Nomenclature

A_{22} = two-body solute interaction coefficient
A_γ = Debye–Hückel proportionality constant
B_{222} = three-body solute interaction coefficient
B_{ii} = second virial coefficient, cm^3/mol
$C(x_2)$ = thermodynamic consistency function
H = Henry's constant based on molality, atm kg/mol
H' = Henry's constant based on mole fraction, atm
I = ionic strength, mol/kg, as given by eq 35
M_1 = molecular weight of water, kg/mol
P = total pressure
P^S = saturation (vapor) pressure
R = gas constant, J/mol K
T = temperature, K
a_{22} = two-body interaction coefficient in eq 14
b = interaction coefficients in eq 14
c_{ij} = molecule–ion and ion–ion interaction coefficient
f = fugacity, atm
g^{E*} = excess Gibbs energy of the system in unsymmetric form, J/mol
m_i = molality of species i, mol/kg
n = number of moles
v_i = molar volume of i, cm^3/mol
$\bar{v}_i$ = partial molar volume of i, cm^3/mol
x_i = stoichiometric mole fraction i in liquid phase, $n_i/(n_{NH_3} + n_{H_2O})$
y_i = mole fraction of i in vapor phase
z_i = molecular mole fraction of i in liquid phase, $n_i/(n_{H_2O} + \sum_{j\neq 1} n_j)$, where j refers to solute species
z_i = ionic charge on species i

Greek Letters

Γ_1 = activity coefficient of water based on mole fraction
Γ_2^* = activity coefficient of ammonia based on mole fraction
$\Lambda_{21}, \Lambda_{12}$ = interaction parameters in Wilson equation
α^0 = characteristic parameter in equation of state proposed by Nakamura et al., L^2 atm/mol^2
$\beta_{ij}^{(0)}$ = dilute-solution interaction parameter, kg/mol
γ_i^* = activity coefficient of solute species i based on molality

μ_i = chemical potential of species i, J/mol
ϕ_i = fugacity coefficient of species i
ω = dummy variable

Subscript

1 = water
2 = ammonia

Superscript

* = unsymmetric convention
∞ = infinite dilution
0 = standard state
L = liquid phase
PO = corrected to zero pressure
S = saturation
v = vapor phase

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Solid–Liquid Equilibria Using UNIFAC

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To calculate the solubility of a solid in a liquid solvent, it is necessary to know the melting temperature and enthalpy of fusion of the solid and the activity coefficient of the solid solute (referred to its pure subcooled liquid) in the solvent. For typical nonelectrolyte systems, this activity coefficient can be estimated from the group-contribution method UNIFAC. Solubilities are calculated for a variety of solids in single and mixed solvents; also, eutectic temperatures and compositions are calculated for some binary systems. Agreement with experiment is good.

While there is an abundance of technical literature on the thermodynamics of vapor–liquid equilibria in mixtures, much less attention has been given to the thermodynamics of solubilities of solids in pure and mixed liquid solvents. Such solubilities are of interest in chemical process design, especially when process conditions must be specified to prevent precipitation of a solid, lest flow lines be plugged.

This work is concerned with a procedure for predicting solubilities of solids in liquids, in nonelectrolyte systems.

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Particular attention is given to polar substances where previously proposed prediction methods are poor. The procedure suggested here is based on the UNIFAC correlation for estimating activity coefficients from group contributions.

Thermodynamic Framework

A solid solute, designated by subscript 2, partly dissolves in a liquid solvent, designated by supscript 1. For the solute, the equation of phase equilibrium is

$$f_2^s = f_2^L \tag{1}$$

where f is the fugacity, superscript s stands for solid phase,

and superscript L stands for liquid phase.

For the fugacity in the liquid phase, we write

$$f_2{}^L = \gamma_2 x_2 f^L{}_{pure\ 2} \tag{2}$$

where x is the mole fraction, γ is the activity coefficient and $f^L{}_{pure\ 2}$ is the fugacity of pure (subcooled) liquid 2 at system temperature.

