The Excess Gibbs Free Energy of Aqueous Nonelectrolyte Solutions

A new thermodynamic model is presented for aqueous solutions of polar nonelectrolytes. The model is based on solute aggregation in an aqueous lattice, which is inferred from spectroscopic, thermodynamic, and physiochemical data. The adjustable model parameters have physical meaning, and are less intercorrelated and temperature-dependent than are the parameters in other models such as the UNIQUAC and NRTL equations, which apply to a more general class of solutions. The model describes observed extrema in the activity coefficients of aqueous solutions, thus pointing out that the behaviors of aqueous and nonaqueous solutions are fundamentally different, and that aqueous solutions cannot be well described with nonaqueous solution models over the whole concentration range. The two-parameter form of the new model can better predict binary vapor-liquid equilibria from liquid-liquid equilibrium data than other two-parameter models, and gives better predictions of ternary liquid-liquid equilibrium using only binary data. It is also shown that the model can be used to describe aqueous solutions of water-soluble polymers.

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Introduction

A goal of thermodynamic modeling is the description of several different properties using the same set of parameters. Many activity coefficient models and equations of state can successfully correlate data, such as vapor-liquid equilibrium (VLE) or liquid-liquid equilibrium (LLE) data, but require different sets of parameters for each. This is of concern to chemical engineers because it suggests that the physical assumptions of the models may not be correct, and extrapolation may therefore be unjustified. Also, a correct thermodynamic model should decrease the amount of data that must be measured. For example, if an accurate model of excess Gibbs free energy is available to describe LLE, it should allow the prediction of VLE as well. Further, the fitted parameters in most thermodynamic models are not unique, but are highly intercorrelated and temperature-dependent. However, one expects that if a thermodynamic model is derived from correct physical assumptions, the adjustable parameters should be related to molecular constants, and assume unique values when fitting data.

Physical chemists have long recognized the unique behavior of water and aqueous solutions. Liquid water has a coordination number of 4 to 5, whereas other liquids have a coordination number of approximately 10. Nevertheless, chemical engineers generally use the same thermodynamic equations to describe aqueous and nonaqueous solutions of nonelectrolytes. It is probably fortuitous that the same models that successfully smooth nonaqueous solution data can also be used to describe some of the features of aqueous solutions. However, in rigorous tests, including the simultaneous description of different properties, dilute solution behavior, and the uniqueness of parameters, these models fail for aqueous solutions because they do not accurately model the physical situation.

This work focuses on the unique nature of aqueous solutions, and on developing a new excess Gibbs free energy model for aqueous solutions with experimentally verifiable assumptions that can simultaneously describe VLE and LLE with a unique set of parameters.

Physical Chemistry of Aqueous Solutions

Throughout this discussion water will be designated as component 1, and the nonaqueous component, which will be referred to as the solute, as component 2. All VLE, LLE, and heat of

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mixing data, unless otherwise noted, are from the compilations of Gmehling et al. (1977), Sorenson and Arlt (1979), and Christensen et al. (1982), respectively. Further, the excess thermodynamic functions presented here will be divided by x_1x_2 to emphasize dilute solution behavior and the asymmetry of the property under consideration.

While most nonaqueous solutions mix endothermically and with small entropic effects, most aqueous solutions mix exothermically and with large ordering effects. For example, Gill et al. (1976) have shown that at 15°C dilute solutions of many C_5 and C_6 hydrocarbons mix exothermically with water. These solutions have large positive excess Gibbs free energies, so that the excess entropy of mixing must be large and negative, indicating ordering. Many polar organic molecules also mix exothermically with water at dilute solute concentrations, but with a large positive excess Gibbs free energy and ordering effects, as shown in Figure 1. Such behavior is exhibited by alcohols, ketones, aldehydes, amines, dioxane, tetrahydrofuran, acetic acid, and many other compounds. Malcolm and Rowlinson (1957) have shown that even a water-soluble polymer (polyethylene glycol) mixes exothermically with water, but with a large positive excess Gibbs free energy. Other observed trends are that G^{EX} is relatively temperature insensitive, while H^{EX} is very sensitive to changes in temperature.

The LLE of binary aqueous solutions is also very different from nonaqueous solutions. While most nonaqueous solutions exhibit an approximately symmetric LLE phase boundary, with both liquid phases of predominantly one component (>0.90), aqueous solution LLE is asymmetric and skewed toward water-rich concentrations, as seen from the data in Sorensen and Arlt (1979). This occurs because $G^{EX}/(RTx_1x_2)$ is so large at these concentrations. Aqueous solutions are also unusual in that they exhibit LLE with a lower critical solution temperature (LCST). This is consistent with the Gibbs-Helmholtz relation, which establishes that in solutions that mix exothermically, G^{EX} increases with increasing temperature and the solution becomes less stable.

Another unique aspect of aqueous solutions is their anomalous behavior at water-rich concentrations. Measurements (Roux et al., 1980; Franks and Ives, 1966; Franks, 1969) of X-ray diffraction, volumetric properties, heat capacities, sound absorption, activation energies for reactions in mixed aqueous solvents, activity coefficients, viscosity, and many other properties, exhibit extrema or other unusual behavior at dilute solute concentrations (below 10 mol % solute). Also, various types of spectroscopic data have shown that solute-solute interactions are more prevalent in water-rich solutions than would be expected based on the overall solution concentration. Nuclear magnetic resonance (NMR) measurements have also shown that tertiary butyl alcohol and trimethylurea aggregate in aqueous solutions (Leiter et al., 1983), and the light-scattering data of Kato (1984), indicate frequent solute-solute interactions in dilute aqueous solutions of butoxy-ethanol. Franks (1979) has interpreted the light-scattering data of Parfitt and Smith (1969) in terms of solute clustering, and Bale et al. (1968) concluded from small-angle X-ray scattering measurements of tertiary butyl alcohol that clusters of like molecules form.

The previously described behavior is often referred to as typical aqueous solution behavior. Multifunctional or highly polar compounds such as methanol, acetonitrile, N,N dimethylformamide, DMSO, urea, and carbohydrates show less evidence of solute aggregation and are not as likely to exhibit anomalous behavior at dilute solute concentrations. Rather than characterizing solutes as belonging to one of these two different classes, here we develop a model that varies continuously between the two, depending on the degree of solute aggregation. The limited degree of aggregation is closely related to solute polarity and is a measure of the ability of the solute to penetrate the water lattice, as discussed by Hildebrand (1968).

