Thermodynamics of Solutions with Solvent and Solute in Different Pure States

Isoactive-solvent (ISAC) theory is a thermodynamic framework for the case where the components of a solution exist in different pure states: liquid solvent and gaseous solutes (absorption of gases); solid solvent and liquid solutes (sorption of liquids); and liquid solvent and solid solutes (solubility of mixed electrolytes). Properties of mixed solutes are predicted from known activities of single solutes by assuming that solute-solute (but not solute-solvent) molecular interactions are ideal. Equations for an ISAC ideal solution are exact in the limiting case of a solution of identical solutes. The thermodynamic potential is a Legendre transformation of the Gibbs free energy: $\Psi = G - \mu_1 n_1$, where the solvent is component number 1. The ISAC standard state is the real single-solute mixture.

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Introduction

The equations of solution thermodynamics are based on the model of an ideal solution, in which the fugacity of every component is proportional to its mole fraction:

$$f_i = K_i x_i \tag{1}$$

In the symmetrical convention, K_i is the fugacity of pure ith liquid. Real mixtures are characterized in terms of activity coefficients (γ_i) defined by:

$$\gamma_i = \frac{f_i}{K_i x_i} \tag{2}$$

Activity coefficients of different components are not independent; relations between them as well as their dependence on temperature, pressure, and composition are concisely described by "excess functions" such as the excess Gibbs free energy:

$$\frac{g^e}{RT} = \sum_i x_i \ln \gamma_i \tag{3}$$

Activity coefficients and their related thermodynamic excess functions are discussed in standard references, e.g., Chapter 6 of Prausnitz, Lichtenthaler and Azevedo (1986) and Chapter 13 of Rowlinson and Swinton (1982).

If the pure state of a solute is not the same as the solvent, the symmetrical convention breaks down. Sorption of gases and liquids in solids, absorption of gases in liquids, polymers dissolved in liquid solvents, and solids (electrolytes and nonelectrolytes) dissolved in liquids belong in this category. In these cases, the unsymmetrical convention is used: K_i in Eq. 1 becomes the Henry constant, which refers to a hypothetical standard state of "infinite dilution." There are, however, formidable problems associated with extending activity coefficients based on Henry's law to multicomponent (ternary and higher) mixtures (Van Ness and Abbott, 1982).

Isoactive Solvent Theory

Isoactive-solvent (ISAC) theory is a thermodynamic framework for solving phase equilibrium problems when the pure components exist in different pure states (solid, liquid, gas). The activities of the constituent solvent-solute binaries must be known. Properties of mixed solutes are predicted from the known activities of single solutes by assuming that solute-solute (but not solute-solvent) molecular interactions are ideal.

Some definitions are required. One component is the solvent and the other components are solutes. For example, the "solvent" could be a liquid containing dissolved solutes (gases or solids) or a solid containing sorbed gases or liquids. Consider a mixture of N components. Let the solvent be component no. 1, and let the solutes be numbered 2, 3, . . . , N. The isoactive solvent potential Ψ is a Legendre transformation (Callen, 1984) of the Gibbs free energy that replaces the amount of solvent by its

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chemical potential as independent variable:

$$\Psi = G - \mu_1 n_1 = \sum_{i=2}^{N} \mu_i n_i \qquad (4)$$

Ψ plays the same role in ISAC theory as the Gibbs free energy (G) in conventional solution thermodynamics. The essential difference is that Ψ exchanges the amount of solvent (n_1) for its chemical potential (μ_1) as natural independent variable. For solutes, let z_i be the mole fraction of ith solute on a solvent-free basis:

$$z_i = \frac{x_i}{1 - x_1} \quad (i = 2, 3, \ldots, N) \qquad (5)$$

"Specific solvent" (σ) is moles of solvent per mole of solute:

$$\sigma = \frac{x_1}{1 - x_1} \qquad (6)$$

It is convenient to express the chemical potential of the solvent as an activity:

$$\mu_1 = \mu_1^* + RT \ln a_1 \qquad (7)$$

where μ_1^* is the conventional standard state of pure solvent.

The thermodynamic derivation of ISAC theory is contained in Appendix A. Since most of the ISAC equations are similar to their counterparts in standard solution thermodynamics, the following comparison of key relations provides a faster and more intuitive introduction to ISAC theory:

Fugacity:

$$\text{Standard:} \quad f_i = f_i^0 \gamma_i x_i \quad (i = 1, 2, \ldots, N) \qquad (8a)$$

$$\text{ISAC:} \quad f_i = f_i^0 \gamma_i' z_i \quad (i = 2, 3, \ldots, N) \qquad (8b)$$

Ideal Solution:

$$\text{Standard:} \quad f_i = f_i^0 x_i \quad (i = 1, 2, \ldots, N) \qquad (9a)$$

$$\text{ISAC:} \quad f_i = f_i^0 z_i \quad (i = 2, 3, \ldots, N) \qquad (9b)$$

Excess Free Energy Function:

$$\text{Standard:} \quad g^e/RT = \sum_{i=1}^{N} x_i \ln \gamma_i \qquad (10a)$$

$$\text{ISAC:} \quad \psi^e/RT = \sum_{i=2}^{N} z_i \ln \gamma_i' \qquad (10b)$$

Gibbs-Duhem Equation:

$$\text{Standard:} \quad \sum_{i=1}^{N} x_i \, d \ln \gamma_i = 0 \quad (\text{constant } T, P) \qquad (11a)$$

$$\text{ISAC:} \quad \sum_{i=2}^{N} z_i \, d \ln \gamma_i' = 0 \quad (\text{constant } T, P, a_1) \qquad (11b)$$

Activity Coefficients:

$$\text{Standard:} \quad \ln \gamma_i = \left[\frac{\partial(G^e/RT)}{\partial n_i}\right]_{T,P,n_j} \quad (i = 1, 2, \ldots, N) \qquad (12a)$$

$$\text{ISAC:} \quad \ln \gamma_i' = \left[\frac{\partial(\Psi^e/RT)}{\partial n_i}\right]_{T,P,a_1,n_j} \quad (i = 2, 3, \ldots, N) \qquad (12b)$$

The activity of the solvent (a_1) is an independent variable; the *amount* of solvent is determined by the equation:

$$\sigma^e = -\left[\frac{\partial(\psi^e/RT)}{\partial \ln a_1}\right]_{T,P,z_i} \qquad (13)$$

where σ^e is excess specific solvent:

$$\sigma^e = \sigma - \sum_{i=2}^{N} z_i \sigma_i^0 \quad (\text{constant } T, P, a_1) \qquad (14)$$

Equation 13 has no equivalent in conventional solution thermodynamics.

The ISAC model of an ideal solution is illustrated in Figure 1 for a ternary mixture; the curves are loci of constant activity (a_1) of the solvent. An ISAC ideal solution is defined entirely in terms of the behavior of single-solute (binary) mixtures. On the middle locus, for example, point A is the standard state for component number 2, and point B is the standard state for component number 3. Since $\gamma_i' = 1$ for each solute, it follows from the above equations that $\psi^e = 0$ and $\sigma^e = 0$. An ISAC ideal solution is thermodynamically consistent as demonstrated by substitution of $\gamma_i' = 1$ in Eq. 11b.

Example

Differences between the standard and ISAC conventions are understood best in terms of an example for a ternary liquid mixture containing one solvent (no. 1) and two solutes (nos. 2 and 3). All three pure components are liquids and the vapor is a perfect gas. Assume that the *solute* interactions are ideal in the ISAC sense, so that $\psi^e = 0$, $\sigma^e = 0$, and $\gamma_2' = \gamma_3' = 1$. However, solute-solvent interactions are nonideal: for single-solute solu-

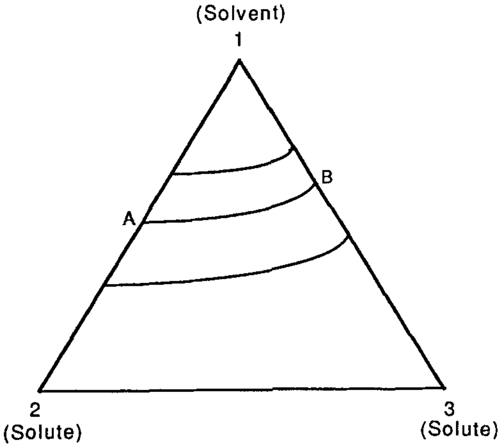

Figure 1. Ternary phase diagram of two solutes (nos. 2 and 3) in solvent (no. 1).

