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THERMODYNAMICS OF CONDENSED IONIC SYSTEMS

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ABSTRACT

In considering the thermodynamics of condensed ionic systems, primary emphasis will be given to those types which have not been widely investigated, at least until recently. Special attention will be given to systems continuously miscible from the fused salt to dilute solution in a polar solvent. Mixed fused salts will also be considered as well as phase separation and critical phenomena for any type of ionic system. The most important theories are given briefly; the status of more complex or less important theories is described. Semi-empirical equations are discussed where they are the best method of representing the experimental data.

1. INTRODUCTION

Condensed liquids or solids may be broadly classified into three types, metals, salts, and molecular liquids or solids, and mixtures of any one, two, or possibly all three types. Pure substances or mixtures of a given type are now quite well investigated, at least with respect to structure and thermodynamic properties, although much remains to be learned about fused salts (ionic liquids) at very high temperatures. But mixtures of components of different types are relatively novel and of particular current interest.

The primary emphasis in this paper will be on mixtures of molecular and ionic liquids with some comparative discussion of mixed fused salts and other systems. Very dilute solutions of

salts in water have been widely studied and Debye-Hückel theory provides a basis for their description. But for solvents of lower dielectric constant or for multiple charged ions, there are complications which will be discussed. Emphasis will also be given to systems concentrated in the ionic component. Some systems are completely miscible to the fused salt; others show two liquid phases while still others have a high but limited solubility of a solid salt.

Ionic systems differ from nonelectrolytes because of the long-range nature of coulombic forces. The first result is the extreme limitation on any inequality of density of positive and negative charges. For almost all purposes one may assume exact electroneutrality. Often this electroneutrality applies on such a small scale that the long-range aspect of interionic forces is effectively eliminated; one says that these forces are screened and only the short-range component is still effective. Then the properties of the system can be calculated by methods essentially similar to those for nonelectrolytes. But if an ionic solution becomes dilute, in a solvent or in a gaseous plasma, the screening is eventually lost and a different treatment is necessary.

Another basic factor is the relative magnitude of the electrical or coulombic interaction energy compared to thermal energy. If the maximum coulombic energy is comparable to or less than thermal energy, the electrical forces will be called weak. Certain approximations and corresponding properties arise for weak electrical forces in contrast to other behavior for strong electrical forces.

More precisely we define an electrical length

$$\ell = \beta e^2 / 4\pi\epsilon_0 D \quad (1)$$

where e is the protonic charge, D the dielectric constant or relative permittivity and ϵ_0 is the permittivity of free space. Most of the literature on electrolyte solutions, however, is written in electrostatic units (esu); the corresponding equations are obtained by substituting $(4\pi)^{-1}$ for ϵ_0 . If the shortest interionic distance is a and the ionic charges are z_i and z_j , the criterion becomes $z_i z_j \ell / a$. If this quantity significantly exceeds unity, then the electrical forces are strong; otherwise they are weak.

In some cases, plasmas for example, a fixed minimum interionic distance may not be defined. Comparison of a mean interionic distance, $c^{-1/3}$, with ℓ is then useful, but the quantity $z_i z_j \ell c^{1/3}$ is not a maximum ratio of coulombic to thermal energy.

We now turn to the theory which describes the transition from a random distribution of ions at low concentration in a solvent to an alternating charge distribution at high concentration.

2. SCREENING OF INTERIONIC FORCES

2.1 Debye-Hückel Theory

The special properties of dilute electrolytes constituted a major puzzle for physical chemists in early years of this century. It had already been determined empirically that there was an unexpected square root dependence on concentration for several properties when in 1923 Debye and Hückel (1) (DH) proposed a beautifully simple theory which confirmed this result and provided both working equations and a physical picture of dilute electrolytes. In particular, the theory gave the screening relationship for the interionic potential.

There are two major portions of Debye-Hückel theory: (1) the derivation of the distribution function for the charge density and (2) the derivation of macroscopic thermodynamic or kinetic properties. Since there are now much improved methods for the second step (2), the original imaginary charging process will not be presented. But the original Poisson-Boltzmann method is still a most valuable approach to the first step and we now review it.

One begins by considering a local electrostatic potential $\psi_i(r)$ in the vicinity of an ion i . This must conform to the Poisson equation

$$\nabla^2 \psi_i(r) = -\rho_i(r)/\epsilon_0 D \quad (2)$$

where $\rho_i(r)$ is the mean charge density.

Next it is assumed that the local concentration of ions is influenced by their electrostatic energy in accordance with the Boltzmann relationship. Thus the radial distribution functions for ions of charges $z_j e$ around the ion of charge $z_i e$ are

$$g_{ij} = \exp[-\beta z_j e \psi_i(r)] \quad (3)$$

where $\beta = (kT)^{-1}$. With average ion concentrations c_j , the mean charge density becomes

$$\rho_i = \sum_j c_j z_j e g_{ij} \quad (4)$$

If this expression is substituted into the Poisson equation, no simple solution can be obtained. Debye and Hückel made the drastic but still useful assumption that the electrical forces were weak, i.e., that the electrostatic energy was small enough in relation to thermal energy that the exponential in g_{ij} could be expanded and only the first two (linear) terms retained, yielding

$$\rho_1 = \sum_j c_j z_j e - \sum_j c_j z_j^2 e^2 \beta \psi_1(r) \quad (5)$$

It is apparent that the first term on the right is just the mean charge density which must be zero. The Poisson equation now becomes

$$\nabla^2 \psi_1 = \kappa^2 \psi_1 \quad (6)$$

with

$$\kappa^2 = 4\pi\ell \sum_j c_j z_j^2 \quad (7)$$

This linearized Poisson-Boltzmann equation is easy to solve. With a hard-core, ionic diameter a employed in the boundary conditions, one obtains ψ_1 and then, if for the moment we ignore the linearization approximation, the distribution functions

$$g_{ij} = \exp(-z_i z_j q) \quad (8)$$

with

$$q = [\ell/(1 + \kappa a)r] \exp[-\kappa(r-a)] \quad (9)$$

The most important aspect of this result is the final factor which shows that the effect of the central charge diminishes exponentially as $\exp(-\kappa r)$. Thus κ^{-1} is the screening length, and electrostatic forces are converted to short-range forces if κr is large. Indeed, if κa is large, all of the interionic interactions are effectively short range. Note also that κ^2 contains the factor $\sum_j c_j z_j^2$. In macroscopic (molality) units this is called the ionic strength which is defined as

