

## Thermodynamics of solubility in mixed solvent systems

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**Abstract** - A general equation for the solubility of a completely-ionized solute which dissolves congruently in a mixed solvent in terms of (a) the solubilities of the solute in the individual solvents, (b) properties of the pure mixed solvent system, and (c) parameters which have molecular significance has been deduced using both classical thermodynamics and exact statistical thermodynamic theory of liquids. The equation from classical thermodynamics contains three terms which sum to zero: an excess logarithmic solubility relative to a defined ideal logarithmic solubility, an excess logarithmic activity coefficient, and an excess standard chemical potential. The ideal logarithmic solubility is linear in the solvent mole fraction. A method is described for estimation of the excess logarithmic activity coefficient if the Pitzer parameters for the salt in one pure solvent and the dielectric constant and density of the pure solvent mixture are known. The remaining term, the excess standard chemical potential, can be correlated with the theory of Kirkwood and Buff to define selective solvation term for the salt as a whole, and this term can be evaluated if the molar volume and the excess Gibbs energy of the solvent mixture are known. Examples from published experimental data are discussed.

### INTRODUCTION

Solubilities of non-electrolyte or electrolyte solutes in mixed solvents have been used, along with appropriate classical thermodynamic theory, to deduce Gibbs energies of transfer from a reference pure solvent to the mixed solvent (ref. 1). Because little knowledge is available on activity coefficients in mixed solvents, especially for electrolytes, use of solubility data has been restricted, for the most part, to systems in which the solubility is sufficiently low that activity coefficients can either be neglected or can be estimated with reasonable certainty. Thus, while significant theoretical advances in the molecular interpretation of Gibbs energies of transfer have been made recently (ref. 1), the formulation of a general solubility equation for use in critical evaluation of solubilities in mixed solvents has yet to be achieved. Such an equation would describe, ideally, the solubility of a solute in a mixed solvent in terms of: (a) the solubilities of the solute in the individual solvents, and (b) parameters which can be used directly in molecular theories of solubility. The most general theoretical approach to the derivation of a solubility equation would use both classical thermodynamics and exact statistical thermodynamic theories of liquids, and it is this extended concept of thermodynamics that is used in this paper.

Exact statistical thermodynamic theories are analogous to classical thermodynamic theories, in that they are independent of the specific form of the molecular interaction energies. In classical thermodynamics, solubility equilibrium is described in terms of chemical potentials, which are related to solubilities through definitions of activity coefficients. In exact statistical theories, exemplified by the theory of Kirkwood and Buff (ref. 2, 3, 4) as modified by Hall (refs. 5, 6) and by Marcus (ref. 7), solubility equilibrium is described in terms of molecular correlation functions, which in turn are related by exact equations to the chemical potentials. The correlation functions, in particular the radial distribution function, thus provide a direct link between microscopic and macroscopic pictures of liquids, and also provide criteria which must be satisfied by specific models of interactions in the liquid, such as ion-multipole interactions which lead to selective solvation.

The specific aim of this paper is to examine the application of thermodynamics (in the extended sense) to the solubility of a single completely-ionized salt which dissolves congruently in a mixed two-component solvent. Once the appropriate equations are established, some illustrations of their application to experimental data and their relation to current theories of solvation will be discussed briefly.

The method for investigating the thermodynamics of solubility in a two-component solvent in terms of solubilities in the pure solvents involves a procedure which has been described previously (ref. 8) but less completely than here. We shall show that the definition of an *ideal solubility in a mixed solvent* follows from thermodynamic analysis.

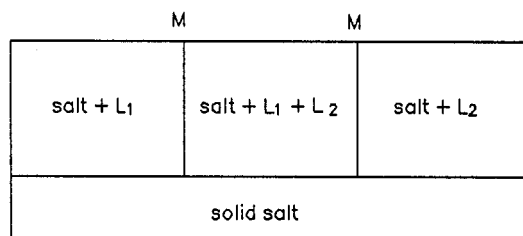
### CLASSICAL THERMODYNAMICS AND SOLUBILITY EQUILIBRIUM IN MIXED SOLVENTS

The Gibbs energy for transfer of a congruently-dissolving solid to a saturated solution is a minimum, and the same minimum affinity holds for transfer to a mixed solvent or to each of the pure solvents. The conditions for equilibrium are thus:

$$\begin{aligned}(\mu_s^* - \mu_s^{(12)})\delta\xi &= 0 \\(\mu_s^* - \mu_s^{(1)})\delta\xi &= 0 \\(\mu_s^* - \mu_s^{(2)})\delta\xi &= 0\end{aligned}\tag{1}$$

where  $\xi$  is the degree of advancement,  $\mu_s$  the chemical potential of the solute in solution,  $\mu_s^*$  the chemical potential of the pure solid, and superscripts (1), (2), (12) designate quantities in solvents 1, 2 and the mixture of solvents 1 and 2, respectively. The system is illustrated in Fig. 1, where the common solid phase underlies three saturated solution phases containing, respectively, pure solvent 1, pure solvent 2, and mixed solvent 12, each separated from the other by a membrane semipermeable to the salt only. The system is analogous to that of two different salts in a single