Solid lines are loci of constant solvent activity (a_1). Points A and B are the single-solute standard states for the middle locus.

tion 1-2, let the excess Gibbs free energy be $g^e_{12}/RT = C_{12}x_1^0x_2^0$ so that:

$$\ln \gamma_1^0 = C_{12}(x_2^0)^2$$
$$\ln \gamma_2^0 = C_{12}(x_1^0)^2$$

The superscript ^{0} identifies the single-solute solution, which is the standard state in the ISAC convention. The activity of the solvent in 1-2 solution is

$$a_1 = x_1^0\gamma_1^0 = x_1^0 e^{C_{12}(1-x_1^0)^2}$$

Note that the standard-state mole fraction x_1^0 is an implicit function of solvent activity (a_1). Assume a similar set of equations for single-solute solution 1-3, with binary constant C_{13}. Let:

$$C_{12} = 1.5$$
$$C_{13} = 1.0$$

and

$$P_1^s = 1 \text{ bar}$$
$$P_2^s = 2 \text{ bar}$$
$$P_3^s = 3 \text{ bar}$$

In conventional solution thermodynamics, fugacities for the liquid mixture are calculated as a function of the ternary composition (x_1, x_2, x_3). Independent variables in the ISAC convention are the solvent activity and solvent-free mole fractions. Let:

$$a_1 = 0.7$$
$$z_2 = 0.6$$
$$z_3 = 0.4$$

Since $z_2 + z_3 = 1$, only a_1 and z_2 are independent. Numerical solution of the equation for the activity of the solvent at $a_1 = 0.7$ yields:

$$x_2^0 = 0.57009$$
$$x_3^0 = 0.40673$$

These mole fractions identify the ISAC single-solute reference states at $a_1 = 0.7$. The mole fraction of solvent in the ternary mixture is given by Eq. 14 for an ideal solution:

$$\sigma = z_2\sigma_2^0 + z_3\sigma_3^0$$
$$\frac{x_1}{1-x_1} = z_2\left[\frac{x_1^0}{1-x_1^0}\right]_{12} + z_3\left[\frac{x_1^0}{1-x_1^0}\right]_{13}$$
$$\frac{x_1}{1-x_1} = z_2\left[\frac{1-x_2^0}{x_2^0}\right] + z_3\left[\frac{1-x_3^0}{x_3^0}\right]$$
$$\frac{x_1}{1-x_1} = 0.6\left[\frac{0.42991}{0.57009}\right] + 0.4\left[\frac{0.59327}{0.40673}\right] = 1.03592$$

and $x_1 = 0.50882$. Then from Eq. 5:

$$x_2 = z_2(1 - x_1) = 0.29471$$
$$x_3 = z_3(1 - x_1) = 0.19647$$

From Eqs. 8a and 9b:

$$f_1 = P_1^s a_1 = 1(0.7) = 0.7000 \text{ bar}$$
$$f_2 = f_2^0 z_2 = P_2^s\gamma_2^0 x_2^0 z_2$$
$$= 2(1.31948)(0.57009)(0.6) = 0.90266 \text{ bar}$$
$$f_3 = f_3^0 z_3 = P_3^s\gamma_3^0 x_3^0 z_3$$
$$= 3(1.42187)(0.40673)(0.4) = 0.69398 \text{ bar}$$

In the ISAC convention $\gamma_2' = \gamma_3' = 1$ but in the standard convention:

$$\gamma_1 = \frac{f_1}{P_1^s x_1} = \frac{a_1}{x_1} = 1.3757$$
$$\gamma_2 = \frac{f_2}{P_2^s x_2} = 1.5315$$
$$\gamma_3 = \frac{f_3}{P_3^s x_3} = 1.1774$$

In the ternary mixture, $\psi^e/RT = 0$, but $g^e/RT = \Sigma x_i \ln \gamma_i = 0.3200$.

This example serves to clarify the following points:

1. Thermodynamic equilibrium data must be available for each solvent-solute pair in the solution.
2. The ISAC standard state is the real single-solute mixture; therefore, the ISAC formulation of ideal mixing of solutes applies even when the solvent and solutes exist in different pure states.
3. Since the practical independent variables are mole fractions (x_i), implementation of the ISAC convention requires an additional, iterative calculation for the unknown activity of the solvent in the standard state.
4. As a predictive tool, ISAC theory works best when nonidealities of solute-solvent molecular interactions dominate. The equations for an ISAC ideal solution are exact in the limiting case of a solution of identical solutes.

Appendix A is a thermodynamic derivation of fundamental equations for the ISAC convention. The relationship of Ψ to the semigrand ensemble of statistical mechanics and McMillan-Mayer solution theory is given in Appendix B.

Ternary Vapor-Liquid Equilibria

The section may be skipped if the objective is to predict equilibrium properties of mixed solutes where the solutes exist in a different state than the solvent. Here the ISAC convention is used to predict multicomponent (ternary and higher) vapor-liquid equilibrium (VLE) from data for the constituent binaries when all of the components are liquids, so that ISAC may be compared with the Wilson, NRTL and UNIQUAC equations. ISAC equations for activity coefficients developed in this section will be applied later to systems of mixed solutes.

Consider a ternary mixture of three liquids and designate the solvent as component no. 1 and the solutes as component nos. 2 and 3. Solute-solute interactions are not assumed to be ideal. Although the choice of solvent is arbitrary in this case, best results are obtained when the solvent is the component that introduces the greatest degree of nonideality to the system; the

2-3 binary is the pair with the smallest excess Gibbs free energy g^e. Experimental data must be available for the solute-solvent binaries (g^e_{12} and g^e_{13}) and for the solute-solute binary (g^e_{23}). The objective is to predict activities inside the triangle of Figure 1 using experimental data for the three sides of the triangle.

The top region of the triangle in Figure 1 is the focus of interest for mixed-solutes (nos. 2 and 3) in a solvent (no. 1). The bottom region of the triangle does not exist as a homogeneous solution when the solutes have a pure state different from the solvent. The bottom region of the triangle is a single solute (no. 1) in mixed solvents (nos. 2 and 3); in this case, the top part of the triangle does not exist as a homogeneous solution. Here both cases, mixed solutes and mixed solvents, can be examined at once because all three components are liquids.

