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Kenneth S. Pitzer

May 1981

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The Treatment of Ionic Solutions over the Entire Miscibility Range

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(Abstract)

Conductance and thermodynamic properties are considered for several ionic systems continuously miscible from the fused salt to dilute solution in water or another polar solvent. Over most of the composition range, the activities of the respective components of the ionic systems show the same patterns of behavior and can be represented by the same equations that were developed for nonelectrolytes. Consideration is also given to ionic systems of large but finite solubility, including mixed electrolytes. The dominant factor in the behavior of these systems is the strength of ion solvation in competition with intermolecular forces in the solvent and direct interionic forces. Strong ion solvation yields negative deviations from ideal solution behavior and vice versa.

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Introduction

Few systems have been studied which are miscible continuously from the fused salt to dilute solution in water or a similar solvent. But their behavior in the very high concentration range is found to be relatively simple and less complex than in the dilute range. The writer [1] has presented equations representing the thermodynamic properties of two systems of this type. A very simple equation of the van Laar or regular solution type is adequate over most of the concentration range but a Debye-Hückel term is needed for dilute solutions. These results are consistent with the following general picture of structural patterns. The fused salt has a disordered ionic lattice with alternating positive and negative charges. As water (or other polar molecular solvent) is added, it fits between ions with the appropriate orientation of protons near anions and unshared electrons near cations. But the alternating charge pattern remains until the solution is quite dilute; then that pattern is lost and the ions are randomly distributed at infinite dilution. The Debye-Hückel theory describes this last transition from alternating charges to random location of ions. But in the more concentrated range, the important aspect is the relative strength of ion hydration energies in comparison to the sum of direct anion-cation attraction and intermolecular attraction in pure solvent. If ion hydration energies are stronger, one finds negative departures from ideal solutions and vice versa.

After a brief survey of conductance data, which indicates whether systems are fully or only partially ionized, these thermodynamic relationships are explored in some detail. Another section presents methods

appropriate for ionic systems of large but finite solubility with emphasis on mixed electrolytes and solubility relationships.

Conductance

In using conductance data as an indicator of the degree of ionization over wide ranges of composition it is best to consider the viscosity-conductance product. While the macroscopic viscosity is not a perfect indicator of the resistance to ionic motion, it is the best measure that is generally available. Figure 1 shows the $\eta\Lambda$ product for three systems which exemplify the patterns of behavior that are commonly found. System A is $\text{LiClO}_3 - \text{H}_2\text{O}$ at 131.8°C which was investigated by Campbell and Paterson [2]. The very moderate reduction in $\eta\Lambda$ from very dilute to more concentrated solutions was shown to follow the theory for ion interaction in fully dissociated electrolytes. At the other extreme of composition the viscosity decreases very rapidly from a value for the pure fused salt 113 times that for water. The writer is not aware of any theoretical analysis appropriate to this region with a little water in a fused salt. But with the conductance itself increasing rather rapidly with addition of water it does not seem likely that there is any departure from full ionization even though the $\eta\Lambda$ product decreases somewhat. Presumably this full ionization extends throughout the intermediate concentration range.

System B is tetra-n-butylammonium picrate and n-butyl alcohol at 91°C , investigated by Seward [3]. In this system the viscosity changes less rapidly near the fused salt and the $\eta\Lambda$ product is more nearly constant; again complete ionization is indicated for the range of high concentration. But with the lower dielectric constant of butyl alcohol

(compared to water) there is incomplete ionization in dilute solutions. This phenomenon is well understood. But less widely recognized is the redissociation which occurs as the concentration increases further. Davies [4] explained this redissociation by the rapid decrease of ion activity coefficients with increase in ionic strength. This decrease is so extreme for 1-1 electrolytes in low dielectric solvents or for 2-2 and higher valence types in water that it overcomes the normal tendency toward increase in association with concentration. Silvester and the writer [5] have also considered this effect for high-valence electrolytes in water. This redissociation phenomenon can also be discussed in terms of the decrease in electrical screening length with increase in concentration. An ion pair widely separated by solvent from other ions acts as a neutral species, but the same two ions in pure fused salt or very concentrated solution behave as dissociated ions.

