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Abstract

The electrical conductance and thermodynamic properties (activities) are described for the few aqueous electrolytes which have been investigated over the full range from fused salt to pure water. The activities are quite well represented by a simple equation originally proposed by van Laar for non-electrolytes. Comments are made concerning the properties of various strong electrolytes up to saturation concentration and their dependence on temperature up to 300°C. These properties are accurately represented by virial-coefficient equations. Such equations have been used by Harvie and Weare to calculate all of the solubility relationships in the sea-water-related system Na-K-Mg-Ca-Cl-SO_4-H_2O; the agreement with experiment is excellent.

INTRODUCTION

In considering the properties of very concentrated aqueous solutions, first consideration will be given to those few systems which have been investigated over the complete range in composition from dilute aqueous electrolyte to dilute solution of water in fused salt. In this connection, a few of the simple methods and equations found successful for non-electrolyte solutions will be used. Surprisingly, these methods appear to have been ignored by investigators of very concentrated electrolytes, but it will be shown that they are effective. The activity of water, measurable by its vapor pressure, is an important property and particularly so since the Gibbs-Duhem equation allows the activity of the other component to be calculated from the information on water. Conductance is also important, especially for the insight it gives concerning the state of dissociation of charged species.

The composition range for most systems of interest is limited by solubility. Indeed the solid-solution equilibrium is a matter of great importance itself. In such cases the pure liquid salt is not available as a reference state and the alternate choice is the infinitely dilute reference state. Under these circumstances the best approach is the extension of methods and equations appropriate to dilute electrolytes to higher concentrations up to the solubility limit. The properties of sodium chloride, as a typical fully ionized electrolyte, are considered over a wide range in temperature and to saturation concentration. Various methods of expressing such properties are discussed and the writer's preference, the virial coefficient method, is described in detail. Results of very recent calculations of solubility relationships for sea-water-related systems by Harvie and Weare (1979) are reported as an indication of the capacity of these equations to represent the properties of concentrated solutions up to the solubility limit.

While no detailed discussion will be given of the underlying statistical mechanical theory for these systems, it should be remembered that such theory is now well established. The writer has given an elementary summary, Pitzer (1977), where references are given to more detailed presentations. However, accurate calculations are very burdensome and are just becoming feasible on the largest computers. Thus theory is not about to displace experiment in obtaining numerical values for properties of these complex solutions. But it is possible, and frequently not very difficult, to determine theoretically the approximate characteristics of a system, and it is no longer useful to propose complex ad hoc theories since it is possible to determine whether the assumptions are or are not valid.

SIMPLE EXAMPLES WITH WIDE COMPOSITION RANGES

For our first experimental examples we consider a few cases where the salt melts at not too high a temperature. Thus the entire range from dilute aqueous solution to fused salt is accessible. $LiClO_3$ at 132°C is an example. The melting points of salts are depressed for salt mixtures; hence it is also convenient to consider such systems as $(Li,K)NO_3-H_2O$ where the full range is accessible at 119°C. Here the cation fraction is constant at 50% and the properties are essentially those of a two-component water-salt mixture.

The conductance of several such systems has been measured, Campbell and Paterson (1958), Campbell, Debus, and Kartzmark (1958). Its meaning with respect to the state of ionization of the system is most readily judged from the equivalent conductance-viscosity product which is shown in Fig. 1 for $LiClO_3$ over the full 0-100% range and for $LiNO_3$ to high concentration. In the dilute aqueous solution range the well-known electrostatic effects cause a reduction in conductance from its limiting value. For these examples the equations based on complete ionic dissociation are adequate; there is no need to assume any ionic association. In the middle range the $\eta\Lambda$ product passes through a shallow minimum but, in the absence of an exact theory, it is not possible to draw any precise conclusions. The near constancy of the $\eta\Lambda$ product, however, suggests continued full ionization. The increase in $\eta\Lambda$ in approaching the pure fused salt is striking for $LiClO_3$. For the addition of a little water to the fused salt, the viscosity decreases faster than the conductance increases. The writer is not aware of any theoretical analysis of this region; such a study would be interesting.

There are also organic systems which have been investigated over the full range from dilute electrolyte solution to fused salt. An example is tetra-n-butylammonium picrate in n-butyl alcohol, Seward (1951). In this case there is ion-pairing in the dilute solution range with a sharper drop in the $\eta\Lambda$ product. The minimum in $\eta\Lambda$ occurs at about 5% salt after which that product rises to about the same value as it had at infinite dilution in the alcohol solvent. Thus there appears to be a re-dissociation in the intermediate composition range; this effect will be discussed further below. This and other organic electrolyte-fused salt systems are discussed in an interesting review by Kraus (1954).

Let us turn now to the thermodynamic properties of the simple inorganic systems with particular attention to the activity of water as measured by its vapor pressure above the solution. This has been measured for $(Li,K)NO_3-H_2O$ by Tripp and Braunstein (1969), for that system, for $LiNO_3-H_2O$, and for several others by Braunstein and Braunstein (1971), for $LiCl-H_2O$ by Gibbard and Scatchard (1973), and for $(Ag,Tl)NO_3-H_2O$ by Trudelle, Abraham, and Sangster (1977). Robinson and Stokes (1965) summarize earlier results for other systems including $NH_4NO_3-H_2O$. The activity of water for many of these systems is shown in Fig. 2. 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 (1923) correction applicable as the concentration increases.

The similarity of the curves on Fig. 2 to those for nonelectrolyte solutions is striking. The dashed line representing $a_1 = x_1$ can be called "ideal-solution behavior" for these systems, as it is for nonelectrolytes, 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, it seems worthwhile to explore the use for these systems of the simple equations for nonelectrolytes. One of the simplest and most successful had its origin in the work of van Laar (1906) and has been widely used, with modified theoretical interpretation, by Hildebrand, Scatchard, Guggenheim, and others; the term "regular solutions" is sometimes used for this behavior. For the activity of either component, referenced to the pure liquid, one has

$$\ln a_1 = \ln x_1 + w_1 z_2^2 \tag{1a}$$

$$\ln a_2 = \ln x_2 + w_2 z_1^2 \tag{1b}$$

$$z_1 = n_1/[n_1 + \nu n_2(b_2/b_1)] \tag{1c}$$

$$z_2 = \nu n_2/[n_1(b_1/b_2) + \nu n_2] \tag{1d}$$

$$w_2 = w_1(b_2/b_1) \tag{1e}$$

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

$$\ln a_1 = \ln x_1 + wx_2^2 \tag{2a}$$

$$\ln a_2 = \ln x_2 + wx_1^2 \tag{2b}$$

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. 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 and subsequently to compare the values with ratios of molal volumes. Pitzer and Brewer (1961) give, in their chapter 21, a discussion of this type of equation for nonelectrolytes including both thermodynamic relationships and derivations from simple statistical models. Such equations can, of course, be used for nonelectrolyte solutions where water is one component.

Equation (1) was fitted 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 $(Ag,Tl)\,NO_3$-H_2O and $w_1 = -0.89$, $(b_1/b_2) = 1.2$ for $(Li,K)NO_3$-H_2O. Water is component 1 and the salt component 2. 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.

It can be questioned whether one should use the mole fraction on an ionized basis, as was done above, or on an unionized molecular formula basis. The ionized basis is clearly the correct one in the limit of high dilution in water, but this is not too compelling an argument since the region of primary application is the very concentrated solutions. Statistical arguments related to the restriction from random distribution of the ions by electrostatic forces throughout the composition range (including the pure fused salt) might be persuasive, but are complex and have not been developed clearly. Purely empirical tests were made for the two systems for which data are available across the full range of composition. For the system $(Ag,Tl)NO_3$-H_2O the ionized basis is superior with a standard deviation of fit of only 0.003 for the range 0.0 to 0.9 in x_1 whereas the unionized basis yields a standard deviation almost ten times larger. For the system $(Li,K)NO_3$-H_2O, however, there was little difference with standard deviations of 0.008 and 0.010, respectively. The optimum values of w_1 and (b_1/b_2) are quite different on the unionized basis from the values given above for the ionized basis. It seems to the writer that the ionized basis is more reasonable for systems known to be primarily in ionic form and the empirical evidence gives at least some support to that conclusion.

With experimental data for the activity of water, one can, of course, integrate the Gibbs-Duhem equation to obtain the activity of the salt, over the same range in composition, without the use of any model or semi-empirical equation. But equation (1) appears to fit so well that its use is very convenient. As presented, the constant of integration is evaluated for the pure-liquid reference state for each component. Thus equation (1b) gives the activity of the salt in relation to the pure fused salt. Since this form is obtained by integrating the Gibbs-Duhem equation over composition to the fused salt, $x_1 = 0$, $x_2 = 1$, the Debye-Hückel range is avoided and no error from that source is introduced.