According to Eq. A5, ψ is identical with g along the 2-3 side of the triangle in Figure 1 where $\mu_1 = 0$. Therefore, at zero solvent activity:

$$\lim_{a_1 \to 0} \psi^e(a_1, z_2) = g^e_{23}(z_2) \tag{15}$$

At the opposite extreme of unit activity the solute-solute nonidealities vanish:

$$\lim_{a_1 \to 1} \psi^e(a_1, z_2) = 0 \tag{16}$$

The limiting value of σ^e along the 2-3 side of the triangle in Figure 1 is:

$$\begin{aligned} \lim_{a_1 \to 0} \sigma^e &= \sigma - z_2\sigma_2^0 - z_3\sigma_3^0 \\ &= x_1 - z_2 x_{12}^0 - z_3 x_{13}^0 \\ &= a_1\left[\frac{1}{\gamma_1^\infty} - \frac{z_2}{(\gamma_1^\infty)_{12}} - \frac{z_3}{(\gamma_1^\infty)_{13}}\right] \end{aligned} \tag{17}$$

x_{1j}^0 is the mole fraction of solvent in the 1-j pair at its standard state. The dependence of the Henry's constant (γ_1^∞) on composition is needed in Eq. 17. Assume that:

$$\ln \gamma_1^\infty = z_2 \ln (\gamma_1^\infty)_{12} + z_3 \ln (\gamma_1^\infty)_{13} \tag{18}$$

Equation 18 is a first approximation for mixed solvents; more refined expressions (Prausnitz, Lichtenthaler and Azevedo, 1986) are available. From Eq. 13:

$$\lim_{a_1 \to 0}\left(\frac{\partial(\psi^E/RT)}{\partial a_1}\right)_{z_i} = -\lim_{a_1 \to 0}\left(\frac{\sigma^e}{a_1}\right) = -\lim_{a_1 \to 0}\left(\frac{\partial \sigma^e}{\partial a_1}\right)_{z_i} \tag{19}$$

As explained in Appendix A, temperature is constant and the effect of pressure on the liquid phase is neglected. Combining the last three equations:

$$\lim_{a_1 \to 0}\left(\frac{\partial(\psi^e/RT)}{\partial a_1}\right)_{z_i} = z_2 e^{-K_2} + z_3 e^{-K_3} - e^{-(K_2 z_2 + K_3 z_3)} \tag{20}$$

where $K_i \equiv \ln (\gamma_1^\infty)_{1i}$. The activity coefficients of the solvent at infinite dilution are obtained from $\ln (\gamma_1^\infty)_{1i} = \lim_{x_1 \to 0}(dg^e_{1i}/dx_1)$. Equation 13 also relates the slope $(\partial\psi^e/\partial a_1)$ to σ^e at $a_1 = 1$, but since $\lim_{a_1 \to 1}(\sigma^e)$ is of the form $(\infty - \infty)$, σ^e is finite but indeterminate.

Thus the limits of ψ^e at $a_1 = 0$ and $a_1 = 1$, Eqs. 15 and 16, as well as its slope at $a_1 = 0$, Eq. 20, are known properties of the constituent binary solutions. An equation that satisfies these boundary conditions is:

$$(\psi^e/RT) = g - a_1[s(1 - a_1) + g a_1] \tag{21}$$

where

$$g(z_2) \equiv \left(\frac{g^e_{23}}{RT}\right) \tag{22}$$

and

$$s(z_2) \equiv e^{-(K_2 z_2 + K_3 z_3)} - z_2 e^{-K_2} - z_3 e^{-K_3} \tag{23}$$

Other properties are calculated from Eq. 21. Using Eq. A25:

$$\sigma^e = a_1[2 g a_1 + s(1 - 2a_1)], \tag{24}$$

and from Eq. A19:

$$\begin{aligned} \ln \gamma_2' &= (1 - a_1^2)(\ln \gamma_2)_{23} - a_1(1 - a_1)(s + z_3 s') \\ \ln \gamma_3' &= (1 - a_1^2)(\ln \gamma_3)_{23} - a_1(1 - a_1)(s - z_2 s') \end{aligned} \tag{25}$$

where $(\gamma_2)_{23}$ and $(\gamma_3)_{23}$, the activity coefficients in the 2–3 binary solution, are calculated from g^e_{23} in the usual way and

$$s' = \left(\frac{\partial_s}{\partial z_2}\right)_{T,P,a_1} = (K_3 - K_2)e^{-(K_2 z_2 + K_3 z_3)} - e^{-K_2} + e^{-K_3} \tag{26}$$

The three independent variables for an ISAC bubble-point pressure calculation are T, x_1 and x_2. Since $x_3 = (1 - x_1 - x_2)$, the composition of the liquid phase is known; z_2, z_3 and σ are given by Eqs. 5 and 6. The unknowns are P, y_1, y_2, y_3 and a_1. Combining Eqs. 14 and 24:

$$\sigma^e = \sigma - z_2\sigma_2^0 - z_3\sigma_3^0 = a_1[2 g a_1 + s(1 - 2a_1)] \tag{27}$$

g and s are explicit functions of z_2, Eqs. 22 and 23. σ_i^0 is a function of x_{1i}^0 given by Eq. 6. In the single-solute solutions, a_1 is an explicit function of x_{1i}^0, and this function can be inverted to get $x_{1i}^0(a_1)$. Therefore σ_i^0 is an implicit function of a_1, which is the only unknown in Eq. 27. After solving Eq. 27 for a_1, the solute activities a_2^0 and a_3^0 are calculated at their standard states: x_{12}^0 in the 1-2 binary and x_{13}^0 in the 1-3 binary, respectively. Then ternary activities are obtained from Eq. A22. Finally the equations for fugacity:

$$\begin{aligned} P y_1 \Phi_1 &= P_1^s a_1 \\ P y_2 \Phi_2 &= P_2^s a_2^0 \gamma_2' z_2 \\ P y_3 \Phi_3 &= P_3^s a_3^0 \gamma_3' z_3 \end{aligned} \tag{28}$$

in combination with:

$$y_1 + y_2 + y_3 = 1 \tag{29}$$

are solved simultaneously for P and the vapor-phase mole frac-

Table 1. Ternary Systems

System No.	Component No. 1	Component No. 2	Component No. 3	g^e_{23}/RT	g^e_{1i}/RT
1	methyl acetate	acetone	acetonitrile	0.00	0.05
2	acetonitrile	benzene	carbon tetrachloride	0.03	0.35
3	water	acetone	1,4-dioxane	0.08	0.45
4	water	acetone	ethanol	0.18	0.39
5	chloroform	n-heptane	ethanol	0.55	0.18

tions y_i. Φ includes the Poynting correction for the effect of pressure on the binary standard states, as well as the fugacity coefficients of the pure and mixed vapors (Van Ness and Abbott, 1982). The P_i^s are the vapor pressures of the pure saturated liquids at saturation.

We compared predictions by Eqs. 27–29 with experimental data for bubble-point pressures for five ternary systems listed in Table 1. g^e_{ij} refers to the maximum value of the excess Gibbs free energy at the temperature of the experiment in Table 2. The first component is the solvent, selected so that the 2–3 system is the most nearly ideal pair (except for the last system). The solute-solute interactions are nearly ideal for the first two systems, but nonideal for the last three systems. Table 1 also contains the average value of $(g^e_{1i}/RT)_{max}$ for the solute-solvent binaries; the first ternary system is nearly ideal in the conventional sense, but the last four mixtures are nonideal. The fifth system is not well suited to the ISAC model of ideal (or nearly ideal) solute-solute interactions; in fact, heptane and ethanol are on the verge of splitting into two liquid phases. However, the fifth system was included to cover the complete spectrum of solute-solute interactions, from ideality to large positive deviations from Raoult's law.

Table 2. ISAC Error in Calculated Bubble-Point Pressure

System No.	Reference	T, K	No. Points	ΔP_{exper} %	ΔP_{calc} %
1	DiElsi et al. (1978)	323.15	21	0.1	0.1
2	Clark & Missen (1974)	318.15	62	0.6	0.6
3	Loehe et al. (1981)	323.15	79	0.2	1.0
4	Chaudhry et al. (1980)	323.15	57	0.1	0.7
5	Abbott et al. (1975)	323.15	92	0.2	1.8

RMS errors in the calculated bubble-point pressure are listed in Table 2 and compared to the estimated experimental error. The first two systems are in complete agreement with experiment. Beginning with the third system, the predictions show systematic deviations proportional to the nonidealities (g^e_{23}) of the solute-solute interactions. For example, for system no. 3, the RMS error in P was 1.0%, compared to an estimated experimental uncertainty of 0.2%. Figures 2 and 3 compare calculated and experimental values of vapor-phase mole fraction for two cuts through the ternary phase diagram; the RMS error is $\Delta y = 0.002$. Experimental values of y were calculated (Loehe, Van Ness and Abbott, 1981) using the Gibbs-Duhem equation.