In aqueous systems most strong electrolytes behave essentially as example A up to the solubility limit whereas 2-2 and higher valence types show a tendency toward the ion association and redissociation pattern of example B.

In addition there are typical weak electrolytes such as example C in Fig. 1 which is acetic acid-water at room temperature. Here the pure acetic acid is not a fused salt but rather a polar molecular liquid showing some self dissociation. In the dilute aqueous range there is strong ion association and no redissociation. We shall not consider this type of system further in this paper, but it should be recognized as an important category.

There is a fourth type of system, not shown on Fig. 1, which is a strong, fully ionized electrolyte in dilute and even moderately concentrated solution, but the pure solute is a molecular liquid rather than a fused salt. Examples include the common acids HClO_4 and HNO_3 (also HCl under high pressure). The monohydrates, H_3OClO_4 , etc., approximate fused salts and their behavior at lower concentrations follows the pattern of example A. With special definitions these systems could be considered in a manner similar to those of type A which are the subject of the remainder of this paper.

Activity. Simple Treatment for High Concentration

The vapor pressure of water and thereby the water activity has been measured over the entire composition range for very few systems. We shall consider two; in each case a mixed nitrate was used to depress the melting point and avoid a high pressure of steam. The system $(\text{Ag}, \text{Tl})\text{NO}_3\text{-H}_2\text{O}$ was measured at 98.5°C by Trudelle, Abraham, and Sangster [6]. The system $(\text{Li}, \text{K})\text{NO}_3\text{-H}_2\text{O}$ was measured at very high concentration at 119°C and higher temperatures by Tripp and Braumstein [7]. Isopiestic measurements were made for this system and several others, including $\text{LiCl-H}_2\text{O}$, at somewhat lower concentrations and at 100 to 150°C by Braumstein and Braumstein [8]. These isopiestic data at 100°C can be converted to water activities by use of the vapor pressure data of Gibbard and Scatchard [9] for $\text{LiCl-H}_2\text{O}$. These results are shown on Fig. 2 together with those for several systems of finite but great solubility [9, 10].

The composition variable is the mole fraction on an ionized basis, i.e., $x_1 = n_1/(n_1 + \nu n_2)$ where n_1 and n_2 are moles of water and salt, respectively, and ν is the number of ions in the salt. On this basis Raoult's law applies in the very dilute range, with the Debye-Hückel [11] correction applicable as the concentration increases. Much of the published work on fused salt systems has composition reported on the unionized rather than the ionized basis. Theory clearly supports the ionized basis. Also the writer [12] tested the empirical representation of the properties of the two systems cited above and found a clear advantage for the ionized basis.

The similarity of the curves on Fig. 2 to those for non-electrolyte solutions is striking. The dashed line representing $a_1 = x_1$ can be called "ideal-solution behavior" for these systems, as it is for non-electrolytes; but it is realized that a statistical model yielding that result would be more complex for the ionic case. Also the Debye-Hückel effect is a departure from this ideal behavior. Nevertheless, the properties of these systems are represented quite well by the simple equations for nonelectrolytes. One of the simplest and most successful had its origin in the work of van Laar [13] and has been widely used since. Prausnitz [14] discusses this and related equations as well as the contributions of Margules, Hildebrand, Scatchard, Guggenheim, and others to this topic. For the activity of either component, referenced to the pure liquid, one has

$$\ln a_1 = \ln x_1 + w_1 z_2^2 \quad (1a)$$

$$\ln a_2 = \nu(\ln x_2 + w_2 z_1^2) \quad (1b)$$

$$\Delta G_m/RT = n_1 \ln x_1 + \nu n_2 \ln x_2 + w_1 n_1 z_2 \quad (1c)$$

$$z_1 = n_1/[n_1 + n_2(b_2/b_1)] \quad (1d)$$

$$z_2 = \nu n_2/[n_1(b_1/b_2) + \nu n_2] = 1 - z_1 \quad (1e)$$

$$w_2 = (b_2/b_1)w_1 \quad (1f)$$

Note first that if (b_1/b_2) is unity, z_1 and z_2 reduce to the mole fractions x_1 and x_2 . Then one has the even simpler equations