If the fused salt does not exist at the temperature of interest, one normally uses the infinitely dilute solute standard state. While these equations can easily be converted to that basis, the results are not immediately useful for two reasons: (1) Debye-Hückel effects are significant in the dilute range and are not considered, and (2) the usual composition scale for the solute standard state is molality rather than mole fraction. Both of these problems can be overcome, but the more complex relationships will not be given here.

In the nonelectrolytes the non-ideality parameter w relates to the ratio to thermal energy (kT) of the difference between the intermolecular potential energy of attraction of unlike species as compared to the mean of the corresponding intermolecular potentials of attraction for pairs of like molecules. A greater mutual attraction of unlike species gives a negative deviation from ideality for systems such as mercury-cadmium and acetone-chloroform among nonelectrolytes and for $LiCl-H_2O$, for $LiNO_3-H_2O$, and very mildly for $(Li,K)NO_3-H_2O$. Where the intermolecular attraction for unlike pairs is less than the mean for like pairs one has a positive deviation from ideality in systems such as benzene-cyclohexane, CS_2-acetone, and mercury-tin, as well as in $(Ag,Tl)NO_3-H_2O$ and $NH_4NO_3-H_2O$. That Li^+ ion tends to be more strongly hydrated than K^+, Ag^+, Tl^+, or NH_4^+ is well-known. Thus the relative positions of the upper curves on Fig. 2 is readily understood and it appears that a Li, K mixture somewhat richer than 50% in K would yield ideal behavior in the MNO_3-H_2O system. It is interesting to note, however, the substantial difference between the lithium nitrate and lithium chloride curves. On this picture the H_2O-cation and H_2O-anion attractions must be compared with cation-anion and water-water attractions. Thus it is clear that the effect of different anions is of comparable significance to that of different cations, as observed, even when the anions are not ordinarily regarded to be hydrated.

This treatment of very concentrated electrolytes in a manner analogous to that of nonelectrolytes seems to me to be the simplest and most useful approach, but it has not been used to the writers knowledge. A favorite method has been the use of the Brunauer-Emmett-Teller adsorption isotherm as proposed by Stokes and Robinson (1948). Here the rationale is that the fused salt can attract water molecules, presumably to the surfaces of the cations, much as water is attracted to the surface of a crystal. As more water is added, the binding energy per molecule decreases gradually to that of pure water in a dilute solution or with a multilayer film. Braunstein and Braunstein (1971) and Trudelle, Abraham, and Sangster (1977) summarize the results of fitting several sets of recent data to the BET equation which is

$$a_w(1-x_w)/x_w(1-a_w) = 1/cr + (c-1)\ a_w/cr \qquad (3)$$

where $a_w = a_1$ is the activity of water, x_w is its mole fraction on an unionized basis and both c and r are empirical parameters. While this equation fits reasonably well up to $x_w = 0.65$, the fit is not as good as that for equation (1). Above $x_w = 0.65$ the B.E.T. equation is much less satisfactory. Also equations (1) and (2) have the great convenience of a simple form expressing the activity as an explicit function of the mole fraction and an equally simple expression for the activity of the fused salt component.

In a paper 25 years after that proposing the BET method, Stokes and Robinson (1973) developed a more elaborate equation which was based on successive hydration equilibria but also included the Debye-Hückel equation; this equation fitted very accurately the data for several inorganic salts up to saturation at 25°C.

It is well to keep in mind the number of empirically evaluated constants for the various treatments. We include only those related primarily to the extremely concentrated range and omit those related to Debye-Hückel terms, if included. The simplest nonelectrolyte type of equation (2) has one constant whereas the more general van Laar equation (1) has two. The BET equation (3) also has two empirical constants while the later Stokes and Robinson equation has three.

Now that there are experimental data for fused salt-water solutions over the full range of composition, it will be interesting to explore appropriate statistical models and semi-empirical equations related thereto. Existing equations, however, represent the data rather well, as discussed above. There is no reason to doubt the general picture of a mixture of ions and water molecules departing somewhat from randomness because of electrostatic as well as short-range interparticle forces.

NONLINEAR ELECTROSTATIC EFFECTS AND ION PAIRING

For singly charged ions in water the electrostatic energy at closest approach does not substantially exceed thermal energy; hence one may treat electrostatic effects in a linear approximation as did Debye and Hückel (1923). But as Bjerrum pointed out, for higher-charged ions in water or for singly charged ions in solvents of lower dielectric constant, this linear approximation is inadequate. The nonlinear effect may be treated as an ion-pairing equilibrium of a special type where the equilibrium constant cannot be determined accurately until another parameter, usually the interionic distance of "dissociation", has also been specified. But as Gronwall, LaMer, and Sandved (1928) showed and Guggenheim (1959) and others have emphasized, it is not necessary to consider an association equilibrium; it is equally correct in thermodynamics to treat these nonlinear effects with a more complex expression for the activity coefficient of the fully-dissociated solute. The early equations including these nonlinear effects were inconveniently complex, but Pitzer and Mayorga (1974) proposed a very simple expression which adequately represents this phenomenon and is usually more convenient to use than the association equilibrium.

This electrostatic ion pairing is quite different from the association of a typical weak electrolyte such as acetic acid. In the weak electrolyte the fraction dissociated decreases continuously until the pure component is a molecular liquid with possibly a small fraction of self-dissociation. The distinctive differences for the nonlinear electrostatic effects are well illustrated by the organic fused salt system mentioned above, tetrabutylammonium picrate-butyl alcohol, Seward (1951). As is shown in Fig. 4, the equivalent conductance (or the $\eta\Lambda$ product) decreases rapidly in the dilute solution range to a value at 1% picrate less than one fourth that at infinite dilution. Above 5% picrate, however, the viscosity-conductance product increases, and it is slightly higher for pure picrate than for the infinitely dilute solution. Thus the pure picrate is clearly a fused salt-not a molecular liquid- and the ion pairs present at 1% concentration must redissociate in the range above 10%.

This redissociation of ion pairs was discussed in detail by Davies (1962) who showed that it could be explained in terms of reasonable activity-coefficient behavior in connection with an association equilibrium. Fuoss and Kraus (1933) explained the increase in equivalent conductance past the minimum as the formation of triple ions. Their picture could be extended to quadruple ions, etc., until the pure fused salt becomes a single giant ion with internal conductance. But Davies showed that the assumption of these larger ions was not necessary.

Typical 2-2 electrolytes have such high melting points that their aqueous solutions cannot be investigated over the full range in composition to the pure liquid. But the solids which separate are usually crystals with hydrated cations and an ionic structure, e.g., $MgSO_4 \cdot 7H_2O$. Davies suggests that the maximum ion pairing for $ZnSO_4$ is between 0.1 and 0.2 m at 25°C and for higher valence types it occurs at even lower concentration, possibly 0.01 m for $LaFe(CN)_6$, a 3-3 electrolyte. Thus it seems feasible for many purposes, at least, to regard very concentrated aqueous solutions of 2-2 or other high-valence salts as fully ionized fused salts with hydrated cations and with additional water present. It is in the dilute range that one must consider either ion pairing or a special activity expression including the non-linear electrostatic effects. Since the latter method is compatible with complete ionization at higher concentration, this is an added advantage to that choice.

GENERAL TREATMENT EXTENDING TO CONCENTRATED SOLUTIONS

Most aqueous solutes are limited in solubility far short of the fused salt and one wishes a general representation of their properties valid through the dilute range up to saturation. In contrast to the extreme range of composition discussed above, for which there are few examples, in these more moderate concentrations there are experimental data at 25° for very many salts, acids, and bases, and, with diminishing abundance, data extend down to 0°C and up to 300°C with a few cases extending even higher. Most of the data are for 1 atm pressure but above 100°C the pressure must be higher; also there are some measurements at 25°C and high pressure.

Most basic theoretical studies use the simple charged-hard-core model and emphasize relatively low concentrations (up to 1 or 2 molal for activity or osmotic coefficients). Within the expected accuracy of this charged-hard-core model, good agreement is obtained in this range for 1-1 electrolytes. Ramanathan and Friedman (1971) treated a model with a more reasonable continuous short range potential and obtained good agreement with plausible potentials for the alkali halides. These theories have greater difficulties with 2-2 or other highly charged species but good progress is being made. For conductance the most exact theories are valid only for dilute solutions but there do not appear to be any qualitatively important differences between theory and experiment up to 1 molal for 1-1 electrolytes.

Over the wide range of temperature to 300°C and concentration to 10 m, sodium chloride shows only very moderate and slow changes in its properties, Silvester and Pitzer (1977), Pitzer, Bradley, Rogers, and Peiper (1979). The principal change is the increase in the Debye-Hückel parameter which lowers both activity and osmotic coefficients. The osmotic coefficient for NaCl is shown on Fig. 5; the curves were calculated by the methods described in the next section. The behavior of a typical 2-1 electrolyte, $MgCl_2$, is shown on Fig. 6, based on the work of Holmes, Baes, and Mesmer (1978). Thus there is no reason to assume less than complete ionization or other qualitative departures from the familiar properties at room temperature. Although other solutes have not been studied as extensively, many "strong" electrolytes clearly retain their character in a similar manner. Of course, there are weak electrolytes showing partial ionization at room temperature and their treatment through dissociation equilibria is familiar. Also a few solutes show special properties; ZnI_2 for example is a relatively normal strong electrolyte below 0.5 m but at higher concentrations becomes highly complexed and yields a negative transference number for Zn.