Vapor compositions were reported for system 2. For the ISAC equations, the RMS deviation from experiment is $\Delta y = 0.005$.

For comparison, the average error in bubble-point pressure for system 5 obtained from the UNIQUAC equation is 1.6%. For the other systems, the ISAC predictions are as good or bet-

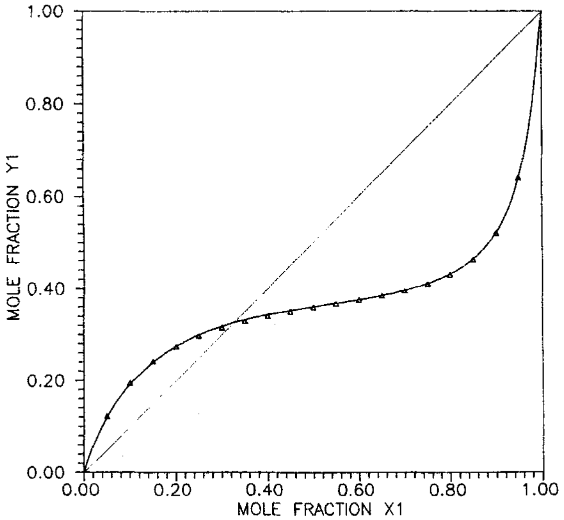

Figure 2. VLE of water(1)-acetone(2)-dioxane(3) at 323.15 K.

Mole fraction water in vapor (y_1) as a function of mole fraction water in liquid (x_1) on locus (x_3/x_2) = 10. Solid line is ISAC prediction based on binary data and triangles are experimental data (Loehe, Van Ness and Abbott, 1981).

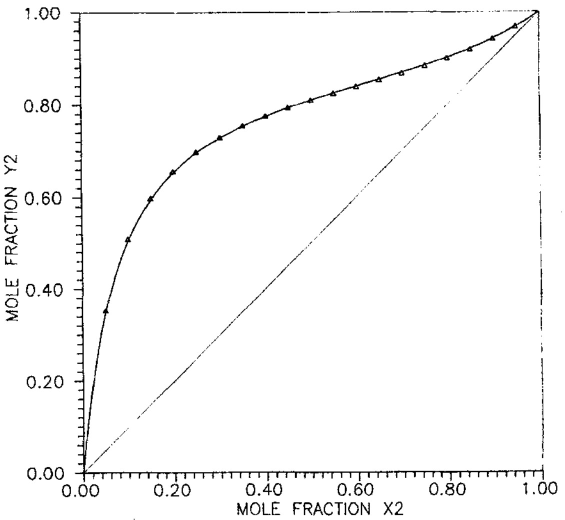

Figure 3. VLE of water(1)-acetone(2)-dioxane(3) at 323.15 K.

Mole fraction acetone in vapor (y_2) as a function of mole fraction acetone in liquid (x_2) on locus (x_1/x_3) = 3. Solid line is ISAC prediction based on binary data and triangles are experimental data (Loehe, Van Ness, and Abbott, 1981).

ter (Kopatsis, 1985) than the UNIQUAC equations. The UNIQUAC equations are more convenient to use for VLE calculations, but cannot be applied unless all of the components are liquids in their pure state. The purpose here is to compare ISAC with established methods before applying it to mixtures with components in different standard states.

To summarize the results of using the ISAC convention to predict multicomponent VLE from binary data:

1. For mixed solutes, the ISAC equations are very accurate for systems with nonideal solute-solvent molecular interactions and nearly ideal solute-solute interactions. Similar results should be expected for systems in which the solutes and solvent exist in different pure states.
2. The accuracy of ISAC predictions deteriorates as solute-solute interactions become more nonideal. Results for systems 3–5 in Table 2 indicate that errors of several percent, which are nearly an order of magnitude larger than the experimental error, appear when the solutes are nonideal. These errors are due to ternary effects that cannot be predicted from binary data alone. Comparable errors are anticipated for ISAC predictions of the phase behavior of a solute in nonideal mixed solvents, when solute and solvent exist in different pure states.

ISAC Predictions for Ideal Mixed Solutes

When solute-solute molecular interactions are ideal or nearly ideal, phase equilibria of mixed solutes can be predicted from single-solute data using $\gamma_i' = 1$, $\psi^e = 0$, and $\sigma^e = 0$. Details of the solution algorithm are highly specific to the type of phase equilibria: sorption of gaseous solutes in a solid adsorbent, solubility of gaseous solutes in a liquid solvent, solubility of solid electrolytes in a liquid solvent, etc. Each type of system uses a different convention to report single-solute phase equilibrium. For adsorption, the activity of the adsorbent must first be calculated from single-gas adsorption isotherms. The activity of a gas dissolved in a liquid solvent is modeled, for example, by the Krichevsky-Ilinskaya equation (Prausnitz, Lichtenthaler, and Azevedo, 1986). For electrolyte solutions, the activity of the solvent in its standard state is available directly from isopiestic measurements, but there is the complication of dissociation of solutes. Finally, the problem is posed differently in each case: for adsorption the independent variables are temperature, pressure and vapor composition; for solubility of gases in liquids, the independent variables are temperature, pressure and solvent-free mole fraction of solutes in the vapor phase; and for electrolyte solutions the independent variables are the temperature and molalities of the solutes. Adsorption and solutions of strong electrolytes are considered next. Prediction of solubility of mixed gases is considered in a separate paper (Myers and Myers, 1988).

Gas Adsorption Equilibria

In this case the "solvent" is the solid adsorbent and the solutes are the adsorbates. Consider adsorption of a binary gas mixture. Adsorbate-adsorbate interactions within the pores of the adsorbent are assumed to be ideal in the ISAC sense, with $g_{23}^e = 0$.

Several changes in nomenclature are necessary. The chemical potential of crystalline adsorbents like carbon or zeolites must be expressed in terms of mass:

$$\mu_1 = \left(\frac{\partial G}{\partial m_1}\right)_{T,P,n_j} \tag{30}$$

and Eq. 6 is modified so that specific solvent is mass of adsorbent per mole of solute: $\sigma = m_1/n$. In adsorption terminology, the dependent variable is $1/\sigma$, the total amount adsorbed per unit mass of adsorbent. The chemical potential of the adsorbent in the single-gas standard state is given by Eq. A7:

$$-d\mu_1 = (1/\sigma_i^0)d\mu_i^0 = (1/\sigma_i^0)RTd\ln f_i^0 \tag{31}$$

The adsorbent "solvent" is nonvolatile and the vapor pressure of the adsorbate is often subatmospheric. Assuming a perfect gas vapor:

$$-d\mu_1 = RT(1/\sigma_i^0)\frac{dP_i^0}{P_i^0} \tag{32}$$

Integrating:

$$\mu_1 - \mu_1^* = -RT\int_0^{P_i^0}\frac{(1/\sigma_i^0)}{P_i^0}\,dP_i^0 \tag{33}$$

This integral is evaluated using experimental data for the adsorption isotherm: $(1/\sigma_i^0) = \mathcal{F}(P_i^0)$. The fugacity of the adsorbate in its "single-solute" standard state is simply its pressure (P_i^0) over the adsorbent, so from Eq. 9b:

$$Py_i = P_i^0(\mu_1)z_i \tag{34}$$

where z_i is adsorbent-free mole fraction of ith adsorbate. Equation 34 has been used extensively in the field of adsorption where it is called ideal-adsorbed-solution (IAS) theory (Myers, 1987). The second key equation is for the excess solvent:

$$\sigma^e = \sigma - \sum_{i=2}^{N}(z_i\sigma_i^0) = 0 \tag{35}$$

In terms of adsorption variables, Eq. 35 asserts that the reciprocal of the total amount adsorbed is a linear function of reciprocal amounts adsorbed in the standard state.

