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Thermodynamic Modeling of the Solubility of Salts in Mixed Aqueous–Organic Solvents

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A semiempirical thermodynamic model is proposed for prediction of the solubility of salts in mixed aqueous–organic solvents. This model requires only standard thermodynamic properties for the pure components and for the solutes at infinite dilution in each solvent. The new method is illustrated with predictions of solubility for several salts in mixtures of water with methanol and ethanol. The method developed here could be of particular interest for process calculations and design of low-energy extractive crystallization methods for production of salts from aqueous solutions.

(1) Introduction

The solubility of solutes in mixed solvents is of great practical importance. Mixtures of solvents are routinely used to manipulate physical properties, such as the density, viscosity, volatility, etc., or certain chemical properties, such as stability, flammability, or ability to dissolve specific compounds. Mixed solvents are often encountered in distillation or extraction operations.

Recently developed extractive crystallization processes, for example, provide a method for removing a salt from aqueous solution with much less energy than that required by conventional multiple-effect evaporators (Weingaertner et al., 1991). In commonly used solvent systems for liquid–liquid extraction, such as tri-*n*-butyl phosphate/water or 3-methyl-1-butanol/water, organic phases often contain appreciable amounts of water, with mole fractions of up to 0.5 in some cases (Marcus, 1990). In all these applications the presence of a salt in the liquid phase may have a substantial influence on the phase behavior of the system. Reliable models for prediction of the thermodynamic properties of mixed solvent/salt systems are therefore highly needed (Sander et al., 1986; Marcus, 1990; Zerres and Prausnitz, 1994).

Sander et al. (1986) proposed a semiempirical formalism to calculate the effect of salts on vapor–liquid equilibria. Their model combines a term of the Debye–Hückel type with an “artificial” composition-independent dielectric constant (about 50 at 25 °C for alcohol/water mixtures) and a modified UNIQUAC term with concentration-dependent parameters. Although these authors were successful in calculating vapor–liquid equilibria with their method, they pointed out that much work remains to be done before a reliable description of liquid phase nonideality is achieved. The authors emphasized the need for a satisfactory description of the dependence of the standard chemical potential for the ions on solvent composition. They also indicated that, until progress is made in the solution of this problem, it will not be possible to describe quantitatively phenomena such as salt solubilities or liquid–liquid equilibria in salt-containing mixtures.

Marcus (1990) showed that the solubility of a solute in a binary mixed solvent depends primarily on the

preferential solvation of the solute by the individual components of the solvent mixture. The preferential solvation of solutes was analyzed in terms of the quasi-lattice quasi-chemical (QLQC) method and the inverse Kirkwood–Buff integral method. The author stated that the QLQC method could, in principle, permit approximate predictions of solubility in binary solvent mixtures, provided the required independent data are available. These data include (i) the standard molar Gibbs energies for transfer of the solute from its standard state into the standard state in each solvent, (ii) the Gibbs energy of mixing of the solvents for the equimolar mixture, and (iii) a lattice adjustable parameter. In practice, however, the approximations inherent in the QLQC model can hamper the calculation of solubility from completely independent data.

The aim of the present work is to develop a new predictive method for engineering calculations of the solubility of salts in mixed solvents from independent thermodynamic data. In contrast to currently available methods for representation of phase equilibria in mixed solvents containing electrolytes (Chen et al., 1980; Mock et al., 1986; Macedo et al., 1990; Marcus, 1990; Zerres and Prausnitz, 1994), our proposed approach requires only standard thermodynamic properties for the pure solute and for the same solute at infinite dilution in each of the solvents. The nonideality of a salt-free solvent mixture is described by the NRTL equation, with parameters obtained from the activity coefficients of the cosolvents at infinite dilution. The thermodynamic framework presented here is based on a generalization of our earlier work, which has been applied to calculate the solubility of salts in binary and multicomponent aqueous solutions (Kolker and de Pablo, 1995a,b).

(2) Solvent Composition Dependence of the Standard Chemical Potential of a Solute in Solution

To calculate the activity coefficient of a solute (component 2) in a mixed solvent, we apply a method originally developed for binary aqueous solutions (Kolker and de Pablo, 1995a). For convenience, Appendix A gives a condensed version of the necessary equations.