$$\ln a_1 = \ln x_1 + w x_2^2 \quad (2a)$$

$$\ln a_2 = \nu(\ln x_2 + w x_1^2) \quad (2b)$$

$$\Delta G_m/RT = n_1 \ln x_1 + \nu n_2 \ln x_2 + w n_1 x_2 \quad (2c)$$

In either equations (1) or (2) the non-ideality parameter w (sometimes written w/RT) arises from the difference between the intermolecular attraction of unlike species as compared to the mean of the intermolecular attraction for pairs of like species. If we ignore effects of volume or coordination-number differences, the quantity w for non-electrolyte and for electrolyte systems can be expressed in terms of short range energies of interparticle attraction ϵ_{ij} and the effective coordination number c as follows:

Nonelectrolyte A - B

$$wkT = c\Delta\epsilon = c[\epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})]$$

Electrolyte (MX) - Water (W)

$$wkT = c\Delta\epsilon = (c/2)(\epsilon_{MW} + \epsilon_{XW} - \epsilon_{MX} - \epsilon_{WW})$$

The second parameter in equation (1), (b_1/b_2) , is sometimes ascribed to the ratio of the volumes of the molecules or to the ratio of molal volumes in the liquid. (Originally van Laar related b_1 and b_2 to the b quantity in the van der Waals equation, which is in turn related to the volume of the molecules, but this relationship to an approximate equation for the imperfect gas is less useful.) In some systems, especially metallic solutions, equation (1) is still quite satisfactory but (b_1/b_2) departs greatly from the ratio of molal or atomic volumes. For fused salt-water mixtures it seems best to regard (b_1/b_2) as a freely adjustable parameter.

Equation (1) was fitted [1] to the two systems remaining liquid over the full range of composition with the results $w_1 = 1.02$, $(b_1/b_2) = 0.50$ for $(\text{Ag,Tl})\text{NO}_3\text{-H}_2\text{O}$ and $w_1 = -0.89$, $(b_1/b_2) = 1.2$ for $(\text{Li,K})\text{NO}_3\text{-H}_2\text{O}$. Water is component 1 and the salt component 2. In each salt the cation fraction is about 0.5 and is fixed; hence the system can be treated as if it involved a single pure salt. For the latter system the simpler equation (2) serves almost as well with $w = -0.80$ (this implies $b_1/b_2 = 1.0$). The calculated curves based on equation (1) are compared with the experimental data in Fig. 3 where it is apparent that the agreement is excellent.

Given the equation for the activity of water one can, from thermodynamics, calculate the activity of the salt and the total Gibbs energy of mixing. The former is given by equation (1b) or (2b), and the latter by equation (1c) or (2c). Figure 4 shows the Gibbs energy of mixing for the two systems as well as that for an ideal solution with $w = 0$. It is clear that the deviations from ideality are substantial; indeed, if w_1 were much larger than that for $(\text{Ag,Tl})\text{NO}_3$, phase separation would occur.

Activity. Debye-Hückel Effects

Although the agreement in Fig. 3 appears to be almost perfect, there is a small discrepancy in the dilute range where the transition occurs from an alternating charge distribution of ions to a random distribution. This is the phenomenon which received much attention from physical chemists in the early years of this century and which was first explained with a simple theoretical equation by Debye and Hückel [11] in 1923. From our present viewpoint, it is interesting that so much attention was given to such a small discrepancy. But we shall see that, from a different viewpoint, the effect is substantial.

Clearly electrostatic forces cause a departure from a random distribution of ions throughout the composition range except in the limit of infinite dilution. Possibly this departure from randomness is nearly constant at most compositions; this would be consistent with, but probably is not required for, the observed agreement with equation (1). In any case, the ionic distribution does become random in the limit of zero solute concentration, and it is desirable to include this aspect in a more complete equation. This can be accomplished by adding a Debye-Hückel term to equation (1). We wish to use mole fraction (on an ionized basis) as the measure of composition. Also it seems best to adopt an extended form of Debye-Hückel equation which gives some recognition to the repulsive forces between ions. The form obtained by the writer [15, 16] from the pressure equation of statistical mechanics is especially simple for the solvent activity; with conversion to a mole fraction basis, the electrical contribution to the activity coefficient of the solvent becomes

$$\ln \gamma_1^{el} = 2(1000/M_1)^{1/2} A_\phi I_x^{3/2} / (1 + \rho I_x^{1/2}) \quad (3)$$

where M_1 is the molecular weight of the solvent and A_ϕ is the usual Debye-Hückel parameter (for molality and the osmotic coefficient).