Equations 33–35 are the solution-thermodynamics version of adsorption. In adsorption thermodynamics, the theory is that adsorption takes place in a two-dimensional phase lying next to the surface and within the potential field of the adsorbent, which is assumed to be inert so that $\mu_1 = \mu_1^*$. Then an additional work term ΠdA is introduced, where Π is the two-dimensional spreading pressure and A is the specific surface area of the solid. The equivalent of Eq. 33 in adsorption thermodynamics is:

$$\frac{\Pi A}{RT} = \int_0^{P_i^0}\frac{(1/\sigma_i^0)}{P_i^0}\,dP_i^0 \tag{36}$$

In adsorption thermodynamics, standard states of the adsorbates are at equal Π; in solution thermodynamics, the standard states are fixed by the chemical potential μ_1 of the adsorbent. Although the physics and terminology are different, the adsorption and solution models are equivalent thermodynamically.

The application of IAS theory to multicomponent adsorption has been studied extensively; IAS is accurate at low surface coverage but systematic errors are sometimes observed at high coverage (Valenzuela and Myers, 1984). The conclusion is the same as that obtained for multicomponent VLE data: the more ideal the adsorbate-adsorbate interactions, the more accurate

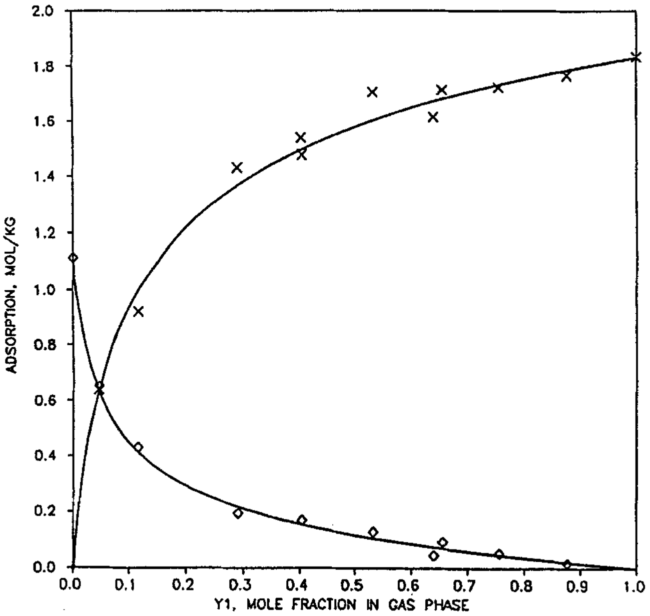

Figure 4. Adsorption of mixtures of propylene (X) and ethylene (◇) on carbon molecular sieve at 323.15 K and 13.575 kPa.

Points are data of Nakahara, Hirata, and Mori (1982) and solid lines are predicted by IAS theory using the single-gas isotherms in Figure 5.

the results. One of the examples for which IAS is in quantitative agreement with experiment is shown on Figure 4; the predictions are based on the single-gas adsorption isotherms of propylene and ethylene on Figure 5.

If mixed-gas adsorption data are found to be nonideal, they can be handled in terms of a ψ^e function similar to Eq. 21 for VLE. In the case of adsorption, g^e can be any of the conventional equations (Wilson, UNIQUAC, etc.) provided the variation in the activity of the adsorbent (a_1) is taken into account. However, the s function has no physical meaning because the adsorbent does not exist at infinite dilution. Observing that ($\Pi A/RT$) in adsorption thermodynamics is equivalent to ($-\ln a_1$) in solution thermodynamics, a suitable ψ^e function for adsorption is:

$$\psi^e = g^e(1 - e^{C(\Pi A/RT)}) \tag{37}$$

where C is a constant for a particular adsorbent. It follows from Eq. 13 that the "excess solvent" (excess reciprocal amount adsorbed) is:

$$\sigma^e = -C\left(\frac{g^e}{RT}\right)e^{C(\Pi A/RT)} \tag{38}$$

Equations 37 and 38 are proposed for correlating mixed-gas adsorption data that are nonideal. g^e can be represented, for example, by two parameter models (Wilson, UNIQUAC, etc.). These models have been used previously to describe adsorbed-phase activities in terms of conventional equations for vapor-liquid equilibrium, but the effect of spreading pressure (or the activity of the adsorbent) was neglected. According to Eq. 37, even relatively small changes in spreading pressure have a strong influence on adsorbate activities.

Ideal-adsorbed-solution theory is a special case of ideal isoactive-solvent theory in which the "solvent" is the solid adsorbent and the "solutes" are adsorbed gases.

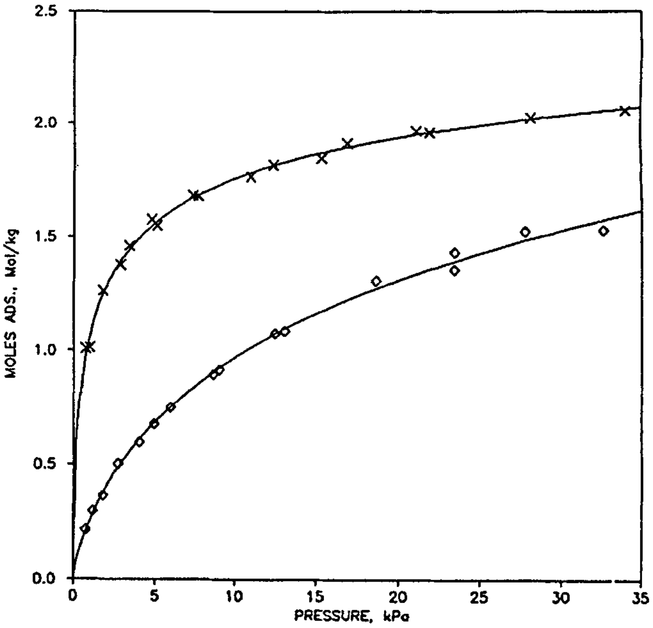

Figure 5. Single-gas adsorption isotherms of propylene (X) and ethylene (◇) on carbon molecular sieve MSC-5A at 323.15 K.

Solutions of Strong Electrolytes

The monographs of Horvath (1985) and Zemaitis, Clark, Rafal and Scrivner (1986) review the thermodynamics of electrolyte solutions. Consider a solution of two nonvolatile strong electrolytes (nos. 2 and 3) dissolved in a solvent (no. 1). Equilibrium data on single solutes can be used to predict equilibria for mixed solutes, for which experimental data are relatively scarce. For nonvolatile solutes there is one equilibrium equation:

$$P\Phi_1 = P_1^s a_1 \tag{39}$$

For bubble-point pressure calculations, temperature and composition (molalities m_i of each solute) are given and a_1 is unknown. Assume that the solute-solute interactions are ideal so that $\psi^e = \sigma^e = 0$. From Eqs. A13 and A23:

$$\sigma = z_2\sigma_2^0 + z_3\sigma_3^0 \tag{40}$$

z_i is mole fraction of ith solute: $z_i = m_i/(\Sigma m_i) = m_i/m$. Since σ is moles of solvent per mole of solute, its reciprocal is proportional to the molality of the solution:

$$(1/\sigma) = M_1 m \tag{41}$$

where M_1 is the molecular weight of the solvent in kg/mol. At the single-solute standard state:

$$(1/\sigma_i^0) = M_1 m_i^0 \tag{42}$$

The standard state molalities m_i^0 are functions of a_1; the relation between molality and solvent activity is expressed in terms of the osmotic coefficient (ϕ) of the solvent:

$$\ln a_1 = -\phi M_1(\Sigma_i m_i) \tag{43}$$

where m_i is the molality of the ith ion in mol/kg and summation is over all ions present, assuming total dissociation for strong electrolytes. Since σ and z_i are specified, a_1 is the only unknown in Eq. 40. Its solution is obtained numerically, for example, by Newton's method in terms of the functions $m_i^0 = m_i^0(a_1)$.