To extend this method to a solvent mixture, we begin by examining the dependence of the activity coefficient

of a solute at infinite dilution, $\ln \gamma_2^\infty$, on solvent composition. This quantity represents a difference of the chemical potentials of component 2 in the standard state in the solvent mixture and this component at the standard state of a "pure supercooled liquid state" (Kolker and de Pablo, 1995a), i.e.

$$\ln \gamma_2^\infty = (\mu_2^* - \mu_2^\circ)/RT \quad (1)$$

where μ_2^* is the standard chemical potential of component 2 at the reference state of a "hypothetical ideal solution of unit concentration" (Zerres and Prausnitz, 1994) and μ_2° is the standard chemical potential of pure supercooled component 2. Clearly, the value of μ_2^* depends on the composition of the solvent mixture. We now proceed to develop an expression for such a composition dependence.

Let component 1 be a first solvent (water), component 2 be a solute (e.g., a salt), and component 3 be a second solvent (organic cosolvent). We express the solvent composition by the solute-free mole fraction, z_3 , of the organic cosolvent. The mole fraction of water (in the solute-free mixture) is then $z_1 = 1 - z_3$.

We express the standard chemical potential of the solute in a mixed solvent, μ_2^* , as the sum of two contributions which we attribute to each of the two solvents in the mixture

$$\mu_2^* = z_1 \mu_{21}^* + z_3 \mu_{23}^* \quad (2)$$

In eq 2, μ_{21}^* is the standard chemical potential of solute 2 in solvent 1 of the mixture and μ_{23}^* is the standard chemical potential of a solute 2 in solvent 3 of the mixture (both at the reference state of a hypothetical ideal solution of unit concentration). In writing eq 2, we assume that the solvent mixture is a hypothetical fluid composed of two distinct regions, one containing molecules of 1 and another one containing molecules of 3. These two regions, however, interact with each other by bringing the chemical potentials of components 1 and 3 to their values in the solute-free mixture (as opposed to their values as pure solvents). This is just a useful conceptual aid for development of a suitable expression for the standard chemical potential and bears little resemblance to the actual solvent mixture.

We assume that chemical potentials μ_{21}^* and μ_{23}^* depend on the chemical potentials of the solvents μ_1 and μ_3 , respectively; i.e., $\mu_{21}^* = \mu_{21}^*(\mu_1)$ and $\mu_{23}^* = \mu_{23}^*(\mu_3)$. Chemical potentials μ_1 and μ_3 are functions of the pressure P , the temperature T , and the composition of the solvent, z_3 ; i.e., $\mu_1 = \mu_1(P, T, z_3)$ and $\mu_3 = \mu_3(P, T, z_3)$. We therefore write

$$\begin{aligned} \left(\frac{\partial \mu_{21}^*}{\partial z_3} \right)_{P,T} &= \frac{d\mu_{21}^*}{d\mu_1} \left(\frac{\partial \mu_1}{\partial z_3} \right)_{P,T} = RT \frac{d\mu_{21}^*}{d\mu_1} \left(\frac{\partial \ln a_1}{\partial z_3} \right)_{P,T} \\ \left(\frac{\partial \mu_{23}^*}{\partial z_3} \right)_{P,T} &= \frac{d\mu_{23}^*}{d\mu_3} \left(\frac{\partial \mu_3}{\partial z_3} \right)_{P,T} = RT \frac{d\mu_{23}^*}{d\mu_3} \left(\frac{\partial \ln a_3}{\partial z_3} \right)_{P,T} \end{aligned} \quad (3)$$

where a_1 and a_3 are the activities of solvents 1 and 3 in their solute-free mixture. Similarly

$$\left(\frac{\partial \mu_{21}^*}{\partial P} \right)_{T,z_3} = \frac{d\mu_{21}^*}{d\mu_1} \left(\frac{\partial \mu_1}{\partial P} \right)_{T,z_3} \text{ and}$$

$$\left(\frac{\partial \mu_{23}^*}{\partial P} \right)_{T,z_3} = \frac{d\mu_{23}^*}{d\mu_3} \left(\frac{\partial \mu_3}{\partial P} \right)_{T,z_3} \quad (4)$$

The derivatives $(\partial \mu_1 / \partial P)_{T,z_3}$ and $(\partial \mu_3 / \partial P)_{T,z_3}$ are the partial molar volumes of the solvents in their solute-free

mixture, i.e.

$$\left(\frac{\partial \mu_1}{\partial P} \right)_{T,z_3} = \bar{v}_1$$

$$\left(\frac{\partial \mu_3}{\partial P} \right)_{T,z_3} = \bar{v}_3$$

The derivatives $(\partial \mu_{21}^* / \partial P)_{T,z_3}$ and $(\partial \mu_{23}^* / \partial P)_{T,z_3}$ are the partial molar volumes of the solute at the standard state in solvents 1 and 3 in the mixture, respectively

$$\left(\frac{\partial \mu_{21}^*}{\partial P} \right)_{T,z_3} = \bar{v}_{21}^*$$

$$\left(\frac{\partial \mu_{23}^*}{\partial P} \right)_{T,z_3} = \bar{v}_{23}^*$$