$$I = (1/2) \sum_i m_i z_i^2 \quad (10)$$

with m_i the molality of the i^{th} ions. If the ionic strength is high, the electrical forces are strongly screened. The linearized charge density is

$$\rho_1 = -z_1 e q \sum_j c_j z_j^2 \quad (11)$$

The second step, the statistical derivation of thermodynamic properties is now best carried out by a method that considers short-range as well as electrostatic forces. This is done on the McMillan-Mayer basis at osmotic equilibrium between solution and pure solvent. One method is the pressure or virial equation which yields the pressure of a plasma or the osmotic pressure for a solution

$$p = \frac{c}{\beta} - \left(\frac{1}{6}\right) \sum_i \sum_j c_i c_j \int_0^\infty r \frac{\partial u_{ij}}{\partial r} g_{ij} 4\pi r^2 dr \quad (12)$$

where c is the total concentration and u_{ij} is the interparticle potential, which is assumed to be pairwise additive. The first term c/β is just the ideal-gas or ideal-solution term. After an appropriate treatment for the hard core repulsion at $r = a$, one has

$$p = c/\beta - (1/6) \sum_i \sum_j c_i c_j \int_a^\infty (\partial u_{ij}/\partial r) g_{ij} 4\pi r^3 dr \\ + (2\pi a^3/3\beta) \sum_i \sum_j c_i c_j g_{ij}(a) \quad (13)$$

where $g(a)$ is the value of $g(a+\epsilon)$ as $\epsilon \rightarrow 0$. The osmotic coefficient for a solution is

$$\phi = \beta p/c \quad (14)$$

provided that p is now the osmotic pressure.

The first double sum on the right in equation 13 relates to the electrostatic forces while the last term arises from the repulsive forces of the hard cores. It is the former that is unique for ionic systems and is of special interest. With the linearized charge distribution the electrical and ideal terms yield

$$p(1+e\ell) = c/\beta - \kappa^3/24\pi\beta(1+\kappa a). \quad (15)$$

It is also useful to define the mean square ionic charge

$$\langle z^2 \rangle = \sum_i c_i z_i^2 / c \quad (16)$$

whence

$$\kappa^2 = 4\pi \langle z^2 \rangle \ell c \quad (17)$$

and the osmotic coefficient is

$$\begin{aligned}\phi^{el} - 1 &= -\kappa^3/24\pi c(1+\kappa a) \\ &= -\langle z^2 \rangle_{\ell} \kappa/6(1+\kappa a)\end{aligned}\quad (18)$$

The electrostatic length ℓ was defined earlier; it is about 7 Å for water at room temperature.

One may use the Gibbs-Duhem equation to obtain the activity coefficient from the osmotic coefficient

$$\ln \gamma_{\pm} = \phi - 1 + \int_0^m (\phi - 1) d \ln m. \quad (19)$$

This equation is strictly valid for m the molality rather than the concentration. In dilute solutions molality is quite accurately proportional to the concentration. Then the electrostatic contribution to $\ln \gamma_{\pm}$ is

$$\ln \gamma_{\pm}^{el} = - \frac{\langle z^2 \rangle_{\ell}}{6} \left[\frac{2}{a} \ln(1+\kappa a) + \frac{\kappa}{1+\kappa a} \right]. \quad (20)$$

It is also interesting to obtain the electrical contribution to the Helmholtz energy (or, practically for solutions, the Gibbs energy)

$$A^{el}/V\kappa T = (\kappa^2/12\pi a) \ln(1+\kappa a) \quad (21)$$

or

$$A^{el}/N\kappa T = -(\langle z^2 \rangle_{\ell}/3a) \ln(1+\kappa a). \quad (22)$$

In the limit at low concentration κa becomes small as compared to unity and one obtains the Debye-Hückel limiting laws (DHLL)

$$\ln \gamma_1^{el} = -\langle z^2 \rangle_{\ell} \kappa/2 \quad (23)$$

$$\phi^{el} - 1 = -\langle z^2 \rangle_{\ell} \kappa/6. \quad (24)$$

Since κ^2 is proportional to c , each of these expressions yields the dependence on the square root of the concentration. It should be remembered, however, that these are valid only if a is large enough to make the linearization approximation valid.

2.2 Exact Solutions for the Primitive Model

Let us turn now to the short-range forces between the ions. The primitive model which has been assumed so far

$$u_{ij} = z_i z_j e^2 / 4\pi\epsilon_0 D r \quad \text{for } r > a \quad (25a)$$

$$u_{ij} = +\infty \quad \text{for } r < a \quad (25b)$$

is quantitatively valid at long distances but purely qualitative at short distances for real systems. The hard core assumption may be reasonably satisfactory as a cut-off for the electrical effects. But one cannot expect this hard core model to represent accurately all of the kinetic effects of short-range forces on the thermodynamic properties of real systems. Nevertheless, the exact mathematical solution for the primitive model is of considerable interest. This problem has received much attention in recent years. While the best solutions are cumbersome mathematically, there is good enough agreement among various methods to give confidence in the results. Probably the Grand Canonical Monte Carlo (GCMC) method of Valleau and Cohen (3) yields the most reliable results for high charge types. Ordinary Monte Carlo as well as several other methods appear to be accurate for 1-1 electrolytes in water. The final results from various methods have been compared in excellent papers by Rasaiah, et al. (4) and by Valleau, et al. (5) for electrical parameters appropriate for aqueous 1-1 and 2-2 electrolytes, respectively, and for low and moderate concentrations.

At higher concentration and for stronger electrical forces the primitive model yields a critical point and separation into two phases. For a plasma, the phases are gas and liquid. For a solution there is a dilute phase with ions largely paired (see Section 5.1 below) and a concentrated phase which is reasonably described as a solvated fused salt. The primitive model has the characteristics required for a theory of corresponding states, i.e., a potential fully determined by length and intensity scaling factors (6). The reduced variables may be taken as

$$c^* = ca^3 \quad (26)$$

$$\beta^* = \langle z^2 \rangle \ell / a. \quad (27)$$

Although the mathematical accuracy is less than for lower ranges of c^* or β^* , the critical point was located by Stell, et al. (7) as near $\beta^* = 0.010$ and $\beta^* = 12$. Friedman and Larsen (8) have given an excellent discussion of corresponding states for the primitive model ionic fluid. We will return to this matter of phase separation below in Section 5.3.

