameters and standard deviations from regressing experimental data are shown in Table 2.

Figure 2 shows two systems where the solute-free binaries form nearly ideal solutions. The agreement is more qualitative, and certainly not as good as shown in Figure 1. Extensive examination of solute-free binaries[36] show that a maximum in f_{23}^{+} is usually found in mixtures with strong solvent nonideality, whereas the f_{23}^{+} in nearly ideal mixtures (where the absolute magnitude of f_{23}^{+} is <2) are generally monotonic. Figure 3 shows f_{23}^{+} plotted as a function of composition for the nearly ideal binary solution of chlorobenzene/ aniline and the strongly nonideal case of ethanol/*n*-heptane. In general, we have found that parameters estimated from mixtures where the solute-free binary is nearly ideal usually have larger standard deviations while those found for

Table 2. Estimated Values of the Parameters in Eq. 13 and Their Corresponding Standard Deviations Found from Optimization

Solute (1)	Solvent (2)	f_{12}^0	σ
Beta carotene	Acetone	1.92	0.40
Beta carotene	Cyclohexane	3.87	0.33
Beta carotene	n-Hexane	2.82	0.38
Beta carotene	Toluene	5.75	1.09
Beta carotene	MEK	5.81	0.49
Benzoic acid	Carbon tetrachloride	−0.11	0.77
Benzoic acid	n-Heptane	−2.47	1.37
Benzoic acid	n-Hexane	0.07	1.01
Benzoic acid	Cyclohexane	−0.03	0.98
Paracetamol	Ethyl acetate	5.95	1.04
Paracetamol	Water	8.70	0.54
Paracetamol	Methanol	−0.40	0.85
Paracetamol	Ethanol	1.82	0.88
Paracetamol	Dioxane	3.61	0.79
Anthracene	n-Hexane	−0.77	0.04
Anthracene	n-Heptane	−0.63	0.04
Anthracene	n-Octane	−0.49	0.05
Anthracene	Cyclohexane	−0.54	0.06
Anthracene	2-Methyl-1-propanol	0.28	0.08
Anthracene	1-Propanol	−0.15	0.05
Anthracene	1-Butanol	−0.44	0.06
Anthracene	2-Propanol	1.70	4.04
Anthracene	2-Butanol	0.40	0.12
Anthracene	2-Pentanol	4.86	4.17
Anthracene	Ethyl acetate	1.56	0.11
Anthracene	MTBE	8.02	1.03
Naphthalene	Water	7.15	1.13
Naphthalene	Methanol	18.45	5.31
Naphthalene	Ethanol	7.20	1.89
Naphthalene	2-Propanol	9.46	1.89
Naphthalene	1,2-Propanediol	−84.06	13.75
Naphthalene	Acetone	7.70	1.31
Salicylic acid	1,2-Propanediol	−31.38	6.13
Salicylic acid	Ethanol	5.46	1.21
Salicylic acid	Water	−4.98	0.97

nonideal mixtures have lower standard deviations. This indicates that estimation of parameters characterizing the solute–solvent interaction is best done in mixtures where the solute-free binary forms a substantially nonideal solution. Mixtures with numerically small values of f_{23}^+ are largely insensitive to changes in f_{1j}^0. This means that the excess solubilities in these mixtures are small and approximately independent of the nature of the solute.

### Excess solubility in binary mixed solvents—prediction

To test the predictive capability of the approach, Figure 4 shows an example of two moderately successful predictions of data sets 15 and 17 in Table 1. The excess solubility prediction of Figure 4 require measured solubility data in four systems for estimation of the parameter values between beta carotene and each of the solvents. The parameters used in Figure 4 are based on simultaneous reduction of the sets 13, 14, 16, and 18, giving the f_{1j}^0 values for beta carotene (1) with $'j'$ = acetone (1.88 ± 0.47), toluene (10.36 ± 3.97), MEK (6.14 ± 0.69), and hexane (2.87 ± 0.50). These parameters are different from those in Table 2, because prediction is tested here. Figure 4 shows trends of the excess solubility which are qualitatively correct and the experimental results are within the error bars.