All the experimental results cited above indicate ordering to produce increased solute-solute and water-water interactions. While qualitative evidence for both of these effects comes from NMR data, the light-scattering data mentioned above quantitatively establish that solute aggregation is the dominant effect. Other experimental evidence for solute aggregation comes from the freezing point depression data for dilute aqueous solutions of alcohols of Kozak et al. (1968). From fitted virial coefficients, they predicted that large "alcohol micelles" were significant at dilute solute mole fractions. Also, Cramer (1977), in his study of the transfer of organic compounds from an organic solvent to water, pointed out that existing theories fail to quantitatively describe the incremental increase of S^{EX} with each additional methylene group. He therefore postulated that the entropic effect is colligative in nature and this can be explained by solute aggregation.

Speedy (1984) and Speedy and Mezei (1985) used statistical arguments and computer simulations to show that naturally occurring holes in aqueous solutions tend to cluster, and that sol-

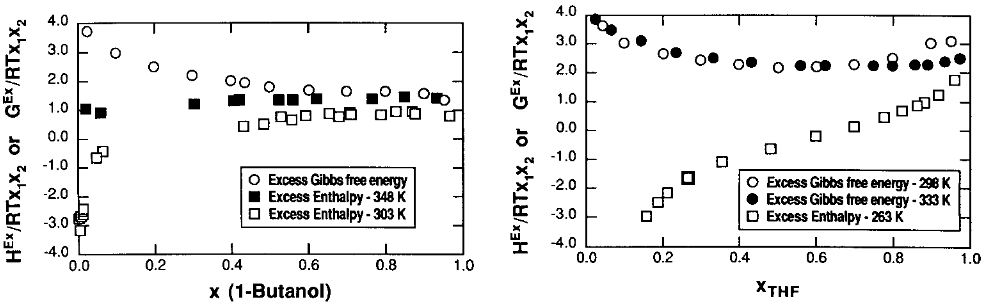

Figure 1a.

Figure 1b.

Figure 1. Excess Gibbs free energy and enthalpy.

a. Water/1-butanol, temp. 298K unless otherwise indicated
b. Water/tetrahydrofuran

ute molecules can fill the holes, resulting in clusters of solute molecules. Thus, solute aggregation is not only due to solute-water repulsions, but is also a natural consequence of how the solute fills the aqueous lattice.

Based on this evidence, it is not unreasonable to assume that water-rich solution behavior is dominated by solute aggregation. However, most current models of aqueous solutions deemphasize solute-solute interactions, and are variations of water models. Franks (1979) and Shealy (1985) have reviewed aqueous solution models, many of which are complex, contain numerous adjustable parameters, describe limited concentration ranges, and are difficult to use for multicomponent solutions. In contrast, models used by chemical engineers do not distinguish between aqueous and nonaqueous solutions, contain physically unjustifiable assumptions, cannot simultaneously describe VLE and LLE, and have adjustable parameters that are highly intercorrelated, temperature-dependent, and not related to molecular constants.

Physical Assumptions for the New Model

Our goal is to develop an excess Gibbs free energy model based on the physical chemistry of aqueous solutions. Physical chemists are interested in simultaneously describing G^{EX}, H^{EX}, S^{EX}, and heat capacity. Since this is so difficult, frequently used models are mathematically complex and contain many adjustable parameters. The chemical engineer's interest in G^{EX} (for phase equilibrium calculations) is fortunate because G^{EX} is a much simpler function than either H^{EX} or S^{EX}. Barclay and Butler (1938) pointed out that enthalpic and entropic effects are correlated and their sum, therefore, has simple concentration and temperature dependencies. Consequently, it is not surprising that models generally used by chemical engineers which can describe G^{EX} do not also describe H^{EX} or S^{EX}.

The proposed model assumes that solute aggregation is the dominant source of nonideality at low solute concentrations, and that at higher concentrations the solution nonidealities are of a relatively simple form; this new model will be referred to as the solute aggregation (SA) model. It is important to note that we are not considering solutes to aggregate due to the chemical forces between them; indeed many of the solutes considered do not exhibit strong interactions. Instead it is exclusion by the water lattice that causes the solute to aggregate (Hildebrand, 1968; Speedy, 1984; Speedy and Mezei, 1985).

As the solute concentration increases, hydrogen bonding of water is broken down, resulting in enthalpic and entropic changes. Experimental G^{EX} information from VLE data indicate that the sum of these effects gives a concentration dependence of G^{EX} that is deceptively simple, and that the structure of water need not be explicitly considered. The temperature dependence of G^{EX} is small for such mixtures for the same reason, so that if G^{EX} can be modeled successfully at one temperature, the model should suffice at other temperatures as well.

Only the simplest type of solute aggregation will be considered—clusters of pure solute. At infinite dilution of solute the number of solute molecules per cluster is unity; the cluster size increases with solute concentration until it reaches a maximum (corresponding to the maxima observed in physiochemical properties), and then decreases with further increases in concentration as the water lattice breaks down.

Finally, size difference effects such as taken into account in the Flory-Huggins model have not been included in the new model. Except for aqueous polymer solutions considered later, the size differences between the species we consider are not so large as to require incorporation of these effects.

Model Development

The starting point for the SA model development is

$$G^{EX}/RT = H^{EX}/RT - S^{EX}/R \tag{1}$$

Heat of mixing data for aqueous solutions, of which Figure 1a is an example, show that at higher temperatures (above 70°C) H^{EX} approaches one-constant Margules behavior. G^{EX} will therefore be modeled at higher temperatures, but since G^{EX} is insensitive to temperature, this model should be valid at lower temperatures as well. Consequently, we will use

$$H^{EX} = CRTx_1x_2 \tag{2}$$

To calculate the excess entropy, S^{EX}, we must compare the entropy of solute molecules occupying holes in the aqueous lattice to the ideal entropy of mixing monomers of solute and water. Our model is that the number of holes in an aqueous lattice is assumed to be approximately constant. When solute is first added, only a fraction of the holes are filled. As more solute is added, the holes are occupied first with monomers and then with larger and larger aggregates of solute molecules. When the average aggregate size approaches a limiting value, the water lattice begins to break up, more holes are created, and the aggregate size decreases.