Fig. 1. Schematic representation of solubility equilibria for a single salt in pure solvents  $L_1$  and  $L_2$  and mixed binary solvent; M - membranes semipermeable to salt only.



solvent in isopiestic equilibrium, where the common vapour phase replaces the solid phase, and the three systems contain pure salt 1 and solvent, pure salt 2 and solvent, and mixed salts and solvent, each separated from the other by membranes semipermeable to the solvent only. This system has been discussed by Sangster and Lenzi (ref. 9) using a different method than that used here; however, the present method yields the same results without assuming *a priori* the form of the equation for the osmotic coefficient for a solvent containing a mixture of salts.

The first of the equilibrium conditions in eqn. (1) can be considered to be the criterion for minimization of the chemical affinity of the system, subject to the constraints given by the second and third conditions. Thus, the second and third conditions can be multiplied by, respectively, Lagrange multipliers  $-\alpha$  and  $-\beta$ , and the three equations can be added to give:

$$[\mu_s^* - \mu_s^{(12)} - \alpha(\mu_s^* - \mu_s^{(1)}) - \beta(\mu_s^* - \mu_s^{(2)})]\delta\xi = 0\tag{2}$$

The terms in the chemical potential of the solid disappear with the choice  $\alpha + \beta = 1$ , so that, on rearrangement,

$$\mu_s^{(12)} = (1-\beta)\mu_s^{(1)} + \beta\mu_s^{(2)}\tag{3}$$

Because the chemical potential terms in eqn (3) are mutually equal, the remaining Lagrange multiplier  $\beta$  is clearly an arbitrary dimensionless quantity with the characteristics of a fraction, such as solvent mass or mole fraction, volume fraction, or any other fractional quantity. The most

convenient choice is  $\beta = x_2^{(12)}$ , the solvent mole fraction of solvent component 2. The chemical potential of the salt in solvent  $i$ , with  $i = 1, 2$  or  $12$ , is:

$$\mu_s^{(i)} = \mu_s^{o(i)} + \nu RT \ln[\gamma_s^{(i)} m_s^{(i)} (\nu_+^{\nu} \nu_-^{\nu})^{1/\nu} / m^\circ] \quad (4)$$

where  $R$  is the gas constant,  $T$  the thermodynamic temperature,  $\nu$  the sum of the stoichiometric coefficients  $\nu_+$  and  $\nu_-$  of ions of the completely-ionized salt,  $\mu_s^{o(i)}$ ,  $\gamma_s^{(i)}$ ,  $m_s^{(i)}$  the standard chemical potential, activity coefficient (molality scale) and molality of the solute in solvent  $i$  and  $m^\circ = 1 \text{ mol kg}^{-1}$  the standard molality. Substitution of eqn (4) into (3) gives:

$$\begin{aligned} \ln(m_s^{(12)}/m^\circ) &= (1-x_2^{(12)}) \ln(m_s^{(1)}/m^\circ) + x_2^{(12)} \ln(m_s^{(2)}/m^\circ) \\ &+ (1-x_2^{(12)}) \ln(\gamma_s^{(1)}/\gamma_s^{(12)}) + x_2^{(12)} \ln(\gamma_s^{(2)}/\gamma_s^{(12)}) \\ &- ((1-x_2^{(12)}) \Delta_{tr} G_{1 \rightarrow 12}^\circ + x_2^{(12)} \Delta_{tr} G_{2 \rightarrow 12}^\circ) / \nu RT \end{aligned} \quad (5)$$

where

$$\Delta_{tr} G_{i \rightarrow 12}^\circ = \mu_s^{(12)} - \mu_s^{(i)} \quad (6)$$

is the Gibbs energy of transfer from solvent  $i$  to mixed solvent  $12$ .