For the solid phase we assume that there is no solubility of component 1. It then follows that

$$f_2{}^s = f^s{}_{pure\ 2} \tag{3}$$

As discussed elsewhere (Prausnitz, 1969) we can calculate the ratio $(f^s/f^L)_{pure\ 2}$ from

$$\ln\left(\frac{f^s}{f^L}\right)_{pure\ 2} = \frac{\Delta h_f}{RT}\left[\frac{T}{T_m} - 1\right] \tag{4}$$

where Δh_f is the enthalpy of fusion, T_m is the melting temperature of pure substance 2, and T is the temperature of the system. Equation 4 neglects correction terms proportional to Δc_p (specific heat difference between liquid and solid) because the required c_p data are usually not available and because these corrections tend to be small in comparison with uncertainties in the activity coefficient.

For the solids considered here, enthalpies of fusion and melting temperatures are taken from standard references (Landolt–Börnstein, 1961; Weast, 1974).

When eq 4 is substituted into eq 2, the desired solubility x_2 can readily be found provided that the activity coefficient γ_2 is known as a function of composition. If components 1 and 2 are chemically similar, we can use the approximation $\gamma_2 = 1$ and thereby obtain the ideal solubility. For example, for naphthalene, phenanthrene, and anthracene in benzene near room temperature, calculated ideal solubilities are in good agreement with experiment.

For nonpolar systems, we can estimate the activity coefficient using the Hildebrand–Scatchard theory of regular solutions (Hildebrand et al., 1970). Such estimates often give good results; they are particularly useful for calculating solubilities in cryogenic systems, as discussed by Preston (Preston and Prausnitz, 1970).

For nonpolar as well as polar systems, activity coefficients for solid-solubility calculations can often be estimated from vapor–liquid equilibrium data at higher temperatures. Such data are correlated using some semiempirical equation such as Wilson, NRTL, or UNIQUAC, whose characteristic binary parameters are extrapolated with respect to temperature. Experimental data and binary parameters have been correlated for a large number of systems by Gmehling and Onken (1977).

Activity Coefficients from UNIFAC

A group-contribution method, called UNIFAC, has been developed for estimating activity coefficients in nonelectrolyte liquid mixtures (Fredenslund et al., 1975; 1977a; 1977b; Gmehling and Onken, 1977; Onken and Gmehling, 1977). This method is useful for calculating the activity coefficient γ_2 in eq 2.

The activity coefficient consists of two parts: the combinatorial contribution, due mostly to differences in molecular size and shape, and the residual contribution, arising mostly from differences in intermolecular forces of attraction. For a component i in a multicomponent solution

$$\ln \gamma_i = \ln \gamma_i{}^c + \ln \gamma_i{}^R \tag{5}$$

$$\ln \gamma_i{}^c = \ln \frac{\Phi_i}{x_i} + \frac{z}{2}\, q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \tag{6}$$

where

$$l_i = \frac{z}{2}\,(r_i - q_i) - (r_i - 1)$$

The coordination number z is taken to be 10. The area fraction θ and the segment fraction Φ are related to the mole fraction x through

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}; \qquad \phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{7}$$

where pure-component parameters r_i and q_i are, respectively, measures of molecular (van der Waals) volumes and molecular surface areas. These, in turn, are given by group contributions R_k and Q_k according to

$$r_i = \sum_k \nu_k{}^{(i)} R_k; \quad q_i = \sum_k \nu_k{}^{(i)} Q_k \tag{8}$$

where $\nu_k{}^{(i)}$, always an integer, is the number of groups of type k in molecule i. Group contributions R_k and Q_k are given by Fredenslund et al. (1977a; 1977b).

The residual contribution to activity coefficient γ_i is given by

$$\ln \gamma_i{}^R = \sum_{\substack{k \\ \text{all groups in} \\ \text{the solution}}} \nu_k{}^{(i)} [\ln \Gamma_k - \ln \Gamma_k{}^{(i)}] \tag{9}$$

where Γ_k is the group residual activity coefficient and $\Gamma_k{}^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i. In eq 9, the term $\ln \Gamma_k{}^{(i)}$ is necessary to attain the normalization that activity coefficient γ_i becomes unity as $x_i \rightarrow 1$.