Equation 40 can be written is terms of molalities:

$$\frac{m_2}{m_2^0} + \frac{m_3}{m_3^0} = 1 \quad (\text{constant } a_1) \tag{44}$$

This equation was first proposed on a empirical basis by Zdanovskii (1936) and is a very good approximation for mixtures of strong electrolytes with a common ion such as NaCl—KCl—H_2O. Equation 44 can be applied to the prediction of solvent activity (a_1) given m_1 and m_2 for the mixed solutes; the standard-state molalities m_1^0 and m_2^0 are implicit functions of a_1.

Zdanovskii's rule is effective for predicting activities of solutions of strong electrolytes with a common ion. For binary solutes without a common ion, cross-ion effects must be taken into account:

$$\sum_{i=2}^{5} \left(\frac{m_i}{m_i^0}\right) = 1 \tag{45}$$

where the summation is over the four electrolytes resulting from dissolution of two solutes without a common ion. For example, consider a solution prepared from 1 mole of CaS_2O_3 + 2 moles of NaCl. The ion concentrations are $\{Ca^{2+}, Na^+, S_2O_3^{2-}, Cl^-\} = \{1, 2, 1, 2\}$. The same solution can be prepared from 1 mole of $CaCl_2$ plus 1 mole of $Na_2S_2O_3$. The concentrations of the four electrolytes $\{CaS_2O_3, NaCl, CaCl_2, Na_2S_2O_3\}$ depend on ionic concentrations, not the starting mixture. Since these compounds do not actually exist in solution, their concentrations must be defined; let the concentration m_i of any compound be proportional to the product of its cation and anion concentrations ($m^+ \times m^-$):

$$m_i = \left(\frac{m^+z^+}{\sum_+ m^+z^+}\right)\left(\frac{m^-}{\nu_i^-}\right) = \left(\frac{m^-z^-}{\sum_- m^-z^-}\right)\left(\frac{m^+}{\nu_i^+}\right) \tag{46}$$

where m^+, z^+ and ν_i^+ are the actual molality of the cation in solution, its charge, and the number of cations in the compound, respectively. Similarly m^-, z^- and ν_i^- are the actual molality of the anion in solution, its charge (absolute value), and the number of anions in the compound, respectively. The other factors in Eq. 46 are required to preserve the electroneutrality of the compound: $(\nu_i^+z^+) = (\nu_i^-z^-)$, and the electroneutrality of the solution: $\Sigma_+(m^+z^+) = \Sigma_-(m^-z^-)$. Equation 46 also satisfies the mass balance requirement that $m^+ = \Sigma_i m_i \nu_i^+$ for each cation and $m^- = \Sigma_i m_i \nu_i^-$ for each anion. For the example given above, Eq. 46 yields the molalities $\{CaS_2O_3, NaCl, CaCl_2, Na_2S_2O_3\} = \{0.5, 1.0, 0.5, 0.5\}$.

For a solution of two strong electrolytes without a common ion, experimental single-solute data on the activity or osmotic coefficient of the solvent as a function of the molality of the solute m_i^0 are needed for four electrolytes, the original two plus the two cross-ion pairs. In a bubble-point pressure problem, the first step is to calculate the four molalities m_i by Eq. 46 using the known ionic concentrations. Then Eq. 45 is solved iteratively for a_1, yielding the vapor pressure and the osmotic coefficient of the solvent. The practical application of Eq. 45 is to solve for the osmotic coefficient or activity of the solvent as a function of the composition of the solution. Composition may be expressed as a function of the molalities of A^+B^- and C^+D^-, or the molalities A^+D^- and C^+B^-, or in terms of the four ionic molalities. For the purpose of comparing ideal ISAC theory with experimental isopiestic (constant vapor pressure of solvent) data, the procedure is reversed: given the solvent activity a_1, find the binary solute concentrations. Let the concentration be expressed in terms of solute nos. 2 and 3 as solvent-free mole fraction:

$$z_2^* = \frac{m_2^*}{m_2^* + m_3^*} \tag{47}$$

where $m_4^* = m_5^* = 0$. The superscript * indicates the choice of solute nos. 2 and 3 to express initial concentration. Combining the last three equations and defining $r = m_3^*/m_2^*$, the concentration under isopiestic conditions is given by:

$$m_2^* = \frac{\nu_2^+z_2^+ + \nu_3^+z_3^+r}{\dfrac{\nu_2^+z_2^+}{m_2^0} + \dfrac{\nu_3^+z_3^+r^2}{m_3^0} + \dfrac{\nu_2^+\nu_3^-z_4^+r}{\nu_4^-m_4^0} + \dfrac{\nu_2^-\nu_3^+z_5^+r}{\nu_5^-m_5^0}} \tag{48}$$

where ν_i^+ and z_i^+ refer to the number of cations and their charge

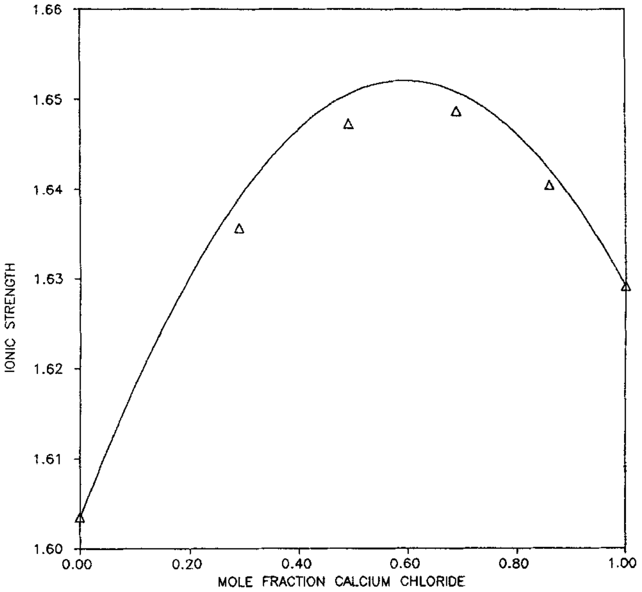

Figure 6. Ionic strength of aqueous solutions of $Mg(NO_3)_2$ + $CaCl_2$ as a function of mole fraction of $CaCl_2$ at 298.15 K and at constant activity of water.

Solid line is prediction of ideal ISAC theory and triangles are experimental isopiestic data of Platford (1971).

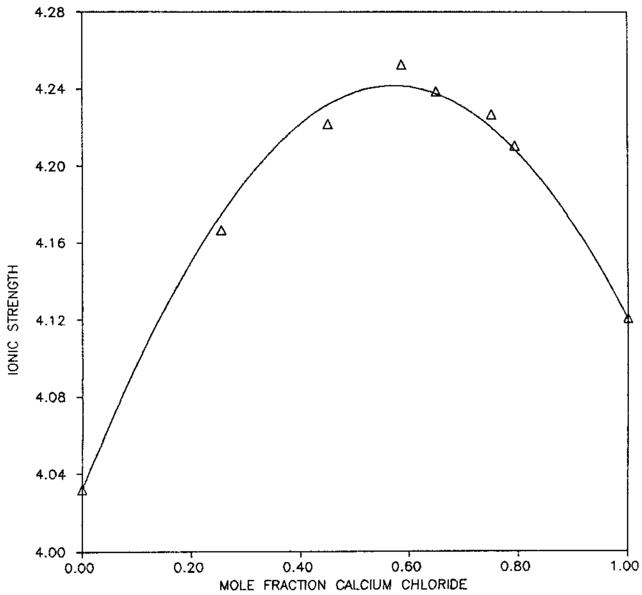

Figure 7. Ionic strength of aqueous solutions of $Mg(NO_3)_2$ + $CaCl_2$ as a function of mole fraction of $CaCl_2$ at 298.15 K and at constant activity of water.
Solid line is prediction of ideal ISAC theory and triangles are experimental isopiestic data of Platford (1971).