To model this process, consider first the mixing of water with occupied holes and then the filling of the occupied holes with additional solute. There is no entropy change associated with the second step since the solute monomers are not chemically bound—any solute monomer can go into any hole. The unoccupied holes need not be considered since they do not affect mixture properties. The mole fraction of occupied holes is equal to the mole fraction of solute aggregates, x_2', which can be related to the mole fraction of solute monomers, x_2, by:

$$x_2' = (x_2/m)/(x_2/m + x_1) = \mu x_2/D \tag{3}$$

with

$$D = \mu x_2 + 1 - x_2$$
$$\mu = 1/m$$
$$x_1' + x_2' = 1$$

where m is the average number of solute molecules per aggregate. The entropy of mixing the occupied holes in the aqueous lattice with solute monomers is

$$S^{MIX} = -R[x_1' \ln x_1' + x_2' \ln x_2'] \tag{4}$$

therefore

$$S^{EX} = -R[x_1' \ln x_1' + x_2' \ln x_2' - x_1 \ln x_1 - x_2 \ln x_2] \tag{5}$$

Substituting Eqs. 2, 3, and 5 into Eq. 1 yields (see appendix)

$$\frac{G^{EX}}{RTx_1x_2} = C - \frac{\ln D}{x_1x_2} + \frac{\mu}{Dx_1}\ln \mu + \frac{1-\mu}{D}\ln(1-x_2) + \frac{(\mu-1)(1-D)}{D}\ln x_2 + (\mu-1)\ln(1-x_1) \quad (6)$$

We have used the simple empirical expression below to model the concentration dependence of the average number of solute molecules in a solute cluster, m,

$$m = 1/\{1 + x_1(A-1)[1 - \exp(-B(1-x_1))]\} \quad (7)$$

Note that this expression satisfies the boundary conditions that $m \rightarrow 1$ as $x_1 \rightarrow 1$ and as $x_1 \rightarrow 0$.

Figure 2 shows the average number of solute molecules per cluster, m, vs. concentration for the case of $A = 0.3$, $B = 40$. Recalling that $\mu = 1/m$, Eq. 7 can now be used in Eq. 6. Figure 3 shows that if the first four entropic terms of Eq. 6 (that is, the second, third, fourth, and fifth terms) are neglected, the results obtained are similar in form to those when the complete equation is used. (Since activity coefficients are derivatives of G^{EX}, it is not evident that a simplification of G^{EX} will be satisfactory for the activity coefficients. However, we have tested the phase behavior predictions of the complete and simplified models, and have found the results to be comparable. Further, the difference between the two can be minimized by adjusting the values of the parameters A and C.)

Making this simplifying mathematical assumption results in the final form of the SA model

$$G^{EX}/(RTx_1x_2) = C + x_1(A-1) \cdot \{1 - \exp[-B(1-x_1)]\}\ln(1-x_1) \quad (8)$$

The expressions for the activity coefficients of this model are

$$\ln \gamma_1 = 2V\frac{(1-x_1)}{x_1} - W(1-x_1) + C(1-x_1)^2$$

$$\ln \gamma_2 = V\frac{(2x_1-1)}{1-x_1} + Wx_1 + Cx_1^2 \quad (9)$$

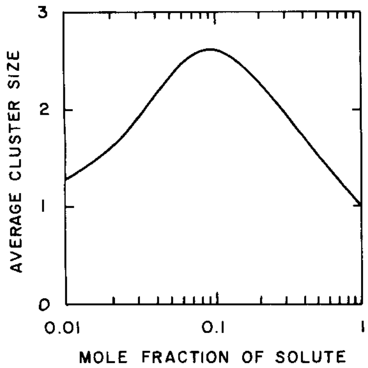

Figure 2. Average cluster size vs. solute mol fract. using Eq. 7 with $A = 0.3$, $B = 40$.

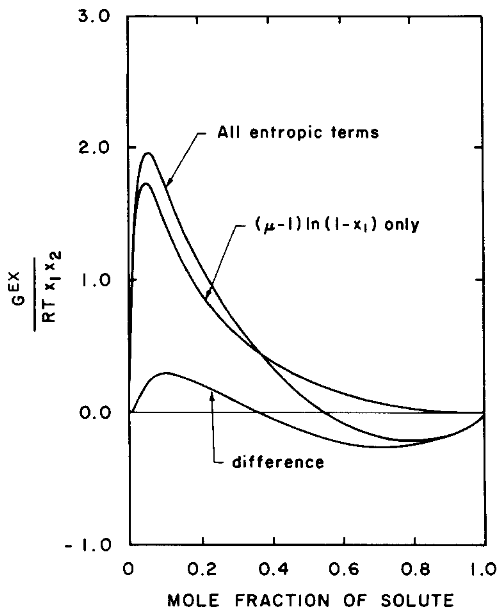

Figure 3. Excess Gibbs free energy using complete Eq. 6 and only first and last terms.

where

$$V = x_1^2(1-x_1)(A-1)(1-Z)\ln(1-x_1)$$

$$W = x_1^2(1-x_1)(A-1)\left[\frac{(1-Z)}{1-x_1} + BZ\ln(1-x_1)\right]$$

$$Z = \exp[-B(1-x_1)]$$

Equation 8 has the three adjustable constants: A, B, and C. Aqueous solution LLE phase compositions, which typically range from 0.40 to 1.0 mol frac. water, can be used to determine two of these parameters. The third parameter can be found by fitting the infinite dilution activity coefficient of water from VLE data. The resulting expression is capable of simultaneously describing VLE and LLE data. Table 1 shows the fitted parameters for a number of different solutes. The B parameters usually lie in the range of 30 to 60. The maximum in $G^{EX}/(RTx_1x_2)$, which is determined by the value of B, is also given. In almost all cases the maximum lies in the range of 0.03 to 0.07 mol frac. solute, which is where extrema occur for many physiochemical properties of aqueous solutions. If we set B equal to a constant value of 40, we obtain the two-parameter version of the model in which the maximum of $G^{EX}/(RTx_1x_2)$ occurs at 0.045 mol frac. solute for all solutions. The A parameter in the model is approximately equal to the reciprocal of the maximum cluster size. Fitted values of A range from 0.2 to 0.9. Average cluster sizes of as large as 5 ($A = 0.2$) are physically reasonable in view of the studies of Kozak et al. (1968) and Desnoyer et al. (1983).