If one's primary interest, however, is in real systems and their measured properties, it is preferable to use semi-empirical methods. Theory does not yet provide accurate results for

realistic models of the short-range, interionic forces (or better, including solvent molecules as well as ions and their various interacting forces). Thus, one is especially interested in simple theoretical equations which represent all important phenomena, even if they are quantitatively approximate with respect to those aspects which will be treated empirically.

2.3 An Extended Debye-Hückel Theory

One very simple but useful equation is obtained (2,9) if the exponentials for the DH distribution functions are expanded to three terms (hence a designation DH3). The result for the osmotic coefficient is

$$\phi-1 = -\frac{\langle z^2 \rangle}{6(1+\kappa a)} \frac{\ell \kappa}{c} + c \frac{2\pi a^3}{3} + \frac{\pi \langle z^2 \rangle \ell^2 a^2}{3(1+\kappa a)^2} \quad (28)$$

The short range forces have introduced two terms; the first is exactly proportional to the concentration and independent of ionic charge. It is just the repulsive term of the van der Waals equation for a non-ideal gas. The last term, which arose from the third terms in the exponential expansions, is also proportional to c at low c but then diminishes as κa becomes comparable to unity.

If one regards a as an empirical quantity, the DH3 equation is rather effective for real systems (9). But much more important are the ideas; the last two terms constitute an apparent "second virial coefficient" with a constant term and a second term diminishing rather rapidly with increase in ionic strength.

2.4 Semi-Empirical Equations

A very successful system of semi-empirical equations is based on these ideas with some modification of the exact mathematical form (9). These equations retain the form of the first term and adopt a standard value of a in that term which is a great convenience in calculations for mixed electrolytes (10). These equations predict successfully the chemical potential of each component of complex electrolyte mixtures from parameters determined from simple electrolytes (10,11).

The treatment of dilute or moderately concentrated aqueous electrolytes has been reviewed elsewhere (12) and will not concern us further. Let us turn now to ionic systems so concentrated that the interionic forces are screened to a short range.

3. MIXTURES WITH FORCES SCREENED TO SHORT RANGE

Among the ionic systems so concentrated that coulombic forces are screened to very short range are molten salts including mixtures of molten salts. There are MC and MD studies of the structure of both pure and mixed fused salts. A recent MD study of the LiCl-KCl mixture by Lantelme and Turq (13) shows very clearly the alternating charge pattern. The Li-Cl and K-Cl distribution functions change only slightly on mixing. The energy of mixing is calculated and agrees quite well with the experimental enthalpy of mixing discussed below. These calculations use a potential including, in addition to the coulombic term, a soft repulsive term and dispersion-force terms with parameters fitted to the properties of the ionic crystals and derived from theory.

Since much of the work on mixed fused salts and other highly screened ionic systems is related to the theories for nonelectrolyte solutions, we review that field briefly.

The statistical mechanics of nonelectrolyte solutions, with truly shortrange intermolecular forces, has been extensively investigated and widely reviewed (14-16). The simplest result is that for random mixing of molecules which yields for the entropy of mixing

$$\Delta_m S = -R \sum_i n_i \ln x_i \quad (29)$$

where a macroscopic, constant-pressure basis is now used with n_i the number of moles of the i^{th} species with mole fraction

$$x_i = n_i / \sum_j n_j. \quad (30)$$

Systems with this entropy of mixing and no heat or volume change or mixing are said to be ideal solutions or mixtures.

The next level of refinement still assumes random mixing but recognizes small differences in the energy of interaction between neighboring molecules. This yields an additional term for the Gibbs energy of mixing

$$\Delta_m G = RT \sum_i n_i \ln x_i + \sum_{i>j} n_i x_j A_{ij}. \quad (31)$$

The parameters A_{ij} are related in simple lattice calculations to the coordination number C , the intermolecular energies ϵ_{ij} , and the Avogadro number N_A as follows:

$$A_{ij} = CN_A(2\epsilon_{ij} - \epsilon_{ii} - \epsilon_{jj})/2. \quad (32)$$

The use of a lattice model for the liquid state is questionable, but the same result has been obtained by other methods also. However, these derivations imply that the various molecules are nearly equal in size and mix without significant change in volume.

If there are only two components, equation 31 becomes

$$\Delta_m G = RT(n_1 \ln x_1 + n_2 \ln x_2) + A n_1 x_2. \quad (33)$$

The chemical potential of either component is conveniently expressed by its activity. These are

$$\ln a_1 = \ln x_1 + A x_2^2 / RT \quad (34)$$

$$\ln a_2 = \ln x_2 + A x_1^2 / RT. \quad (35)$$

These equations are most clearly applicable to simple mixtures of fused salts with a common cation or anion, for example, LiCl-NaCl (17-18). In the disordered lattice of the liquid, it is assumed that anion sites and cation sites remain distinct. The Li^+ and Na^+ are mixed nearly randomly on the cation sites. The mole fractions x_1 and x_2 then refer to fractions among cations. On an ideal basis, i.e., $A = 0$, this is known as the Temptkin model (19).

If both anions and cations are mixed, the extension is clear, at least for random mixing. Now the entropy of mixing is

$$\Delta_m S = -R \left(\sum_i^{+ \text{ions}} n_i \ln x_i^c + \sum_j^{- \text{ions}} n_j \ln x_j^a \right) \quad (36)$$

where the x_i^c are cation fractions and the x_j^a are anion fractions. The total solution must remain electrically neutral, of course.

One can, instead, take all of the ions to be randomly mixed without regard to sign. While this seems a poor approximation for a fused salt near its melting point, it is realized at very high temperature or at high dilution in a solvent. If all ions have the same magnitude of charge, it is readily shown that the entropy of mixing equations on the fully random basis yield the same results as those just given.

Let us demonstrate this for the simple case of the equimolar mixture LiCl-LiBr-NaCl-NaBr. Now the mole fraction of each ion is 1/4 on the fully random basis for the mixture, but it is 1/2 for each ion in a pure salt. Thus

$$\begin{aligned}
\Delta_m S/R &= -\sum n_i (\ln x_i^m - \ln x_i^o) \\
&= -[\ln(1/4) - \ln(1/2)] \sum n_i \\
&= (\ln 2) \sum n_i
\end{aligned} \tag{37}$$

where the sum covers both + and - ions. This is the same result as that given by equation 36 for this example. This equality can be proven (17) for a general composition, but the equations are more complex.