in the *i*th electrolyte, and ν_i^- and z_i^- are the number of anions and their charge (absolute value) in the *i*th electrolyte. Component nos. 4 and 5 refer to the cross-ion electrolytes. Since single-solute molalities (m_i^0) are functions of solvent activity (a_1), Eq. 48 gives the molality of the initial solution ($m_4^* = m_5^* = 0$) in terms of its temperature, solvent activity, and solvent-free mole fraction of electrolyte z_2^*. The molality of the initial solution $\{m_2^*, m_3^*\}$ determines the molality of individual ions and the ionic strength of the solution:

$$I = \frac{1}{2} \sum_i (m_i z_i^2) \tag{49}$$

Equations 48 and 49 give the ionic strength I of mixed-solutes nos. 2 and 3 as a function of their mole fraction z_2^* at constant a_1. A result is shown on Figures 6 and 7 for aqueous solutions of magnesium nitrate and calcium chloride. It may seem peculiar for the *concentration,* not the activity, to be the dependent variable, but this is the way to compare ISAC theory with experimental isopiestic data (constant solvent activity). The ionic strength is given as a function of the mole fraction of calcium chloride (solvent-free basis). The solid line obtained from Eqs. 48 and 49 is based on experimental single-solute data $m_i^0(a_1)$ for the electrolytes $Mg(NO_3)_2$ and $CaCl_2$, and their cross-ion pairs $MgCl_2$ and $Ca(NO_3)_2$. No mixed-solute data were used to make this prediction. Similar results were obtained with other systems of binary solutes with and without common ions. Figures 6 and 7 provide striking confirmation of ISAC predictive capacity because the experimental maxima were predicted from single-solute data.

Conclusions

1. Ideal ISAC theory is a general method of predicting phase equilibria in multicomponent systems when the solvent and the solutes exist in different pure states.

2. Accuracy of ISAC predictions improves with the ideality of solute-solute interactions. In the limit of identical solutes, ideal ISAC theory is exact.

3. The ISAC convention can be applied to phase equilibria of a solute in a mixed solvent. In this case, activities in the solvent-solvent binary, as well as the activity of the solute in each pure solvent, must be known. The accuracy of predictions are comparable to those from the UNIQUAC equation for predicting activities in ternary liquid mixtures from parameters for the constituent binaries.

Acknowledgment

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Notation

A = specific surface area, m^2/kg
a = activity
C = constant, Eq. 37
E_j = energy of *j*th quantum state
$\mathcal{F}$ = function of x
f = fugacity
G = Gibbs free energy
g = value of G per mole of solute, Eq. A5; dimensionless g^e, Eq. 22
h = enthalpy per mole of solute
I = ionic strength, Eq. 49
K = $\ln \gamma_1^\infty$; constant, Eq. 1
k = Boltzmann constant
M = molecular weight, kg/mol
m = molality, mol/kg; mass, kg, Eq. 30
N = number of components present; number of molecules, Eq. B1
n = amount, mol
P = pressure, Pa
P^s = vapor pressure at saturation, Pa
Q = canonical partition function, Eq. B1
R = Gas constant
r = ratio, m_3^*/m_2^*
S = entropy, J/K
s = value of S per mole of solute, J/(mol · K), Eq. A16; function, Eq. 23
s' = partial derivative of s, Eq. 26
T = absolute temperature
V = volume
v = value of V per mole of solute
w = $w_{22} + w_{33} - 2w_{23}$, exchange energy, J
X = any extensive variable, Eq. A3
x = mole fraction in liquid phase; value of X per mole of solute, Eq. A3
y = mole fraction in vapor phase
Z = partition function, Eq. B5
z = mole fraction of solute on solvent-free basis, Eq. 45; ionic charge, Eq. 46

Greek letters

γ = activity coefficient, standard convention
γ' = activity coefficient, ISAC convention
Δ = partition function, Eq. B3
μ = chemical potential, J/mol
ν = number of ions in compound
Π = spreading pressure, N/m, Eq. 36
σ = mole of solvent per mole of solute
Φ = vapor-phase fugacity coefficient, Eq. 28
ϕ = osmotic coefficient, Eq. 43
Ψ = isoactive-solvent free energy, J
ψ = value of Ψ per mole of solute, J/mol

Superscript

$*$ = standard state of pure substance or state of ∞ dilution, Eqs. 7, A8, A22; initial solution, Eq. 47

$+$ = cation
$-$ = anion
0 = standard state of single-solute solution
∞ = value at state of infinite dilution
e = excess function, Eqs. A13–A17
id = ideal change upon mixing
m = change upon mixing

Subscript

1 = solvent
i = ith solute
ij = $i-j$ binary mixture

Appendix A: Derivation of Isoactive-Solvent Theory

Consider a mixture of N components. Let the solvent be component no. 1, and let the solutes be numbered 2, 3, . . . , N. Starting with the definitions of isoactive solvent potential (Ψ), solute mole fractions (z_i), and specific solvent (σ) in Eqs. 4–6, it follows that:

$$d\Psi = -SdT + VdP - n_1 d\mu_1 + \sum_{i=2}^{N} \mu_i dn_i \qquad \text{(A1)}$$

Phase equilibrium corresponds to minimum Ψ at constant T, P and μ_1. These conditions are realized, for example, in isopiestic measurements of the concentrations of solutions of mixed nonvolatile salts in equilibrium via the vapor phase with the same solvent. For mixed solutes, the ISAC standard state of each solute is its equilibrium single-salt solution.

It follows from Eqs. 4 and A1 that:

$$-SdT + VdP - n_1 d\mu_1 = \sum_{i=2}^{N} n_i d\mu_i \qquad \text{(A2)}$$

which is the Gibbs equation (Prausnitz, Lichtenthaler, and Azevedo, 1986). Extensive variables (X) such as S, V, and n_i are transformed into molar intensive variables (x) as follows:

$$x = X/n \qquad \text{(A3)}$$

where n is the total amount of solute in the multicomponent mixture:

$$n = \sum_{i=2}^{N} n_i \qquad \text{(A4)}$$

x is amount of X per mole of solute: $\psi = \Psi/n$, $s = S/n$, $v = V/n$, etc. Special nomenclature (z_i, σ) was introduced in Eqs. 5 and 6 for the case when X is the amount of one of the components. With these definitions, Eq. 4 becomes:

$$\psi = g - \sigma\mu_1 = \sum_{i=2}^{N} z_i \mu_i \qquad \text{(A5)}$$

and Eq. A2 is written:

$$-sdT + vdP - \sigma d\mu_1 = \sum_{i=2}^{N} z_i d\mu_i \qquad \text{(A6)}$$

Thermodynamic variables are now defined on a solvent-free basis: the quantities s, v and σ are molar extensive variables *per mole of solute*. For a single-solute solution, Eq. A6 reduces to:

$$-s_i^0 dT + v_i^0 dP - \sigma_i^0 d\mu_1 = d\mu_i^0 \qquad \text{(A7)}$$

The standard state identified with the superscript 0 refers to the single-solute (binary) mixture at T, P and μ_1 of the multicomponent (ternary or higher) solution. s_i^0 is the entropy per mole of solute, v_i^0 is the volume per mole of solute, and σ_i^0 is "specific solvent" in the $1 - i$ binary solution.

The dT and dP terms in Eqs. A6 and A7 are dropped in the following derivation. Therefore, the results are limited to isothermal conditions. At constant T and μ_1, the pressure varies but the vdP term is negligible compared to the other terms for a condensed (liquid or solid) phase. Neglect of the effect of pressure is acceptable as long as the mixture is sufficiently far removed from its gas-liquid critical point.

