Lawrence Berkeley National Laboratory

Recent Work

Title

THERMODYNAMICS OF AQUEOUS ELECTROLYTES AT VARIOUS TEMPERATURES, PRESSURES, AND COMPOSITIONS

Permalink

<https://escholarship.org/uc/item/0m41b3n8>

Author

Pitzer, K.S.

Publication Date

1979-09-01

MASTER

LBL-9788

CONF-791063--1

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

To be presented at the Conference on Thermodynamics of
Aqueous Systems with Industrial Applications, Arlie House,
Washington, D. C., October 22-24, 1979

THERMODYNAMICS OF AQUEOUS ELECTROLYTES AT VARIOUS
TEMPERATURES, PRESSURES, AND COMPOSITIONS

Kenneth S. Pitzer

September 1979

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

MASTER

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

THERMODYNAMICS OF AQUEOUS ELECTROLYTES AT VARIOUS TEMPERATURES, PRESSURES, AND COMPOSITIONS

Kenneth S. Pitzer

Department of Chemistry and Lawrence Berkeley Laboratory,
University of California, Berkeley, CA 94720

Early in this century there was great interest in the apparently anomalous properties of aqueous electrolytes. The anomaly concerned the limiting behavior at low concentration. While several investigators contributed substantially to the resolution of this problem, it was the classic work of Debye and Hückel (1) which provided a simple yet adequate explanation of the effect on thermodynamic properties of the long-range electrostatic forces between ions in solution. The experimental work of that era tended to emphasize dilute solutions at room temperature. While Debye and Hückel recognized the short-range repulsive forces between ions by assuming a hard-core model, the statistical mechanical methods then available did not allow a full treatment of the effects of this hard core. Only the effect on the electrostatic energy was included -- not the direct effect of the hard core on thermodynamic properties.

As is often the case, after the intense activity of the 1920's, the investigation of aqueous electrolytes proceeded at a more relaxed pace. But careful and systematic experimental research continued in this area and was summarized by Harned and Owen (2) and by Robinson and Stokes (3) in their

excellent monographs. The latter volume contains in the appendix a comprehensive set of tables of the osmotic and activity coefficients of the common inorganic solutes at 25°C and at concentrations up to 6 M in most cases.

Major theoretical advances were made, principally by Mayer, in creating an adequate statistical mechanical theory in which both long-range electrostatic forces and short-range forces of whatever origin were properly considered. Friedman has contributed greatly to further theoretical advances and will discuss recent work in this symposium. Also important are the Monte Carlo calculations of Card and Valleau (4). The writer has published (5) an elementary review of these theoretical advances; more advanced reviews are available by Friedman (6) and by Andersen (7). The result is that the properties of univalent aqueous electrolytes based on the hard core and other simple models (8) are now known from reliable theory up to a concentration of 1 or 2 M. While the actual interionic potentials of mean force doubtless differ somewhat from the models treated, the resulting thermodynamic properties will be similar. Thus we have good theoretical guidance in selecting forms of equations for semi-empirical use. For more highly charged ions or a solvent with substantially lower dielectric constant the situation is somewhat more complex, but the theory is reasonably satisfactory and is being further improved.

From the thermodynamic viewpoint, the basic statistical theory is still too complex to provide useful working equations, but it does suggest forms of equations with some theoretical

terms, and other terms including parameters to be evaluated empirically. In general, the theoretical terms arise from the electrostatic interactions which are simple and well-known while the empirical terms relate to short-range inter-ionic forces whose characteristics are qualitatively but not quantitatively known from independent sources. But, as we shall see, this division is not complete - there are interactions between the two categories.

In recent years there has been a resurgence of experimental research on aqueous inorganic electrolytes emphasizing the broader domain of high temperatures or high pressures or both. Also many organic solutes have been investigated at room temperature. Thus most of the pure aqueous electrolytes likely to be of engineering interest have been investigated at room temperature, a substantial number have been studied over the 0 - 50°C range, and a smaller but increasing number at high pressures and at temperatures to 300°C or occasionally higher.