Figure 4 shows the excess Gibbs free energy computed from VLE data for the water/ethanol mixture at three different temperatures, and Table 2 gives values of the two fitted parameters for the NRTL, UNIQUAC, and SA ($B = 40$) equations. We have chosen the NRTL and UNIQUAC models for comparison since they are among the best of the general two-parameter

Table 1. Fitted Parameters for Various Solutes

Solute	$\ln \gamma^{\infty}_{water}$	LLE Phase x_{solute}		$\frac{H^{EX}}{(RTx_1x_2)_{x_{water}\to 0}}$	A	B	Max. $\frac{G^{EX}}{RTx_1x_2}$	C
Mixtures with Upper Critical Solution Temperature								
1-Butanol	1.67 (60°C)	0.0158	0.441 (60°C)	1.5 (55°C)	0.257	45	0.040	1.65
Cyclohexanone	2.20 (90°C)	0.0144	0.615 (90°C)	2.5 (50°C)	0.386	60	0.032	2.09
Ethyl acetate	2.15 (55°C)	0.0130	0.805 (55°C)	3.6 (25°C)	0.108	30	0.050	2.37
Methyl acetate	2.22 (50°C)	0.0765	0.654 (30°C)	3.4 (25°C)	0.609	40	0.044	2.20
Isobutyl alcohol	1.37 (106°C)	0.0240	0.369 (100°C)	1.7 (75°C)	0.243	30	0.050	1.35
Furfural	2.03 (66°C)	0.0213	0.667 (60°C)	2.8 (20°C)	0.250	25	0.061	2.07
Acrylonitrile	2.00 (79°C)	0.0330	0.827 (60°C)	3.2 (45°C)	0.626	40	0.044	2.48
Acrolein	2.58 (92°C)	0.1820	0.472 (80°C)	3.0 (30°C)	0.572	40	0.044	2.09
2-Butanone	1.99 (74°C)	0.0469	0.581 (80°C)	2.8 (60°C)	0.579	40	0.044	2.14
Aniline	1.76 (100°C)	0.0152	0.670 (100°C)	——	0.120	30	0.050	2.04
Near-Critical Mixtures (Upper and Lower Critical Solution Temperature)								
2-Butanol	1.15 (80°C)	0.0390	0.299 (80°C)	1.3 (75°C)	0.299	22	0.067	1.10
3-Methylpyridine	1.10 (70°C)	0.0286	0.162 (60°C)	−0.7 (25°C)	0.422	45	0.040	1.19
2-Butoxyethanol	0.96 (110°C)	0.0195	0.153 (110°C)	——	0.366	60	0.032	0.963
Tetrahydrofuran	2.05 (70°C)	0.1180	0.363 (80°C)	2.0 (25°C)	0.651	20	0.071	2.08

thermodynamic models. It should be kept in mind that they were not developed specifically for use with the aqueous solutions of interest here. It is interesting to note that while the excess Gibbs free energy for this system is not very temperature-dependent, the values of the NRTL and UNIQUAC parameters are; in contrast, the SA model parameters are not nearly as temperature-dependent. The decrease of the A parameter with increasing temperature suggest that the cluster size or ordering increases with temperature, which is consistent with the exothermic heat of mixing for this system at water-rich concentrations.

Figure 5 is a parameter intercorrelation diagram for the NRTL, UNIQUAC, and SA equations. Constant values of the objective function, the average absolute deviation in pressure (AADP), are plotted as a function of the relative change in the model parameters for the water/ethanol data at 55°C. Note that the ellipse for the SA model is much smaller and more nearly circular, indicating that the model parameters are not as intercorrelated as in the UNIQUAC equation, and that finding a unique solution is simpler. These factors are important for making multicomponent predictions from fitted binary data.

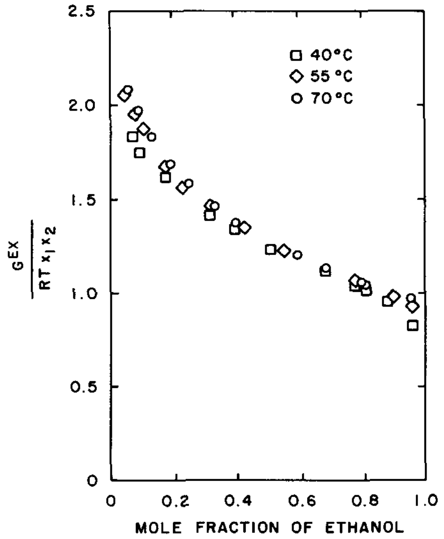

Figure 4. Excess Gibbs free energy for water/ethanol system at various temperatures.

The two-parameter SA model ($B = 40$) can better predict VLE from LLE data, as seen in Figure 6, which shows experimental $x - y$ data and predictions of SA and UNIQUAC models using parameters determined from LLE. Since LLE phase compositions are generally in the range of 0.40 to 0.99 mol frac. water, another test for a model is to use such data to predict the infinite dilution activity coefficient of water. Table 3 shows that the SA model gives better predictions of infinite dilution activity coefficients than do the UNIQUAC and modified UNIQUAC equations. The NRTL equation ($\alpha = 0.3$) predictions are not as good as the UNIQUAC predictions and therefore are not shown here.