$$A_\phi = (1/3)(2\pi N_o d_w / 1000)^{1/2} (e^2 / DkT)^{3/2} \quad (4)$$

I_x is the ionic strength on a mole fraction basis

$$I_x = \frac{1}{2} \sum z_i^2 x_i \quad (5)$$

where x_i is the mole fraction of ion i . Also ρ is a parameter related to the closest approach of ions but increased by the factor $(1000/M_1)^{1/2}$ from the parameter b used on the molality basis.

For our case of a 1-1 electrolyte these equations reduce to

$$I_x = \frac{1}{2} x_2 \text{ and}$$

$$\ln \gamma_1^{el} = (500/M_1)^{1/2} A_\phi x_2^{3/2} / (1 + \rho x_2^{-1/2} x_2^{1/2}) \quad (6)$$

For both of the examples considered here the value, $\rho = 14.9$, was found to be quite satisfactory for the "closest approach" parameter [1]. As noted above this parameter is much larger on a mole fraction basis than that for molality or molar concentration.

If this expression for the electrostatic contribution is combined with equation (1), we have (for a 1-1 electrolyte)

$$\ln \gamma_1 = w_1 z_2^2 + (500/M_1)^{1/2} A_\phi x_2^{3/2} / (1 + \rho x_2^{-1/2} x_2^{1/2}) \quad (7)$$

$$a_1 = x_1 \gamma_1 \quad (8)$$

This expression fits the experimental data for the two systems

$(Ag, Tl)NO_3-H_2O$ and $(Li, K)NO_3-H_2O$ very well with standard deviations in a_1 of 0.003 and 0.002, respectively. The parameters are $w_1 = 0.835$, $(b_1/b_2) = 0.56$ for $(Ag, Tl)NO_3-H_2O$ at $98.5^\circ C$. For $(Li, K)NO_3-H_2O$ the

data are at 119°C near the fused salt and at 100°C for the less concentrated solutions. Since w represents an energy divided by kT , the w values were adjusted correspondingly, with the result $w_1 = -1.124$ at 100°C, -1.070 at 119°C, $(b_1/b_2) = 1.0$. The Debye Hückel parameter, $A_\phi = 0.461$ at 100°C, was taken from Bradley and Pitzer [17].

The Debye-Hückel term in equations (6) and (7) has no theoretical significance beyond the dilute range, possibly $x_2 < 0.1$, but it is a very smooth function of small magnitude over the concentrated range. Hence its effect for concentrated solutions can be compensated by small changes in w_1 and (b_1/b_2) .

Other thermodynamic properties may be derived from equation (3) for the Debye-Hückel or electrical effect. The electrical, excess Gibbs energy is

$$\Delta G^{\text{ex,el}}/RT = -(\sum n_k)(1000/M_1)^{1/2} (4A_\phi I_x/\rho) \ln(1 + \rho I_x^{1/2}) \quad (9)$$

where the sum includes all species, neutral as well as ions. For the electrical, excess Gibbs energy of mixing of a single 1-1 salt with a solvent this yields

$$\frac{\Delta G_m^{\text{ex,el}}}{RT} = 2n_2 \left(\frac{1000}{M_1} \right)^{1/2} \left(\frac{2A_\phi}{\rho} \right) \ln \left(\frac{1 + \rho^{1/2}}{1 + \rho^{1/2} x_2^{1/2}} \right) \quad (10)$$

This expression can be added to equation (1c) or equation (2c) to yield the complete equation for the Gibbs energy of mixing.

