A Hydration Model of Aqueous Solutions of Inorganic Electrolytes at High Temperature and Pressure

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HPL-94-51
May, 1994

activity coefficients, conductivity, degree of dissociation, distribution coefficient, electrolytes, hydration, ideal solution, ionic dissociation, solubility, steam

The classical model of electrolytic solutions fails to explain the correlations of Styrikhovich, of Martynova and of Marshall. An expanded version which includes the hydration processes inherent in solubilization and ionic dissociation processes was shown to be internally inconsistent.

A new hydration model of aqueous solutions of inorganic electrolytes at high temperature and pressure, based on a novel interpretation of ionic dissociation at high temperature and pressure, is proposed. The model yields a unifying treatment of electrolytic solutions at high temperature and pressure valid over the whole range of electrolytes from the weakest to the strongest, in liquid and vapor phases as well as in cases where the solvent is diluted with an inert fluid.

The proposed model accounts for the correlations of Styrikhovich, of Martynova and of Marshall, and shows that these correlations are particular cases of the more general relations derived from that model by rigorous thermodynamic reasoning. The proposed model also predicts the gradual conversion of electrolytes in aqueous solutions into non-electrolytes as the water density is decreased, whether by dilution with an inert solvent or by pressure reduction (at supercritical conditions), consistent with observed trends. The power of the model for practical applications is demonstrated by working out an example of interest to the electrical power industry. The results predict an observed trend not understood before.

In principle, the model is not restricted to applications at infinite dilution. It is therefore of practical importance to determine the range of concentrations at which the model still applies.

Formerly published as HPL-90-06. HPL-90-06 was reprinted from the *Proceedings of the 1987 Symposium on Chemistry in High Temperature Aqueous Solutions* with permission of the Electric Power Research Institute.

INTRODUCTION

BACKGROUND

Marshall and his colleagues at the Oak Ridge National Laboratory (ORNL) made a thorough investigation of various electrolytic solutions over a wide range of temperatures and pressures [1-9]. NaCl solutions were investigated most extensively. Quist and Marshall [3] experimentally determined the electrical conductivity and equivalent conductance of these NaCl solutions (0.1-0.001 *m*) to 800°C and to 4000 bars, covering the density range from 1 to 0.3 g/cm^3. They found that, at constant temperature and low density, the conductivity of these solutions decreases with the density and appears "to approach a value near zero at densities near 0.2 g/cm^3, ...(indicating)... that there is very little (dissociation) of sodium chloride at lower densities" [3]. They obtained limiting equivalent conductances by fitting "the experimental data to equations expressing conductance as a function of concentration" [3]. Below densities of about 0.65 g/cm^3 there was no good fit because NaCl behaves as a weak electrolyte:

$$NaCl(aqueous) = Na^+(aqueous) + Cl^-(aqueous) \qquad (1)$$

for which the equilibrium constant K1 is:

$$K1 = [Na^+][Cl^-]/[NaCl] \qquad (2)$$

where the brackets indicate the thermodynamic activity of the bracketed species. In the limit of infinite dilution:

$$K1 = \alpha^2 * C/(1 - \alpha) \qquad \text{(infinite dilution limit)} \qquad (3)$$

where C represents the concentration of the solute (NaCl in this case), and α is the degree of dissociation defined as:

$$\alpha = C_+/C = C_-/C = C_d/C \qquad (4)$$

where the positive and negative subscripts represent the cation Na^+ and the anion Cl^-, respectively, and subscript d represents the dissociated fraction. Under such conditions, "it is necessary to use a conductance equation that includes a conventional equilibrium constant" for the dissociation of NaCl [3]. From the fit, both the limiting equivalent conductance and the equilibrium constant are determined provided the electrolyte is not too weak (K1 > 0.0001). Even so, the fit deteriorated with decreasing densities: about 1% or less standard deviation at 0.7 g/cm^3 and above, 2% at 0.65 and 0.6, 4% at 0.55, 7% at 0.5, and 10% at 0.45 g/cm^3. "At the lower densities the uncertainty becomes progressively larger as NaCl becomes a weaker electrolyte"[3]. However, Quist and Marshall found the following [3]:

1. At constant temperature of 100°C and above, the limiting equivalent conductance of these solutions is linear with the density.