Most practical systems, however, are mixtures rather than pure electrolytes. The experimental measurement of a wide variety of mixtures over closely spaced grids of composition would be very burdensome. It is here, for mixed electrolytes, that theory, confirmed by a limited number of experiments, is particularly valuable. The electrostatic interactions are all simply defined; also the short-range forces between a pair of ions of different sign are the same in a mixed electrolyte as in the pure electrolyte comprising

that pair of ions. Thus a proper definition of terms will allow the evaluation of all of these effects in mixtures from information on the various pure electrolytes. It is for the effect of short-range forces between ions of the same sign that new terms arise for mixtures. But ions of the same sign repel one another and are unlikely to be so close together that their short-range forces have a large effect. Indeed Bronsted (9) postulated that these differences among short-range interactions among ions of the same sign could be ignored and Guggenheim (10) developed detailed equations on that basis. Kim and the writer (11) found that such differences were not completely negligible for mixtures of singly charged ions or for 2-1 charged mixtures but that they were very small. Also these difference terms can be evaluated from existing measurements on simple mixtures of the most important ions. Thereafter, for complex mixtures of practical importance, all of the important terms are known and only very small terms must be neglected from lack of information.

From the preceding paragraphs it is clear that the capacity to calculate the properties of a variety of mixed electrolytes depends on an adequate theoretical structure within which the available experimental data can be organized. Thus the primary emphasis for the remainder of this paper will be the description of this structure of semi-empirical equations. The array of substances for which experimental data are available will be described in general terms but there is not sufficient space to list results in detail. Also a severe

test of predictions for mixed electrolytes will be reported.

But before turning to the detailed consideration of electrolytes of moderate concentration, it is interesting to note the properties of a few systems which exist as liquids from pure fused salts to dilute aqueous solutions.

Miscible Electrolytes

There are two systems for which the vapor pressure and thereby the activity of water has been measured over the full range of composition from fused salt to dilute solution in water. In each case the salt is a simple mixture of approximately equal molal proportions. The system $(\text{Ag}, \text{Tl})\text{NO}_3$ was measured at 98°C by Trudelle, Abraham, and Sangster (12) while $(\text{Li}, \text{K})\text{NO}_3$ was measured in the most concentrated range at 119°C by Tripp and Braunstein (13) and over the remainder of the range at 100°C by Braunstein and Braunstein (14). These results are shown on Figure 1 which also includes similar data for several systems of large but limited solubility. The composition variable is the mole fraction on an ionized basis, i.e., $x_1 = n_1/(n_1 + vn_2)$ where n_1 and n_2 are moles of water and salt, respectively, and v is the number of ions in the salt. On this basis Raoult's law applies in the very dilute range, with the Debye-Hückel correction applicable as the concentration increases.

The similarity of the curves on Figure 1 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 (15) and has been widely used since. Prausnitz (16) discusses this and related equations as well as the contributions of Margules, Hildebrand, Scatchard, Guggenheim, and others to this topic. For the activity of either component, referenced to the pure liquid, one has

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

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

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

$$z_2 = v n_2 / [n_1 (b_1/b_2) + v n_2] \quad (1d)$$

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

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

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

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

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, although 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.

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 $(\text{Ag,Tl})\text{NO}_3\text{-H}_2\text{O}$ and $w_1 = -0.89$, $(b_1/b_2) = 1.2$ for $(\text{Li,K})\text{NO}_3\text{-H}_2\text{O}$. Water is component 1 and the salt component 2. 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 Figure 2.

These results shown in Figures 1 and 2 demonstrate the similarity of the effects of short-range forces on the properties of nonelectrolytes and concentrated electrolytes. One finds both positive and negative deviations from ideality and these effects may be ascribed to the difference between the intermolecular potential energy of attraction of unlike species to the mean of the corresponding potentials for pairs of like molecules. Previous discussion of these systems has focused on the hydration of the positive ion as the dominant

effect, but we see in Figure 1 that the shift from nitrate to chloride is comparably important. Just as for nonelectrolytes, one must consider all intermolecular forces in electrolytes.

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 have been overcome, and the more complex relationships are being presented elsewhere (17). However, for most purposes, the virial coefficient equations for electrolytes are more convenient and have been widely used. Hence our primary presentation will be in those terms.