The group residual activity coefficient is related to the composition and temperature through

$$\ln \Gamma_k = Q_k[1 - \ln \sum_m \theta_m \psi_{mk} - \sum_m (\theta_m \psi_{km}/\sum_n \theta_n \psi_{nm})] \tag{10}$$

Equation 10 also holds for $\ln \Gamma_k{}^{(i)}$. In this equation, θ_m is the area fraction of group m and the sums are over all groups

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{11}$$

where X_m is the mole fraction of group m in the mixture. The group interaction parameter ψ_{mn} is given by

$$\psi_{mn} = \exp - \left[\frac{U_{mn} - U_{nn}}{RT}\right] = \exp - (a_{mn}/T) \tag{12}$$

where U_{mn} is a measure of the energy of interaction between groups m and n. The group-interaction parameters a_{mn} and a_{nm} ($a_{mn} \neq a_{nm}$) have been systematically evaluated from a large body of vapor–liquid and liquid–liquid equilibrium data. For many group interactions, these parameters are listed by Fredenslund et al. (1977a; 1977b).

Results

Solubilities were calculated for several solutes in a variety of solvents using eq 2 and 4 with activity coefficients calculated from UNIFAC.

Figure 1 shows a temperature-composition diagram for the system ethanol–benzene; the ideal solubility ($\gamma = 1$) is indicated by the dashed line while the solubility predicted with UNIFAC is indicated by the continuous line. Experimental data are shown by points. In this system there are positive deviations ($\gamma > 1$) from Raoult's law in the liquid phase and therefore the observed results lie appreciably above those calculated assuming an ideal liquid mixture.
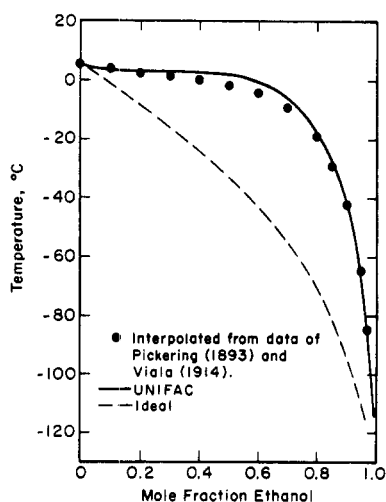
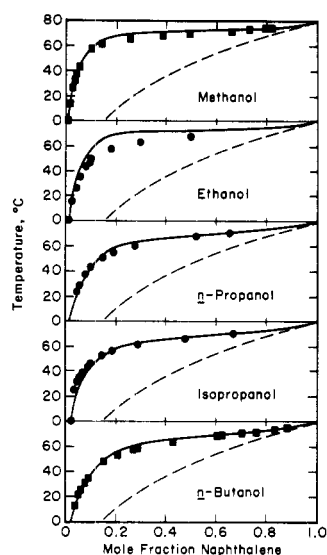**Figure 1.** Solid–liquid equilibria for ethanol–benzene.

Figure 2. Solid–liquid equilibria for five binary naphthalene–alcohol systems: —, UNIFAC; - - -, ideal; ●, data from Sunier (1930); ■, data from Ward (1926).
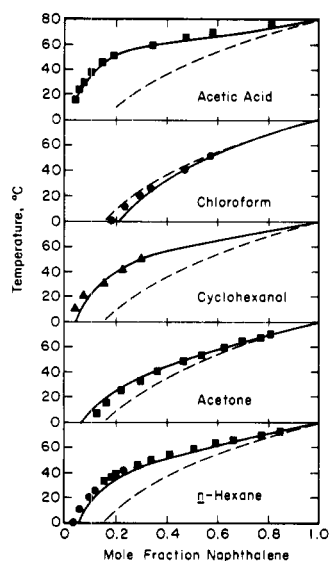

Figure 3. Solid–liquid equilibria for five binary systems containing naphthalene: —, UNIFAC; - - -, ideal; ●, data from Hildebrand (1920); ■, data from Ward (1926); ▲, data from Weissenberger (1927).