With this brief discussion emphasizing the absence of qualitative changes in the nature of most electrolytes up to saturation concentration, we turn to the quantitative representation of these properties. The chemical potential of both solute and water are of primary interest, usually expressed as activity and osmotic coefficients, but other properties such as enthalpies and molal volumes are related through thermodynamics to derivatives of these coefficients. The following comments relate to "strong" electrolytes; the state of ions related to carbonic, phosphoric, and similar acids must be handled by the appropriate dissociation equilibria.

There are two general methods of expressing these quantitative properties of individual strong electrolytes which arise from the differences in short-range interionic forces. One pattern, first proposed by Bronsted (1922) and improved by Guggenheim (1935) and others, can be described as a virial expansion in increasing powers of the molality. Such series expressions in virial coefficients are an accepted method for describing the properties of non-ideal gases. For electrolytes one must add a Debye-Huckel term for the electrostatic effects, but the remaining effects of short-range forces may be expressed as accurately as desired by a series in increasing powers of molality. Such extended virial series were used by Scatchard (1968) and Scatchard, Rush, and Johnson (1970). However, it was noted by Mayer (1950) that the interaction of short-range forces and electrostatic forces yields a dependence of the virial coefficients on the electrical concentration usually expressed as ionic strength. By recognizing this dependence, the virial series converges much more rapidly. The writer and his associates have refined this virial-coefficient or ion-interaction approach and extended its applicability to relatively high concentration, Pitzer (1973), Pitzer and Mayorga (1973), Pitzer and Mayorga (1974), Silvester and Pitzer (1977). These equations are given in the next section. For weak electrolytes the dissociation equilibrium must be considered but further departures from ideal behavior can be expressed by virial coefficients. This was demonstrated for phosphoric acid, Pitzer and Silvester (1976), and for sulfuric acid, Pitzer, Roy, and Silvester (1977).

One of the great advantages of the ion-interaction or virial-coefficient method is the ease by which it is extended to mixed electrolytes. Indeed in the early Bronsted or Guggenheim forms all virial coefficients related to the differences between the interactions of ions with the same sign of charge were assumed to be zero. Then all non-zero parameters could be evaluated from pure electrolytes yet the equations gave the properties of mixtures. It has proved that the interaction terms for different ions of the same sign, although small, are not completely negligible. These can be obtained from experiments on very simple mixtures such as $LiCl-HCl-H_2O$, and thereafter the properties of mixtures of unlimited complexity can be calculated, Pitzer and Kim (1974).

The virial coefficient approach was applied to sea water and related systems by Whitfield (1975), and very recently Harvie and Weare (1979) have applied this method to the prediction of solubility equilibria in the sea water-related system $Na-K-Mg-Ca-Cl-SO_4-H_2O$ with remarkable success. Some of their results will be discussed below.

The alternate general method for expressing the individual properties of electrolytes at high concentration has been the assumption of association equilibria such as $Na^+ + SO_4^= = NaSO_4^-$. Davies (1962) discusses this procedure in which a standard activity coefficient equation is adopted which is typical of the highest curves observed. Then any appreciable lowering of the activity coefficient is ascribed to an association equilibrium. At high molality further association to triple ions of various types must be assumed; this process can be continued indefinitely as required.

This ion association method is, of course, just an extension to many electrolytes of the ion-pairing equilibrium discussed above for the non-linear electrostatic effects that occur only for high-valence types in water. As long as the fraction associated is rather small, the mathematical effect of an ion association is the same as that of a negative contribution to a virial coefficient; there is a reduction in the activity coefficient of the parent solute which is linear in molality for a binary association or a second virial coefficient. Thus it is possible to represent the observed properties of electrolytes by assuming a sufficient number of ion association equilibria and this can be extended to mixtures, see Garrels and Thompson (1962), Garrels and Christ (1965), and Helgesen (1969). Especially for complex mixtures the simultaneous solution of numerous non-linear equations for the various association equilibria becomes burdensome, but computer-based methods are available, Helgesen, Brown, Nigrini, and Jones (1970).

The choice between virial-coefficient and ion-association methods is not one of principle but rather one of convenience for a given accuracy. Since the writer believes, possibly with prejudice, that the virial-coefficient method is more convenient, it will be emphasized here. This convenience arises primarily from the fact that a desired activity coefficient is given by a single equation which can be solved directly, even though it may have many terms, whereas several simultaneous equations must be solved in the ion-association method. Also the virial coefficient method appears to yield better results in some cases. But the choice is for the user to make.

Before concluding this section three other theoretical methods should be mentioned although none has yet been applied as widely as those already discussed. First, one can use a series in increasing powers of the activities of various solutes instead of a power series in the concentrations of the solutes (the virial coefficient method). This activity series is related to the grand partition function of statistical mechanics. Wood, Lilley, and Thompson (1978) recently extended this method to electrolytes by the inclusion of a Debye-Hückel term and applied it to several examples. More rapid convergence is obtained (than for the concentration series) in cases of rather strong ion pairing. But the concentrations are directly measured whereas the activities must ordinarily be inferred indirectly; thus the virial series is much more convenient for most practical calculations.

A second approach is based on "corresponding states" in a manner somewhat analogous to the familiar treatment of the gas-liquid behavior of nonelectrolytes by dimensionless reduced variables. One may similarly define dimensionless variables for an ionic system by taking the ratio of thermal energy to an interionic energy, the ratio of the volume per ion to the cube of a characteristic interionic distance, etc. Friedman and Larsen (1979) have discussed the theoretical results for the hard core ionic model as well as some experimental data on this basis. Differences from a particular shape of interionic potential curve (such as the hard core model) will cause departures from a corresponding states pattern of behavior. It is not yet clear how useful this approach will be, but it deserves further exploration.

A third approach involves the assumption of some sort of lattice model or of long-range order in the solution. Pytkowicz, Johnson, and Curtis (1977) propose one model and cite earlier work of this type. Although, lattice models have occasionally suggested forms of equations that were useful empirically for liquid systems, this empirical success did not establish the correctness of the model. Indeed alternate models frequently lead to the same expression for a thermodynamic property of a complex liquid. The fact that some activity coefficient curves show rather closely a dependence on the cube root of the concentration over a finite range was cited as evidence for a diffuse lattice-like structure by Frank and Thompson (1959), but this range is at low concentration (0.002-0.05 m) where there is now a firm theoretical basis, and Rasaiah, Card, and Valleau (1972) showed that the apparent cube-root behavior was a mathematical accident. Since lattice models have not demonstrated any over-all empirical superiority for aqueous electrolytes, and they suffer from the inherent contradiction in the assumption of long-range order for a liquid, they will not be discussed in detail. If lattice models are to be useful in the future, it will be for very concentrated solutions. Even in that range a fused salt model, although more complex, would be more realistic and probably could be handled by modern theoretical methods.

VIRIAL COEFFICIENT EQUATIONS, SOLUBILITY EQUILIBRIA

In this section we will outline briefly the equations of the virial-coefficient method and comment on their application to the calculation of equilibria with various solid phases by Harvie and Weare (1979). Additional details concerning the derivation of the equations and the evaluation of empirical parameters can be found in the series of papers of Pitzer, Mayorga, Kim, and Silvester (1973-1977).

A general equation is assumed for the excess Gibbs energy of the virial form

$$G^{ex}/n_w RT = f(I) + \sum_i \sum_j \lambda_{ij}(I)\, m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk}\, m_i m_j m_k \qquad (4)$$

where G^{ex}/n_w is the excess Gibbs energy per kilogram of solvent and m_i, m_j, etc., are the molalities of the various ions or neutral solutes present. The long-range electrostatic forces lead to the Debye-Hückel term f(I) where I is the ionic strength. Short-range interparticle-potential effects are taken into account by the virial coefficients λ_{ij} for binary interactions, μ_{ijk} for ternary, etc. As noted above, electrostatic effects lead to an ionic strength dependence on λ for ionic interactions. For μ this is neglected; also μ is omitted if all ions are of the same sign. While fourth virial coefficients could be added, they do not appear to be needed for most applications. Indeed the third virial coefficients are so small that they can often be omitted at moderate concentration (I up to about 2).