In eqn (5), the first set of terms on the right-hand side defines the ideal solubility in a mixed solvent:

$$\ln(m_s^{(12)}/m^\circ)^{id} = (1-x_2) \ln(m_s^{(1)}/m^\circ) + x_2 \ln(m_s^{(2)}/m^\circ) \quad (7)$$

while the remaining excess terms account for solute-solute and solute-solvent interactions. Thus eqn (5) can be written:

$$[\ln(m_s^{(12)}/m^\circ)]^E + [\ln \gamma_s^{(12)}]^E + [\mu^{o(12)}]^E / \nu RT = 0 \quad (8)$$

where

$$[\ln(m_s^{(12)}/m^\circ)]^E = \ln(m_s^{12}/m^\circ) - (1-x_2^{(12)}) \ln(m_s^{(1)}/m^\circ) - x_2^{(12)} \ln(m_s^{(2)}/m^\circ) \quad (9)$$

$$[\ln \gamma_s^{(12)}]^E = \ln \gamma_s^{(12)} - (1-x_2^{(12)}) \ln \gamma_s^{(1)} - x_2^{(12)} \ln \gamma_s^{(2)} \quad (10)$$

$$\begin{aligned} [\mu_s^{o(12)}]^E &= \mu_s^{o(12)} - (1-x_2^{(12)}) \mu_s^{o(1)} - x_2^{(12)} \mu_s^{o(2)} \\ &= (1-x_2^{(12)}) \Delta_{tr} G_{1 \rightarrow 12}^\circ + x_2^{(12)} \Delta_{tr} G_{2 \rightarrow 12}^\circ \end{aligned} \quad (11)$$

It should be noted that a change in definition of the activity coefficients could eliminate the term involving the Gibbs energies of transfer. Thus, choosing the reference chemical potential as the chemical potential of the supercooled pure liquid solute at the given temperature and pressure, and the mole fraction of the solute as the composition variable would give the same reference chemical potential for the solute in each solution. This choice has value for non-electrolyte solutes. However, for electrolytes, which are the main concern in this paper, interpretation of the activity coefficients is more convenient using the molality scale and the conventional infinite-dilution standard state, and it is this choice of standard state that gives rise to the necessity of Gibbs energies of transfer.

It is clear that eqn. (5) could be written at once, given the equality of the chemical potentials in eqn. (1). The derivation given here shows that eqn. (5) is the form of relation that follows at once from formal thermodynamic reasoning, and emphasizes the arbitrary choices that are made in identifying the Lagrange multipliers.

Definition of an ideal solubility only has value if real systems exist which approximate closely to the definition. An actual example is found in the system is NaCl-H<sub>2</sub>O-D<sub>2</sub>O (refs. 8, 10), where the logarithm of the solubility at 25°C is a linear function of the solvent mole fraction within

experimental error (Fig. 2). The immediate conclusion is that the activity coefficients and the Gibbs energies of transfer both follow simple mixing rules, which from eqns. (10) and (11) are:

$$\begin{aligned} \ln \gamma_s^{(12)} &= (1-x_2^{(12)}) \ln \gamma_s^{(1)} + x_2^{(12)} \ln \gamma_s^{(2)} \\ (1-x_2^{(12)}) \Delta_{tr} G_{1 \rightarrow 12}^\circ + x_2^{(12)} \Delta_{tr} G_{2 \rightarrow 12}^\circ &= 0 \end{aligned} \quad (12)$$

In systems which exhibit non-ideal solubility in a mixed solvent, deviations from the ideal solubility involve both the Gibbs energies of transfer and the activity coefficients, and we turn to statistical thermodynamic theories to clarify the significance of these terms and to provide practical methods for obtaining their general mathematical form.

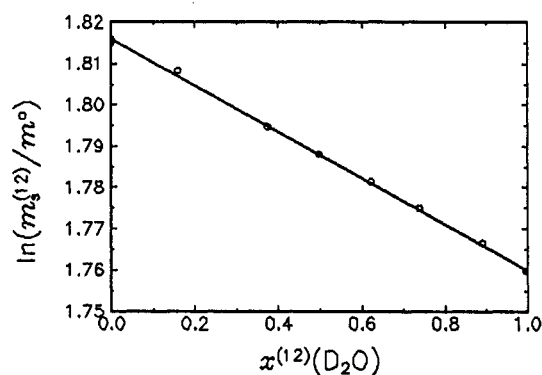


Fig. 2. Ideal logarithmic solubility of NaCl in  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures at  $25^\circ\text{C}$  (ref. 10). Points: experimental data; line drawn through solubilities in pure solvents. Dielectric constants (ref. 11):  $\text{H}_2\text{O}$ , 78.54;  $\text{D}_2\text{O}$ , 78.06. See text for symbols.