Similar results are given in Figure 2 which presents solubilities for binary mixtures containing naphthalene and

Table I. Solubility of Naphthalene[e] in Various Solvents at 40 °C

solvent	solubility, mol %		data ref
	UNIFAC	exptl	
methanol	4.8	4.4	a
ethanol	5.4	7.3	b
1-propanol	9.3	9.4	b
2-propanol	9.3	7.6	b
1-butanol	11.1	11.6	a
n-hexane	25.9	22.2	a
cyclohexanol	20.5	22.5	c
acetic acid	12.5	11.7	a
acetone	35.8	37.8	a
chloroform	47.0	47.3	d

[a] Sunier (1930). [b] Ward (1926). [c] Weissenberger (1927). [d] Hildebrand (1920). [e] Pure component data for naphthalene: T_m = 80.2 °C; Δh_f = 4494 cal/mol. Ideal solubility of naphthalene is 44.0 mol %.

Table II. Solubility of Anthracene[c] in Various Solvents at 20 °C

solvent	solubility, mol %		data ref
	UNIFAC	exptl	
acetone	0.25	0.31	a
diethyl ether	0.45	0.29	a
chloroform	1.82	0.94	a
ethanol	0.04	0.05	a
carbon tetrachloride	0.53	0.41	a
phenol[d]	1.13	0.99	a
cyclohexane	0.31	0.12	a
methanol	0.03	0.02	a
1-propanol	0.06	0.06	a
2-propanol	0.06	0.04	a
aniline	0.27	0.35	a
n-hexane[e]	0.24	0.18	b

[a] Fohl et al. (1966). [b] Hildebrand et al. (1917).
[c] Pure component data for anthracene: T_m = 216.5 °C; Δh_f = 6898 cal/mol. [d] Solubility at 60 °C. [e] Solubility at 25 °C. Ideal solubility of anthracene is 0.86 mol % at 20 °C, 1.05 mol % at 25 °C, and 3.58 mol % at 60 °C.

Table III. Solubility of Phenanthrene[c] in Various Solvents at 20 °C

solvent	solubility, mol %		data ref
	UNIFAC	exptl	
diethyl ether	13.8	13.3	a
n-hexane[d]	7.0	4.8	b
acetone	9.7	14.5	a
chloroform	26.4	23.8	a
ethanol	1.02	1.23	a
carbon tetrachloride	15.8	14.5	a
acetic acid	2.55	1.92	a
methanol	0.91	0.64	a
carbon disulfide	18.5	23.5	a

[a] Henstock (1922). [b] Hildebrand et al. (1917). [c] Pure component data for phenanthrene: T_m = 96.3 °C; Δh_f = 4456 cal/mol. [d] Solubility at 25 °C. Ideal solubility of phenanthrene is 20.6 mol % at 20 °C and 23.4 mol % at 25 °C.

any one of five alcohols, and in Figure 3, which presents solubilities for binary mixtures containing naphthalene and any one of five polar organic solvents. As in Figure 1, there is good agreement between experiment and solubilities calculated using UNIFAC.

Solubilities for naphthalene, anthracene, and phenanthrene in various solvents are given in Tables I, II, and III. For these fused-ring solutes, no new group-interaction parameters were used. The calculations shown are based on group-interaction parameters previously reported from