At dilute solute concentrations, the SA model predicts a maximum in the activity coefficient of the solute and a minimum in the activity coefficient of water, Figure 7, which is confirmed by a large amount of experimental evidence for aqueous solutions. For example, the freezing point depression data of Okamato et al. (1978) for a wide range of solutes show minima in the activity coefficient of water at dilute solute concentrations. Lebert and Richon (1984) have measured the infinite dilution activity coefficients of alcohols in water, and have obtained lower values than those from the extrapolation of VLE data, Table 4. An explanation for this is that a maximum exists in the activity coefficient of the alcohol at low mole fractions. Mikhailov

Table 2. Fitted Model Parameters for Water/Ethanol

Temp. °C	UNIQUAC J/mol		NRTL (α = 0.3) J/mol		SA (B = 40) A	SA (B = 40) C
40	753	699	−12.1	4,190	0.813	1.16
55	163	988	−314	5,132	0.738	1.16
70	−126	1411	−406	5,546	0.701	1.15

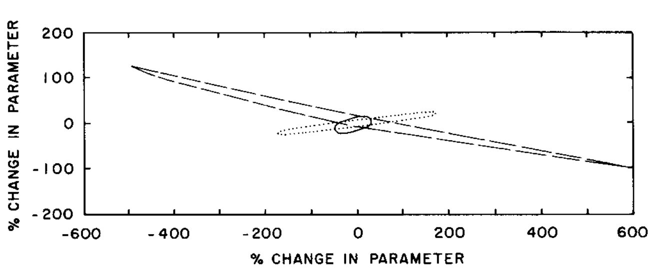

Figure 5. Equal error contours as a result of parameter variations in fitting VLE data for water/ethanol system at 55°C.

——— NRTL, AADP = 0.4 kPa; ----- UNIQUAC, AADP = 0.4 kPa; ——— SA, AADP = 1.3 kPa

(1968) has derived an equation that describes such behavior, and Franks (1979) has stated that this is one of the physically more accurate models; however, it is not widely used due to its complexity and the number of adjustable parameters. In contrast, this behavior is predicted here with the relatively simple solute aggregation model which contains only two (or three) adjustable parameters.

The differences between the SA and UNIQUAC models are a function of the hydrophilicity or hydrophobicity of the solute. The SA model is substantially better for hydrophobic solutes such as 1-butanol, cyclohexanone, etc. (as shown in Figure 6 and Table 3), which are partially miscible with water and exhibit large entropic mixing effects, and the model can better predict VLE from LLE for such solutes. As the solute becomes more hydrophilic (ethanol, methanol, acetone) the SA model does not fit VLE data quite as well as UNIQUAC, but the differences are small, Table 5.

Finch (1981) has cited evidence that water-soluble polymers also aggregate. Assuming that the Flory-Huggins theory provides a reasonable approximation for size effects, that the vapor phase is ideal, and that the mass fraction is a good approximation for volume fraction (since volumetric data are not generally available for such solutions), we have that

$$m_i \gamma_i' P_i^{VAP} = y_i P \tag{10}$$

where m_i is the mass fraction of the solute and γ_i' is the mass-based activity coefficient. The only simultaneous measurement of monomer and polymer VLE and LLE has been reported by Malcolm and Rowlinson (1957) for dioxane (cyclic dimer) and polyethylene glycol. Figure 8 shows the mass-based activity coefficient of water determined from vapor-liquid equilibrium data as a function of mass fraction, and demonstrates that when size effects are accounted for, the water/solute interactions are independent of molecular weight. The solid line in this figure is an SA model fit of the polyethylene glycol 500 LLE where the mass fractions of solute in each phase are 0.032 and 0.350. Thus, the SA model describes both the VLE and LLE of these aqueous polymers up to 80 mass % polymer. At larger mole fractions of solute the Flory-Huggins contribution is the dominant contribution to the free energy; the inability of the SA model to describe solutions with mass fraction of solute greater than 0.80 may therefore be due to the Flory-Huggins approximation.

Table 3. Infinite Dilution Activity Coefficients

Solute	$\ln \gamma^\infty_{water}$	Δ_{SA}	$\Delta_{UNIQUAC}$	ΔModified UNIQUAC
1-Butanol	1.67	−0.14	−0.71	−0.39
Cyclohexanone	2.20	−0.22	−0.79	−0.77
Ethyl acetate	2.15	0.24	−0.06	0.03
Methyl acetate	2.22	0.02	−0.39	−0.30
Furfural	2.03	0.13	−0.46	−0.45
Acrylonitrile	2.00	0.48	0.27	0.33
Acrolein	2.58	−0.49	−0.98	−0.94
2-Butanone	1.99	0.14	−0.48	−0.44
Isobutyl alcohol	1.37	0.00	−0.54	−0.31
Aniline	1.70	0.35	−0.29	−0.17
Average	—	0.22	0.50	0.41

$\Delta_{model} = \ln \gamma^\infty_{water}(model) - \ln \gamma^\infty_{water}$

Multicomponent Mixtures

The development of a multicomponent form of the SA model requires a statement about the clustering and interactions of the multiple solutes. Roux et al. (1980) have pointed out that aqueous solutions of alcohols, amines, amine oxides, and alkoxyethanols are often similar to micellar systems. Aqueous solutions will therefore be considered as a mixed micellar system in which the different solutes form "micelles." The concept of aggregates used for binary aqueous solutions in the previous section therefore still applies, but in this case the aggregates are composed of mixtures of different solutes. As before, it is assumed that the aggregates contain no water molecules.

The multicomponent aqueous solution is considered to be a pseudobinary solution, with aqueous and nonaqueous compo-

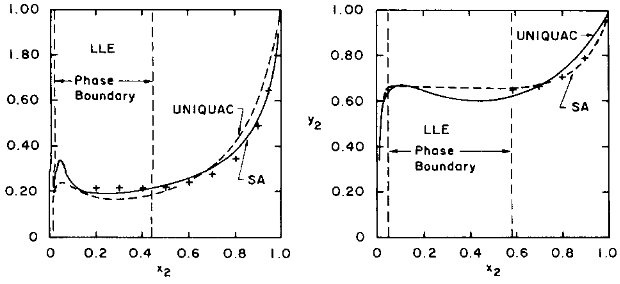

Figure 6. Predictions of VLE from LLE data.

Left, water/1-butanol, 60°C
Right, water/2-butanone, 73.6°C

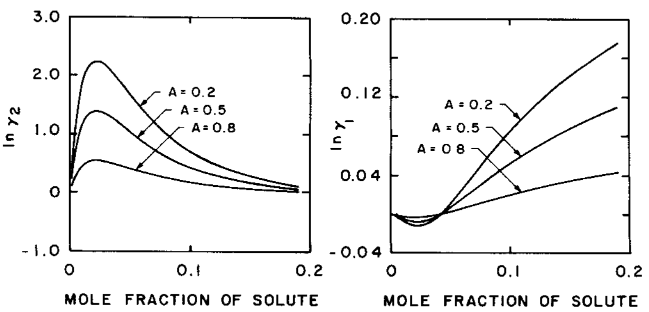

Figure 7. SA model predictions for solute (2) and water (1) activity coefficients at low solute concentrations for various values of parameter *A*.