Since one cannot vary individual ion concentrations but must maintain electrical neutrality, individual λ and μ values are not accessible. Only combinations corresponding to electrical neutrality are measureable or are needed. It is also true that individual ion activity coefficients are not measureable (by macroscopic methods); nevertheless, it is convenient to use individual ion expressions which can then be combined for any neutral combination. One then obtains for the osmotic coefficient ϕ and the activity coefficient γ_M of a cation M or γ_X of an anion X,

$$(\phi-1) = \frac{2}{(\sum_i m_i)} \Bigg\{ - \frac{A_\phi \, I^{3/2}}{1+bI^{1/2}} + \sum_c \sum_a m_c m_a (B^\phi_{ca} + ZC_{ca})$$

$$+ \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} (\Theta^\phi_{cc'} + \sum_a m_a \psi_{cc'a}) + \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} (\Theta^\phi_{aa'}$$

$$+ \sum_c m_c \psi_{aa'c}) \Bigg\} \tag{5a}$$

$$\ln \gamma_M = z^2_M F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c (2\Theta_{Mc} + \sum_a m_a \psi_{Mca})$$

$$+ \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} \psi_{aa'M} + |z_M| \sum_c \sum_a m_c m_a C_{ca} \tag{5b}$$

$$\ln \gamma_X = z^2_X F + \sum_c m_c (2B_{cX} + ZC_{cX}) + \sum_a m_a (2\Theta_{Xa} + \sum_c m_c \psi_{Xac})$$

$$+ \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} \psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca}. \tag{5c}$$

Here m_c is the molality of cation c with charge z_c and correspondingly for anion a. Sums over c or a cover all cations or anions, respectively. B's and Θ's are measureable combinations of λ's whereas C's and ψ's are combinations of μ's. Equations (5b, c) are strictly valid only when combined to yield an activity of a neutral species or a difference of activities between equally charged species.

The electrostatic function f must contain the Debye-Hückel limiting law with the parameter

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

but it proves empirically advantageous to take an extended form. Among alternatives, the form found best was

$$f(I) = -4A_\phi I b^{-1}\ \ln(1+bI^{1/2}) \tag{6}$$

with b = 1.2 chosen for all electrolytes in water. At 25°C the value of A_ϕ is 0.391. The appropriate derivatives give the term in Eq. (5a) for ϕ. For the activity coefficient it is convenient to define

$$\begin{aligned} F = {} & -A_\phi[I^{1/2}/(1+bI^{1/2}) + (2/b)\ln(1+bI^{1/2})] + \sum_{\substack{\cancel{b}\\ c}} \sum_a m_c m_a B'_{ca} \\ & + \frac{1}{2}\sum_c \sum_{c'} m_c m_{c'}\, \Theta'_{cc'} + \frac{1}{2}\sum_a \sum_{a'} m_a m_{a'}\, \Theta'_{aa'} \end{aligned} \tag{7}$$

which includes both the Debye-Hückel term with A_ϕ and certain derivatives of the second virial terms.

The coefficients, B_{MX}, are functions of ionic strength. Again an empirical choice was made among theoretically plausible forms for B_{MX} and the following was chosen with $\beta^{(1)}$ and $\beta^{(2)}$ parameters fitted to the data for each solute.

$$B^{\phi}_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} e^{-\alpha I^{1/2}} \tag{8a}$$

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} g(\alpha I^{1/2}) \tag{8b}$$

$$B'_{MX} = \beta^{(1)}_{MX} g'(\alpha I^{1/2})/I, \tag{8c}$$

where the functions g and g' are given by

$$g(x) = 2[1 - (1+x)e^{-x}]/x^2 \tag{9a}$$

$$g'(x) = -2[1 - (1 + x + 1/2\ x^2)e^{-x}]/x^2 \tag{9b}$$

with $x = \alpha I^{1/2}$. In Eqs. (8) the form given is for 1-1 and 1-2 electrolytes for which the value $\alpha = 2$ was chosen emperically. For higher valence types, such as 2-2 electrolytes, an additional term is added and Eqs. (8) become

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} e^{-\alpha_1 I^{1/2}} + \beta^{(2)}_{MX} e^{-\alpha_2 I^{1/2}} \tag{10a}$$

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} g(\alpha_1 I^{1/2}) + \beta^{(2)}_{MX} g(\alpha_2 I^{1/2}) \tag{10b}$$

$$B'_{MX} = \beta^{(1)}_{MX} g'(\alpha_1 I^{1/2})/I + \beta^{(2)}_{MX} g'(\alpha_2 I^{1/2})/I. \tag{10c}$$

In this case the values of $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$ are assigned. In lieu of an ion pairing equilibrium, the additional term in Eqs. (10) with a negative $\beta^{(2)}$ accounts for the increased tendency of higher valence types to associate in solution.

The use of this modified functional form for the second virial coefficient rather than the explicit recognition of ion association greatly simplifies calculations.

The parameters, C_{MX}, are related to the tabulated parameters of Pitzer and Mayorga (1973), C^{ϕ}_{MX}, as follows,

$$C_{MX} = C^{\phi}_{MX}/2|z_M z_X|^{1/2} \qquad (11)$$

also the quantity Z is defined to be

$$Z = \sum_{i} m_i |z_i| = 2 \sum_{c} m_c z_c \qquad (12)$$

The mixed electrolyte terms in Θ and Ψ account for differences among interactions between ions of like sign. The defining equations for the second virial coefficients, Θ_{ij}, are given by Eqs. (13),

$$\Theta^{\phi}_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) + I\,{}^{E}\theta'_{ij}(I) \qquad (13a)$$

$$\Theta_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) \qquad (13b)$$

$$\Theta'_{ij} = {}^{E}\theta'_{ij}(I) \qquad (13c)$$

θ_{ij}, a single parameter for each pair of anions or each pair of cations, is the only adjustable parameter in Eqs. (13).

The terms ${}^{E}\theta_{ij}(I)$ and ${}^{E}\theta'_{ij}(I)$ account for the electrostatic effects of unsymmetrical mixing. Equations for calculating these terms were derived by Pitzer (1975); this effect was discovered by Friedman (1962). The important features of ${}^{E}\theta_{ij}(I)$ and ${}^{E}\theta'_{ij}(I)$ are that they depend only on the charges of the ions i and j and the total ionic strength. They do not constitute additional parameterization. ${}^{E}\theta_{ij}(I)$ and ${}^{E}\theta'_{ij}(I)$ are zero when the ions i and j are of the same charge. Although these terms are important for 1-3 mixtures, such as HCl-$AlCl_3$, they did not appear to be really needed for simple 1-2 mixtures. However, Harvie and Weare (1979) have found these special electrostatic terms to be important for the $CaSO_4$-NaCl system and some more complex mixtures involving singly and doubly charged ions.

These virial-coefficient equations have been found by various authors to represent accurately the properties of electrolyte mixtures to quite high concentration. Recent examples include NaCl-$SrCl_2$, Macaskill, White, Robinson and Bates (1978), and HCl-KCl, Macaskill and Bates (1978). Most impressive, however, are the results of Harvie and Weare (1979) on the very complex solutions arising from evaporation of and partial precipitation from sea water.

Tables 1 and 2 give the values of the parameters needed for the Na-K-Ca-Mg-SO_4-Cl-H_2O systems; most were obtained by Pitzer and Mayorga (1973) or Pitzer and Kim (1974) but several improvements and additions were made by Harvie and Weare (1979). Many of the subsystems are reasonably well fitted by other treatments, such as those of Kharaka and Barnes (1973), of Truesdale and Jones (1974), or Plummer, Jones, and Truesdell (1976), while Harvie and Weare obtain excellent agreement throughout. However, for the $CaSO_4$-NaCl-H_2O system, where the other treatments fail, Harvie and Weare also obtain excellent agreement as shown in Fig. 7. The results for the related $CaSO_4$-Na_2SO_4-$NaCl$-H_2O system are similar and are shown on Fig. 8. Finally, the invariant points for the system Na-K-Mg-Cl-SO_4- H_2O at 25°C are shown in Table 3 which compares the calculated results of Harvie and Weare with, in parentheses, the experimental values of Braitsch (1971). The agreement is remarkably good and probably within experimental error at most points, at least. These solubility results depend, of course, on the properties of the solids as well as those of the solution, it is evident that the both sets of properties must have been calculated accurately to obtain agreement over such a wide range of conditions.

The systems just discussed involve only strong electrolytes. Many geochemical systems include carbonates, phosphates, or others salts of weak acids and their treatment would also require consideration of the dissociation equilibria; indeed this would extend to sulfates at low pH where the HSO_4^- ion is formed.

CONCLUSIONS

It is shown that the properties of fully ionized aqueous electrolyte systems can be represented by relatively simple equations over wide ranges of composition. There are only a few systems for which data are available over the full range tc fused salt. A simple equation commonly used for nonelectrolytes fits the measured vapor pressure of water reasonably well and further refinements are clearly possible. Over the somewhat more limited composition range up to saturation of typical salts such as NaCl, the equations representing thermodynamic properties with a Debye-Hückel term plus second and third virial coefficients are very successful. A stringent test is offered by the calculation of all of the solubility relationships of the system Na-K-Mg-Ca-Cl-SO_4-H_2O and the calculated results of Harvie and Weare show excellent agreement with experiment.