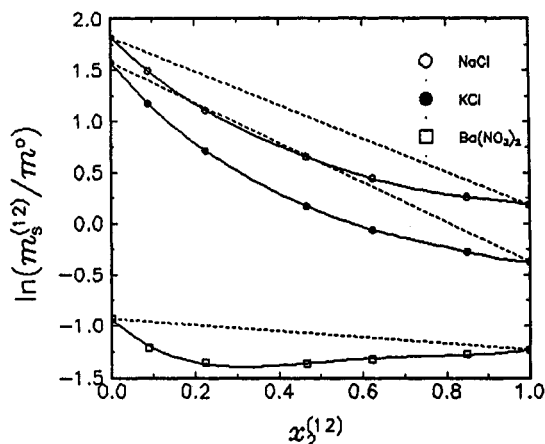


Fig. 3. Solubilities of NaCl, KCl and  $\text{Ba}(\text{NO}_3)_2$  in  $\text{H}_2\text{O}-\text{En}(\text{OH})_2$  mixtures at  $25^\circ\text{C}$  (ref. 13).

As an illustration of the application of the thermodynamic principles, solubilities of NaCl, KCl and  $\text{Ba}(\text{NO}_3)_2$  in water (w)-ethylene glycol [ $\text{En}(\text{OH})_2$ ] mixtures (ref. 12) are shown in Fig. 3, along with the ideal solubility lines. Note that the excess solubility is negative, indicating that the sum of the excess logarithmic activity coefficient and the excess standard chemical potential must be positive. The other contributions to the total solubility curve will be discussed in the following sections.

### THE EXCESS LOGARITHMIC ACTIVITY COEFFICIENT

Few published data are available from which general principles can be established for evaluation of activity coefficients in mixed solvent systems. The most direct procedure, especially where salts with high solubility are in question, would be to use Pitzer's equations for activity coefficients. Here an important assumption is involved: the dielectric constant in the Pitzer electrostatic term is the bulk dielectric constant, which implies that counterions are effectively excluded from the neighborhood of a given ion where preferential solvation takes place. Koh *et al.* (ref. 13) have analyzed emf data for the systems alkali metal chloride-water-methanol by Pitzer's equations, and have evaluated the interaction parameters  $\beta^{(0)}$  and  $\beta^{(1)}$ . The equation for the mean activity coefficient of the salt is (ref. 14):

$$\ln \gamma_s = z_M z_X f^\gamma + m(2\nu_M \nu_X / \nu) B_s^\gamma + m^2(2\nu_M \nu_X / \nu)^{3/2} C_s^\gamma \quad (13)$$

with

$$\begin{aligned} f^\gamma &= A^\phi x \\ A^\phi &= (1/3)(2\pi N_A d)^{1/2} (e^2 / 4\pi \epsilon_0 D kT)^{3/2} \\ &= 8.60323(d/\text{kg m}^{-3})^{1/2} D^{-3/2} \text{ at } 25^\circ\text{C} \\ x &= I^{1/2} / (1 + 1.2I^{1/2}) + (5/3) \ln(1 + 1.2I^{1/2}) \\ B_s^\gamma &= 2(\beta_s^{(0)} + \beta_s^{(1)} y) \\ y &= [1 - \exp(-2I^{1/2})(1 + 2I^{1/2} - I/2)] / 4I \end{aligned} \quad (14)$$

Here,  $z_i$  is the charge number of ion  $i$ ,  $A^\phi$  is the Debye-Hueckel osmotic parameter,  $N_A$  Avogadro's constant,  $d$ ,  $D$  the solvent density and dielectric constant,  $e$  the elementary charge,  $\epsilon_0$  the permittivity of vacuum,  $k$  the Boltzmann constant and  $I$  the ionic strength divided by the standard molality.

Analysis of the results of Koh *et al.* (ref. 13) shows that  $\beta^{(0)}$  is either constant for each alkali chloride, or varies linearly with solvent mole fraction, and is generally much smaller than  $\beta^{(1)}$ , while  $\log \beta^{(1)}$  is a linear function of  $\log D$ , with a different slope for each salt; for CsCl, there are two slopes, delineating two ranges of solvent composition. An example is given in Fig. 4. This behaviour is not unexpected, since  $\beta^{(0)}$  is a measure of interactions between pairs of like ions and  $\beta^{(1)}$  of interactions between pairs of unlike ions, i.e.,  $\beta^{(1)}$  is analogous to an ion pairing parameter (ref. 14). The Bjerrum theory of ion pair formation (see ref. 15) indeed gives the ion pair formation constant as a function of  $D$  which depends on the particular ion pair.