It follows from eqs 4 that $d\mu_{21}^*/d\mu_1 = \bar{v}_{21}^*/\bar{v}_1$ and $d\mu_{23}^*/d\mu_3 = \bar{v}_{23}^*/\bar{v}_3$. Substituting these derivatives into eqs 3 and integrating by parts gives

$$\frac{1}{RT} \mu_{21}^* = \frac{1}{RT} \mu_{21,0}^* + \frac{\bar{v}_{21}^*}{\bar{v}_1} \ln a_1 - \int_0^{z_3} \ln a_1 \frac{\partial}{\partial z_3} \left(\frac{\bar{v}_{21}^*}{\bar{v}_1} \right) dz_3 \quad (5)$$

and

$$\frac{1}{RT} \mu_{23}^* = \frac{1}{RT} \mu_{23,0}^* + \frac{\bar{v}_{23}^*}{\bar{v}_3} \ln a_3 - \int_{z_3}^1 \ln a_3 \frac{\partial}{\partial z_3} \left(\frac{\bar{v}_{23}^*}{\bar{v}_3} \right) dz_3 \quad (6)$$

where $\mu_{21,0}^*$ is the standard chemical potential of the solute in pure solvent 1 (a hypothetical ideal solution of unit concentration) and $\mu_{23,0}^*$ is the standard chemical potential of the solute in pure solvent 3 (also a hypothetical ideal solution of unit concentration). Substituting eqs 5 and 6 into eq 2, we find the following solvent composition dependence for the standard chemical potential of the solute:

$$\begin{aligned} \frac{1}{RT} \mu_2^* &= \frac{1}{RT} (z_1 \mu_{21,0}^* + z_3 \mu_{23,0}^*) + z_1 \frac{\bar{v}_{21}^*}{\bar{v}_1} \ln a_1 + \\ &\quad z_3 \frac{\bar{v}_{23}^*}{\bar{v}_3} \ln a_3 - z_1 \int_0^{z_3} \ln a_1 \frac{\partial}{\partial z_3} \left(\frac{\bar{v}_{21}^*}{\bar{v}_1} \right) dz_3 + \\ &\quad z_3 \int_{z_3}^1 \ln a_3 \frac{\partial}{\partial z_3} \left(\frac{\bar{v}_{23}^*}{\bar{v}_3} \right) dz_3 \end{aligned} \quad (7)$$

Substituting eq 7 into eq 1 gives a solvent composition dependence for $\ln \gamma_2^\infty$.

As discussed by Kolker and de Pablo (1995a), the right-hand side of eq 1 is regarded as the Gibbs free energy required to bring component 2 from a condensed pure phase (in the standard state) to an infinitely dilute solution. Following the notation used in that work, we denote such a quantity by $-g_{22}$, i.e.

$$\frac{1}{RT} (\mu^\circ - \mu_2^*) = g_{22} \quad (8)$$

Our subsequent calculations of activity coefficients require knowledge of g_{22} to determine the parameters appearing in the relevant equations. Substituting eq 7 into eq 8, we have

$$g_{22} = z_1 g_{22}^{(1)} + z_3 g_{22}^{(3)} - z_1 \frac{\bar{v}_{21}^*}{\bar{v}_1} \ln a_1 - z_3 \frac{\bar{v}_{23}^*}{\bar{v}_3} \ln a_3 + \\ z_1 \int_0^{z_3} \ln a_1 \frac{\partial}{\partial z_3} \left(\frac{\bar{v}_{21}^*}{\bar{v}_1} \right) dz_3 - z_3 \int_{z_3}^1 \ln a_3 \frac{\partial}{\partial z_3} \left(\frac{\bar{v}_{23}^*}{\bar{v}_3} \right) dz_3 \quad (9)$$

where $g_{22}^{(1)}$ and $g_{22}^{(3)}$ are the values of g_{22} for binary solutions of solute 2 in solvent 1 and in solvent 3, respectively. For a binary solution (solute-single solvent), g_{22} is given by eq A4 of Appendix A.

Before eq 9 can be applied, we need to determine (i) the free energies $g_{22}^{(1)}$ and $g_{22}^{(3)}$, (ii) the activities of the solvents in their solute-free mixture, and (iii) the ratios \bar{v}_{21}^*/\bar{v}_1 and \bar{v}_{23}^*/\bar{v}_3 and their solvent composition dependence. The next sections outline procedures for calculation of these quantities.