Table 4. Experimental and Extrapolated Values of Limiting Activity Coefficients of Alcohols

Alcohol	Exp. at 25°C (Okamoto et al., 1978)	VLE Extrap. (Gmehling et al., 1977)
Methanol	1.65	1.87 (25°C) 2.04 (35°C) 2.05 (40°C)
Ethanol	3.27	4.09 (20°C) 4.46 (30°C) 5.06 (40°C) 4.17 (40°C)
1-Propanol	10.9	16.0 (25°C) 17.1 (30°C) 16.3 (30°C) 17.3 (40°C)
1-Butanol	45.1	72.0 (25°C)

nents. The molar excess Gibbs free energy of the mixture will be calculated from

$$G^{EX} = G_{1s}^{EX} + G_{ss}^{EX} \tag{11}$$

where G_{1s}^{EX} and G_{ss}^{EX} are the aqueous-solute and solute-solute contributions, respectively. The SA model will be used to describe G_{1s}^{EX} and any of the common thermodynamic models can be used to describe G_{ss}^{EX}. We use the multicomponent form of the two-constant Margules equation because it is simple and satisfactory for describing many nonaqueous mixtures.

To calculate the entropic portion of G_{1s}^{EX} we consider a two-step process. First, N_2 moles of solute 2 are mixed with N_3 moles of solute 3 to obtain

$$S_{23}^{MIX} = -R(\overline{x}_2 \ln \overline{x}_2 + \overline{x} \ln \overline{x}_3) \tag{12}$$

where

$$\overline{x}_2 = N_2/(N_2 + N_3) \quad \text{and} \quad \overline{x}_3 = 1 - \overline{x}_2$$

and S_{23}^{MIX} is the molar entropy change of the process. Now add N_1 moles of water to the $N_2 + N_3$ moles of solute. Since the entropy of mixing of the solutes has already been considered, and the entropy of mixing water and solutes is identical for each solute, the species type of each solute molecule is unimportant. Assume again that the (mixed) solute forms an average cluster size of m. The cluster mole fractions of water and (mixed) solute, x'_1 and x'_s are defined by

$$x'_s = (x_s/m)/(x_s/m + x_1) \tag{13}$$

Table 5. UNIQUAC and SA Model Fits of Aqueous VLE Data

System	SA AADP kPa	SA AADy	UNIQUAC AADP kPa	UNIQUAC AADy
Water/methanol	0.30	0.0075	0.23	0.0069
Water/ethanol	0.43	0.0118	0.14	0.0075
Water/acetone	0.87	0.0110	1.08	0.0070

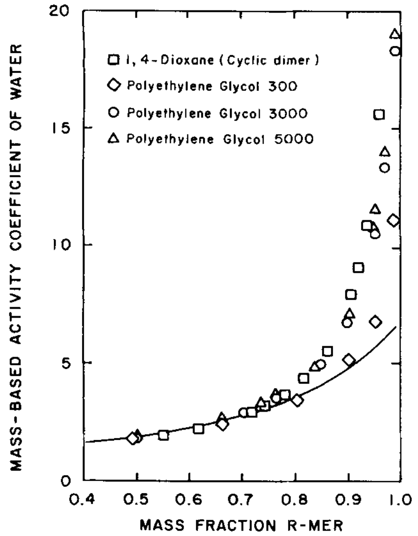

Figure 8. Mass-based activity coefficients of water in water/r-mer mixtures with dioxane (cyclic dimer) and various polyethylene glycols.
□ ◇ ○ △ Experiment
—— SA model

where

$$x'_1 = 1 - x'_s$$

$$x_s = x_2 + x_3$$

$$x_2 = N_2/(N_1 + N_2 + N_3)$$

$$x_3 = N_3/(N_1 + N_2 + N_3)$$

$$x_1 = 1 - x_2 - x_3$$

The molar entropy of mixing water and (mixed) solute is

$$S_{1s}^{MIX} = -R(x'_1 \ln x'_1 + x'_2 \ln x'_2) \tag{14}$$

Now assume that the total molar entropy for both steps, S_{123}^{MIX} can be calculated from

$$\begin{aligned} S_{123}^{MIX} &= S_{1s}^{MIX} + (x_2 + x_3)S_{23}^{MIX} \\ &= -R[x'_1 \ln x'_1 + x'_s \ln x'_s + (x_2 + x_3)\overline{x}_2 \ln \overline{x}_2 \\ &\quad + (x_2 + x_3)\overline{x}_3 \ln \overline{x}_3] \end{aligned} \tag{15}$$

Therefore, the molar excess entropy is

$$\begin{aligned} -S_{123}^{EX}/R &= x'_1 \ln x'_1 + x'_s \ln x'_s \\ &\quad + (x_2 + x_3)\overline{x}_2 \ln \overline{x}_2 + (x_2 + x_3)\overline{x}_3 \ln \overline{x}_3 \\ &\quad - x_1 \ln x_1 - x_2 \ln x_2 - x_3 \ln x_3 \end{aligned} \tag{16}$$

Noting that $\overline{x}_2 = x_2/(x_2 + x_3)$ and $\overline{x}_3 = 1 - \overline{x}_2$, Eq. 16 reduces to

$$\begin{aligned} -S_{123}^{EX}/R &= x'_1 \ln x'_1 + x'_s \ln x'_s + x_2 \ln \overline{x}_2 \\ &\quad + x_3 \ln \overline{x}_3 - x_1 \ln x_1 - x_2 \ln x_2 - x_3 \ln x_3 \\ &= x'_1 \ln x'_1 + x'_s \ln x'_s - x_1 \ln x_1 - x_2 \ln (x_2 + x_3) \end{aligned}$$

$$
\begin{aligned}
&- x_3 \ln (x_2 + x_3) \\
&= x_1' \ln x_1' + x_s' \ln x_s' - x_1 \ln x_1 - (1 - x_1) \ln (1 - x_1)
\end{aligned}
\tag{17}
$$

and is identical to the entropic contribution in a binary mixture (which is expected since the multicomponent development is a pseudobinary one). This same result is obtained regardless of the number of solute species. Following the development for binary solutions, the entropic portion of G_{1s}^{EX} is

$$
S^{EX}/R = x_1^2(1 - x_1)(A - 1) \cdot \{1 - \exp[-B(1 - x_1)]\} \ln (1 - x_1) \tag{18}
$$

where it is assumed the solute mixture A parameter is a linear function of the pure solute A parameters

$$
A = (x_2A_2 + x_3A_3 + x_4A_4 + \ldots)/(x_2 + x_3 + \ldots)
$$

Note that since the B parameter is approximately the same for all solutes in binary mixtures, it is reasonable to use this same value ($B = 40$) in the multicomponent model as well.