2. The slope of the straight lines so obtained is independent of temperature.

3. At 400°C and above, the limiting equivalent conductance is independent of temperature.

4. Other solutions exhibited the same relational form [2,5].

The preceding allows reliable extrapolation of the limiting equivalent conductance to low densities. Then, the corresponding equilibrium constant K1 is calculated. Quist and Marshall found that Log K1 is linear with the logarithm of the water density ρ_w, at constant temperature, whether that density is varied by pressure changes or by mixing with an inert diluent and that the same relational form applied to other electrolytes [1-9].

THE HYDRATION MODEL OF IONIC DISSOCIATION AT HIGH TEMPERATURE AND PRESSURE

I. MODEL DESCRIPTION

Quist and Marshall's explanation for the linearity of Log K1 with Log ρ_w, based on Franck's earlier work [10], essentially is as follows [1-9]:

A. Water is a participant in the dissociation reaction, as follows:

$$NaCl.mH_2O + kH_2O = Na^+.pH_2O + Cl^-.jH_2O \qquad (5)$$

B. The "complete" equilibrium constant for reaction 5 then is:

$$K^o = [Na^+.pW][Cl^-.jW]/[NaCl.mW][W]^k \qquad (6)$$

where W represents H_2O (water).

C. Since the participation of water in the dissociation reaction is included, K^o is a function of temperature only.

D. In the limit of infinite dilution, activities equal concentrations:

$$K^o = \alpha^2 * C/(1-\alpha)(C_{w,p})^k \qquad \text{(infinite dilution limit)} \qquad (7)$$

Where $C_{w,p}$ is the pure water concentration at pressure P.

E. Comparison with equation 3 then yields:

$$K^o = K1/(C_{w,p})^k \qquad (8)$$

F. And in logarithmic form: $\text{Log } K1 = \text{Log } K^o + k\text{Log } C_{w,p}$ (9)

G. Inherent in the model is an essential distinction between the water bound in the hydrate complexes and the remaining or "free" water. Therefore, molal concentration units loose all their practical advantages. Quist and Marshall give additional arguments for using molar concentrations[3].

H. According to Eq. 9, Log K1 should vary linearly with the logarithm of the water density (proportional to its molar concentration C_w). QED.

II. MODEL ANALYSIS

A. Matheson's Analysis:

Matheson examined the above model and found it internally inconsistent. His argument may be clarified and summarized essentially as follows [11]:

1. The activities and, therefore, the "constants" in Eqs. 2 and 6, are not defined until standard states are specified.

2. Standard states chosen at a fixed pressure are independent of the system pressure and the corresponding equilibrium constants K(T) are functions of temperature only.

3. Often, standard states are chosen at the same pressure as that of the electrolytic solution. Therefore, such "standard states" vary together with the experimental pressure of the solution.

4. Such varying "standard states" are called <u>reference states</u> to distinguish them from those chosen at a fixed pressure. The corresponding "equilibrium constants" K(T,P) usually vary with that pressure.

5. The relation between the two "constants" is [12]:

   $$K(T) = Y * K(T,P) \tag{10}$$

   with $$Y = (y_+ y_- / y_a) \tag{11}$$

   where y_+, y_- and y_a represent the activity of the reference state of the cation, the anion and the associated species, respectively.

6. Introducing the activity coefficients, Eq. 2 is written as:

   $$K1 = \Gamma 1 * C_+ * C_- / C_a = \Gamma 1 * (C_d)^2 / C_a \tag{12}$$

   with $$\Gamma 1 = \gamma_+ * \gamma_- / \gamma_a \tag{13}$$

   where γ_+, γ_- and γ_a represent the activity coefficients for the cation, the anion and the associated species, respectively.

7. In electrolytic solutions, <u>reference states</u> usually are chosen such that all activity coefficients equal unity in the limit of infinite dilution. Therefore, in that limit, Eq. 12 becomes:

   $$K1(T,P) = \alpha^2 C/(1-\alpha) \qquad \text{(infinite dilution limit)} \tag{14}$$

8. Similarly Eq. 8 should be:

   $$K^o(T,P) = K1(T,P)/(C_{w,p})^k \qquad \text{(infinite dilution limit)} \tag{15}$$

   from which:

   $$K^o(T) = Y0 * K^o(T,P) = Y0 * K1(T,P)/(C_{w,p})^k \qquad \text{(limit)} \tag{16}$$

   where $$Y0 = Y/(y_w)^k \tag{17}$$

9. In logarithmic form, Eq. 16 becomes:

   $$\text{Log } K1(T,P) = \text{Log } K^o(T) - \log Y0 + k\text{Log } C_{w,p} \qquad \text{(limit)} \tag{18}$$

10. Therefore, to validate Eq. 9, it must be proved that:

$$\text{Log } YO = 0 \qquad \text{i.e.:} \qquad YO = 1 \qquad (19)$$

which is impossible.