Table 3 shows values of estimated parameters for paracetamol (solute) with four different solvents estimated from four different sets of measured data, labeled I–IV. The sets of data in I are 3 and 6 from Table 1 giving parameter values for predicting the excess solubility in sets 1, 4, and 5. We have excluded set 2 in this procedure because dioxane only appears in a single data set. Similar combinations of training/testing sets may be built as shown in Figure 5. On the left is shown the data sets used for estimation of the paracetamol/solvent parameter values. These are then used to predict the excess solubility in the mixtures shown on the

(a)

(b)
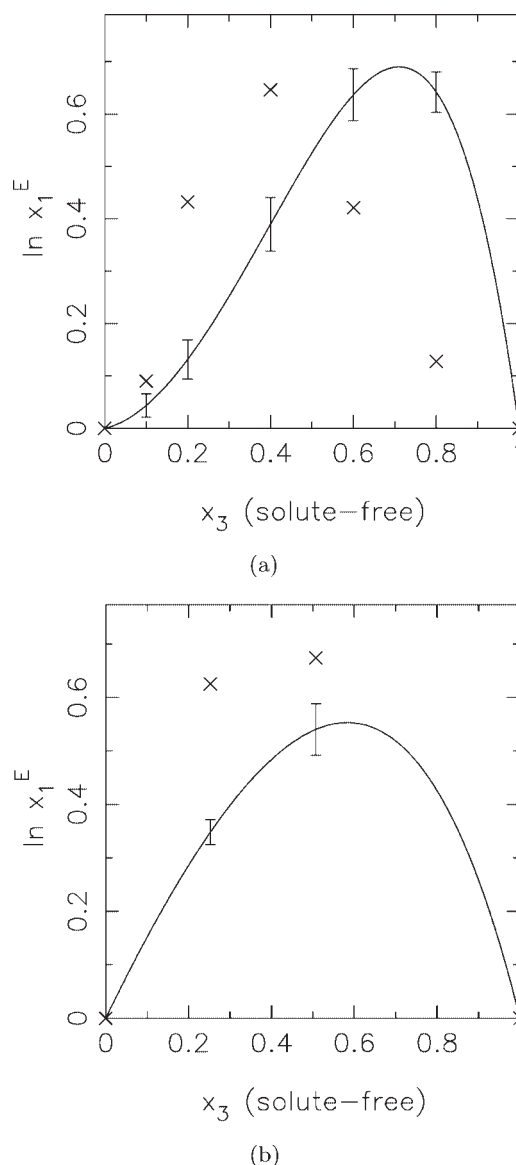
Figure 2. Estimated and experimental excess solubility of solid solutes in binary mixed solvents: (a) Paracetamol(1)/methanol(2)/water(3), and (b) beta carotene(1)/MEK(2)/toluene(3).

The solute-free binary mixture forms a close-to-ideal solution in these systems, and the data/model agreement is not as good as that in the more nonideal mixtures.
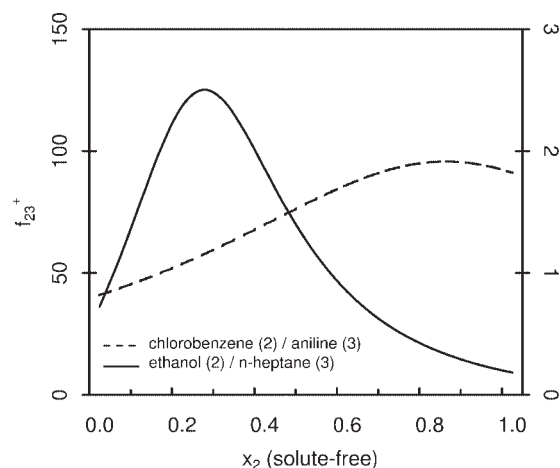
Figure 3. Total correlation function integral factor f_{23}^+ of a nearly ideal and a nonideal system.
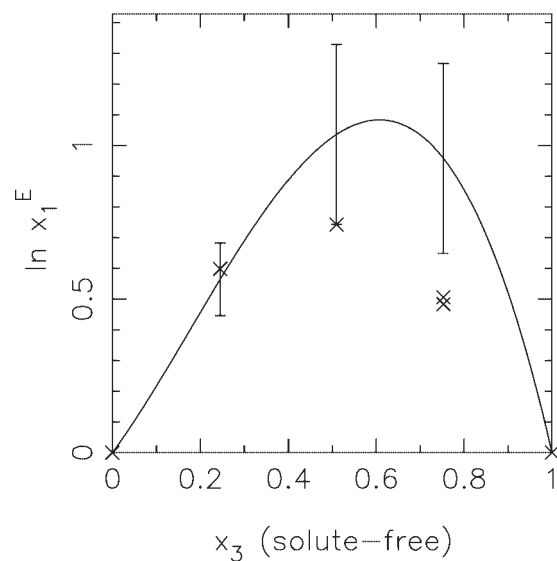
The values of chlorobenzene/aniline refers to the right ordinate, while ethanol/n-heptane refers to the left ordinate. Data taken from Ref. 36.