The heat of mixing is obtained by temperature differentiation of equation 31.

$$\Delta_m H = \sum_{i>j} n_i x_j (A_{ij} - T \partial A_{ij} / \partial T). \tag{38}$$

If the statistical model were exactly correct, the A's would be independent of temperature and $\partial A / \partial T = 0$. While this is usually approximately true, it is seldom exactly the case. Then there are small terms involving $\partial A_{ij} / \partial T$ in the entropy of mixing which indicate a departure from purely random mixing. All of this is very reasonable, but it is not easy to construct an exact statistical model showing this behavior.

Table 1. Nonideal Gibbs Energies and Entropies of Mixing of Fused Salts at 933 K

	A/RT	$-R^{-1} \partial A / \partial T$
AgCl-LiCl	1.13	-0.08
AgCl-NaCl	0.43	0.24
AgCl-KCl	-0.46	-0.32

The heat of mixing for a large number of simple fused salts was measured by Hersh and Kleppa (20) who also report work of others on the Gibbs energy of mixing where available. Table 1 gives these results for the AgCl-LiCl, AgCl-NaCl, and AgCl-KCl systems as values of A/RT and $-R^{-1} \partial A / \partial T$. While the latter, the nonideal entropy term, is smaller than the nonideal Gibbs energy term (or the enthalpy term), it is not negligible.

3.1 Corresponding States for Fused Salts

In this case there are useful theories for the nonideality parameter values. A first edition was presented by Reiss, et al. (21,22), and is based on a theory of corresponding states for fused salts. The statistical theory for corresponding states for nonelectrolytes (6) arises from the assumption of a universal function for the intermolecular potential scaled with respect to

distance and energy. This can also be assumed for an ionic system; indeed the primitive, hard-core model, equation 25, is of that form with a the distance factor and $z_i z_j$ the energy factor. One can further note that like-charged ions repel one another, hence the hard core diameter is unimportant for those interactions. The only essential distance factor is that for hard-core repulsion of unlike ions.

Actually a hard core model is not required for corresponding states. It is only necessary that the repulsive force in each salt must follow a universal function with a scaling factor a .

Reiss, et al., showed that many properties of pure fused salts were quite well described by the corresponding states relationships. And they showed by an expansion as conformal solutions that the heat of mixing parameter (our $A_{ij} - T\partial A_{ij}/\partial T$) should be proportional to $[(a_2 - a_1)/a_1 a_2]^2$ where a_1 is taken to be the sum of ionic radii for salt 1 and a_2 the sum of radii for salt 2. This relationship is shown on figure 1. Note that in this case all systems show a positive deviation from ideal behavior.

Davis and Rice (23) extended this development by including terms for ion-induced dipole and dispersion force interactions. The coefficients for these terms were obtained from experiments or theory and are separate from the coulombic term. This is an extension from corresponding states. Hersh and Kleppa (20) discuss their calorimetric results in terms both of the simpler corresponding states theory, which is quite successful for the mixed alkali halides, and in terms of the extended theory which is needed for more complex cases. The Davis and Rice theory can yield the negative deviations from ideal behavior which are observed for the mixtures involving silver salts.

3.2 Other Simple Theoretical Models

There are many other models from which theories have been developed; many are pertinent only to special situations and others seem unduly complex in proportion to their accuracy or relationship to real systems. Two theories do deserve at least brief description. First is the mean field or van der Waals theory adapted to ionic systems. Here it is assumed that the structure of the fluid is determined by the sudden repulsive forces and that attractive forces merely contribute a general cohesive force or mean field. The ionic forces can be shown (24,25) to contribute, approximately, a term $-Ac^{1/3}$ per particle to the energy or $-Ac^{4/3}/3$ to the pressure. Derivation of A is complex but a simple approximation is

$$A = Me^2/8\pi\epsilon_0 D \quad (40)$$

Figure 1. The heat of mixing of fused nitrates with the indicated alkali cations as a function of the conformal solution parameter.

where M is a sort of Madelung constant with a magnitude about 1.75 for a simple 1-1 electrolyte.

For hard-core repulsive forces, one can adopt the excellent Carnahan and Starling (26) expression, and the pressure is then

$$p/ckT = (1 + y + y^2 - y^3)/(1-y)^3 - Ac^{4/3}/3 \quad (41)$$

where $y = \pi a^3 c/6$ is the hard core packing fraction. Similar expressions are available for other thermodynamic properties.

Another simple model is called the mean spherical approximation (MSA). This starts with the Ornstein-Zernicke equation which defines a "direct correlation function" $C_{ij}(r)$.

$$g_{ij}-1 = C_{ij} + \sum_k c_k \int (g_{ik}-1) C_{kj} d^3 r_k. \quad (42)$$

This direct correlation function is expected to depend primarily on the "direct" potential between a pair of particles with little regard for more distant particles. Specifically, the MSA assumptions for an ionic system are (27,28)

$$C_{ij}(r) = -z_i z_j e/r \quad \text{for } r > a \quad (43a)$$

$$g_{ij}(r) = 0 \quad \text{for } r < a. \quad (43b)$$

These equations can be solved for the pair distribution functions.

There are several ways of deriving thermodynamic properties from approximate pair distribution functions. In this case the result from the virial equation is much less satisfactory than that from the so-called energy equation. In this case the internal energy is first calculated for infinite temperature for the hard core model. Then it is integrated to finite temperature including electrical effects, and finally differentiated with respect to volume to yield the pressure. The results are first stated as differences of the ionic system from that of uncharged hard spheres. For the Helmholtz energy one obtains

$$\frac{A}{VRT} = \frac{\tilde{A}}{VRT} + \frac{3x^2 + 6x + 2 - 2(1+2x)^{3/2}}{12\pi a^3} \quad (44)$$

with $x = \kappa a$ and $\tilde{A}$ the Helmholtz energy of the uncharged system at the same concentration. The osmotic coefficient is

$$\phi = \tilde{\phi} + \frac{3x[1 + (1+2x)^{1/2}] - 2(1+2x)^{3/2} + 2}{12\pi a^3 c} \quad (45)$$

where $\tilde{\phi}$ is the value for the uncharged system. Again the Carnahan and Starling (26) expression can be used for the uncharged system and the result is an analytical expression which is easily evaluated.

The MSA is a linearized theory and subject to the same limitation as Debye-Hückel theory to electrostatic energies less than or about equal to thermal energy. For this range of weak electrostatic forces, MSA gives a good approximation for the hard sphere model even to very high concentrations. In view of the simplicity of the final results, it is quite useful.