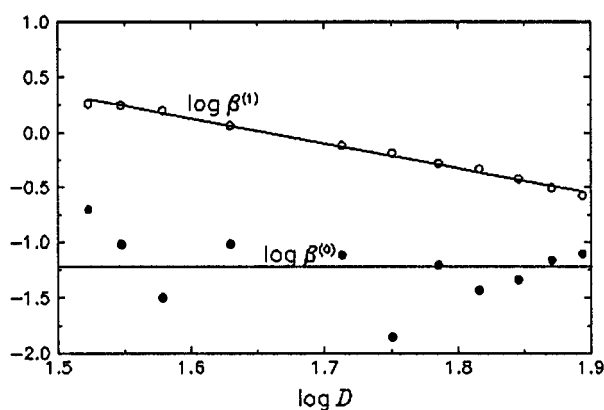


Fig. 4. Dependence of  $\log \beta^{(0)}$  and  $\log \beta^{(1)}$  on  $\log D$  for NaCl in  $\text{H}_2\text{O}$ -MeOH mixtures at  $25^\circ\text{C}$  (from data in ref. 13).

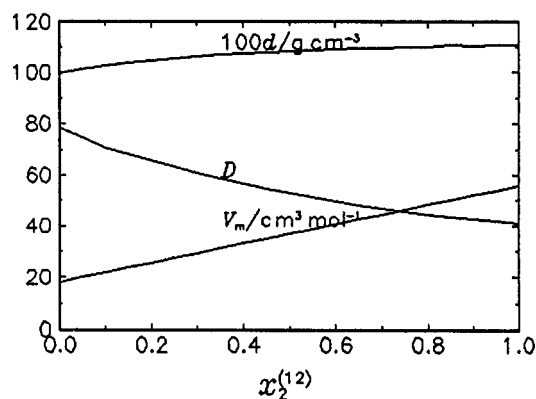


Fig. 5. Density, molar volume and dielectric constant of  $\text{H}_2\text{O}$ -En(OH) $_2$  mixtures at  $25^\circ\text{C}$ .

These observations provide a general strategy for estimation of the activity coefficients in solvent mixtures if we know the solubilities, densities and dielectric constants for the pure solvent mixtures, and the Pitzer parameters for one salt-solvent mixture. For the data on salts in water-ethylene glycol mixtures at  $25^\circ\text{C}$ , the Pitzer parameters are known for solutions in pure water (ref. 14): for NaCl,  $\beta^{(0)} = 0.0765$ ,  $\beta^{(1)} = 0.2994$ ,  $C^\gamma = 0.001905$ , from which  $\ln \gamma_s^{(1)} = 0.01044$  for the saturated solution with  $m = 6.160 \text{ mol kg}^{-1}$ . Fig. 5 shows the necessary density (estimated from linear dependence on mass fraction, as in ref. 16) and dielectric constant data (ref. 11) for the pure solvent mixtures. For the saturated solution of the salt in En(OH) $_2$ ,

$$\ln \gamma_s^{(2)} = \ln \gamma_s^{(1)} + \ln(m_s^{(1)}/m_s^{(2)}) - \Delta_{tr} G_{1 \rightarrow 2}^\circ / \nu RT \quad (15)$$

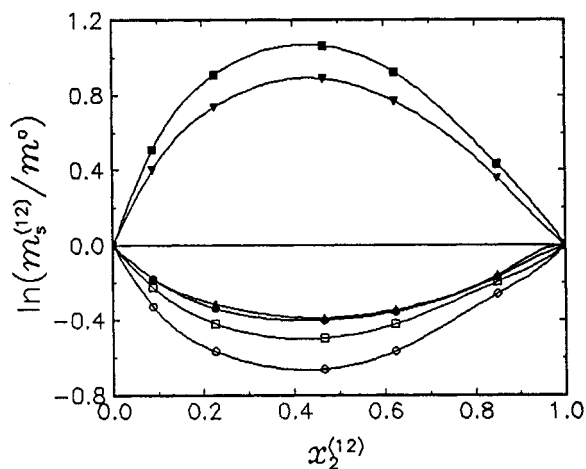
from which, with the Gibbs energy of transfer from water to En(OH) $_2 = 7000 \text{ J mol}^{-1}$  (ref. 11),  $\ln \gamma_s^{(2)} = 0.2369$ . Now assume that  $\beta^{(0)}$  is independent of  $D$ , and that the coefficient  $C^\gamma$  is constant. The value  $\beta^{(1)} = 4.596$  can then be calculated for NaCl in En(OH) $_2$ , and the index  $n$  in the equation