(3) The Quantities $g_{22}^{(1)}$ and $g_{22}^{(3)}$

Thermodynamic data necessary to calculate $g_{22}^{(1)}$ for binary aqueous solutions are available in the literature. These data have already been collected by Kolker and de Pablo (1995a) and need not be given here.

For an organic phase, the Gibbs free energy of formation of inorganic salts in the solvent (component 3) at infinite dilution, ΔG_{2m}^∞ , is generally not available. (Subscript m indicates that ΔG_{2m}^∞ is in the molal scale.) This prevents calculation of $g_{22}^{(3)}$ directly from eq A4. This quantity, however, can be obtained from solubility data. Since the mole fraction at saturation is very low for most inorganic salts in organic solvents (usually, $x_2^{\text{sat}} \approx 10^{-3}-10^{-4}$), the salts' activity coefficient can be regarded as an activity coefficient at infinite dilution, $\ln \gamma_2^\infty$. In this case, the equation of solubility takes the form (Kolker and de Pablo, 1995):

$$-RT \ln \gamma_2^\infty x_2^{\text{sat}} = \Delta H_0 \left(1 - \frac{T}{T_0} \right) + \sum_k \Delta H_k \left(1 - \frac{T}{T_k} \right) - \\ \Delta c_p \left[T_0 - T \left(1 + \ln \frac{T_0}{T} \right) \right] \quad (10)$$

where ΔH_0 and T_0 are the salts' enthalpy and temperature of fusion and Δc_p is the change of heat capacity upon fusion. The second term is added to the right-hand side of eq 10 if k phase transitions occur in the crystal structure of a salt, each with enthalpy change ΔH_k at temperature T_k . An explicit expression for $\ln \gamma_2^\infty$ has the form (Kolker and de Pablo, 1995a)

$$RT \ln \gamma_2^\infty = \Delta G_{2m}^\infty(T) - \Delta G_2^\circ(T) + RT \ln \frac{1000}{M_3}$$

where $\Delta G_{2m}^\infty(T)$ is the Gibbs energy of formation of the salt at infinite dilution in the organic solvent in the molal scale at the temperature of the system, $\Delta G_2^\circ(T)$ is the Gibbs energy of formation of the pure supercooled liquid salt at the temperature of the system, and M_3 is the molecular weight of the solvent. Note that the reference state we use here is a "pure supercooled fused salt". The relation between $\Delta G_2^\circ(T)$ and the more readily available Gibbs energy of formation of a crystal salt, $\Delta G_{2,\text{cr}}^\circ(T)$, is given by

$$\Delta G_2^\circ(T) = \Delta G_{2,\text{cr}}^\circ(T) + \Delta H_0(1 - T/T_0) - \\ \Delta c_p \left[T_0 - T \left(1 + \ln \frac{T_0}{T} \right) \right] + \sum_k \Delta H_k \left(1 - \frac{T}{T_k} \right)$$

Substituting these last two relations into eq 10, we arrive at the following expression for the difference $\Delta G_{\text{org}} = \Delta G_{2,\text{cr}}^\circ(T) - \Delta G_{2m}^\infty(T)$

$$\Delta G_{\text{org}} = RT \ln \frac{x_2^{\text{sat}} 1000}{M_3} \quad (11)$$

Equation 11 permits calculation of $g_{22}^{(3)}$ based on eq A4 (see Appendix A). If the solubility of a salt in the organic solvent is not small enough (e.g., HgCl_2 in pure alcohols), then eqs 10 and 11 are not valid. In such a case, ΔG_{org} can be determined from solubility data using the equation of solubility (Kolker and de Pablo, 1995a).

(4) Activities of the Solvents in a Solute-Free Mixture

Interactions between water and a cosolvent are described by an equation of the NRTL type. The necessary parameters can be determined from the activity coefficients at infinite dilution, which are available for solutions of many organic solvents in water, $\ln \gamma_3^\infty$, and water in organic solvents, $\ln \gamma_1^\infty$ (Reid et al., 1987). We have the following two equations for τ_{13} and τ_{31}

$$\ln \gamma_1^\infty = -[\tau_{13} \exp(\tau_{13}/n_{33}^\circ) + \tau_{31}] \\ \ln \gamma_3^\infty = -[\tau_{31} \exp(\tau_{31}/n_{11}^\circ) + \tau_{13}] \quad (12)$$