The enthalpic contribution for the water-solute interactions will be described using a multicomponent form of the one-constant Redlich-Kister expansion

$$
H_{1s}^{EX}/RT = C_2x_1x_2 + C_3x_1x_3 + C_4x_1x_4 + \ldots \tag{19}
$$

Thus, the multicomponent form of the SA model description of the water-solute interactions is equal to the sum of Eqs. 18 and 19

$$
\begin{aligned}
\frac{G_{1s}^{EX}}{RT} &= x_1^2(1 - x_1)\left(\frac{\sum_{i=2}^{M} A_i x_i}{\sum_{2}^{M} x_i} - 1\right) \\
&\quad \cdot \{1 - \exp[-B(1 - x_1)]\} \ln (1 - x_1) + x_1 \sum_{i=2}^{M} C_i x_i
\end{aligned}
\tag{20}
$$

where components 2 through M are solutes. Also G_{ss}^{EX} is described using a multicomponent form of the two-constant Redlich-Kister expansion (i.e., the two-constant Margules equation)

$$
\frac{G_{ss}^{EX}}{RT} = \sum_{i=3}^{M} \sum_{j=2}^{i-1} x_i x_j (\Lambda_{ij} x_i + \Lambda_{ji} x_j) \tag{21}
$$

The sum of Eqs. 20 and 21 is a new expression for the excess Gibbs free energy of multicomponent aqueous solutions. The corresponding expressions for the activity coefficient are

$$
\begin{aligned}
\ln \gamma_1 &= 2V\left(\frac{1 - x_1}{x_1}\right) - (1 - x_1)W + \sum_{i=2}^{M} x_i \sum_{j=2}^{M} C_j x_j \\
&\quad - 2 \sum_{j=3}^{M} \sum_{i=2}^{j-1} (x_i^2 x_j \Lambda_{ij} + x_j^2 x_i \Lambda_{ij})
\end{aligned}
$$

$$
\begin{aligned}
\ln \gamma_n &= V \frac{2x_1 - 1}{1 - x_1} + x_1 W - \frac{x_1^2}{1 - x_1} \\
&\quad \cdot (1 - Z) \ln (1 - x_1) \sum_{i \neq 1,n}^{M} x_i (A_i - A_n) \\
&\quad + x_1 C_n - x_1 \sum_{i=2}^{M} x_i C_i \\
&\quad + \sum_{j \neq 1,n}^{M} [2\Lambda_{nj} x_n x_j (1 - x_n) + x_j^2 \Lambda_{jn} (1 - 2x_n)] \\
&\quad - 2 \sum_{\substack{j=3 \\ (i,j \neq n)}}^{M} \sum_{i=2}^{j-1} (x_i^2 x_j \Lambda_{ij} + x_j^2 x_i \Lambda_{ji})
\end{aligned}
\tag{22}
$$

where V, W, and Z are defined in Eq. 9.

That the SA model predicts ternary LLE using parameters derived from binary data better than the more general UNIQUAC equation is shown in Figure 9. As pointed out by Anderson and Prausnitz (1978), the most difficult type of ternary LLE to describe are those with a plait point, which is the type of LLE we have considered. Since the SA model gives better ternary predictions and the model parameters are not highly intercorrelated, fitting ternary LLE data is simpler using the SA model. The modified UNIQUAC equation gave predictions that were not significantly different from, or better than, those of the UNIQUAC equation, and were not as good as those obtained with the SA model. For other cases we examined, such as the water/diethyl ether/acetone and water/methyl acetate/acetone systems, where solute aggregation is not important, the predictions of the SA and UNIQUAC models are of about similar accuracy. In the water/diethyl ether/acetone system this is because the ether is so hydrophobic that phase separation is primarily due to enthalpic effects (the A parameter is small, but $C = 3.24$ for this mixture). However, the advantage of the SA model over UNIQUAC is greatest when phase separation is due largely to entropic effects. In the case of the water/methyl acetate/acetone mixture the phase separation is again largely enthalpic because methyl acetate is somewhat hydrophilic, and solute aggregation is less significant.

Application of the Solute Aggregation Model

The SA model describes the vapor-liquid and liquid-liquid equilibria of hydrophobic solutes in aqueous solution better than more general models because it focuses on the unique physical chemistry of such solutions. In particular, emphasis has been put on describing entropic effects in water-rich solutions of hydrophobic solutes. In order to develop a simple model, we have not used complicated expressions for the enthalpy of mixing or size difference effects, both of which could be added to improve the model. Nevertheless, the simple physically-based aqueous solution model developed here has been shown to be quite good for aqueous solutions.

One caveat does apply when using the SA model at very low (0 to 0.01) mole fractions of solute. In this range G^{EX}/x_1x_2 (and S^{EX}/x_1x_2) are strong functions of concentration, and the intercept at infinite dilution of solute is difficult to measure. In the SA model formulated here S^{EX}/x_1x_2 does not contribute to the infinite dilution activity coefficient of the solute. Further, the simple one-constant Margules expression was used to model the excess enthalpy. As a consequence, while other solution models