There have been many efforts to apply the MSA to hard spheres of different sizes or other more complex models (29,30). Other work (31) has developed extensions of MSA to correct approximately for the linearization approximation. The simplicity of the MSA result is lost, however, in these extensions which require fairly extensive calculations. There has been little use of either the simple MSA or its extensions for mixed systems but it has been shown to be fairly satisfactory for pure fused salts. Although electrical forces are very strong for fused salts, they are very strongly screened.

4. MISCIBLE FUSED SALT - MOLECULAR LIQUID SYSTEMS

4.1 Range for Full Screening

Mixtures of polar molecular liquids such as water with fused salts are more complex than mixed fused salts and few examples have been investigated. High pressure is required to confine the solvent as a liquid at the melting point of most salts. There are a few examples where a mixture of two salts was used to reduce the melting point. If the salt composition is fixed, the system can be treated as having two components.

Consider first the range of high concentration where the screening is great enough that Debye-Hückel effects can be ignored. Figure 2 shows the solvent water activity as function of mole fraction for a number of examples, some of limited but large solubility. The sources of these experimental data are given in references (32) and (33). The curves are very similar to those for nonelectrolyte solutions with examples of both positive and negative deviations from ideality.

Since the salt is assumed to be fully dissociated, the composition variable is the mole fraction on an ionized basis. It was noted above, Section 3, that the use of mole fractions based on full mixing of all ions gave the correct results for mixed fused salts even though the charge alternation pattern is certainly dominant. In other words the decrease in entropy because of nonrandomness of distribution of positive and negative ions remains essentially constant as the system is diluted by some additional particles. With n_2 moles of a salt of formula MX and n_1 moles of solvent, one has

Figure 2. Activity of water for water-salt solutions over a very wide range of composition.

$$x_1 = n_1 / (n_1 + 2n_2) \quad (46a)$$

$$x_2 = 2n_2 / (n_1 + 2n_2) \quad (46b)$$

and the equations corresponding to 31 and 35 are

$$\Delta G_m = RT(n_1 \ln x_1 + 2n_2 \ln x_2) + An_1 x_2 \quad (47a)$$

$$\ln a_1 = \ln x_1 + Ax_2^2 / RT \quad (47b)$$

$$\ln a_2 = 2(\ln x_2 + Ax_1^2 / RT). \quad (47c)$$

The meaning of A is now slightly different than that for nonelectrolytes, equation 32 above. Now

$$A = CN_A (\epsilon_{MS} + \epsilon_{XS} - \epsilon_{MX} - \epsilon_{SS}) / 2 \quad (48)$$

where M, X refer to the ions and S to the solvent. Thus a negative A indicates that the ion hydration energies are larger, more negative, than the sum of the ion-ion and solvent-solvent attractions. The ion-ion interaction is, of course, on a short-range, screened basis. These equations fit the data for (Li,K)NO₃-H₂O quite well. But for other systems and for better agreement, somewhat more flexible equations are required. In the case of nonelectrolytes, it is well-known since the work of van Laar (34)

and especially since that of Scatchard (35) and of Hildebrand (36) that the nonideality term should involve a volume fraction rather than a mole fraction if the species have substantially different sizes. If q_1 's are proportional to the molecular volumes, one obtains

$$\Delta_m G = RT(n_1 \ln x_1 + 2n_2 \ln x_2) + a_{12} q_1 n_1 Z_2 / RT \quad (49a)$$

$$\ln a_1 = \ln x_1 + a_{12} q_1 Z_2^2 / RT \quad (49b)$$

$$\ln a_2 = 2(\ln x_2 + a_{12} q_2 Z_1^2 / RT) \quad (49c)$$

$$Z_1 = n_1 q_1 / (n_1 q_1 + 2n_2 q_2) \quad (49d)$$

$$Z_2 = 2n_2 q_2 / (n_1 q_1 + 2n_2 q_2) \quad (49e)$$

Only the ratio q_1/q_2 is significant; hence one may take $q_2 = 1$ and omit it hereafter. Often q_1 is adjusted freely without restriction to the actual volume ratio. Now the agreement with the systems (Ag,Tl)NO₃-H₂O and (Li,K)NO₃-H₂O is excellent up to solvent mole fraction at least 0.8 as shown on figure 3. The parameters are, respectively, $q_1 = 0.50$, $a_{12}/RT = 2.04$ and $q_1 = 1.2$, $a_{12}/RT = -0.74$ for the two examples. In each case the cation fraction is approximately 0.5 for the mixed salt.

Figure 3. Comparison of the calculated and experimental activity of water for water-salt solutions over the full range of composition.

4.2 Debye-Hückel Effects

Although the agreement in figure 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 can be corrected by adding a Debye-Hückel term to equation 49. We begin by conversion of equation 18 to mole fractions and to a solvent activity coefficient instead of an osmotic coefficient, which yields

$$\ln \gamma_1^{el} = 2A_x I_x^{3/2} / (1 + \rho I_x^{1/2}) \quad (50)$$

where A_x is the Debye-Hückel parameter on a mole fraction basis.

$$A_x = (1/3)(2\pi N_0 d_1 / M_1)^{1/2} \ell^{3/2}. \quad (51)$$

M_1 is the molecular weight of the solvent and d_1 the solvent density. I_x is the ionic strength on a mole fraction basis

$$I_x = \frac{1}{2} \sum z_i^2 x_i \quad (52)$$

where x_i is the mole fraction of ion i . Also ρ is a parameter related to the closest approach of ions by the relationship (for a mole fraction basis)

$$\rho = a(8\pi \ell N_A d_1 / M_1)^{1/2}. \quad (53)$$

The complete equation for the solvent activity is

$$\ln a_1 = \ln x_1 + a_{12} q_1^2 Z_2^2 / RT + 2A_x I_x^{3/2} / (1 + \rho I_x^{1/2}) \quad (54)$$

At 373 K, $D = 55.4_6$ for water (37), and $A_x = 3.435$. The results are not sensitive to the exact value of ρ ; the value 14.9 was used which corresponds to $a = 5.8 \text{ \AA}$., a reasonable value for the nitrate salts with hydrated positive ions.

The corresponding equations for the other thermodynamic properties are readily derived. We give only the additional, electrical terms to be added to equations 49a and 49c.

$$\Delta_m G^{el} / RT = 4n_2 (A_x / \rho) \ln[(1 + \rho I_x^{1/2}) / (1 + \rho / \sqrt{2})] \quad (55)$$

$$\begin{aligned} \ln a_2^{el} &= 2 \ln \gamma_+^{el} \\ &= -2A_x \left[\frac{2}{\rho} \ln \left(\frac{1 + \rho I_x^{1/2}}{1 + \rho / \sqrt{2}} \right) + \frac{I_x^{1/2} - 2I_x^{3/2}}{1 + \rho I_x^{1/2}} \right] \end{aligned} \quad (56)$$

In each case the pure fused salt is taken as the standard state where $I_x = 1/2$ and these terms become zero. Alternate expressions have been derived (33) for the infinitely dilute standard state for the salt.