where n_{11}° and n_{33}° are the numbers of nearest neighbors for pure solvents 1 and 3, respectively. Having determined parameters τ_{13} and τ_{31} , we can calculate the activity coefficients γ_1 and γ_3 and the activities of the solvents in their binary mixture, $a_1 = \gamma_1 z_1$ and $a_3 = \gamma_3 z_3$, using equations given by Kolker and de Pablo (1995a) and reproduced in Appendix A. For a solute-free solvent mixture, the Debye-Hückel term is zero and the required values of α_{12} and α_{21} are approximated by the expressions $\alpha_{12} = n_{13} + n_{33} \approx n_{33}^\circ$ and $\alpha_{21} = n_{31} + n_{11} \approx n_{11}^\circ$.

The average number of nearest neighbors in water at 25 °C is approximately $n_{11}^\circ \approx 4.6$. For methyl alcohol it is about $n_{33}^\circ \approx 2.5-3$, and for nonyl alcohol it is about 4 (Zachariasen, 1935). In our calculations we use $n_{33}^\circ \approx 3$ for both methanol and ethanol.

(5) Ratios \bar{v}_{21}^*/\bar{v}_1 and \bar{v}_{23}^*/\bar{v}_3

Differentiation of eqs 3 and 4 with respect to pressure, P , gives

$$\left(\frac{\partial \bar{v}_{21}^*}{\partial z_3} \right)_{P,T} = \frac{\bar{v}_{21}^*}{\bar{v}_1} \left(\frac{\partial \bar{v}_1}{\partial z_3} \right)_{P,T} + \left(\frac{\partial \mu_1}{\partial z_3} \right)_{P,T} \frac{\partial}{\partial P} \left(\frac{\bar{v}_{21}^*}{\bar{v}_1} \right) \quad (13)$$

and

$$\left(\frac{\partial \bar{v}_{23}^*}{\partial z_3} \right)_{P,T} = \frac{\bar{v}_{23}^*}{\bar{v}_3} \left(\frac{\partial \bar{v}_3}{\partial z_3} \right)_{P,T} + \left(\frac{\partial \mu_3}{\partial z_3} \right)_{P,T} \frac{\partial}{\partial P} \left(\frac{\bar{v}_{23}^*}{\bar{v}_3} \right) \quad (14)$$

The compressibility of liquids is small, provided they are far from a critical point. The derivatives with

respect to pressure in the right-hand sides of eqs 13 and 14 are therefore assumed to be negligible. In that case, integration of eqs 13 and 14 gives

$$\frac{\bar{v}_{21}^*}{\bar{v}_1} = \frac{\bar{v}_{21,0}^\infty}{v_1^\circ} \quad (15)$$

and

$$\frac{\bar{v}_{23}^*}{\bar{v}_3} = \frac{\bar{v}_{23,0}^\infty}{v_3^\circ} \quad (16)$$

where $\bar{v}_{21,0}^\infty$ and $\bar{v}_{23,0}^\infty$ are the solute partial molar volumes at infinite dilution in pure solvents 1 and 3, respectively, and where v_1° and v_3° are the molar volumes of pure solvents 1 and 3, respectively. In eqs 15 and 16 we used the fact that the partial molar volumes of the solute are the same in the hypothetical standard state of an ideal solution of unit concentration as they are at infinite dilution in the actual solution (Robinson and Stokes, 1965).

From eqs 15 and 16 it follows that the composition dependence of the ratios \bar{v}_{21}^*/\bar{v}_1 and \bar{v}_{23}^*/\bar{v}_3 is negligible. The derivatives of these ratios with respect to composition are therefore assumed to be zero, and the integrals in eqs 5–7 and 9 disappear.

Thus, if the partial molar compressibilities of a solute at infinite dilution and a solvent can be neglected, the solvent composition dependence for the standard chemical potential of the solute is reduced to that given by

$$\begin{aligned} \frac{1}{RT} \mu_2^* = & \frac{1}{RT} (z_1 \mu_{21,0}^* + z_3 \mu_{23,0}^*) + z_1 \frac{\bar{v}_{21,0}^\infty}{v_1^\circ} \ln a_1 + \\ & z_3 \frac{\bar{v}_{23,0}^\infty}{v_3^\circ} \ln a_3 \end{aligned} \quad (17)$$

Equation 9 for g_{22} is reduced to

$$g_{22} = z_1 g_{22}^{(1)} + z_3 g_{22}^{(3)} - z_1 \frac{\bar{v}_{21,0}^\infty}{v_1^\circ} \ln a_1 - z_3 \frac{\bar{v}_{23,0}^\infty}{v_3^\circ} \ln a_3 \quad (18)$$