11. Alternatively, the linear variation of Log K1 with Log C_w could be explained if Log YO = constant, which is unbelievable.

On the above basis, Matheson concluded that:

12. k does not represent the increased hydration of the solute upon dissociation and

13. The linear relationship remains unexplained.

B. Further Analysis:

1. The success of Marshall and coworkers at ORNL is impressive:

Figure 1 [7] shows the constancy of the equilibrium constant K_o for

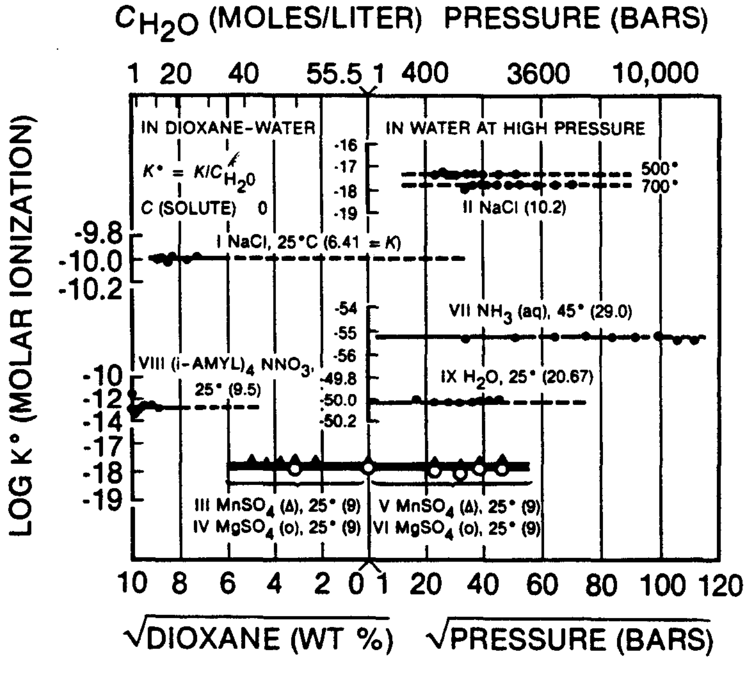

Figure 1 [7]. Invariance of Marshall's complete equilibrium constant $K^o(T)$ over extreme ranges of water densities; whether produced by pressure changes or by mixing with dioxane; for various electrolytes; over an extreme range of temperatures; calculated by Marshall [7] from the values of the conventional equilibrium constant K(T,P) published by various teams: I. Kunze and Fuoss [13]. II. Quist and Marshall [3]. III. Atkinson and Hallada [14]. IV. Dunsmore and James [15]. V. Fisher and Davis [16]. VI. Fisher [17]. VII. Hamann and Strauss [18]. VIII. Fuoss and Kraus [19]. IX. Hamann [20].

various substances investigated by independent groups over temperatures from 25°C to 700°C, and for water concentration changes whether produced by pressure changes or by mixing with an inert diluent [3,4,7,13-20]. Figure 2 [8] shows the linearity of the conventional equilibrium constant K1 with the water concentration C_w, again, for various substances investigated by independent groups over temperatures from 25°C to 700°C, and for water concentration changes whether produced by pressure changes or by mixing with an inert diluent [3,4,7,13-18)].