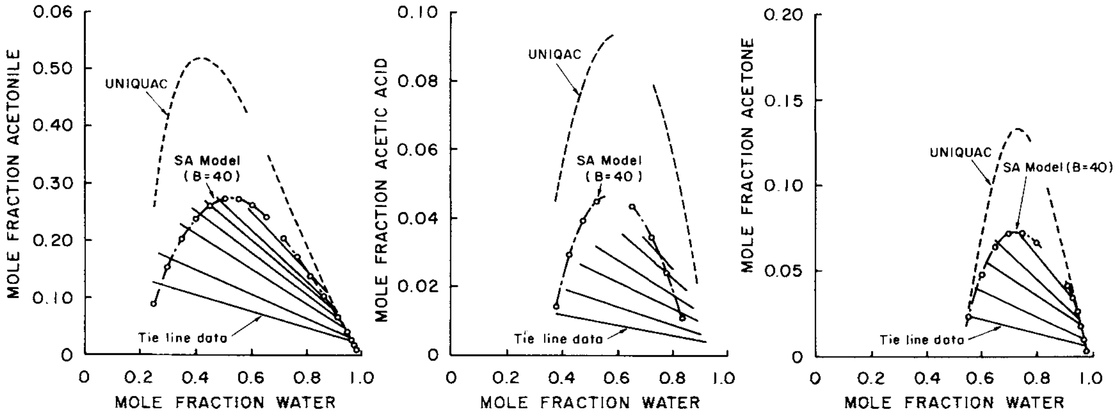

Figure 9. Predictions of ternary LLE from binary data for water with (left) ethyl acetate/acetonitrile, 60°C, (center) 2-butanone/acetic acid, 25°C, (right) 1-butanol/acetone, 30°C.

——— Experimental tie lines; —— - —— SA model predictions
O tie line ends for SA model; ---- UNIQUAC predictions

may overpredict the infinite dilution activity coefficients as they do not describe the maximum in γ at low concentrations, the SA model may underpredict the infinite dilution activity coefficient of the solute. In the range of solute concentrations from 0.01 to 0.1 the SA model is much more accurate than the other models, as discussed here.

Conclusions

The physical chemistry of aqueous solutions shows that aqueous solutions are fundamentally different from nonaqueous solutions. A new model has been proposed for the excess Gibbs free energy of aqueous solutions based on solute aggregation, which is inferred from spectroscopic, thermodynamic, and physiochemical data. The model predicts maxima and minima in the activity coefficients as a function of concentration, as have been observed in aqueous solutions.

The proposed model is simple and its parameters are not as highly intercorrelated or temperature-dependent as in the NRTL and UNIQUAC models. The two-parameter form of the model can better predict VLE from LLE data than the other models considered, and also gives better predictions for ternary LLE using parameters derived from binary data. The proposed model can also describe hydrophilic solutes and water-soluble polymers.

The extrema in activity coefficients in aqueous solutions may have important industrial implications. Many scrubbers and strippers operate at dilute solute concentrations, and therefore the design of such equipment is sensitive to the solution nonidealities. In such cases the use of conventional nonaqueous solution models for aqueous solutions would predict a monotonic increase in the activity coefficient of the solute as its concentration decreased, whereas it is known that solute activity coefficients can exhibit a maximum at dilute solute concentrations. This difference could have an important influence on equipment design. The model developed here would result in a more conservative equipment design.

Notation

A = parameter, Eq. 7
B = parameter, Eq. 7
C = parameter, Eq. 2
D = parameter, Eq. 3
G = Gibbs free energy
H = enthalpy
m = average number of solute molecules per cluster
N = number of moles
P = pressure
P_i^{VAP} = vapor pressure of species i
R = gas constant
T = temperature
V = expression, Eq. 9
W = expression, Eq. 9
x = liquid mole fraction
x' = aggregate or occupied hole mole fraction
y = vapor mole fraction
Z = expression, Eq. 9

Greek letters

γ = activity coefficient
$\mu = 1/m$
Λ = parameter, Eq. 21

Superscripts

EX = excess property
MIX = mixing property
VAP = vapor pressure

Subscripts

$1,2,i$ = species
s = solute

Appendix: Derivation of Binary SA Equation

$$x_1' = \frac{(1-x_2)}{d}; \quad x_2' = \frac{\mu x_2}{d}; \quad D = \mu x_2 + 1 - x_2$$

$$G^{EX} = H^{EX} - TS^{EX}$$

$$\frac{G^{EX}}{RT} = \frac{H^{EX}}{RT} - \frac{S^{EX}}{R}$$

$$= Cx_1x_2 + x_1'\ln x_1' + x_2'\ln x_2' - x_1\ln x_1 - x_2\ln x_2$$

$$= Cx_1x_2 + \frac{1-x_2}{D}\ln\left(\frac{1-x_2}{D}\right)$$

$$
\begin{aligned}
&+ \frac{\mu x_2}{D}\ln\left(\frac{\mu x_2}{D}\right) - x_1 \ln x_1 - x_2 \ln x_2 \\
&= Cx_1x_2 - \frac{1 - x_2}{D}\ln D + \frac{1 - x_2}{D}\ln(1 - x_2) + \frac{\mu x_2}{D}\ln\frac{\mu}{D} \\
&\quad + \frac{\mu x_2}{D}\ln x_2 - (1 - x_2)\ln(1 - x_2) - x_2 \ln x_2 \\
&= Cx_1x_2 - \frac{(\mu x_2 + 1 - x_2)}{D}\ln D + \frac{\mu x_2}{D}\ln \mu \\
&\quad + \frac{(1 - x_2)(1 - D)}{D}\ln(1 - x_2) \\
&\quad + \frac{x_2(\mu - D)}{D}\ln x_2 \\
&= Cx_1x_2 - \ln D + \frac{\mu x_2}{D}\ln \mu \\
&\quad + \frac{x_2(1 - x_2)(1 - \mu)}{D}\ln(1 - x_2) \\
&\quad + \frac{x_2(\mu - 1)(1 - x_2)}{D}\ln x_2
\end{aligned}
$$

$$
\begin{aligned}
\frac{G^{EX}}{RTx_1x_2} &= C - \frac{\ln D}{x_1x_2} + \frac{\mu}{Dx_1}\ln \mu \\
&\quad + \frac{1 - \mu}{D}\ln(1 - x_2) + \frac{\mu - 1}{D}\ln x_2 \\
&= C - \frac{\ln D}{x_1x_2} + \frac{\mu}{Dx_1}\ln \mu + \frac{1 - \mu}{D}\ln(1 - x_2) \\
&\quad + \frac{(\mu - 1)(1 - D)}{D}\ln x_2 + (\mu - 1)\ln x_2
\end{aligned}
$$

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