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Table 1. Parameters for virial coefficient equations at 25°C

M	X	$\beta^{(0)}_{MX}$	$\beta^{(1)}_{MX}$	$\beta^{(2)}_{MX}$	C^{ϕ}_{MX}
Na	Cl	.07650	.2264	--	.00127
Na	SO_4	.01958	1.1130	--	.00497
K	Cl	.04835	.2122	--	-.00084
K	SO_4	.04995	.7793	--	0
Mg	Cl	.35235	1.6815	--	.00519
Mg	SO_4	.22100	3.3430	-37.25	.025
Ca	Cl	.31590	1.6140	--	-.00034
Ca	SO_4	.20000	2.650	-57.70	0

Table 2. Parameters for mixed electrolytes with the virial coefficient equations (at 25°C)

i	j	k	θ_{ij}	ψ_{ijk}
Na	K	Cl	-.012	-.0018
		SO_4		-.010
Na	Mg	Cl	.07	-.012
		SO_4		-.015
Na	Ca	Cl	.07	-.014
		SO_4		-.023
K	Mg	Cl	.0	-.022
		SO_4		-.048
K	Ca	Cl	.032	-.025
		SO_4		0
Mg	Ca	Cl	.007	-.012
		SO_4		.05
Cl	SO_4	Na	.02	.0014
		K		0
		Mg		-.004
		Ca		0

Table 3. Calculated invarient points for the system Na-K-Mg-Cl-SO_4 at 25° from Harvie and Weare (1979) compared with experimental values in parentheses, from Braitsch (1971).

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

FIGURE CAPTIONS

Figure 1. The conductance-viscosity product for water-salt solutions over the full range of composition.

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

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

Figure 4. The conductance-viscosity product for a system showing ion pairing in the dilute range. Note the change of scale at 1%; the system is tetrabutyl ammonium picrate-butyl alcohol.

Figure 5. The osmotic coefficient for sodium chloride solutions at various temperatures.

Figure 6. The osmotic coefficient for magnesium chloride solution at various temperatures.

Figure 7. Comparison of the solubility calculated by Harvie and Weare (1979) and the experimental solubility (points) of gypsum in aqueous NaCl solution at 25°. The dashed curves are calculated by the ion-association methods indicated. This figure is taken from Harvie and Weare (1979).

Figure 8. Comparison of the solubility calculated by Harvie and Weare (1979) (solid curves) and experimental solubilities (points) for gypsum and mirabilite in aqueous NaCl-Na_2SO_4 solution at 25°. The dashed curves are calculated by the ion-association methods indicated. This figure is taken from Harvie and Weare (1979).

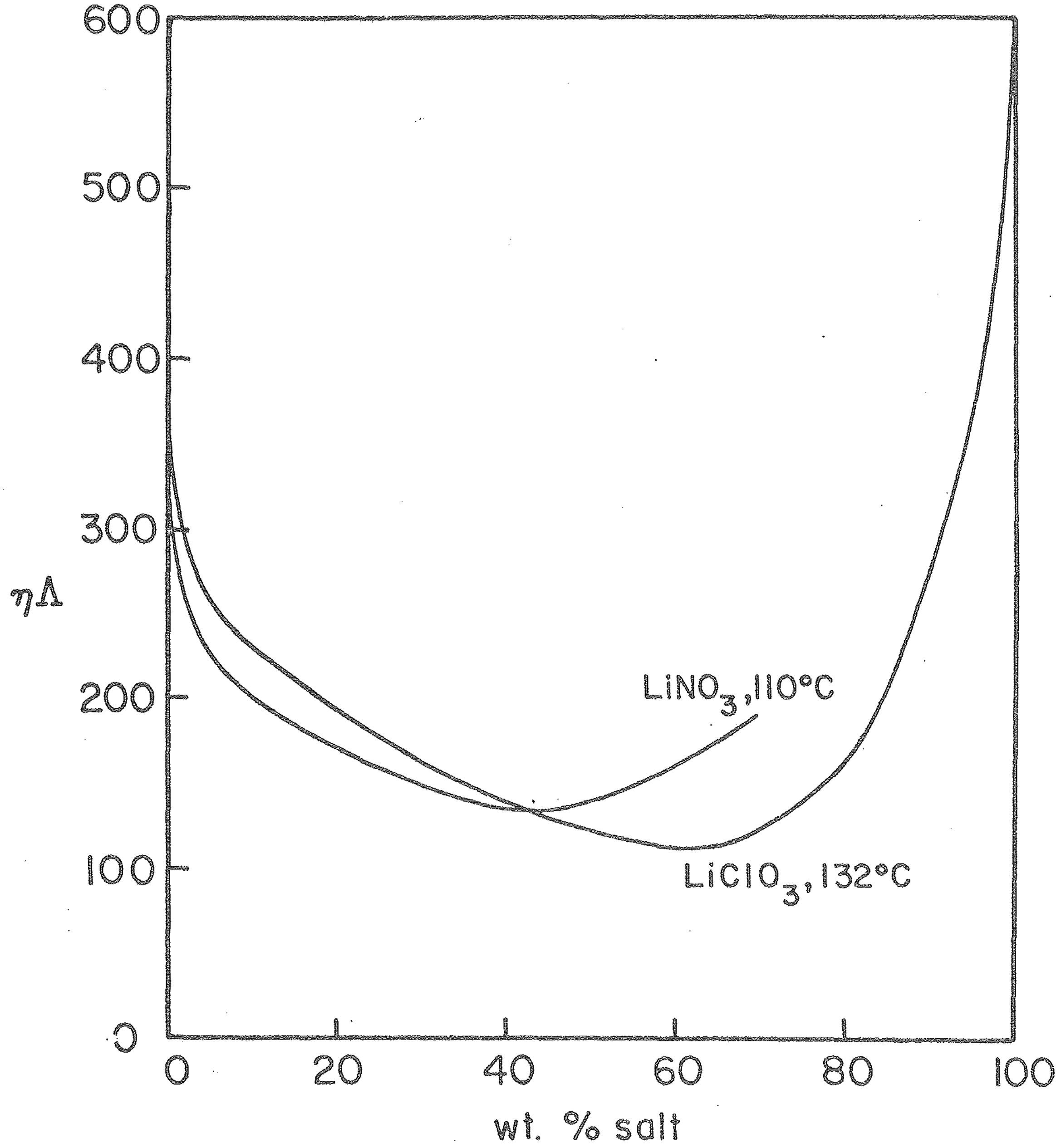

600
500
400
300
200
100
0
ηΛ
0
20
40
60
80
100
wt. % salt
LiNO3, 110°C
LiClO3, 132°C

Figure 1.