Virial Coefficient Equations for Electrolytes

A very effective method of representing the properties of non-ideal gases is by use of a series in increasing powers of density or concentrations. The coefficients, called virial coefficients, are unambiguously related to a particular number of molecules. Thus the first term relates to individual molecules and is the ideal gas law. The second virial coefficient arises from binary intermolecular forces and may be either positive or negative as repulsive or attractive forces predominate. The third virial coefficient arises from triple interactions, etc. The MacMillan-Mayer (18) solution theory established that a formally similar treatment applied to solutes in a solvent provided the intermolecular potentials are replaced by potentials of mean force in that solvent. For electrolytes one must recognize the long-range character of coulombic forces which prevents their inclusion in the virial series. But as Mayer (19) and others have shown, one may combine a Debye-Hückel term for electrostatic effects with a virial series for the effects of short range forces. In this case, however, the virial coefficients depend on the ionic strength as well as the temperature and other properties. These theoretical principles were used by the writer (20) to establish the form of an equation for electrolyte properties in which the virial coefficients are evaluated empirically. Virial type equations were used earlier for electrolytes (10, 21, 22) but without recognition of the ionic strength dependence of the second virial coefficient. The basic equation is

postulated for the excess Gibbs energy from which other functions can be obtained from appropriate derivatives.

$$G^{\text{ex}}/n_w RT = f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k. \quad (3)$$

Here 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).

The derivative equations for osmotic and activity coefficients, which are presented below, were applied to the experimental data for wide variety of pure aqueous electrolytes at 25°C by Pitzer and Mayorga (23) and to mixtures by Pitzer and Kim (11). Later work (24-28) considered special groups of solutes and cases where an association equilibrium was present (H_3PO_4 and H_2SO_4). While there was no attempt in these papers to include all solutes for which experimental data exist, nearly 300 pure electrolytes and 70 mixed systems were considered

and the resulting parameters reported. This represents the most extensive survey of aqueous electrolyte thermodynamics, although it was not as thorough in some respects as the earlier evaluation of Robinson and Stokes (3). In some cases where data from several sources are of comparable accuracy, a new critical evaluation was made, but in other cases the tables of Robinson and Stokes were accepted.

In addition to the activity and osmotic coefficients at room temperature, the first temperature derivatives and the related enthalpy of dilution data were considered for over 100 electrolytes (26, 29). The data for electrolytes at higher temperatures become progressively more sparse. Quite a few solutes have been measured up to about 50°C (and down to 0°C). Also, over this range, the equations using just first temperature derivatives have some validity for rough estimates in other cases. But the effects of the second derivative (or the heat capacity) on activity coefficients at higher temperatures is very substantial.

Sodium chloride has been studied much more thoroughly at high temperature than any other electrolyte. The osmotic coefficient measurements of Liu and Lindsay (30) and various types of measurements of Federov and associates (31) are particularly noteworthy. A preliminary effort to represent all of the data on sodium chloride by virial coefficient equations has been published (32) and a revision is being completed (33).

Over the wide range of temperature to 100°C and concentration to 10 M, sodium chloride shows only very moderate and slow changes in its properties; the principal change is the increase in the Debye-Huckel (34) parameter which lowers both activity and osmotic coefficients. The osmotic coefficient for NaCl at high temperature is shown on Figure 3; the curves were calculated by the virial coefficient equation (33). The behavior of a typical 2-1 electrolyte, MgCl_2 , is shown on Figure 4, which gives both the experimental values of Holmes, Baes, and Mesmer (35) and their curves from a virial coefficient equation. Only a few additional salts have been studied extensively at high temperatures, although solubility information yields less a complete picture for several others (36). However, the general patterns of behavior are simple enough that one can make estimates under some circumstances based on detailed data at room temperature for the solute of interest and high temperature data for other solutes of the same valence type.

The importance of the virial-coefficient equations is especially great for mixed electrolytes. Of the needed virial coefficients for a complex mixture such as sea water, most are determined by the pure electrolyte measurements and all the others of any significance are determined from data on simple mixtures such as NaCl-KCl , NaCl-MgCl_2 , $\text{NaCl-Na}_2\text{SO}_4$, etc., which have been measured. The effect of the terms obtained from mixtures is very small in any case and these terms can be ignored for all but the most abundant species.