Table IV. Calculated and Experimental Eutectics in Binary Mixtures[a]

| system		mol % of component 1		temp, °C	
(1)	(2)	UNIFAC	exptl	UNIFAC	exptl
acetone	diethyl ether	32.0	24.0	−123	−126
acetone	ethanol	24.4	21.0	−124	−119
benzene	1,2-dichloroethane	31.6	32.0	−55	−55
benzene	phenol	65.4	62.5	−7	−6
benzene	ethanol	0.9	1.3	−114	−115
benzene	chloroform	26.8	26.0	−82	−77
benzene	1,4-dioxane	56.9	56.5	−26	−26
benzene	acetonitrile	12.6	5.0	−49	−51
benzene	cyclohexane	26.6	26.5	−48	−44
benzene	nitrobenzene	51.7	50.0	−27	−26
phenol	p-xylene	40.9	42.5	0	4
phenol	naphthalene	83.7	83.8	30	29
ethanol	ethyl acetate	89.7	85.0	−118	−118
acetic acid	p-xylene	59.5	61.6	5	1
acetic acid	benzene	45.3	40.9	−8	−8
acetic acid	cyclohexane	7.4	7.4	−6	−1
nitrobenzene	carbon tetrachloride	12.6	18.6	−37	−35

[a] Data reported in Landolt-Börnstein (1964).
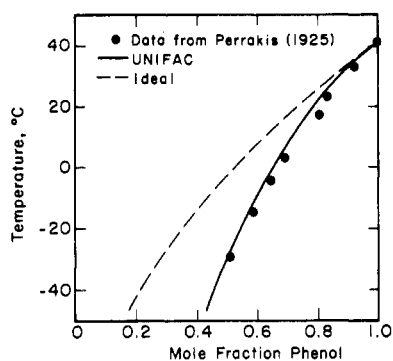
Figure 4. Solid–liquid equilibria for phenol–ethanol.

Figure 6. Solid–liquid equilibria for acetic acid–benzene.

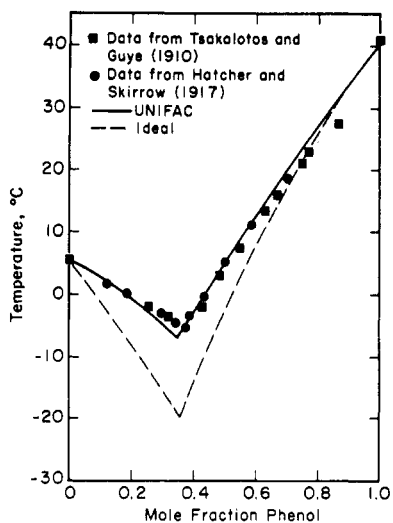**Figure 5.** Solid–liquid equilibria for benzene–phenol.
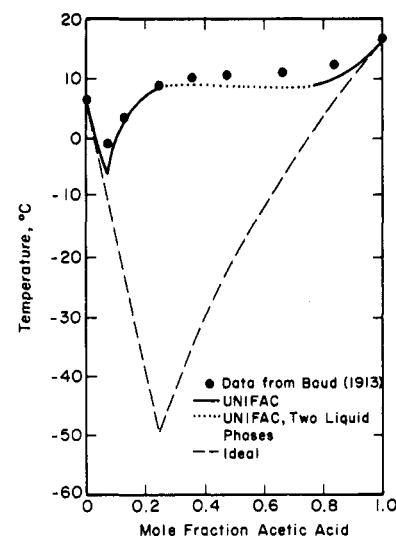
Figure 7. Solid–liquid equilibria for acetic acid–cyclohexane.

data reduction for systems containing benzene.

Figure 4 shows a binary system where there are negative deviations ($\gamma < 1$) from Raoult's law in the liquid phase. In this case the ideal-solubility curve lies above the observed solubilities.

Figures 5 and 6 show two simple eutectic systems where UNIFAC closely predicts the observed eutectic temperature and eutectic composition. Table IV gives calculated and observed eutectic conditions for 17 binary systems. In general, agreement with experiment is good.