With these equations the data are very accurately fitted with the parameters $q_1 = 0.56$, $a_{12}/RT = 1.49$ for $(\text{Ag,Tl})\text{NO}_3\text{-H}_2\text{O}$ and $q_1 = 1.0$, $a_{12}/RT = -1.124$ for $(\text{Li,K})\text{NO}_3\text{-H}_2\text{O}$, both at 373 K. Figure 4 shows the curves for the activity coefficients ($\gamma_1 = a_1/x_1$, $\gamma_{\pm} = a_{\pm}^{1/2}/x_2$) for the latter system. The solid curve shows the results when a Debye-Hückel term is included; the dashed curve is for the case when it is omitted, i.e., equation 49. The difference for $\ln \gamma_1$ can be seen only on the expanded scale of the inset in figure 4 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 49b 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.

Figure 4. The activity coefficients of water and salt over the full range of composition. The dashed lines omit the Debye-Hückel effect whereas the solid lines include it.

One can view the curves for $\ln \gamma_+$ as arising from the integration of the Gibbs-Duhem equation from the pure fused salt ($x_1 = 0$). Up to $x_1 = 0.8$ the result is unambiguous and only a single curve is shown. Thereafter, however, the slope $\partial \ln \gamma_+ / \partial x_1$ is slightly smaller for the true curve than is given by equation 49b. 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 figure 4 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.

5. STRONG UNSCREENED ELECTRICAL FORCES

5.1 Ion Pairing

Consider now the situation where the linearization approximation of Debye-Hückel theory fails and the ions are relatively unscreened. This arises for dilute solutions of salts of 2-2 or higher charge types in water at room temperature or for 1-1 electrolytes in solvents of substantially lower dielectric constant. The solute activity drops below that given by the Debye-Hückel equation at small but finite concentration. This is often described as ion pairing; indeed the population of pairs of oppositely charged ions near one another is higher than Debye-Hückel theory predicts. The exact treatments of the primitive model by Monte Carlo or Molecular Dynamics methods show this effect as do calculations by other methods which avoid the linearization approximation (5).

Even for the primitive model these exact treatments involve very extensive numerical calculations. Thus an alternate treatment is very desirable for the practical handling of experimental data. Such a treatment was first proposed by Bjerrum (38) almost immediately after the Debye-Hückel discovery. Bjerrum assigned all pairs of oppositely charged ions closer than a distance R_B to a separate ion-pair species and assumed an equilibrium between the ion pairs and dissociated ions. We discuss real systems on this general basis.

Bjerrum chose for the dividing distance

$$R_B = z_i z_j \ell / 2$$

which is the minimum in the radial population density of counter ions at very low concentration. While the electrostatic energy is still twice thermal energy at this radius, it is found that the equations of linearized theory give a good approximation for the more distant population as a whole. Presumably this is true because the approximation improves rapidly with increasing radius and with the screening which enters at finite concentration. Bjerrum also offered a theoretical value for the association constant K_A for the primitive model. Since short range forces in real systems certainly differ from this model, it is usually better to assume that the association constant itself is the parameter to be determined empirically. The dividing radius R_B (rather than the hard core diameter a) enters the equation for the activity coefficient of the unassociated ions for the Bjerrum model.

For conductance it is usually assumed (39,40) that ion pairs make no contribution and that equations for fully dissociated electrolytes apply for the separated ions again with the dividing radius R_B replacing the hard core diameter a . In his most recent paper, however, Fuoss (41) further subdivides the ion pair population and assumes some contribution to conductance from a less closely bound type of ion pairs.

Equations for thermodynamic properties of dilute solutions with ion pairing can be found in many references (38,42-44). Since we are considering solutions continuous to the fused salt or at least to high concentration, equations will be given in terms of mole fractions. Thus, if the fraction of solute associated is θ one can define mole fractions of free ions x_i (either + or -), of pairs x_p and a revised value for the solvent x_s

$$x_i = (1-\theta)n_2/[n_1 + (2-\theta)n_2] = I_x \quad (57a)$$

$$x_p = \theta n_2/[n_1 + (2-\theta)n_2] \quad (57b)$$

$$x_s = n_1/[n_1 + (2-\theta)n_2] \quad (57c)$$

Now the Gibbs energy of mixing can be appropriately revised and its derivative with respect to θ equated to zero to yield the ion-pairing equilibrium expression

$$K_x = \frac{x_p}{x_i^2} \exp \left\{ 2A_x \left[\frac{2}{\rho} \ln(1 + \rho I_x^{1/2}) + \frac{I_x^{1/2} - I_x^{3/2}}{1 + \rho I_x^{1/2}} \right] \right\} \quad (58)$$

With ion pairing included, the equation for the solvent activity becomes

$$\ln a_1 = \ln x_s + w_1 z_2^2 + 2A_x I_x^{3/2} / (1 + \rho I_x^{1/2}) \quad (59)$$

with I_x and x_s as defined in equations 57a and 57c, respectively.

The equation for the solute activity becomes rather complex; it is given elsewhere (45).

In dealing with real systems, the best evidence of ion pairing is often conductance rather than thermodynamic measurements. Thus one often obtains θ from the conductance and then determines K_x from equation 58. The other parameters can best be determined from thermodynamic data. This process can be iterated as necessary for self consistency.

This ion pairing treatment is generally quite successful for very dilute solutions in solvents with DT product down to about 3000. At low dielectric constant, however, for even a moderate increase in concentration there is an increase above the expected conductance which Fuoss and Kraus (46) attributed to triple ions. For example, take a Bjerrum distance of 24 Å. Then at 0.01 molar with a central ion pair there is a random probability of 35% that either another ion or ion pair is present within the radius R_B . If this is an ion, one has an ion triplet which contributes $\frac{1}{2}$ to conductance. For thermodynamic properties one must consider both ion triplets and quadruplets. This has been noted for 2-2 electrolytes in water (43,44). Thus the Bjerrum division is self-consistent and generally satisfactory at very low concentration but becomes cumbersome as soon as larger ion clusters have to be included.