To calculate the ratio $\bar{v}_{21,0}^\infty/v_1^\circ$, we write an expression for the mass density of a binary solution of the solute in pure solvent 1

$$\rho_{21} = \frac{x_1 M_1 + x_2 M_2}{x_1 \bar{v}_1 + x_2 \bar{v}_2} \quad (19)$$

Differentiating ρ_{21} with respect to x_2 and taking the limit as $x_2 \rightarrow 0$, we arrive at the following expression:

$$\frac{\bar{v}_{21,0}^\infty}{v_1^\circ} = \frac{M_2}{M_1} - \frac{1}{\rho_1^\circ} \left(\frac{\partial \rho_{21}}{\partial x_2} \right)_{x_2=0} \quad (20)$$

where ρ_1° is the mass density of pure solvent 1. Similarly, for the ratio $\bar{v}_{23,0}^\infty/v_3^\circ$ we have

$$\frac{\bar{v}_{23,0}^\infty}{v_3^\circ} = \frac{M_2}{M_3} - \frac{1}{\rho_3^\circ} \left(\frac{\partial \rho_{23}}{\partial x_2} \right)_{x_2=0} \quad (21)$$

where ρ_3° is the mass density of pure solvent 3.

For aqueous solutions of salts, the density has been measured down to very small concentrations (0.1–0.5 wt %) (Weast, 1971–1972). The derivative appearing

in eq 20 has been calculated numerically using these data. For pure organic solvents, however, the density concentration dependence has been rarely measured because of the very small solubility of inorganic solutes in organic solvents. Most often, only densities at saturation are reported (Linke and Seidell, 1965). We therefore approximate the derivative $(\partial \rho_{23}/\partial x_2)_{x_2=0}$ using only the values of the density of a saturated solution, ρ_{23}^{sat} , and the density of a pure solute-free organic solvent, ρ_3° , i.e.

$$\left(\frac{\partial \rho_{23}}{\partial x_2} \right)_{x_2=0} \approx \frac{\rho_{23}^{\text{sat}} - \rho_3^\circ}{x_2^{\text{sat}}} \quad (22)$$

(6) Results of Solubility Calculations

The solubility of salts which do not form a crystal hydrate in the solid state is described by

$$\begin{aligned} RT \ln \gamma_2 x_2^{\text{sat}} = & -\Delta H_0 \left(1 - \frac{T}{T_0} \right) - \sum_k \Delta H_k \left(1 - \frac{T}{T_k} \right) + \\ & \Delta c_p \left[T_0 - T \left(1 + \ln \frac{T_0}{T} \right) \right] \end{aligned} \quad (22)$$

where x_2^{sat} is the mole fraction of the solute in the saturated solution and γ_2 is its activity coefficient.

In this work we neglect the Debye–Hückel contribution to the activity coefficients in a mixed solvent on the following grounds. According to the Debye–Hückel theory, the electrostatic contribution to the excess Gibbs energy of a solution is proportional to $\rho^{1/2}/(DT)^{3/2}$, where ρ is the density and D is the dielectric constant of the solvent (Pitzer and Simonson, 1986). The dielectric constant D is highly sensitive to solvent composition. When the Debye–Hückel term in the expression for the Gibbs free energy (and accordingly D) is differentiated with respect to solvent composition, it results in a large contribution to the solute's and the solvent's activity coefficients. This contribution predicts, for example, salting out of solvents with a higher D , i.e., salting out of water from water–organic mixtures containing salts. This is contrary to experimental evidence (Sander et al., 1986). As a compromise, Sander et al. (1986) proposed to treat the Debye–Hückel term as if it were independent of composition, with an average dielectric constant equal to 50 at 25 °C. Such an approach is not entirely satisfactory.

Pitzer (1980) and Pitzer and Simonson (1986) have shown that the major portion of symmetrically normalized activity coefficients ($\gamma_2 \rightarrow 1$ as $x_2 \rightarrow 1$), which we also use in this work, is described reasonably well by equations of the nonelectrolyte type (except for very dilute solutions). Based on the results of these authors and also on our own calculations of the solubility of salts in water (Kolker and de Pablo, 1995a), we propose here to ignore the Debye–Hückel term. Our model is applied here to relatively concentrated solutions and to mixed solvents, where electrostatic contributions can be neglected even in the dilute range because ions tend to be much more associated than in water.