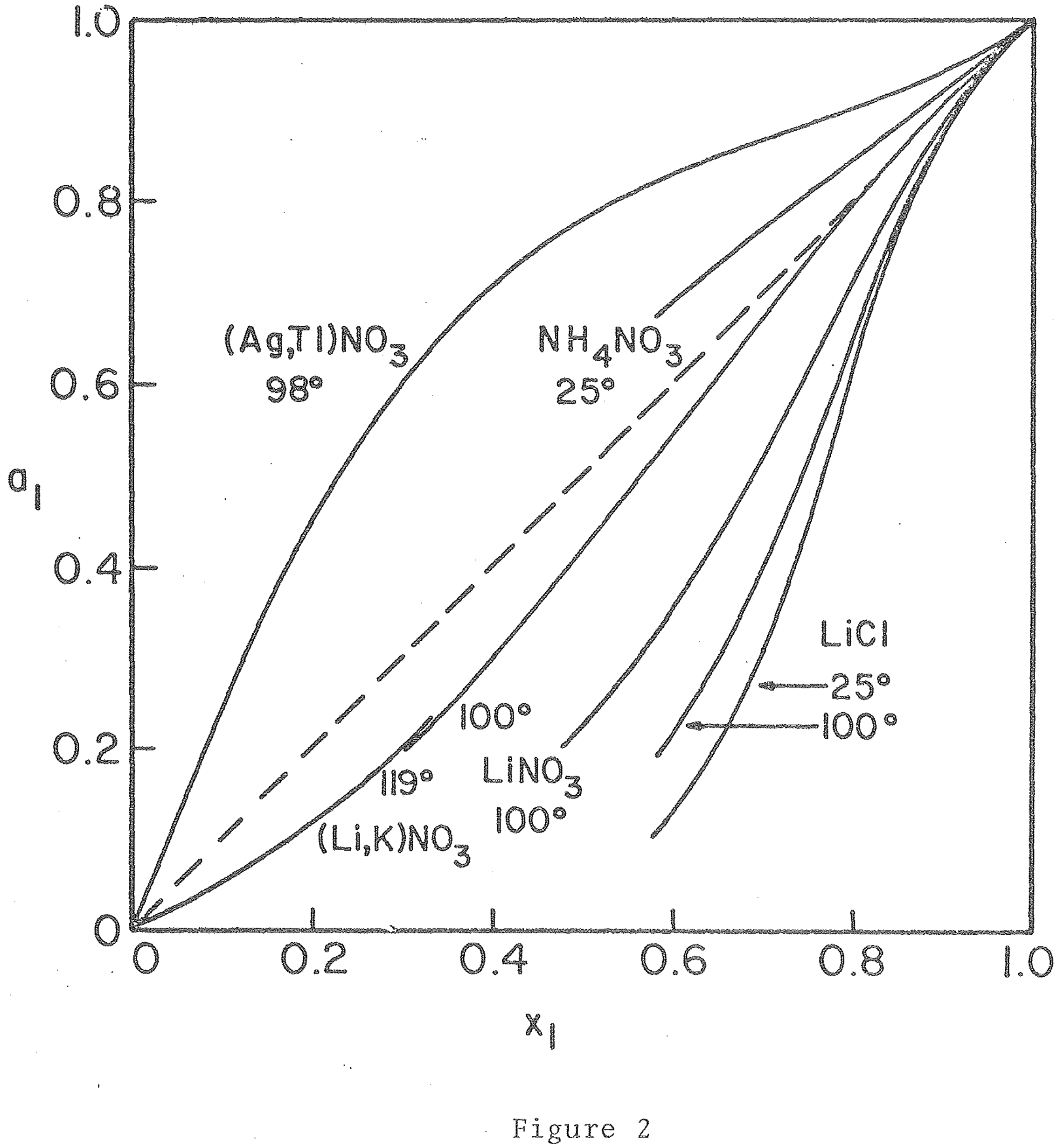
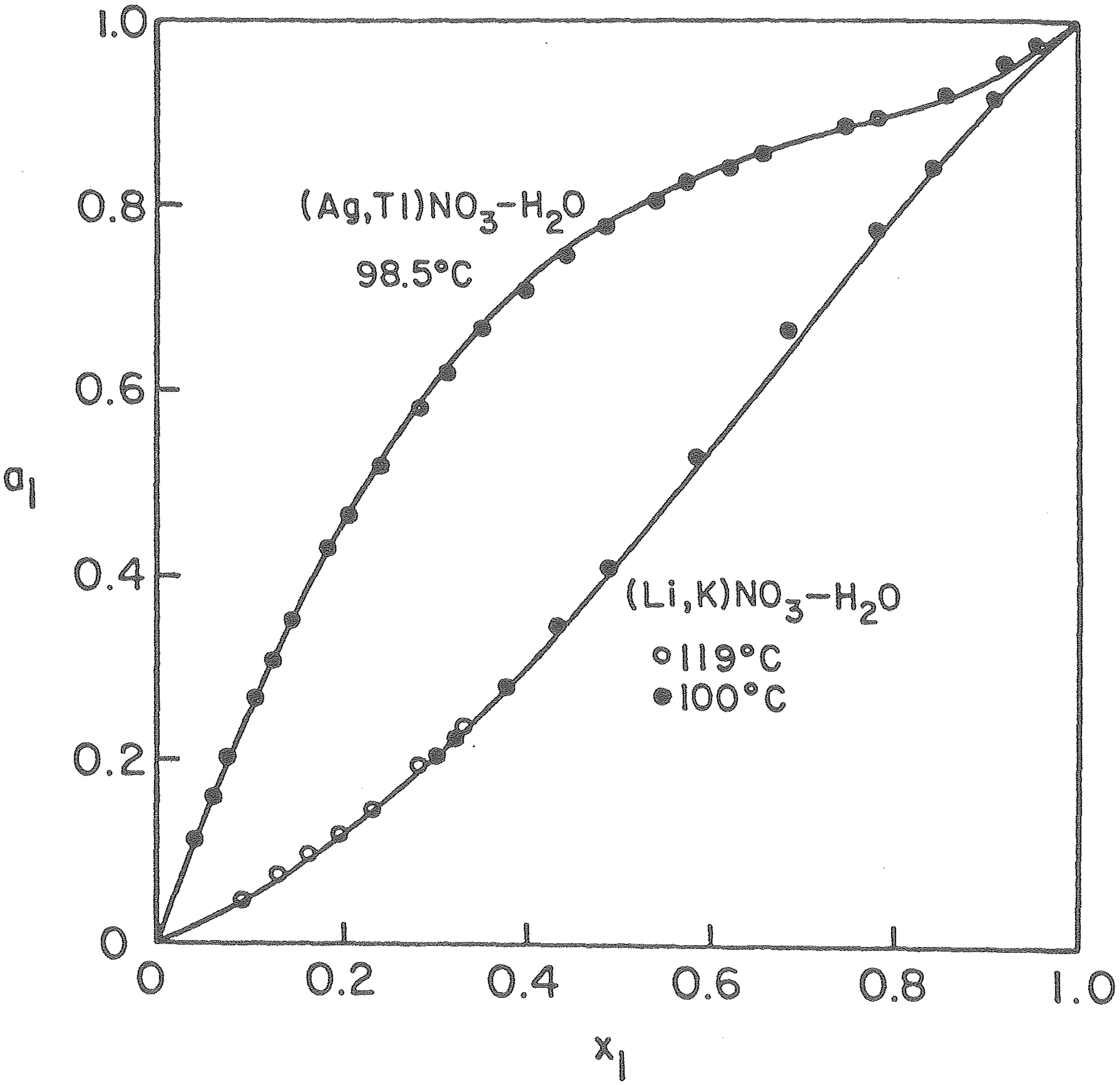

1.0
0.8
0.6
0.4
0.2
0
a_1
0
0.2
0.4
0.6
0.8
1.0
x_1
(Ag,Tl)NO$_3$
98°
NH$_4$NO$_3$
25°
100°
119°
(Li,K)NO$_3$
LiNO$_3$
100°
LiCl
25°
100°

Figure 2



1.0
0.8
0.6
0.4
0.2
0
a_1
0
0.2
0.4
0.6
0.8
1.0
x_1
$(Ag,Tl)NO_3-H_2O$
98.5°C
$(Li,K)NO_3-H_2O$
○ 119°C
● 100°C