An alternate ion-pairing approach with a different division of populations (47) avoids the problem of larger clusters. Assume that around a test ion a Debye-Hückel distribution of other ions extends down to the repulsive force cut off at an effective radius a from a central ion; and then classify as ion pairs the excess of oppositely charged ions. The formal equations for conductance and thermodynamic properties remain the same but the repulsive radius a enters the Debye-Hückel equation for the activity coefficient of the free ions instead of the Bjerrum radius R_B . We discuss below the ionic distribution on this basis.

In his extensive research on ion-pairing, Davies (48) used a definition formally different but practically approximately equivalent to the one just described. He used a standard equation for the activity coefficient of the free ions which corresponds approximately to that for a hard-core repulsive diameter. He also showed that on this basis the fraction associated would reach a

maximum for 2-2 electrolytes in water in the range 0.03 to 0.1 molar and at even lower concentration for several non-aqueous systems. Davies showed that this was consistent with the conductance behavior.

This alternate model for ion pairing was recently applied (45) to the system tetra-n-butylammonium picrate in n-butanol, which is completely miscible above 364 K. Both thermodynamic and conductance data were available; the latter showed strong ion-pairing in the mole fraction range 10^{-4} to 10^{-2} but full ionization for the fused picrate salt.

Of particular interest is the apparent redissociation of the ion pairs with increase of concentration, which seems peculiar. Surely the probability that a positive ion has a near neighbor negative ion does not decrease with increase in concentration. This topic was explored by calculations based on parameters approximating those for the picrate-butanol system; specifically $D = 9.4$, $R_B = 24 \text{ \AA}$, $a = 6.63 \text{ \AA}$, $K_x = 2.65 \times 10^4$ at 373 K.

In considering ion populations in the Debye-Hückel theory it is convenient to use the quantities q and κ defined above in equations 9 and 17, respectively. Also recall the radial distribution functions in both exponential and linearized forms. The essential DH assumption was the linearized charge density which implies (with $g_{++} = g_{--}$)

$$g_{+-} - g_{++} = 2z^2 q \quad (60)$$

For this case $z = 1$ and q is greater than one over a substantial range in radius. Thus the linearized $g_{++} = 1 - q$ is negative which is physically impossible. While it is not without some approximation to assume the exponential form

$$g_{++} = \exp(-q) \quad (61)$$

this cannot be significantly in error for our purpose since it yields values very near zero in the range of special interest. Hence, we assume

$$g_{+-} = 2q + \exp(-q) \quad (62)$$

as an unlike ion distribution consistent with the activity and osmotic coefficients from a Debye-Hückel type of theory.

The total probability $n_{+-}(R)$ of finding an ion of the opposite charge between the hard core distance $6.63 \text{ \AA}$ and radius R is the ion pair fraction plus the product of the concentration of free ions times the volume integral of g_{+-} to R (together with a very small addition for the probability of a second ion pair within R).

This model does not distinguish contact and solvent-separated ion pairs nor does it introduce any realistic detail about short-range forces near hard-core contact. Hence it can only be expected to give a reasonable result on a somewhat coarse-grained basis. One layer of butanol solvent will occupy about 4 to 6 Å. The "ion pair" population is that in excess of the Debye-Hückel distribution and this extends out to at least 24 Å, although it decreases rapidly with increase in radius. Thus it seems that this calculation of n_{+-} is meaningful only for R including at least one solvent layer, i.e., about 12 Å or greater (with all of the "ion pairs" assumed to be within the 12 Å). The result is shown in figure 5 which also shows the ion-pair fraction θ . While the ion-pair fraction decreases above 0.02 molar, the actual probability of finding an ion of opposite charge increases steadily with concentration. Thus there is "redissociation" only in a formal sense. The model as a whole is reasonable and self consistent in terms of ion distribution.

Figure 5. The total probability of finding oppositely charged ions within 12 Å as a function of concentration. Also shown is the ion-pair fraction θ .

The more elaborate statistical calculations which avoid the linearization approximation yield ion distributions similar in most respects to those just described, but direct comparison is not possible because such calculations are unavailable for the parameters of this system. Features that imply triple ions have been discussed by Rossby, et al. (49).

5.2 Unsymmetrical Mixing

If the ions of a given sign in a mixed ionic system all have the same charge, they mix randomly insofar as electrical effects are concerned. Examples are NaCl-KCl or MgCl₂-CaCl₂ in aqueous solution. But there are special electrical effects for mixtures such as NaCl-MgCl₂ or NaCl-CaSO₄ where there is +1:+2 mixing and -1:-2 also in the second example.

An extreme example of unsymmetrical mixing, which has been of recent interest, concerns the iron present in the solar plasma. At $T = 1.7 \times 10^5$ K and $P = 10^{11}$ bar or 10^{16} Pa, $c = 2 \times 10^{31} \text{ m}^{-3}$, $c^{-1/3} = 3.7 \times 10^{-11} \text{ m} = 0.37 \text{ \AA}$, $\lambda = 9.6 \times 10^{-13} \text{ m}$, and $\lambda c^{1/3} = 0.026$; with this small value of $\lambda c^{1/3}$ the hydrogen plasma is influenced only very weakly by electrical forces and the Debye-Hückel limiting law (DHLL) expressions will be valid. The iron present will be highly ionized; $z = +24$ is a reasonable estimate with only the two 1s electrons unionized. Pollack and Alder (50) used the DHLL for the mixed plasma and obtained the result that phase separation should occur even though the average percentage of iron is only 0.002%. They realized that the DHLL was inadequate for the iron-rich phase. But the failure of the linearization approximation (and of the DHLL) has a deeper effect and a better treatment indicates that no phase separation is expected (51).

Recall the linearized expressions for the radial distribution functions:

$$g(\text{H}^+ - \text{H}^+) = g(\text{e}^- - \text{e}^-) = 1 - q(r) \quad (63a)$$

$$g(\text{H}^+ - \text{e}^-) = 1 + q(r) \quad (63b)$$

$$g(\text{Fe}^{+24} - \text{e}^-) = 1 + 24q(r) \quad (63c)$$

$$g(\text{Fe}^{+24} - \text{H}^+) = 1 - 24q(r) \quad (63d)$$

$$g(\text{Fe}^{+24} - \text{Fe}^{+24}) = 1 - 24^2 q(r). \quad (63e)$$

The last three functions for solar conditions are shown in figure 6; the first two depart only slightly from unity and are omitted. The $\text{Fe}^{+24} - \text{e}^-$ and $\text{Fe}^{+24} - \text{H}^+$ functions exceed 2 and drop below zero only at very small r , hence there is no large error in those cases.