Note that, in their work with mixed-solvent electrolyte systems, Mock et al. (1986) also proposed to drop the Debye–Hückel term in their NRTL model on the grounds that the excess Gibbs free energy of electrolyte systems is dominated (in the semidilute and concen-

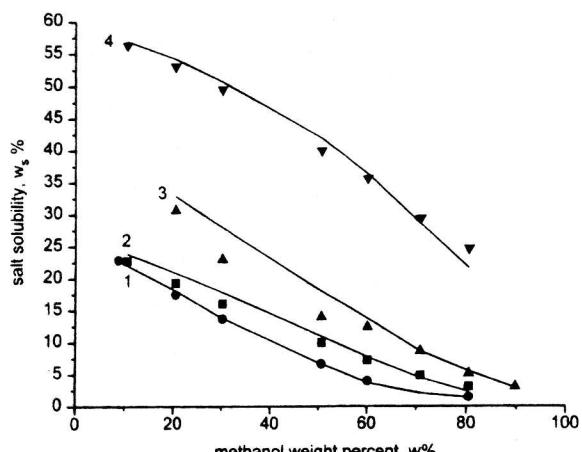


Figure 1. Solubility of salts, w_s %, in mixed water-methanol solvent at 25 °C: (1) KCl, ●; (2) NaCl, ■; (3) KBr, ▲; (4) KI, ▽. The lines show our calculated results. The symbols show experimental data (Linke and Seidell, 1965; Stephen and Stephen, 1963).

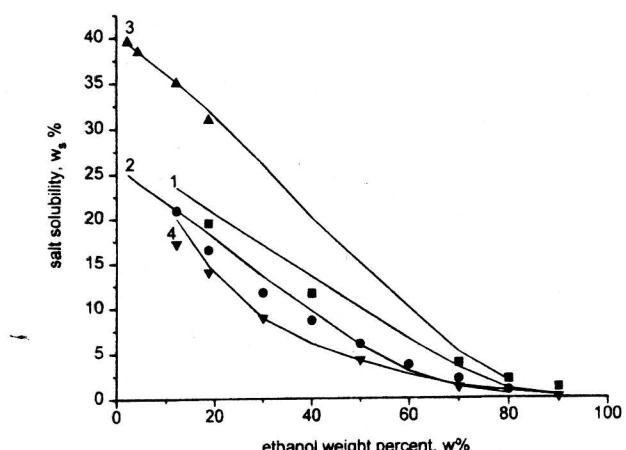


Figure 2. Solubility of salts w_s %, in mixed water-ethanol solvent at 25 °C: (1) NaCl, ■; (2) KCl, ●; (3) KBr, ▲; (4) KNO₃, ▽. The lines show our calculated results. The symbols show experimental data (Linke and Seidell, 1965; Stephen and Stephen, 1963).

trated regions) by the local interactions that govern local composition. Similar arguments were used by Zerres and Prausnitz (1994).

From a purely pragmatic point of view, including the Debye-Hückel term for mixed solvents would limit significantly the predictive ability of our model. Such a term contains an adjustable parameter (a so-called hard-core collision diameter) that was fitted by Pitzer and Simonson (1986) to experimental data for aqueous solutions (but not for organic solvents). These authors proposed to hold it constant for a wide variety of aqueous electrolytes and conditions. In mixed solvents, however, this parameter should depend on composition and such a dependence is unknown.

Figures 1 and 2 show results of our solubility calculations for a number of salts in various mixed water-alcohol mixtures. The agreement between theory and experiment is reasonable, considering that we used no adjustable mixture parameters. Furthermore, we believe that there are ways of improving the performance of the model. One of them would be to carry out a more refined calculation of activities for the solute-free solvent mixture. For simplicity, to determine parameters for the NRTL equation, we use a correlation for activity coefficients at infinite dilution taken from Reid et al. (1987). The advantage of using this correlation is that the experimental information required for a solute-free

mixed solvent is reduced drastically. However, the accuracy of the correlation varies considerably from one system to another.

(7) Conclusions

The thermodynamic framework presented in this work provides a useful procedure for calculating the solubility of salts in ternary systems containing two solvents and a salt. We have shown that from knowledge of pure-component and infinite dilution data for the solute and solvents it is possible to predict the solubilities of various salts in alcohol-water mixtures. The model is applicable over a wide range of salt concentrations and may be useful for the design and operation of extractive-crystallization units.

Preliminary results indicate that our model is also applicable for vapor-liquid calculations of salt-containing solvent mixtures using the same thermodynamic information as that required for solubility calculations. These are reported in an accompanying paper.