A very severe test of these virial-coefficient equations for the sea-water-related Na-K-Mg-Ca-Cl-SO₄-H₂O system has been made by Harvie and Weare (37) who calculated the solubility relationships for all solids which can arise from this complex system. There are 13 invariant points with four solids present and the predicted solution composition in all 13 cases agrees with the experimental values of Braitsch (38) substantially within the estimated error of measurement. In particular, Harvie and Weare found that fourth virial coefficients were not required even in the most concentrated solutions. They did make a few small adjustments in third virial coefficients which had not previously been accurately measured, but otherwise they used the previously published parameters.

There are also many less severe tests (11) of predictions for mixed electrolytes which illustrate the accuracy to be expected in various cases. Thus it is well-established that the virial coefficient equations for electrolytes yield reliable predictions of mixed-electrolyte properties provided the coefficients measurable for the pure electrolyte components are known. The predictions are more accurate if the additional coefficients measurable from simple mixtures are also known but their effect is usually very small.

The working equations for osmotic and activity coefficients, derived from equation (3) are given as equations (4) and (5), respectively. The various secondary relationships are defined in several additional equations stated and briefly described thereafter. Additional details and derivations of equations for the entropy, the heat capacity, and other related functions

can be found in various published papers (11, 20, 23-29, 32-34).

$$\begin{aligned}
 (\phi-1) = & \frac{2}{\left(\sum_i m_i\right)} \left\{ -\frac{A_\phi I^{3/2}}{1+bI^{1/2}} + \sum_c \sum_a m_c m_a (B_{ca}^\phi + ZC_{ca}) \right. \\
 & + \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} (\theta_{cc'}^\phi + \sum_a m_a \psi_{cc'a}) + \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} (\theta_{aa'}^\phi \\
 & \left. + \sum_c m_c \psi_{aa'c}) \right\} \quad (4)
 \end{aligned}$$

Although one wishes activity coefficients for neutral combinations of ions, it is convenient to use equations for single-ion activity coefficients which can then be combined appropriately.

$$\begin{aligned}
 \ln \gamma_M = & z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c (2\theta_{Mc} + \sum_a m_a \psi_{Mca}) \\
 & + \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} \psi_{aa'M} + |z_M| \sum_c \sum_a m_c m_a C_{ca} \quad (5a)
 \end{aligned}$$

$$\begin{aligned}
 \ln \gamma_X = & z_X^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}) + \sum_a m_a (2\theta_{Xa} + \sum_c m_c \psi_{Xac}) \\
 & + \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} \psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca}. \quad (5b)
 \end{aligned}$$

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 measurable combinations of λ 's whereas C 's and ψ 's are combinations of the μ 's in Equation (3). Note that the θ 's and ψ 's are zero and these terms disappear for pure electrolytes.

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

$$A_\phi = (1/3)(2\pi N_0 d_w / 1000)^{1/2} (e^2 / DkT)^{3/2}$$

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

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

with $b = 1.2$ chosen for all electrolytes in water. At 25°C the value of A_ϕ is 0.391. The appropriate derivative gives the term in Equation (4) for ϕ . For the activity coefficient it is convenient to define

$$F = -A_\phi [I^{1/2} / (1 + bI^{1/2}) + (2/b) \ln(1 + bI^{1/2})] + \sum_b \sum_a m_c m_a B'_{ca} \\ + \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} \theta'_{cc'} + \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} \theta'_{aa'} \quad (7)$$

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

The second virial 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 $\beta^{(0)}$ and $\beta^{(1)}$ parameters fitted to the data for each solute.

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha I^{1/2}} \quad (8a)$$

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

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

where the functions g and g' are given by

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

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

with $x = \alpha I^{1/2}$. In Equations (8) the form given is for 1-1 and 1-2 electrolytes for which the value $\alpha = 2$ was chosen empirically. For higher valence types, such as 2-2 electrolytes, where there is a tendency toward ion-pairing, an additional term is added and Equations (8) become

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

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

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

In this case the values of $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$ are assigned.