For the activity of the solute we will consider here only the case of a single 1-1 salt and the pure fused salt standard state, i.e., $a_2 = 1$ at $x_2 = 1$. The activity coefficient is defined by the relationship

$$a_2 = x_2^2 \gamma_{\pm}^2. \quad (11)$$

The full expression for the solute activity coefficient is then

$$\ln \gamma_{\pm} = w_2 z_1^2 - \left(\frac{500}{M_1}\right)^{1/2} A_{\phi} \left\{ \left(\frac{2^{3/2}}{\rho}\right) \ln \left(\frac{1 + \rho 2^{-1/2} x_2^{1/2}}{1 + \rho 2^{-1/2}} \right) + \frac{x_2^{1/2} - x_2^{3/2}}{1 + \rho 2^{-1/2} x_2^{1/2}} \right\} \quad (12)$$

The definitions for solute activity for different valence types, for multicomponent systems with mixed salts, and for the infinitely dilute standard state (as well as the pure fused salt standard state) are complicated, and the optimum set of definitions is not obvious. A possible pattern of definitions was proposed in an earlier paper [1], but it now appears that some changes should be made. The writer expects to return to this question soon.

Figures 5 and 6 show the curves of $\ln \gamma_1$ and $\ln \gamma_{\pm}$ for the systems (Li,K)NO₃ and (Ag,Tl)NO₃, respectively. On Fig. 5 only the experimental points for 100°C are shown; the 119°C data are shown on Fig 3. The solid curves show the results when a Debye-Hückel term is included; the dashed curves are for the case when it is omitted, i.e., equation (1). The difference for $\ln \gamma_1$ can be seen only on the expanded scale of the inset in Fig. 5 where the lower dashed curve gives the simple fit with $\ln \gamma_1 = 0$ at $x_1 = 1$. The data near $x_1 = 0.8$ can be fitted even better if equation (1a) is modified to allow a small offset of $\ln \gamma_1$ at infinite dilution, and this is shown as the upper dashed curve in the inset.

One can view the curves for $\ln \gamma_{\pm}$ as arising from the integration of the Gibbs-Duhem equation from the pure fused salt ($x_1 = 0$). Up to $x_1 \approx 0.8$ the result is unambiguous and only a single curve is shown. Thereafter, however, the slope $\partial \ln \gamma_1 / \partial x_1$ is slightly smaller for the

true curve than is given by equation (1a). Since this slope is multiplied by $[-x_1/(1-x_1)]$ in the integration, the effect of the small change in slope becomes very large as $x_1 \rightarrow 1$. Thus there is a large difference between the two curves for solute activity coefficient in the dilute region.

From Fig. 5 we see that the Debye-Hückel effect is important for solute activity of very dilute solutions even though its effect is small for concentrated solutions or for solvent activity. But more important and less widely recognized is the fact that it is the net effect of short-range forces which is the primary determinant of the thermodynamic properties of these ionic solutions over most of the range of composition. It is this conclusion that I wish to carry over into further discussion of concentrated electrolytes.

Activity. More Complex Treatments

Let us now consider systems that may not be described adequately by equation (1) with two disposable parameters (or equation (2) with one parameter). Also cases of large but limited salt solubility are of much greater general importance than those completely miscible, yet the essential characteristics of very concentrated ionic solutions are the same whether the pure salt is a liquid or a very soluble solid. If the pure salt is not liquid at the temperature of interest, one cannot refer solute activities to that standard state, but other methods are available. The infinitely dilute standard state is the conventional choice, but there are advantages in some cases in the use of a "hydrated fused salt" reference state.

While mole fraction has many advantages as a measure of composition, the use of molality is so widely established for aqueous electrolytes that there are merits in its use when feasible. The pure fused salt has an infinite molality; hence molality must be abandoned for completely miscible systems. But molality can be used satisfactorily for many systems of large but finite solubility.

The use of a hydrated fused salt reference state is illustrated by Fig. 7 which shows the Gibbs energy of mixing a 13 molal solution ($x_2 = 0.319$) with water for HClO_4 , LiNO_3 and AgNO_3 along with the curve for an ideal solution. Robinson and Stokes [10] give the activity and osmotic coefficients needed to calculate these curves. Again the large departures, both positive and negative, from ideality are apparent. For AgNO_3 the positive deviation approaches that for phase separation.

Since the van Laar equation worked so well for the two systems discussed above, one naturally considers equations that have been successful for somewhat more complex nonelectrolytes. Prausnitz [14] discusses several such systems including the Redlich-Kister expansion. Exploratory calculations of this type were not encouraging; a large number of terms were required for an accurate fit even for cases where the behavior appeared to be quite simple.