Figure 6. Radial distribution functions in solar plasma according to classical Debye-Hückel theory. The negative regions are physically impossible and are removed in the corrected calculation.

But the $\text{Fe}^{+24}-\text{Fe}^{+24}$ function becomes large and negative over a major range of r . A negative distribution function is, of course, impossible. Furthermore, this large, negative value of $g(\text{Fe}^{+24}-\text{Fe}^{+24})$ is multiplied by a very large positive $u_{ij}(r)$ in a calculation of the energy or the virial, equation 12.^{ij}

A simple correction to the DHLL was made (50) for the solar plasma problem by setting $g(\text{Fe}^{+24}-\text{Fe}^{+24})$ to zero for the range of radius where it is negative in figure 6. The result for the Gibbs energy is shown in figure 7. The negative curvature of the D-H result indicates phase separation, but this correction for the spuriously negative distribution yields a result with positive curvature across the entire composition range.

For aqueous solutions of moderate concentration the writer (52,53) has calculated the effect of unsymmetrical mixing quite accurately and has incorporated this theoretical term in semi-empirical equations for various thermodynamic properties. The origin of this effect in solutions is the same as that for the solar plasma; the DH radial distribution functions for more highly charged ions of the same sign are too small and often negative. Since the distribution is too small for radii where

Figure 7. The Gibbs energy for iron-hydrogen plasma under solar conditions. The curves are explained in the text.

the interionic energy is large and positive, the error is a negative contribution. Correction for this error raises the internal energy and the Gibbs energy of a phase in proportion to the square of its concentration of the most highly charged ions. Thus the correction stabilizes mixtures as compared to the pure fused salt containing the highly charged ions. In other words it favors keeping the highly charged ions as far apart as possible.

It has been found that these unsymmetrical mixing terms are essential for an accurate treatment of a problem such as the solubility of CaSO_4 in aqueous NaCl . Harvie and Weare (11) treat this problem as well as many more complex problems related to the evaporation of seawater and other natural brines.

5.3 Phase Separation

As mentioned above, when the coulombic energy becomes sufficiently larger than thermal energy, one expects separation into dilute and concentrated phases. A simple ionic model is consistent with corresponding states behavior and the reduced variables $\beta^* = \ell/a$ and $c^* = ca^3$ were defined above in equations 26 and 27.

There are few ionic systems for which there are good experimental measurements of this phase separation. For pure NaCl and KCl , Kirshenbaum, et al., (54) made measurements up to as high a

temperature as was feasible and extrapolated to obtain the estimates for NaCl, $T_c = 3400 \pm 200$ K, $V_c = 266 \pm 60$ cm³ mol⁻¹, $P_c = 350 \pm 130$ atm. For aqueous NaCl the critical curve in T and P is known to 973 K and 1240 bar (55,56), but the density is known only to 823 K (57). At 823 K the critical volume per mole of NaCl is 530 cm³ with $P_c = 760$ bar.

Conversion of these data to the reduced variables, yields the results in Table 2. The value $a = 2.81$ Å for pure NaCl is taken from the sum of ionic radii in the crystal. For the aqueous system the choice of a is more ambiguous. Reduced properties are listed both for the crystallographic value, $a = 2.81$ Å, and for $a = 4.0$ Å to indicate the effect of some increase for a partial hydration layer.

Table 2. The Critical Properties for Phase Separation in Ionic Systems

	β^*	c^*
Pure NaCl($a = 2.81$ Å)	17.	0.10
Aqueous NaCl($a = 2.81$ Å) ⁺	14.6	0.050
Aqueous NaCl($a = 4.0$ Å) ⁺	10.2	0.14
Theory, Stell, et al.(7)	11.8	0.011
Mean Field Theory	8.3	0.08
Theory, McQuarrie(58)	13.1	0.040

⁺ For 823 K.

One cannot expect accurate agreement for β^* and c^* in Table 2. The extrapolated values for pure NaCl are uncertain and the conformity of either real system to the ionic, hard-core model will be approximate at best. Thus the theoretical value of Stell, et al.,(7) for β^* is reasonable, but their value of c^* is too small by at least a factor of 5 and more probably by a factor of 10. The very simple mean field theory, equations 40 and 41, yields much better results for c^* , although the agreement for β^* is not quite as good. The calculation of the critical properties for the ionic model with mean field theory is very simple, but I am unaware of its having been reported previously. A conceptually somewhat more complex theory, the cell theory of Lennard-Jones and Devonshire, was applied to the ionic model by McQuarrie (58). It likewise yields corresponding states behavior; the result for β^* is probably the best among the theories. McQuarrie's value of c^* appears to be too small, but is better than the Stell value by a factor of 4. A semi-empirical theory of Carlson, et al.,(59) fits the properties of pure NaCl about as well as the others, but it will not be considered further because of the extensive array of empirical parameters which it requires.

The reduced critical properties for pure and for aqueous NaCl and for the mean field theory with the hard-core model all agree within a factor of about 2 for both β^* and c^* . This may be as much as can be expected in view of the uncertainties in the data, the hard-core model and the theory. The failure of the several presumably more accurate theories of Stell, et al., for c^* is puzzling. The McQuarrie cell theory and the mean field theory (as well as the semi-empirical theory) all use the ionic lattice energy expression for the electrical energy. This may be the key to their success.

While better theoretical calculations for the ionic, hard-core model are certainly desirable, it is even more important to have good calculations for a more realistic interionic potential such as has been used for MC and MD calculations for liquid alkali halides at lower temperature and higher density. Presumably, MC or MD calculations could be made for the same model but for the critical range of temperature and density.

The interpretation of the results for aqueous NaCl is even more difficult since there is no independent knowledge of the degree of ion hydration near the critical conditions. In treating the aqueous system, the dielectric constant was given the value for pure H₂O at the pressure of the critical point for 823 K. Undoubtedly, the water between ions at critical composition is compressed on the average, but part of this water is strongly attached in ion hydration shells. This ambiguity is even more serious at lower temperatures near the critical point of pure water. The entries in Table 2 are for 823 K, the highest temperature for which there are adequate data.

There are a number of more complex solution systems for which phase separation has been observed. These results are reviewed by Friedman and Larsen (8) in their discussion of the ionic phase-separation phenomenon. The interpretation for these more complex systems is even more ambiguous than for aqueous NaCl, hence it will not be discussed here.

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