Figure 7 shows results for the system acetic acid–cyclohexane. In this case UNIFAC predicts a liquid-phase
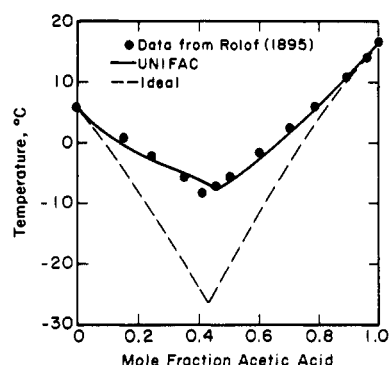
miscibility gap in the mid-composition region.

Few experimental data have been reported on the solubilities of nonelectrolyte solids in mixed solvents. However, since UNIFAC is applicable to ternary and higher systems, UNIFAC may be used to predict solubilities in solvent mixtures. In that case, however, it is necessary to assume that all solvents are insoluble in the solid phase of the solute (eq 3).

Some experimental results have been reported for the solubility of naphthalene in alcohol–water mixtures. These, along with predictions based on UNIFAC, are

Table V. Solubility of Naphthalene in Alcohol–Water Systems[a]

| alcohol	mole fraction alcohol in solvent mixture[b]	temp °C	solubility, mol % ideal	solubility, mol % UNIFAC	solubility, mol % exptl
methanol	0.922	35.7	39.7	2.8	2.4
	0.922	50.6	55.8	4.8	4.6
ethanol	0.906	27.5	32.7	2.6	3.4
	0.906	39.5	43.5	3.8	5.5
	0.743	73.0	47.0	2.0	3.8
1-propanol	0.739	40.9	44.9	3.7	5.6
	0.739	46.7	51.4	4.4	7.4
	0.616	52.1	57.6	3.0	5.7
1-butanol	0.813	21.8	28.3	3.5	4.3
	0.813	29.6	34.1	4.6	5.8
	0.680	30.7	35.3	2.9	4.7
	0.680	43.5	47.7	4.5	8.0

[a] Experimental data from Mannhardt et al. (1943).
[b] Solute-free basis.
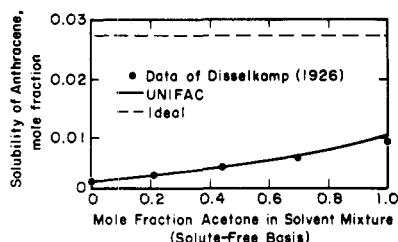
Figure 8. Solubility of anthracene in mixtures of acetone and ethanol at 50 °C.

shown in Table V. In most cases the predictions agree well with experiment and in all cases predictions using UNIFAC are much better than those using the ideal-solution approximation ($\gamma = 1$).

Finally, Figure 8 shows solubilities of anthracene in mixtures of acetone and ethanol at 50 °C; agreement with experiment is very good. While not shown in Figure 8, agreement with experiment is poor at higher temperatures at the acetone-rich end. However, as suggested by Smutek (1967), the high-temperature experimental solubility data are not reliable for acetone-rich solutions, probably because of evaporation of volatile acetone.

Conclusion

Thermodynamics of solid–liquid equilibria, coupled with the UNIFAC group-contribution method for activity coefficients, enables good estimates to be made for the solubilities of typical nonelectrolyte solids in typical liquids, as required in a variety of chemical process-design calculations. Computer programs for that purpose are available from the authors.

Acknowledgment

Nomenclature

a = group-interaction parameter (eq 12)
f = fugacity
l = see eq 6

q = dimensionless van der Waals surface area
Q_k = van der Waals surface area of group k
r = dimensionless van der Waals volume
R = gas constant
R_k = van der Waals volume of group k
T = absolute temperature
U = energy parameter
x = liquid-phase mole fraction
X = liquid-phase group fraction
z = coordination number (= 10)

Greek Letters

γ = liquid-phase activity coefficient
Φ = segment fraction
θ = area fraction
ν = number of groups
Γ = group residual activity coefficient
ψ = see eq 12

Subscripts

1 = solvent
2 = solute
f = fusion
i, j = component
k = molecular group
m = melting in T_m; otherwise refers to molecular group
n = molecular group

Superscripts

c = combinatorial
(i) = molecule i
L = liquid phase
R = residual
s = solid phase

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