Figure 3

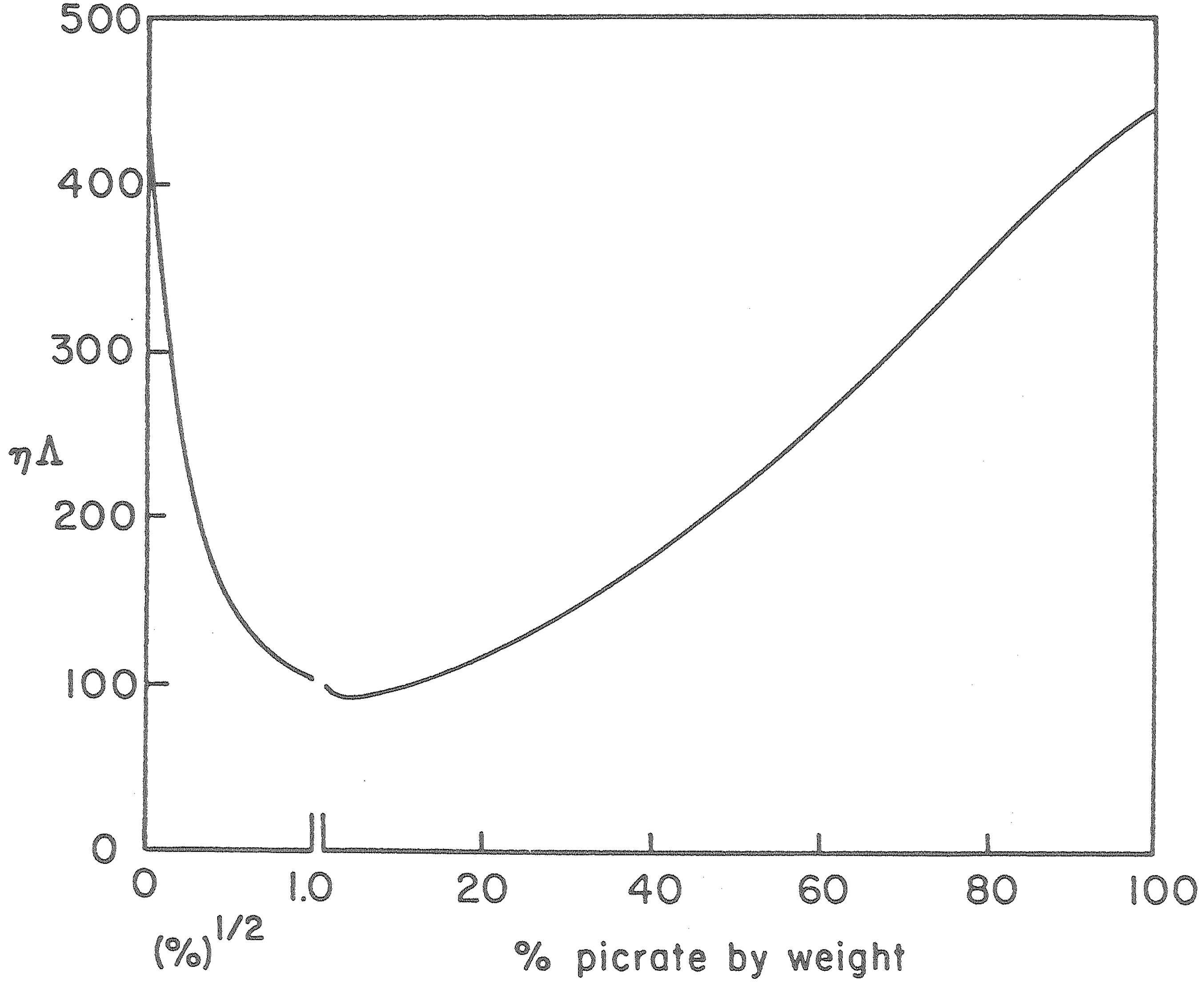

500
400
300
200
100
0
$\eta\Lambda$
0
1.0
20
40
60
80
100
$(\%)^{1/2}$
% picrate by weight

Figure 4

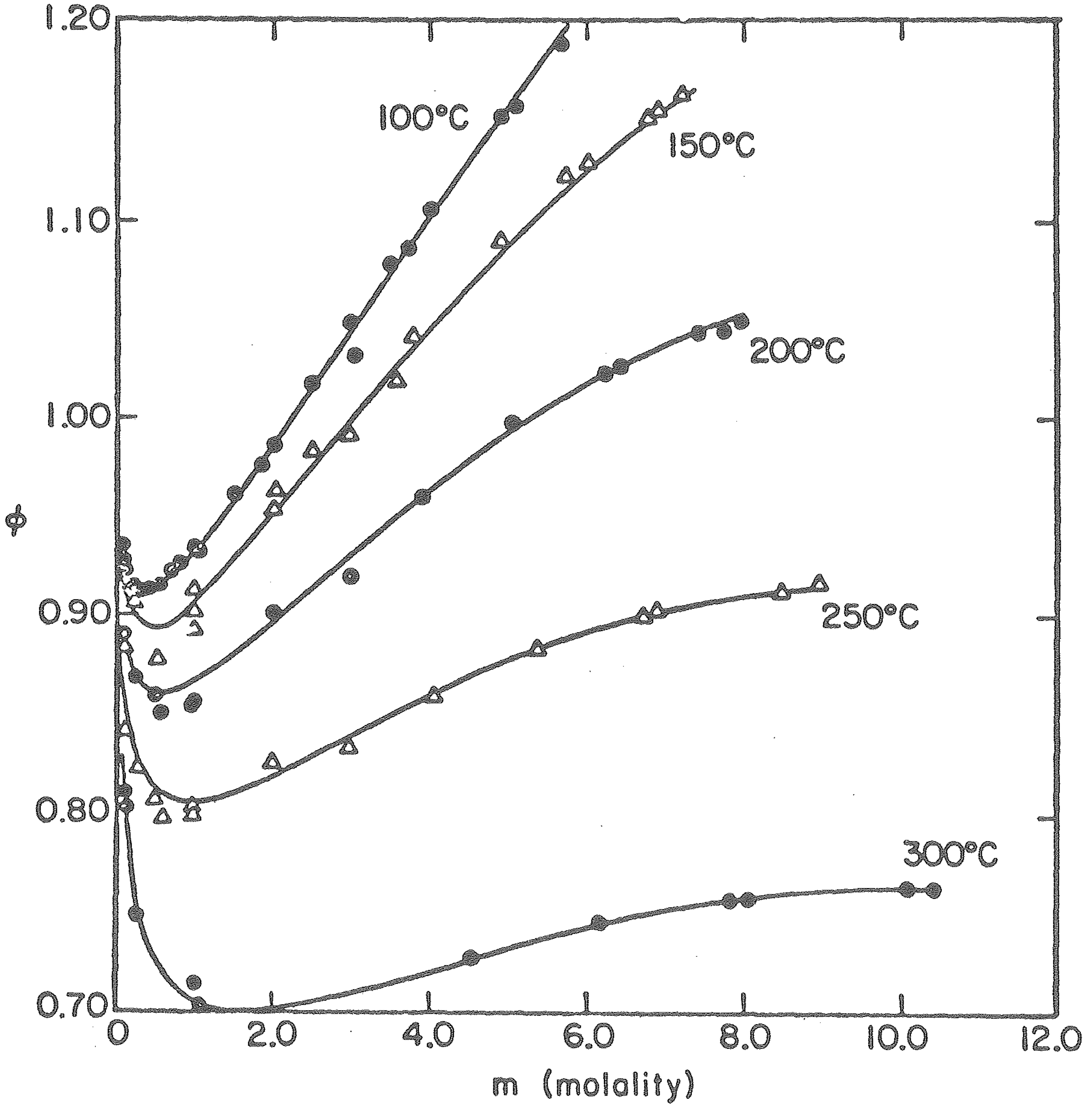

1.20
1.10
1.00
0.90
0.80
0.70
φ
0
2.0
4.0
6.0
8.0
10.0
12.0
m (molality)
100°C
150°C
200°C
250°C
300°C

Figure 5

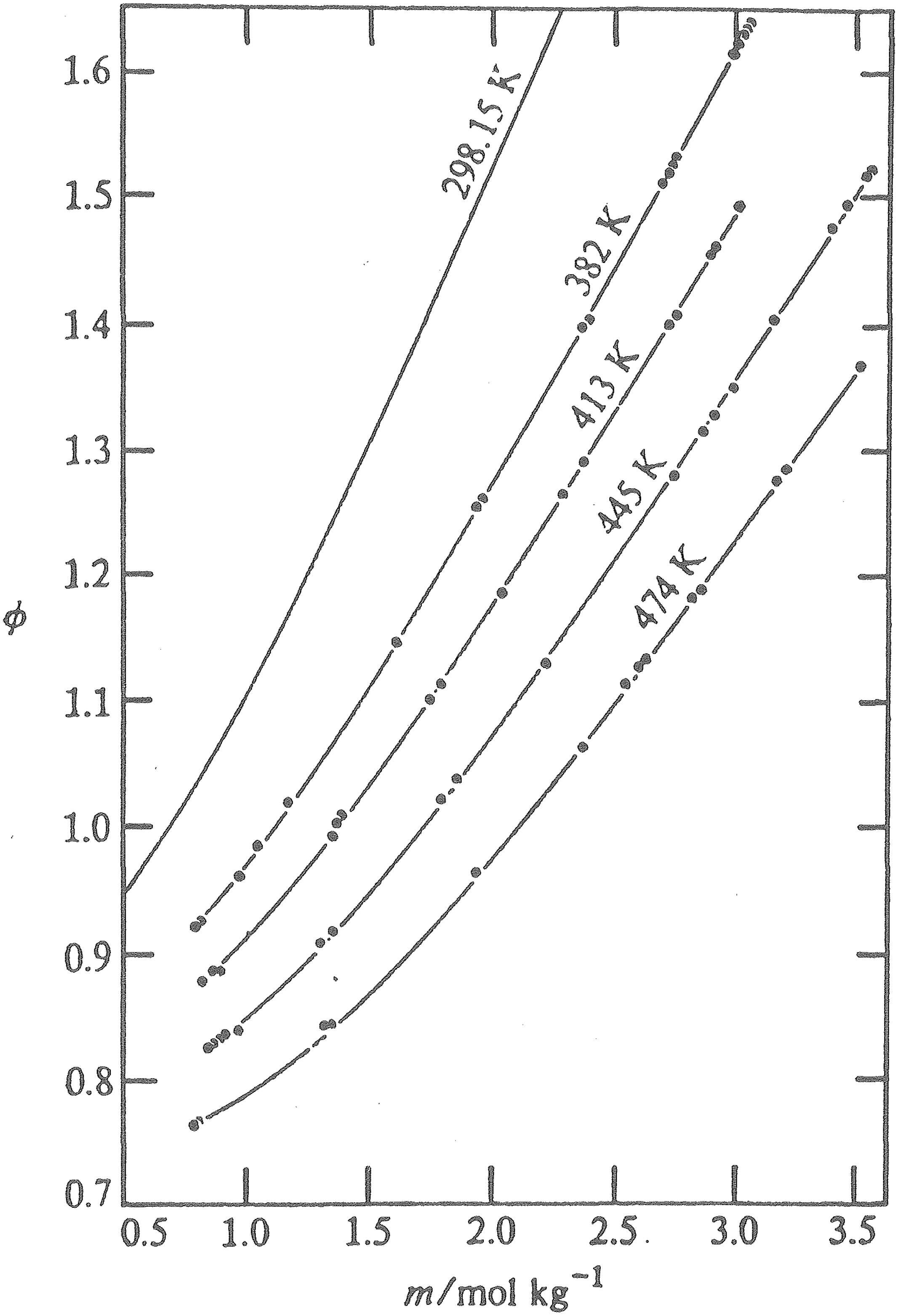

298.15 K
382 K
413 K
445 K
474 K
φ
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.5
1.0
1.5
2.0
2.5
3.0
3.5
m/mol kg⁻¹