(a)

(b)

Figure 4. Predicted and experimental excess solubility of beta carotene in binary solvent mixtures: (a) Beta carotene(1)/acetone(2)/toluene(3), and (b) beta carotene(1)/MEK(2)/n-hexane(3).

right. The estimated parameter values are listed in Table 3 according to their position in Figure 5. Table 3 shows that the procedure chosen from Figure 5 requires relatively little alteration of the parameter values, except for that characterizing paracetamol with methanol. However, the standard deviation for this system is significantly larger compared to the others. These results suggest that the method can reproduce consistent parameter values using different combinations of data from different sources. Figure 6 shows examples of the predicted excess solubility of paracetamol in two solvent mixtures. The estimates in Figure 6a were made from procedure I of Figures 5 and 6b using method IV. Although several data points are outside the range of the prediction intervals, the trends are correct. In particular, the asymmetry of the curve of Figure 6b is consistent with the experimental data.
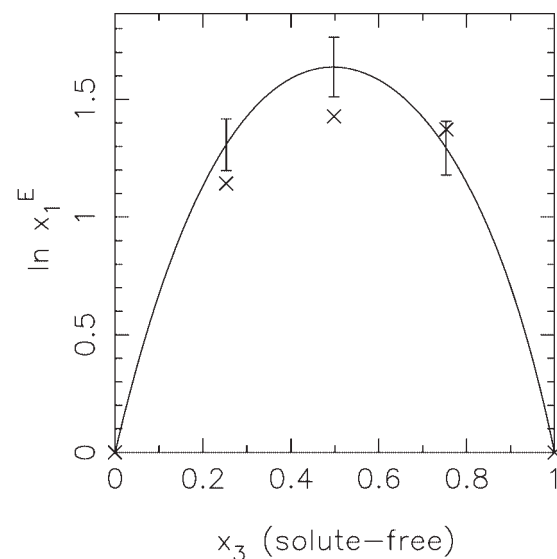
Discussion

The discrepancy among the paracetamol/methanol parameters obtained is probably related to the type of experimental data used. Models originating from fluctuation solution theory work best—in predictive mode—for nonideal systems, and may not describe more ideal systems as well. Methanol forms ideal or close-to-ideal solutions with water, ethanol, and ethyl acetate.

The system water and 1,2-propanediol was not easily described with the above approach. The predictions for Figures 7a,b predict a region of negative excess solubility which

is not confirmed by the data. To examine this problem, an attempt was made to revise the binary solvent parameters using the mixed solvent data with naphthalene. The resulting

Table 3. Estimated Parameter Values (Standard Deviation in Parenthesis) between Paracetamol and Solvents

Solute (1)	Solvent (2)	$f_{12}^0(\sigma)$			
		I	II	III	IV
Paracetamol	Ethyl acetate	6.68 (0.46)	6.80 (0.16)	5.77 (0.07)	5.13 (0.53)
Paracetamol	Methanol	−0.83 (0.32)	4.81 (1.71)	4.81 (1.71)	0.11 (0.41)
Paracetamol	Water	4.28 (0.28)	4.13 (0.37)	4.13 (0.37)	4.83 (1.67)
Paracetamol	Ethanol	5.76 (0.41)	5.91 (0.53)	5.91 (0.53)	3.58 (0.68)