$$\beta^{(1)}(\text{H}_2\text{O})/\beta^{(1)}(\text{En(OH)}_2) = [D(\text{H}_2\text{O})/D(\text{En(OH)}_2)]^n \quad (16)$$

is found to be  $-4.390$ , a reasonable value in terms of Bjerrum theory. This value can then be used to estimate values of  $\beta^{(1)}$  for all mixed solvent systems, and hence the activity coefficients for these systems can also be estimated. The results of these calculations and similar calculations for KCl are shown in Fig. 6. For Ba(NO $_2$ ) $_3$ , no information is available for the Gibbs energy of transfer between water and En(OH) $_2$  for either barium or nitrate ions, so no further analysis can be made. The activity coefficient term is larger in absolute value than the excess solubility itself. Thus errors in the activity coefficients are serious, but difficult to estimate.

Fig. 6. Excess solubility functions for NaCl and KCl in  $\text{H}_2\text{O}-\text{En}(\text{OH})_2$  mixtures at  $25^\circ\text{C}$ .  $[\ln(m_s^{(12)}/m^\circ)]^E$ : ● NaCl, □ KCl;  $[\ln\gamma_s^{(12)}]^E$ : ○ NaCl, △ KCl;  $[\mu_s^{(12)}]^E/2RT$ : ■ NaCl, ▽ KCl.

The excess logarithmic activity coefficient is negative for both NaCl and KCl, indicating that the excess standard chemical potential must be positive at all solvent compositions. The negative value of the excess logarithmic activity coefficient arises from the smaller solubility and larger logarithmic activity coefficient in pure  $\text{En}(\text{OH})_2$  compared with the values in  $\text{H}_2\text{O}$ . The inverse dependence of logarithmic activity coefficient on dielectric constant contributes to the curvature of the plot. Inspection of eqns. (8) through (11) shows that the extrema in all curves in Fig. 6 must occur at the same value of the solvent mole fraction, which is an obvious feature in the figure.



The negative of the sum of the excess logarithmic solubility and the excess logarithmic activity is equal to the excess standard chemical potential, which is shown in Fig. 3. Hall (refs. 5, 6) has applied the Kirkwood-Buff solution theory (ref. 2, 3, 4) to derive equations for preferential solvation of ions in terms of the radial distribution function about the ion, and this derivation has been extended and criticized by Newman (ref. 17) and Marcus (ref. 7). We write these equation for the salt, and find that the dependence of the excess standard chemical potential on solvent composition is given by:

### THE EXCESS STANDARD CHEMICAL POTENTIAL

The negative of the sum of the excess logarithmic solubility and the excess logarithmic activity is equal to the excess standard chemical potential, which is shown in Fig. 3. Hall (refs. 5, 6) has applied the Kirkwood-Buff solution theory (ref. 2, 3, 4) to derive equations for preferential solvation of ions in terms of the radial distribution function about the ion, and this derivation has been extended and criticized by Newman (ref. 17) and Marcus (ref. 7). We write these equation for the salt, and find that the dependence of the excess standard chemical potential on solvent composition is given by:

$$\frac{1}{vRT} \frac{\partial [\mu_s^{(12)}]^E}{\partial x_2^{(12)}} = -\frac{x_2^{(12)}(G_{2s}-G_{1s})}{V_m RT} \frac{\partial \mu_2}{\partial x_2^{(12)}} + \Delta_{tr} G_{2-1}^0 / vRT + \frac{\partial \ln(d^{(12)} m^\circ / c^\circ)}{\partial x_2^{(12)}} \quad (17)$$

Here,  $V_m$  is the molar volume of the pure solvent mixture, and the Kirkwood-Buff integrals for the salt are defined to be

$$v G_{is} = v_+(G_{i+} + G_{i-}) \quad i = 1, 2 \quad (18)$$

where the individual ionic Kirkwood-Buff integrals for the cation (+) -solvent  $i$  interaction are

$$G_{i+} = N_{i+}^* / c_i = \int_0^R 4\pi r^2 (g_{i+} - 1) dr \quad (19)$$

$N_{i+}^*$  is the excess of solvent component  $i$  near the cation,  $g_{i+}$  is the radial distribution function for solvent molecules of type  $i$  around the cation,  $r$  is the radial distance from the ion, and  $R$  is a distance at which the solvent distribution has become essentially uniform, and within which the counterion concentration is negligible. Similar definitions apply for the anion-solvent interaction. The term in the derivative of the chemical potential of the solvent is given by

$$\frac{\partial \mu_2}{\partial x_2^{(12)}} = RT \left[ 1 + \frac{x_2^{(12)}(1-x_2^{(12)})}{RT} \frac{\partial^2 G_m^E}{\partial x_2^{(12)2}} \right] \quad (20)$$