Stokes and Robinson [18] successfully treated nine exceedingly concentrated ionic solution systems with equations based on a successive ion hydration model. They assumed that the cations were hydrated, but the mathematics would be unchanged for the symmetrical electrolytes if the hydration were ascribed to the anions. The successive hydration equilibrium constants for the addition of one water molecule were described by two parameters as follows: $K_1 = K$, $K_2 = Kk$, $K_3 = Kk^2$, $K_4 = Kk^3, \dots$. They included a Debye-Hückel term with a repulsive

diameter, usually $4\text{\AA}$; also they limited the hydration equilibria to a maximum number of water molecules ranging from 4 to 9. Thus if one counts the maximum hydration number but not the Debye-Hückel diameter, they had three disposable parameters. They used volume fraction statistics but used experimental volumetric data so no adjustable parameters were added thereby. The osmotic coefficient was the property fitted and their results are summarized in Table 1. While the standard deviations exceed somewhat the experimental uncertainties, the results are impressive. Also the values of the parameters are qualitatively consistent with other evidence. For example $K_1 = K$ is very large for HClO_4 indicating almost complete hydration to H_3OClO_4 . On the other hand the large differences in parameters between HCl and HClO_4 , between LiCl and LiBr , and again between CaCl_2 and CaBr_2 indicates that the hydration is strongly influenced by anions as well as cations.

Virial coefficient expansions have been used to represent the properties of concentrated electrolytes. A Debye-Hückel term is included together with a power series in molality. For a pure electrolyte, this yields

$$\ln \gamma = D-H(m^{1/2}) + Bm + Cm^2 + Dm^3 + \dots \quad (13)$$

where the Debye-Hückel term $D-H$ may contain an adjustable repulsive diameter or may, following Guggenheim, use a standard value for that parameter. An example of this method is the treatment of CaCl_2 to 10 molal by Staples and Nuttall [19]. They used seven virial coefficients in addition to an adjustable repulsive diameter. The last six virial coefficients alternate in sign. The representation of the data is good, but the physical significance of such a series of virial coefficients is doubtful.

For nonideal gases the second virial coefficient is related by theory to binary intermolecular interactions, the third virial coefficient to ternary interactions, etc. The theory for ionized systems is more complex. However, Mayer [20] has shown that the virial expansion of equation (13) is valid but with an ionic strength (I) dependence for the virial coefficients. That dependence is of practical importance only for the second virial coefficient B . The writer [15] showed that there was also strong empirical support for an ionic strength dependence of B with a sharp variation at low I but a rapid approach to a constant value at large I . On this basis Pitzer and Mayorga [21] were able to represent accurately the thermodynamic properties of a very large number of electrolytes up to about 6 molal with a standard D-H term and only the second and third virial coefficients. The ionic strength dependence of B was expressed by a single parameter specific to each solute. Thus, with the constant component of B and the value of C , there were only three adjustable parameters fitted to each pure electrolyte. Also the third virial coefficient was much smaller than the second -- frequently by two orders of magnitude. While there has been no detailed structural interpretation of these virial coefficients, it is plausible that they represent binary and ternary interionic interactions in the presence of the solvent.

Mixed Electrolytes

The real world is concerned primarily with mixed electrolytes which are of great importance as natural waters, including seawater, and in various industrial processes. Virial expansion equations are readily extended to multicomponent systems but become hopelessly complicated if

high order coefficients are involved. But there is only a single cross or mixing second virial coefficient. Also, if we exclude interactions of three ions of the same sign, there is only a single mixing term at the third level. It is possible to evaluate these terms from simple mixtures with a common ion, such as $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{H}_2\text{O}$, whereupon one may predict the properties of mixed electrolytes of unlimited complexity.

The basic equation [15] in this system is

$$\Delta G^{\text{ex}}/n_w RT = f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \quad (14)$$

where ΔG^{ex} is the excess Gibbs energy, n_w is the number of kg of water, I is the ionic strength, $f(I)$ is a standard Debye-Hückel term, λ_{ij} is a second virial coefficient with ionic strength dependence, and μ_{ijk} is a third virial coefficient. The complete development of this system is lengthy, although straightforward, and was first presented in full for mixed electrolytes by Pitzer and Kim [22]. It has now been given in many papers; hence it will not be repeated here. The general strategy is to combine the λ 's and μ 's in sums or differences corresponding to electrical neutrality. The sum combinations can be evaluated from pure electrolytes and the differences from simple mixtures.