Numerals I−IV refer to values obtained from regression of different sets of experimental data as in Figure 5.
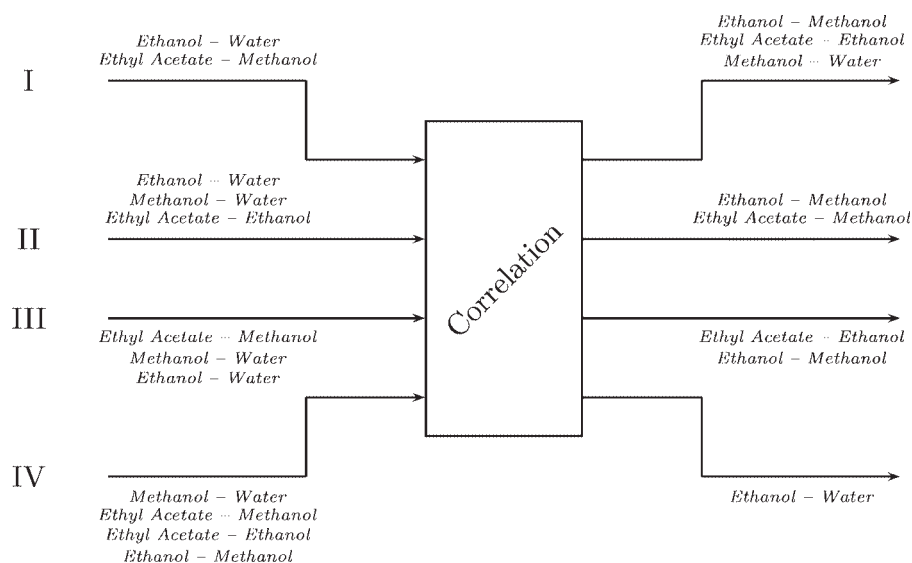
Figure 5. Graphical display of estimation/prediction procedure with varying amount of input data (left side) used to predict the excess solubility in the output (right side).

The listed items are the solvent mixtures in which the solute is dissolved.

solvent parameters were inconsistent with VLE data,[14] suggesting a basic inconsistency of the model and the data. Since the discrepancy is found when the solvent mixture is nearly pure water, the model concept might not be appropriate for hydrophobic attractions of the solute and the dilute nonaqueous solvent. This suggests that careful evaluation of the input data, both excess solubility and the underlying data used to construct the composition dependence of f_{23}^+, will be well worth the effort if quantitative agreement is to be reached in complex cases.

The formalism presented in this article assumes infinite dilution of the solute, thereby removing solute/solute interac-