The second derivative of the excess Gibbs energy of mixing,  $G^E$ , of the solvent component 2 can be found from experimental data on excess Gibbs energies, and is

$$\partial^2 G^E / \partial x_2^{(12)} = -2A_1 + 6(1-2x_2^{(12)})A_2 - (10-48x_2^{(12)} + 48x_2^{(12)2})A_3 \quad (21)$$

with  $A_1 = -1829$ ,  $A_2 = 689$  and  $A_3 = 160 \text{ J mol}^{-1}$  for  $\text{H}_2\text{O-En(OH)}_2$  mixtures (ref. 11). The penultimate term is the standard Gibbs energy of transfer from water to  $\text{En(OH)}_2$ , and the final term (which has not been reported previously) accounts for the change from standard chemical potentials on the amount concentration scale (used in the analysis based on Kirkwood-Buff theory) to standard chemical potentials on the molality scale.

The excess standard chemical potential can be fitted to the polynomial

$$[\mu_s^{o(12)}]^E / \nu RT = x_2^{(12)}(1-x_2^{(12)}) \sum_{n=1}^4 B_n x_2^{(12)(n-1)} \quad (22)$$

with  $B_1 = 6.997$ ,  $B_2 = -9.197$ ,  $B_3 = 8.249$ ,  $B_4 = -2.649$  for NaCl,  $B_1 = 5.789$ ,  $B_2 = -10.147$ ,  $B_3 = 15.950$ ,  $B_4 = -9.667$  for KCl and from which the derivatives can be found. From density data, the molar volume and the correction for difference in standard state can be calculated, from which the value of  $G_{2s}^* - G_{1s}^*$  can be calculated. These quantities are shown in Figs. 7 and 8.

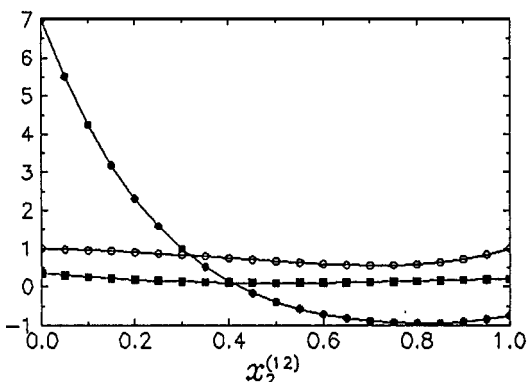


Fig. 7. Quantities required for calculation of solvent sorting by NaCl at 25°C. ●,  $(1/\nu RT)\partial[\mu^{o(12)}]^E/\partial x_2^{(12)}$ ; ○,  $(x_2/RT)^{(12)}\partial\mu_2^{(12)}/\partial x_2^{(12)}$ ; ■,  $\partial \ln(d^{(12)}m_o/c^o)/\partial x_2^{(12)}$ .

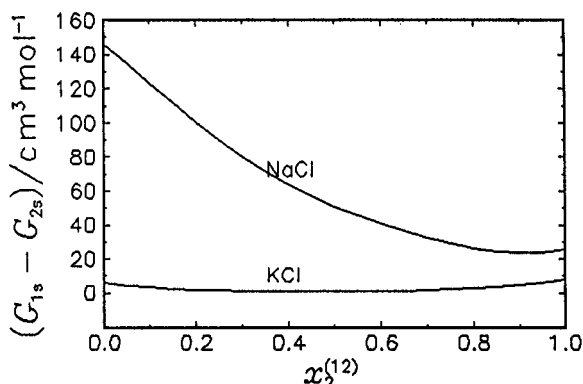


Fig. 8. Difference in Kirkwood-Buff integrals for NaCl and KCl at 25°C from solubilities in  $\text{H}_2\text{O-En(OH)}_2$ .