Figure 6

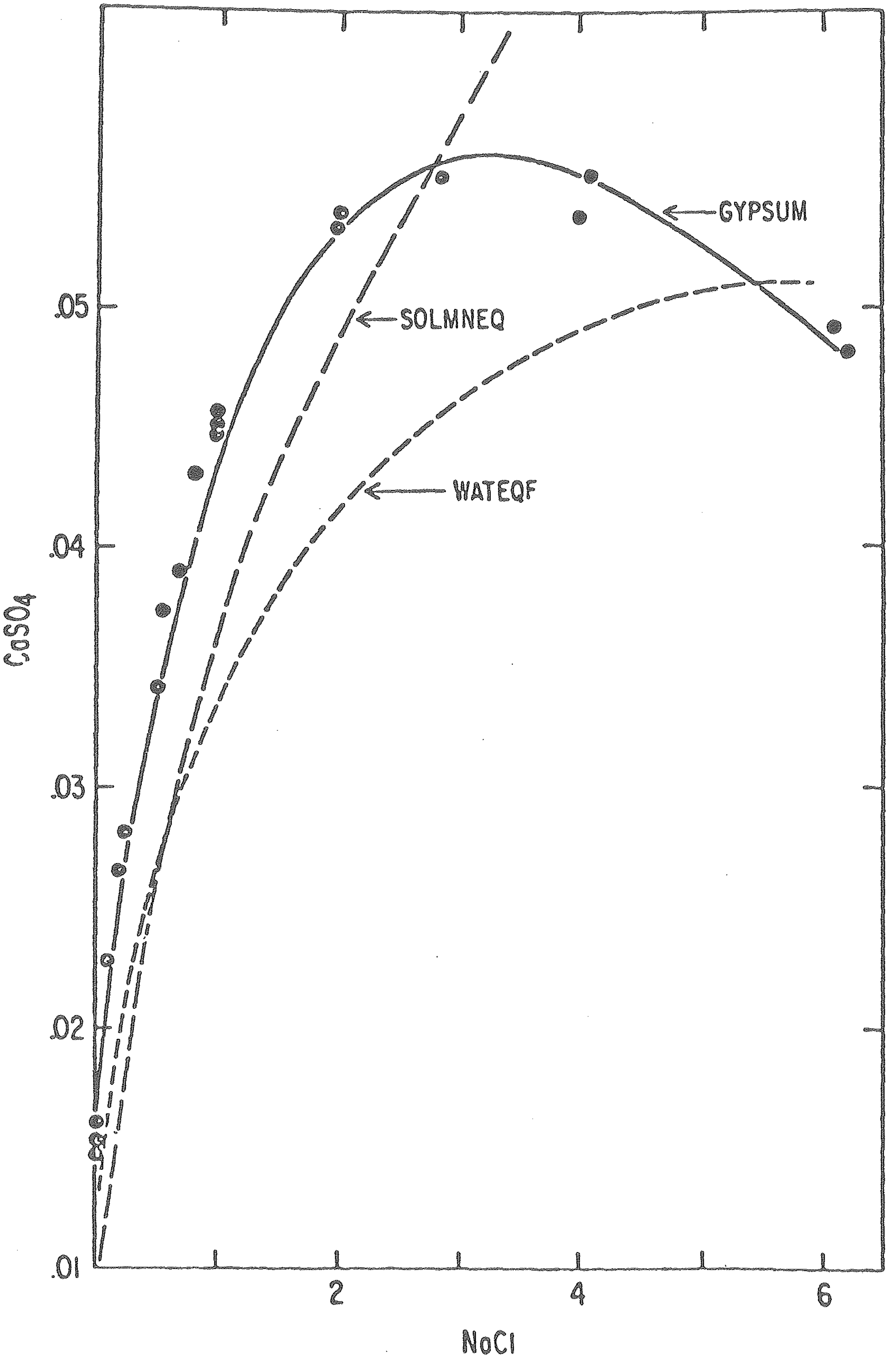


Figure 7

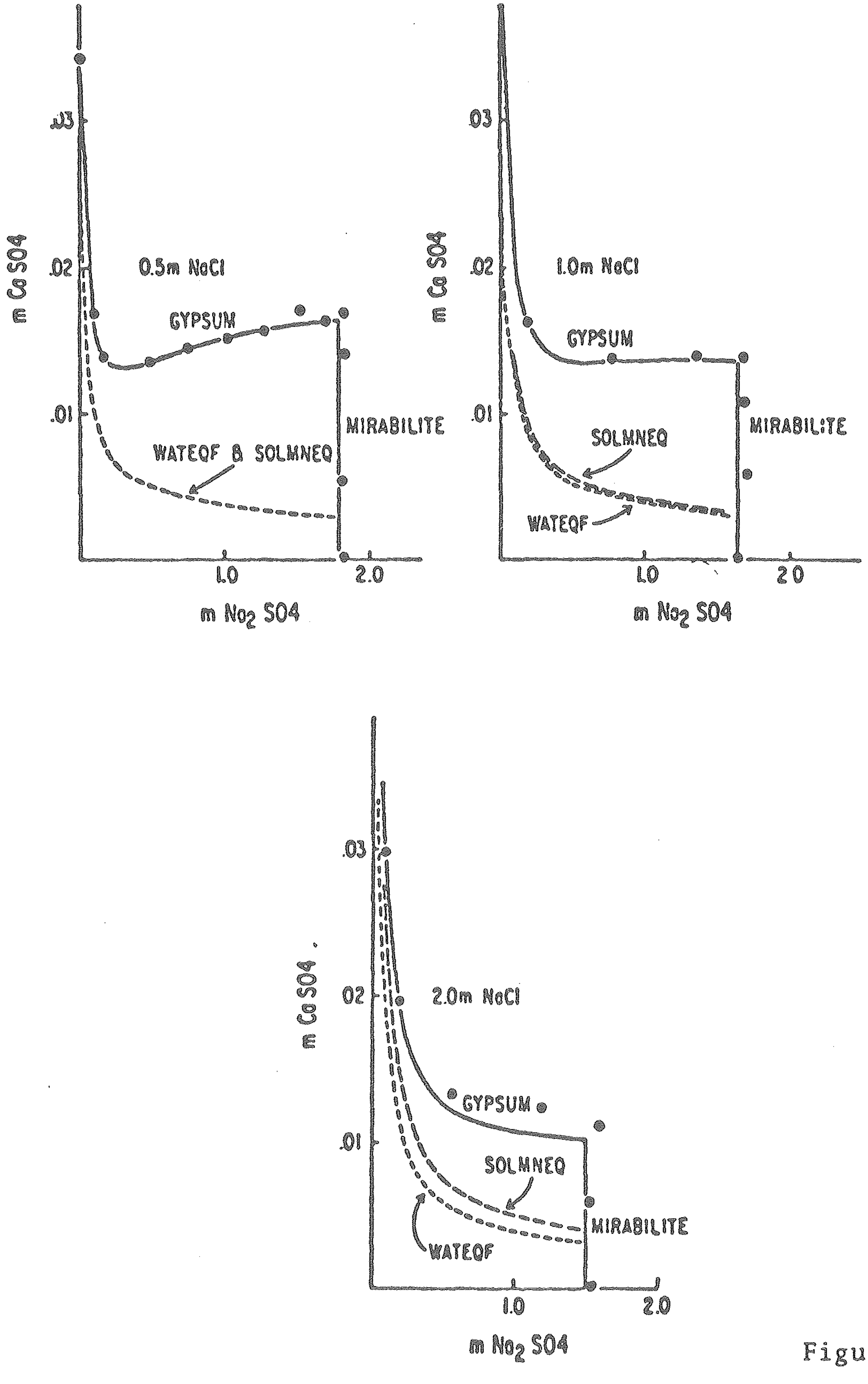

.03
.02
.01
m Ca SO4
0.5m NaCl
GYPSUM
MIRABILITE
WATEQF & SOLMNEQ
1.0
2.0
m Na2 SO4
.03
.02
.01
m Ca SO4
1.0m NaCl
GYPSUM
MIRABILITE
SOLMNEQ
WATEQF
1.0
2.0
m Na2 SO4
.03
.02
.01
m Ca SO4
2.0m NaCl
GYPSUM
SOLMNEQ
MIRABILITE
WATEQF
1.0
2.0
m Na2 SO4

Figure 8

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