tions from the mixture. An expected application is solubility enhancement of such substances as pharmaceuticals and biochemicals. Systems in these categories usually have very low solubilities, below the limit of infinite dilution. However, in cases where the solubility exceeds 1%, Eq. 3 may not be valid. System 6 of Table 1 of paracetamol with methanol and ethanol[15] has the the mole fraction solubility of paracetamol varying from 0.0019 (in water) to 0.0542 (in ethanol). However, the correlation performs well. This suggests that the method is capable of describing the excess solubility in some mixtures with high solubilities, though further investigation of this possibility is needed.
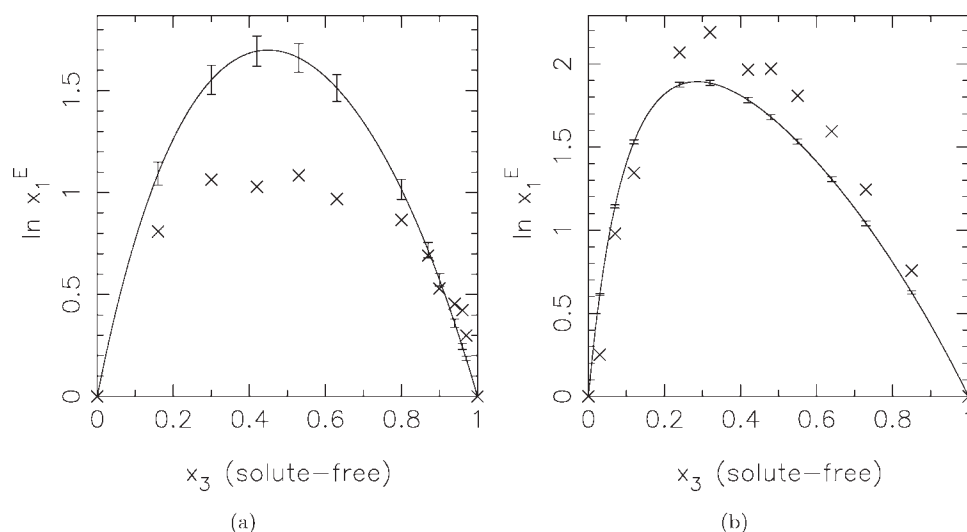
Figure 6. Predicted and experimental excess solubility of paracetamol in binary solvent mixtures: (a) Paracetamol(1)/ethyl acetate(2)/ethanol(3), and (b) paracetamol(1)/water(2)/ethanol(3).
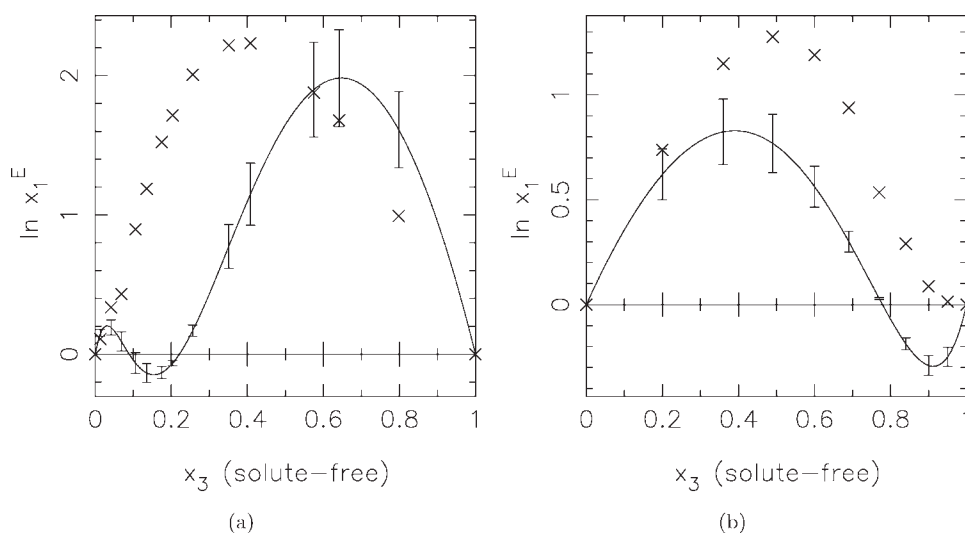
Figure 7. Estimated and experimental excess solubility of naphthalene and salicylic acid in 1,2-propanediol and water: (a) Naphthalene(1)/water(2)/1,2-propanediol(3), and (b) salicylic acid(1)/1,2-propanediol(2)/water(3).

Extension to Multicomponent Solvent Mixtures

Application of the method to mixtures containing more than two solvent species requires a revision of the compositional dependence of the solute activity coefficient. The expansion of the activity coefficient about a reference state of infinite dilution in Eq. 9 has been done only for binary and ternary mixtures.[8] O'Connell[8] presents a general multicomponent expression for the compositional derivative of the chemical potential, and hence the activity coefficient, with constant temperature, pressure, and mole number of other species as a function of the total correlation function integral, given by Eq. 6. Higher order derivative terms can be found from the expansion in Eq. 9, a change in variables, and differentiation of the expression obtained for the derivative.

Conclusions

A theoretical modeling framework has been used to correlate and predict the excess solubilities of solid solutes in a variety of binary solvent mixtures. The model uses one parameter characterizing solute–solvent interaction and an activity coefficient model for the solute-free solvent mixture. The proposed method successfully describes excess solubility behavior in most systems with nearly ideal solvents and all strongly nonideal solvent systems, including those with double extrema in the excess solubility. Prediction of solubilities in pairs of solvents can be made from results found from other mixtures containing the solvent components.

Notation

f = set of pair correlation function integrals, Eq. 8
g = radial (pair) distribution function
G = Gibbs energy
h = total correlation function, $g - 1$
H = Henry's constant
H = total correlation function integral
N = mole number

P = pressure
r = distance between molecular centers
r = residual
R = universal gas constant (8.314 J mol^{-1} K^{-1})
T = absolute temperature
v = volume
x = mole fraction

Greek letters

β = parameter set, $\{f_{12}^0, f_{13}^0\}$
γ = activity coefficient
ΔH = enthalpy of fusion
ρ = molar density
σ = standard deviation of variables

Subscripts and superscripts

$'$ = solute free basis
$\hat{}$ = calculated value
∞ = infinite dilution
$+$ = infinite dilution of solute in mixed solvent
0 = infinite dilution of solute in single solvent
E = excess property
i,j = components
m = fusion or mixture property

Literature Cited

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