The parameters, C_{MX} , are related to the tabulated parameters of Pitzer and Mayorga (23), C_{MX}^ϕ , as follows,

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

also the quantity Z is defined to be

$$Z = \sum_i m_i |z_i| = 2 \sum_c m_c z_c. \quad (12)$$

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 Equations (13),

$$\theta_{ij}^{\phi} = \theta_{ij} + E_{\theta_{ij}}(I) + I E_{\theta'_{ij}}(I) \quad (13a)$$

$$\theta_{ij} = \theta_{ij} + E_{\theta_{ij}}(I) \quad (13b)$$

$$\theta_{ij} = E_{\theta'_{ij}}(I) \quad (13c)$$

θ_{ij} , a single parameter for each pair of anions or each pair of cations, is the only adjustable parameter in Equations (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 (39); this effect was discovered by Friedman (6). 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 (37) have found these special electrostatic terms to be important for the $\text{CaSO}_4\text{-NaCl}$ system and some more complex mixtures involving singly and doubly charged ions.

It would burden this paper excessively to list the parameters for all known electrolytes, even at room temperature. As examples giving the pattern of magnitudes as well as values for widely appearing salts, the values for the $\text{Na-K-Mg-Ca-Cl-SO}_4\text{-H}_2\text{O}$ system are listed in Tables 1 and 2. Most of these are taken from Pitzer and Mayorga (23) or Pitzer and Kim (11) but a few were revised in later work including that of Harvie

and Weare (37). It is apparent that the pure-electrolyte parameters in Table 1 are much larger than those for mixing of ions of the same sign in Table 2. Also the second virial coefficients are much larger than the third virial coefficients in Table 1.

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 to 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 and these coefficients are known for nearly 300 electrolytes at room temperature. These same equations effectively predict the properties of mixed electrolytes. A stringent test is offered by the calculation of all of the solubility relationships of the system Na-K-Mg-Ca-Cl-SO₄-H₂O and the calculated results of Harvie and Weare show excellent agreement with experiment.

Acknowledgements

This research was supported by the Office of Basic Energy Sciences, U. S. Department of Energy, under Contract No. W-7405-Eng-48. I thank Dr. John H. Weare for sending me his results in advance of publication.

References

1. Debye, P. and Hückel, E., Physik. Z. (1923) 24, 185, 334; (1924) 25, 97.
2. Harned, H. S. and Owen, B. B., "The Physical Chemistry of Electrolyte Solutions," 3rd Ed. Reinhold Publishing Co., New York (1958).
3. Robinson, R. A. and Stokes, R. H., "Electrolyte Solutions," Butterworths, London, 1955, revised 1959.
4. Card, D. N. and Valleau, J. P., J. Chem. Phys. (1970) 52, 6232.
5. Pitzer, K. S., Accounts of Chemical Research, (1977) 10, 371.
6. Friedman, H. L. "Ionic Solution Theory," Interscience (1962).
7. Anderson, H. C., "Improvements upon the Debye-Hückel Theory of Ionic Solutions," in "Modern Aspects of Electrochemistry," No. 11, B. E. Conway and J. O'M. Bockris, Eds., Plenum Press, New York, 1975.
8. Ramanathan, P. S. and Friedman, H. L., J. Chem. Phys. (1971) 54, 1086.
9. Bronsted, J. N., Kgl. Dan. Vidensk. Selsk., Mat. Fys. Medd., (1929) 4, (4); J. Am. Chem. Soc., (1922) 44, 877; (1923) 45, 2898.