While methods exist for estimation of preferential solvation by individual ions, still more thermodynamic information, as well as assumptions concerning the splitting of the total term for the salt into its ionic components (see especially refs. 1, 7, 17), are necessary. In this paper, we confine our attention to the immediate interpretation of the terms in the general solubility equation, and make the minimum number of assumptions. The individual Kirkwood-Buff integrals for each solvent can be calculated if the partial molar volumes of the salt at infinite dilution in the solvent mixtures are known (information which is sparse except for the pure components), as well as the isothermal compressibilities of the solvent mixtures. These latter can be estimated closely enough from the isothermal compressibilities of the pure solvents,  $\kappa(i)$  and a simple mixture rule which recognizes that the compressibility is a volume property, with  $V^o$  the molar volume of pure liquid  $i$ :

$$\kappa^{(12)} = [(1-x_2^{(12)})V_1^o\kappa^{(1)} + x_2^{(12)}V_2^o\kappa^{(2)}] / V_m \quad (23)$$

The experimentally accessible values of the individual Kirkwood-Buff integrals plus the partial molar volumes at infinite dilution are then given by:

$$\begin{aligned} G_{s1} + V_s^o &= (G_{s2} - G_{s1})c_2V_2 + \kappa^{(12)}RT \\ G_{s2} + V_s^o &= -(G_{s2} - G_{s1})c_1V_1 + \kappa^{(12)}RT \end{aligned} \quad (24)$$

These values are plotted in Fig. 9. Either this figure or Figure 8 suggests that, even when the limiting partial molar volumes are taken into account, the net preferential solvation of  $K^+$  and  $Cl^-$  ions is small, and almost independent of solvent composition. By contrast, net preferential solvation of  $Na^+$  and  $Cl^-$  ions decreases rapidly as  $En(OH)_2$  is added.

The initial goal has now been reached: description of the excess solubility in terms of the solubilities in the pure solvents, and the properties of the solvent mixture.

### CONCLUSIONS

1. Classical thermodynamics provides a general equation which describes the solubility of a salt in a mixed binary solvent in terms of three contributions: an excess logarithmic solubility relative to a defined ideal logarithmic solubility; an excess logarithmic activity coefficient; and an excess standard chemical potential. The excess logarithmic solubility can be calculated readily from experimental solubility data as a function of solvent composition.
2. With the assumption that the activity coefficient contribution to the excess solubility involves ion interactions in a region where solvent sorting is absent, and that the ion-pair interaction coefficient in Pitzer's equations varies as a power of the dielectric constant, estimates of the activity contribution can be made from known Pitzer parameters in one pure solvent and the solubilities in the two pure solvents.
3. The remaining excess contribution (excess standard chemical potential, or alternatively, excess standard Gibbs energy of transfer) can be correlated with the derivative of the chemical potential of one solvent component with respect to the solvent mole fraction, the molar volume of the solvent, and a term describing net preferential solvation of the ions of the salt.
4. While there are no restrictions on the general concept of the general solubility equation, and on calculation of the excess logarithmic solubility, calculation of the activity coefficient contribution assumes that complete ionization is a suitable reference state for the salt, which may cause difficulties in interpretation, especially in non-aqueous solvent systems, where extensive ion pair and ion multiplet formation is to be expected even in very dilute solutions.
5. As the possibility of direct experimental evaluation of the Kirkwood-Buff integrals becomes more widely realized, this approach is expected to become more widely used in evaluation of solubility data in mixed solvents and in the related areas of Gibbs energies of transfer between solvent pairs and testing of theoretical radial distribution functions. Serious theoretical problems remain to be resolved, in particular, the mutual effects of solvent and counterion sorting near a given ion, which have been treated here by a simple empirical assumption.
6. Recommendations for evaluation of solubility data in mixed solvents include: calculation of at least the excess logarithmic solubility, which can be done readily from experimental data; calculation of the excess logarithmic activity coefficient if possible, especially in very dilute solutions, where this contribution is both smaller and more certain in its calculation; calculation of the excess standard chemical potential. The calculations must, of necessity, be done in the order just given, and should be amply supported by reliable ancillary data.

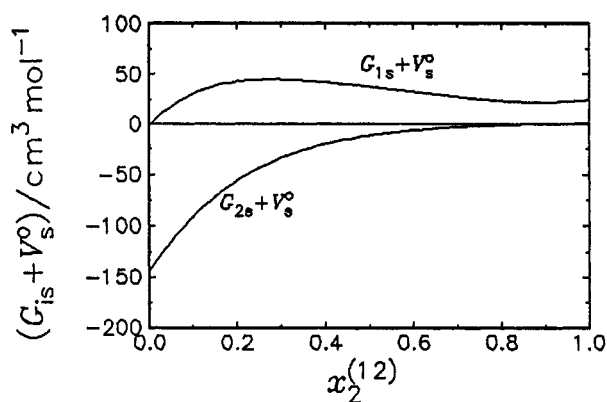


Fig. 9. Individual Kirkwood-Buff integrals plus limiting partial molar volumes for  $NaCl$  at  $25^\circ C$  for  $H_2O$  ( $G_{s1} + V_s^0$ ) and  $En(OH)_2$  ( $G_{s2} + V_s^0$ ).



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