Following the initial application [22] to a considerable array of examples, many other investigators have applied these virial coefficient equations to mixed electrolyte systems. They have proven to be very effective up to saturation for most cases of practical interest. A very impressive application was that of Harvie and Weare [23] who calculated the entire array of solubility equilibria for the system related to seawater evaporation: $\text{Na}-\text{K}-\text{Mg}-\text{Ca}-\text{Cl}-\text{SO}_4-\text{H}_2\text{O}$. The invariant points of this system involve four solid phases and there are thirteen

such invariant points in this case. Harvie and Weare calculated the solution compositions as shown in Table 2. The results agree with the experimental values of Braitch [24] essentially within experimental uncertainty, in each case. While Harvie and Weare evaluated a few previously undetermined small terms, essentially all of the parameters were taken from the earlier papers of Mayorga, Kim, and the writer [21, 22]. Thus the Harvie and Weare calculations constituted predictions of the liquid phase composition, and they extend to many other solubility relationships in addition to the invariant points of Table 2. In several cases previous attempts to calculate these equilibria had yielded serious discrepancies.

The basic statistical mechanical theory for ionized systems [25] gives, in addition to the Debye-Hückel limiting law, various higher-order terms of a purely electrostatic nature. Specifically, these terms depend only on the charges on the ions and the electrical properties of the solvent. Most of these higher-order electrical terms are of no practical importance. They are either negligible or can be included within the virial coefficients without separate consideration. But the higher-order terms for unsymmetrical mixing, i.e., mixing ions of different charge of the same sign, are significant and have a strong ionic strength dependence [26]. A term of this type falls within equation (14) as a contribution to a difference of λ_{ij} 's with special dependence on I ; short range forces contribute in addition a constant term. Since these special electrical terms are fully determined by the ion charges and the properties of water, they do not constitute additional empirical parameters. One example of their importance arises for the solubility of gypsum in sodium chloride solution or seawater. Harvie and Weare

[23] included these terms in their solubility calculations and noted their importance for this case. Rogers [27] has further demonstrated the importance of these terms in a very precise and complete study of gypsum solubility in various solutions containing one or more of NaCl , CaCl_2 , Na_2SO_4 as well as in seawater. Figure 8 shows the effect of the higher-order electrical terms on the activity of CaSO_4 in NaCl solutions saturated with gypsum; the experimental points are from Briggs [28]. It is apparent that this effect is significant for highly concentrated solutions.

From these various results one may reach several conclusions:

1. In ionic systems at high concentration the electrical forces induce a structural pattern with alternation of positive and negative charges. Since this pattern remains essentially constant and by shielding converts long-range coulombic forces into short-range forces, it is ordinarily possible to express the change of properties with composition in the concentrated range without explicit terms for long-range electrical effects.
2. It is the relative strength of short range interspecies attractive forces, i.e., ion hydration in comparison with other effects, which dominates the composition dependence of solution behavior. This effect can be expressed by the same types of equation used for non-electrolytes; virial coefficients, regular solution, speciation by association, etc.
3. Special effects arising from long-range electrical forces do need to be considered explicitly in certain composition ranges: (a) dilute solutions and (b) solutions involving unsymmetrical mixing of ions of the same sign.

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Table 1

Parameters of the Stokes and Robinson treatment for aqueous solutions
at 25°C

Solute	a, Å	n	K	k	σ^a	Max. Molality
KOH	4	5	150.2	0.303	0.018	16
NaOH	4	4	77.6	0.375	0.018	29
HCl	4	6	135	0.338	0.019	16
HClO ₄	4	5	2527	0.192	0.044	16
LiCl	4	5	81.6	0.414	0.015	20
LiBr	4	5	492	0.290	0.017	20
NaCl	3.5	3	61.1	0.368	0.008	6
CaCl ₂	4	9	48.7	0.678	0.041	10
CaBr ₂	4	9	804.6	0.595	0.014	8

^a Standard deviation of osmotic coefficient.