10. Guggenheim, E. A., Phil. Mag. [7] (1935) 19, 588; also Guggenheim, E. A. and Turgeon, J. C., Trans. Faraday Soc., (1955) 51, 747.
11. Pitzer, K. S. and Kim, J. J., J. Am. Chem. Soc. (1974) 96, 5701.
12. Trudelle, M-C., Abraham, M. and Sangster, J., Can. J. Chem. (1977) 55, 1713.
13. Tripp, T. B. and Braunstein, J., J. Am. Chem. Soc. (1954) 73, 1984.
14. Braunstein, H. and Braunstein, J., J. Chem. Thermodynamics (1971) 3, 419.
15. van Laar, J. J., Z. physik. Chem. (1906) 72; (1910) 723.
16. Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria," Prentice-Hall, Inc., Englewood Cliffs, NJ (1969).
17. Pitzer, K. S., in preparation for publication.
18. McMillan, W. G. and Mayer, J. E., J. Chem. Phys., (1945) 13, 276.
19. Mayer, J. E., J. Chem. Phys. (1950) 18, 1426; see also Reference 6.
20. Pitzer, K. S., J. Phys. Chem. (1973) 77, 268.
21. Scatchard, G., J. Am. Chem. Soc. (1968) 90, 3124.
22. Scatchard, G., Rush, R. M. and Johnson, J. S., J. Phys. Chem. (1970) 74, 3786.
23. Pitzer, K. S. and Mayorga, G., J. Phys. Chem. (1973) 77, 2300; J. Soln. Chem., (1974) 3, 539.
24. Pitzer, K. S. and Silvester, L. F., J. Solution Chem., (1976) 5, 269.

25. Pitzer, K. S., Roy, R. N., and Silvester, L. F., J. Am. Chem. Soc., (1977) 99, 4930.
26. Pitzer, K. S., Peterson, J. R., and Silvester, L. F., J. Solution Chemistry, (1978) 7, 45.
27. Pitzer, K. S. and Silvester, L. F., J. Phys. Chem. (1978) 82, 1239.
28. Downes, C. J. and Pitzer, K. S., J. Solution Chem., (1976) 5, 389).
29. Silvester, L. F. and Pitzer, K. S., J. Solution Chem., (1978) 7, 327.
30. Liu, C. and Lindaay, W. T., J. Solution Chem., (1972) 1, 45; J. Phys. Chem., (1970) 74, 341.
31. Puchkov, L. V., Styazhkin, P. S., and Federov, M. K., J. Appl. Chem. (USSR) (1977) 50, 1004; Atonov, N. A., Gilyarov, V. N., Zarembo, V. I., and Federov, M. K., ibid, (1976) 49, 120; and other papers there cited.
32. Silvester, L. F. and Pitzer, K. S., J. Phys. Chem. (1977) 81, 1822.
33. Pitzer, K. S., Bradley, D. J., Rogers, P. S. Z., and Peiper, J. C., paper at Honolulu meeting of the A.C.S. (1979), to be published.
34. Bradley, D. J. and Pitzer, K. S., J. Phys. Chem., (1979) 83, 1599.
35. Holmes, H. F., Baes, C. F., Jr., and Mesmer, R. E., J. Chem. Thermo. (1978) 10, 983.
36. For example, Marshall, W. L., J. Phys. Chem., (1967) 71, 3584.
37. Harvie, C. E. and Weare, J. H., submitted for publication.
38. Braitsch, O., "Salt deposits: their origin and composition," Springer Verlag (1971).

39. Pitzer, K. S., J. Solution Chem., (1975) 4, 249.

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

M	X	$\beta_{MX}^{(0)}$	$\beta_{MX}^{(1)}$	$\beta_{MX}^{(2)}$	C_{MX}^{ϕ}
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 SO ₄	-.012	-.0018 -.010
Na	Mg	Cl SO ₄	.07	-.012 -.015
Na	Ca	Cl SO ₄	.07	-.014 -.023
K	Mg	Cl SO ₄	.0	-.022 -.048
K	Ca	Cl SO ₄	.032	-.025 0
Mg	Ca	Cl SO ₄	.007	-.012 .05
Cl	SO ₄	Na K Mg Ca	.02	.0014 0 -.004 0

Figure Captions

Figure 1. The activity of water for water-salt solutions over a very wide range of composition.

Figure 2. Comparison of the calculated and experimental activity of water for water-salt solutions over the full range of composition.

Figure 3. The osmotic coefficient for sodium chloride solutions at various temperatures.

Figure 4. The osmotic coefficient for magnesium chloride solution at various temperatures.

Fig. 3

Figure 4