For the solvent:

$$\mu_1 = \mu_1^* + RT \ln a_1 \qquad \text{(A8)}$$

where μ_1^* refers to the standard state of pure solvent, which is a function of T. For solutes:

$$\mu_i = \mu_i^0 + RT \ln\left(\frac{f_i}{f_i^0}\right) \quad (i = 2, 3, \ldots, N) \qquad \text{(A9)}$$

The standard state (μ_i^0, f_i^0) is a function of T and a_1. Solute fugacity is defined by:

$$f_i = f_i^0 \gamma_i' z_i \qquad \text{(A10)}$$

The total differential of Eq. A9 at constant temperature is:

$$d\mu_i = d\mu_i^0 + RTd\ln(\gamma_i' z_i) \qquad \text{(A11)}$$

Substitution of Eqs. A7 and A11 into Eq. A6 gives:

$$-\left[\sigma - \sum_{i=2}^{N} z_i \sigma_i^0\right] d\mu_1 = RT \sum_{i=2}^{N} z_i d\ln(\gamma_i' z_i) \qquad \text{(A12)}$$

The quantity in brackets in Eq. A12 is called "excess solvent":

$$\sigma^e = \sigma - \sum_{i=2}^{N} z_i \sigma_i^0 \qquad \text{(A13)}$$

Other important excess functions are:

$$h^e = h - \sum_{i=2}^{N} z_i h_i^0 = h^m - h^{id} \qquad \text{(A14)}$$

$$\psi^e = \psi - \sum_{i=2}^{N} z_i \psi_i^0 - RT \sum_{i=2}^{N} z_i \ln z_i = \psi^m - \psi^{id} \qquad \text{(A15)}$$

$$s^e = s - \sum_{i=2}^{N} z_i s_i^0 + R \sum_{i=2}^{N} z_i \ln z_i = s^m - s^{id} \qquad \text{(A16)}$$

Substitution of Eqs. A5, A9 and A10 into Eq. A15 yields:

$$\frac{\psi^e}{RT} = \sum_{i=2}^{N} z_i \ln \gamma_i' \qquad \text{(A17)}$$

Taking the total differential of Eq. A17 at constant T and using Eqs. A9 and A12, it follows that:

$$d\left(\frac{\psi^e}{RT}\right) = -\sigma^e d \ln a_1 + \sum_{i-2}^{N} \ln \gamma_i' dz_i \tag{A18}$$

ISAC activity coefficients are partial molar variables of the ψ^e function:

$$\ln \gamma_i' = \left[\frac{\partial(n\psi^e/RT)}{\partial n_i}\right]_{T,P,a_1,n_j} \quad (i = 2, 3, \ldots, N) \tag{A19}$$

Comparison of the differential of Eq. A17 with Eq. A18 shows that solute activity coefficients at constant T, P and a_1 obey the equation:

$$\sum_{i-2}^{N} z_i d \ln \gamma_i' = 0 \tag{A20}$$

Therefore, ISAC expressions for activity coefficients of solutes obey an equation similar to the Gibbs-Duhem equation of conventional solution thermodynamics: $(\Sigma x_i d \ln \gamma_i = 0)$. For a ternary mixture, there are four degrees of freedom, so holding T, P and a_1 constant while varying z_2 and $z_3 = (1 - z_2)$ does not violate the phase rule.

For phase equilibrium calculations, one needs the activity relative to pure solute (or its state of infinite dilution in the solvent): $a_i = (f_i/f_i^*)$. The activity in the single-solute reference state is assumed to be known: $a_i^0 = (f_i^0/f_i^*)$. Therefore, for solutes:

$$\frac{f_i}{f_i^*} = \left(\frac{f_i^0}{f_i^*}\right)\left(\frac{f_i}{f_i^0}\right) \tag{A21}$$

Using Eq. A10:

$$\left(\frac{f_i}{f_i^*}\right) = a_i = a_i^0 \gamma_i' z_i \quad (i = 2, 3, \ldots, N) \tag{A22}$$

a_i^0 is solute activity in the single-solute ISAC reference state, γ_i' is the ISAC activity coefficient of the solute, and z_i is the mole fraction of ith solute on a solvent-free basis.

An ISAC ideal solution is defined by $\psi^e = 0$. It follows that:

$$\sigma^e = v^e = h^e = s^e = 0 \tag{A23}$$

$$a_i = a_i^0 z_i \tag{A24}$$

Ideality in the ISAC sense refers only to solute-solute molecular interactions. Conventional excess functions for the single solutes may be highly nonideal, depending on the nature of the solute-solvent binary interactions.

The ISAC convention generates predictions that are thermodynamically consistent because the equations are derived from Eq. A1.

In summary, the key equations for phase equilibrium calculations are Eqs. A17 and A22. The final equation is one obtained from Eq. A18 for which there is no analogy in conventional solution thermodynamics:

$$\sigma^e = -\left[\frac{\partial(\psi^e/RT)}{\partial \ln a_1}\right]_{T,P,z_i} \tag{A25}$$

where σ^e is excess specific solvent from Eq. A13.

Appendix B: Partition Function for Ψ Potential

The partition function Q of a canonical ensemble containing three components nos. 1, 2, and 3 is:

$$Q(N_1, N_2, N_3, V, T) = \sum_j e^{-E_j/kT} \tag{B1}$$

for which the corresponding thermodynamic potential is the Helmholtz free energy (F):

$$F(N_1, N_2, N_3, V, T) = -kT \ln Q(N_1, N_2, N_3, V, T) \tag{B2}$$

The partition function Δ of an isobaric, isothermal ensemble is:

$$\Delta(N_1, N_2, N_3, P, T) = \sum_V Q(N_1, N_2, N_3, V, T) e^{-PV/kT} \tag{B3}$$

The companion function of Δ is the Gibbs free energy (G):

$$G(N_1, N_2, N_3, P, T) = -kT \ln \Delta(N_1, N_2, N_3, P, T) \tag{B4}$$

The above equations are derived in standard texts (McQuarrie, 1976). Here we introduce a new semigrand partition function Z that is related to the isobaric, isothermal ensemble by:

$$Z(\mu_1, N_2, N_3, P, T) = \sum_{N_1} \Delta(N_1, N_2, N_3, P, T) e^{\mu_1 N_1/kT} \tag{B5}$$

Since the Ψ potential defined by Eq. 4 is a Legendre transformation of the Gibbs free energy in which the independent variable variable N_1 is replaced by μ_1, it follows that:

$$\Psi(\mu_1, N_2, N_3, P, T) = -kT \ln Z(\mu_1, N_2, N_3, P, T) \tag{B6}$$

Consider the derivation of Raoult's law by lattice statistics (Hill, 1960). If the exchange energy $w = w_{22} + w_{33} - 2w_{23} = 0$, the canonical partition function for an ideal, binary mixture of components 2 and 3 is:

$$Q(N_2, N_3, T) = (q_2 e^{-cw_{22}/2kT})^{N_2} (q_3 e^{-cw_{33}/2kT})^{N_3} \sum \frac{(N_2 + N_3)!}{N_2! N_3!} \tag{B7}$$

The same Raoult's law expression can be written for Z, for two solutes *at constant chemical potential of the solvent* (μ_1). Because of the presence of the solvent, however, potential energies of solute-solute interactions must be replaced by *potentials of mean force*. This approach is called McMillan-Mayer (MM) solution theory, which asserts that there is a rigorous one-to-one correspondence between the equations of imperfect gas theory and dilute solutions of nonelectrolytes (McQuarrie, 1976). The pressure of the gas maps into the osmotic pressure of the solution. MM solution theory is usually considered in the context of a single solute in a solvent.

In our work, MM theory is extended to mixtures of solutes. If the exchange energy derived from potentials of mean force acting between pairs of solute molecules is zero ($w = 0$), the solution is ideal and Raoult's law can be written for the solutes under conditions of constant chemical potential of the solvent. Raoult's law is exact in the limit when the solutes are identical.

Applications of Raoult's law, as extended to systems in different pure states, goes beyond predicting the behavior of multisolute mixtures from single-solute information. Even when a satisfactory theory of mixtures is available, the concept of nonideality is useful for the quantitative description of the variation of activity with composition.

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