Table 2

Invariant points for the quinary system Na-K-Mg-Cl-SO₄-H₂O at 25°C calculated by Harvie and Weare. Experimental values of Bräitsch are in parentheses

m_{Na}	m_{K}	m_{Mg}	m_{SO_4}	Solid Phases
2.62 (2.69)	1.63 (1.58)	2.08 (1.97)	.84 (.78)	Halite + Sylvite + Glaserite + Schoenite
2.52 (2.41)	1.59 (1.51)	2.16 (2.19)	.84 (.78)	Halite + Leonite + Sylvite + Schoenite
1.16 (1.31)	1.01 (1.10)	3.40 (3.17)	.86 (.79)	Halite + Sylvite + Leonite + Kainite
.48 (.49)	.57 (.64)	4.21 (4.05)	.32 (.29)	Halite + Sylvite + Carnallite + Kainite
.30 (.26)	.22 (.20)	4.75 (4.81)	.40 (.35)	Halite + Kieserite + Carnallite + Kainite
5.20 (5.32)	1.04 (.90)	.95 (.89)	1.31 (1.24)	Halite + Thenardite + Glaserite + Bloedite
3.08 (3.21)	1.31 (1.30)	2.00 (1.85)	1.14 (1.06)	Halite + Glaserite + Bloedite + Schoenite
2.49 (2.96)	1.18 (1.22)	2.40 (2.01)	1.11 (1.05)	Halite + Bloedite + Schoenite + Leonite
1.43 (1.25)	.85 (.72)	3.31 (3.46)	1.14 (1.10)	Halite + Epsomite + Bloedite + Leonite
1.16 (1.18)	.85 (.75)	3.51 (3.54)	1.03 (1.04)	Halite + Epsomite + Leonite + Kainite
.76 (.66)	.50 (.68)	3.95 (4.01)	.81 (.79)	Halite + Kainite + Hexahydrate + Epsomite
.40 (.33)	.23 (.32)	4.57 (4.63)	.59 (.45)	Halite + Kainite + Hexahydrate + Kieserite
.09 (.07)	.02 (.02)	5.74 (5.83)	.06 (.05)	Halite + Bischofite + Kieserite + Carnallite

Figure Captions

1. Degree of ionization as indicated by the viscosity-conductance product. A is $\text{LiClO}_3\text{-H}_2\text{O}$, B is tetra-n-butylammonium picrate -- n-butyl alcohol, C is acetic acid - water.
2. The activity of water for water-salt solutions over the full range of composition.
3. Comparison of the experimental activity of water with that calculated from equation (1).
4. The Gibbs energy of mixing of fused salts with water.
5. The activity coefficients of water and of the salt over the full range of composition. The dashed lines omit the Debye-Hückel effect whereas the solid curves include it.
6. The activity coefficients of water and of the salt over the full range of composition. The dashed curve omits the Debye-Hückel effect whereas the solid curve includes it.
7. The Gibbs energy of mixing of water with concentrated solutions (hydrated fused salts).
8. The activity coefficient of CaSO_4 in solutions of NaCl saturated with gypsum (from Rogers [27]).

Figure 1. Degree of ionization as indicated by the viscosity-conductance product. A is $\text{LiClO}_3\text{-H}_2\text{O}$, B is tetra-n-butylammonium picrate -- n-butyl alcohol, C is acetic acid - water.

Figure 2. The activity of water for water-salt solutions over the full range of composition.

Figure 3. Comparison of the experimental activity of water with that calculated from equation (1).

Figure 4. The Gibbs energy of mixing of fused salts with water.

Figure 5. The activity coefficients of water and of the salt over the full range of composition. The dashed lines omit the Debye-Hückel effect whereas the solid curves include it.

Figure 6. The activity coefficients of water and of the salt over the full range of composition. The dashed curve omits the Debye-Hückel effect whereas the solid curve includes it.

Figure 7. The Gibbs energy of mixing of water with concentrated solutions (hydrated fused salts).

Figure 8. The activity coefficient of CaSO_4 in solutions of NaCl saturated with gypsum (from Rogers [27]).

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