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Appendix A

Here we give equations for the activity coefficients of a binary system in the framework of our approach (Kolker and de Pablo, 1995a). A detailed description of their use has already been presented in that work and need not be given here again.

These equations are

$$\ln \gamma_1 = \ln \gamma_1^* + \ln \gamma_{1DH} \quad (A1)$$

$$\ln \gamma_2 = \ln \gamma_2^* + \ln \gamma_{2DH} \quad (A2)$$

where

$$\ln \gamma_1^* = -[\tau_{12}(A_{12} + A'_{12}x_1x_2)/(x_1A_{12} + x_2)^2 + \tau_{21}(A_{21}^2 + x_1^2A'_{21})/(x_2A_{21} + x_1)^2]x_2^2$$

$$\ln \gamma_2^* = -[\tau_{12}(A_{12}^2 - A'_{12}x_2^2)/(x_1A_{12} + x_2)^2 + \tau_{21}(A_{21} - x_1x_2A'_{21})/(x_2A_{21} + x_1)^2]x_1^2$$

and where $\ln \gamma_{1DH}$ and $\ln \gamma_{2DH}$ are the Debye-Hückel contributions to the activity coefficient of water and that of the electrolyte, respectively. In these equations

$$A_{21} = \exp(\tau_{21}/\alpha_{21}) \quad \text{and} \quad A_{12} = \exp(\tau_{12}/\alpha_{12})$$

$$\tau_{21} = g_{21} - g_{11} \quad \text{and} \quad \tau_{12} = g_{12} - g_{22}$$

$$\alpha_{21} = n_{21} + n_{11} \quad \text{and} \quad \alpha_{12} = n_{12} + n_{22}$$

The g_{ij} are Gibbs free energies of interaction between a species of type i and a central species of type j (in units of RT). The numbers n_{ij} are the average numbers of nearest neighbors of type i which interact with a central species of type j ($i, j = 1, 2$). These equations differ from the commonly used ones (Prausnitz et al., 1986) in three respects: (i) $g_{12} \neq g_{21}$, (ii) $\alpha_{12} \neq \alpha_{21}$, and (iii) α_{ij} are not

regarded as adjustable parameters because they can be expressed in terms of n_{ij} (and the latter can be calculated from molecular information).

To calculate g_{21} , g_{12} , g_{11} , and n_{12}° in terms of g_{22} , n_{11}° , and n_{22}° , we use the following set of four equations

$$\begin{aligned}\tau_{21} \exp(\tau_{21}/n_{11}^\circ) + \tau_{12} &= g_{22} \\ \tau_{12} \exp(\tau_{12}/n_{22}^\circ) + \tau_{21} &= g_{11} \\ n_{12}^\circ/n_{11}^\circ &= \exp(g_{12}/n_{12}^\circ - g_{11}/n_{11}^\circ) \quad (\text{A3}) \\ n_{11}^\circ[\exp(\tau_{21}/n_{11}^\circ) - 2] + n_{12}^\circ[\exp(-\tau_{12}/n_{12}^\circ) - 2] &= 0\end{aligned}$$

where

$$\begin{aligned}g_{22} = (\Delta G_2^\circ - \Delta G_{2m}^\circ)/RT - \ln m_1 + \{\Delta H_0(1 - T/T_0) - \Delta c_p[T_0 - T(1 + \ln T_0/T)] + \sum_k \Delta H_k(1 - T/T_k)\}/RT + \\ 2A_x/\rho \ln(1 + \rho/\sqrt{2}) \quad (\text{A4})\end{aligned}$$

Here ΔG_{2m}° is the Gibbs free energy of formation of the salt at infinite dilution in the molal scale at the temperature of the system, G_2° is the Gibbs free energy of formation of the pure crystal salt at the temperature of the system, m_1 is the molality of a pure solvent ($=55.508$ for water and $1000/M_3$ for an organic cosolvent), ΔH_0 and T_0 are the salt's enthalpy and temperature of fusion, and Δc_p is the change of heat capacity upon fusion. The term $\sum_k \Delta H_k(1 - T/T_k)$ has to be added if k phase transitions occur in the crystal structure of the salt, each with enthalpy change ΔH_k at temperature T_k . Parameters A_x and ρ appear in the expression for the Debye-Hückel contribution for water (Pitzer and Simonson, 1986). The value of n_{12}° is the average number of molecules of type 1 interacting with a molecule of type 2 at infinite dilution (i.e., it is considered as a solvation number), and the value of n_{11}° is the average number of nearest neighbors for a salt-free mixed solvent which is defined as a linear weighted function of these quantities for water and cosolvent.

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