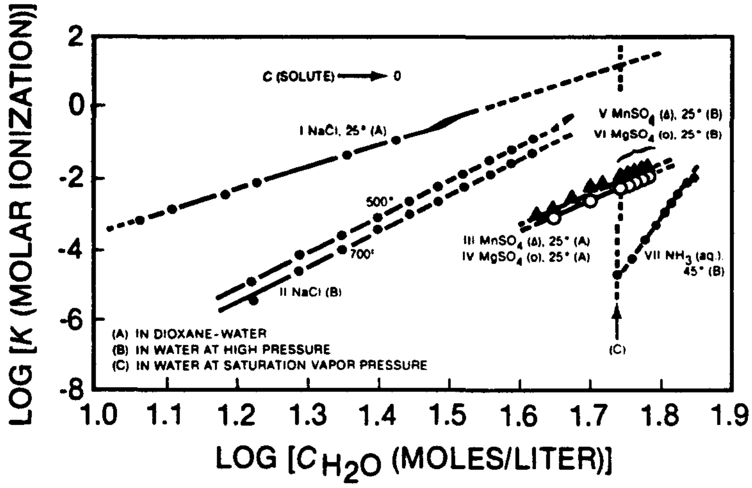

Figure 2 [8]. Linear dependence of conventional equilibrium constants K(T,P), based on molar concentrations, over extreme ranges of water densities; whether produced by pressure changes or by mixing with dioxane; for various electrolytes; over an extreme range of temperatures; calculated by Marshall [7] from the values of the conventional equilibrium constant K(T,P) published by various teams: I. Kunze and Fuoss [13]. II. Quist and Marshall [3]. III. Atkinson and Hallada [14]. IV. Dunsmore and James [15]. V. Fisher and Davis [16]. VI. Fisher [17]. VII. Hamann and Strauss [18].

2. Marshall suggests [8] that Eq. 19 may be considered experimentally established on the basis of the observed straight line relationships. However, the straight lines support just as well the expression:

   $$\text{Log YO} = \text{constant} \qquad (20)$$

   or even: $$\text{Log YO} = (C_{w,p}/C_{w,o})^h \qquad (21)$$

   where $C_{w,o}$ is pure water concentration at the standard pressure.

3. Still, one could make the *ad hoc* assumption that Eq. 19 holds, consistent with the experimentally observed straight lines. It is important to note that Eq. 19 represents an <u>ideal solution</u> property. Indeed, noting that:

   $$d(\text{Log } y_i) = (\nu_i/RT) * dP \qquad (22)$$

(where ν_i represents the partial molal volume of species i in their reference states). Substituting for Y from Eq. 11 into Eq. 17, taking the logarithm on both sides of Eq. 17, differentiating (at constant temperature) then substituting from Eq.22 for the corresponding expressions and rearranging, yields:

$$RT\ d\mathrm{Log}\ Y0 = (\nu_+ + \nu_- - \nu_a - k\nu_w) * dP \qquad (23)$$

In general, the expression on the right side of Eq. 23 is not zero and upon integration from the standard to the reference pressure yields a non-zero value for Log Y0. In ideal solutions, however, each partial molal volume is independent of composition [21]. Therefore, in such solutions at constant temperature, also the algebraic sum of the partial molar volumes in the parenthesis of Eq. 23 is independent of composition and equal to the same sum at equilibrium conditions, i.e. is equal to zero, from which Eq. 19 follows.

4. However, the notion of dissociated ions in ideal aqueous solution appears unacceptable.

C. Summary and Conclusions

No amount of criticism of the theory will make the data disappear. Therefore, we are faced with the following conflict: The high temperature and pressure data appear to indicate ideal solution properties for the hydration model of electrolytic solutions. Such properties are incompatible with the presence of the ion species resulting from the ionic dissociation. In the following, it will be shown that the same conflict arises in other aspects of such solutions.

HYDRATION MODEL OF AQUEOUS SOLUTIONS OF NEUTRAL INORGANIC SOLUTES AT HIGH TEMPERATURE AND PRESSURE

I. MODEL DESCRIPTION

Extensive data are available on solubilities in steam and on steam to liquid distribution coefficients for many simple cases of single compounds [22-26] and it is important to develop reliable correlations for integrating and extrapolating these data. Longton [22] presents Styrikhovich's equation for solubility in steam, and Martynova's relation for steam to liquid distribution coefficients, K_{Di}, with the densities ρ_s and ρ_l of pure steam and liquid, respectively, at the operating temperature and pressure. The relations are:

$$m_{si} = K_{ei}\rho_s^{\ m} \qquad \text{(at solute saturation)} \qquad (24)$$

$$K_{Di} = m_{si}/m_{li} = (\rho_s/\rho_l)^m \qquad (25)$$

where m_{si} and m_{li} are the molal concentrations of species i in the steam and liquid, respectively, and K_{ei} is the equilibrium constant for the solubilization process (of substance X) considered as a hydration reaction:

$$X\ \text{(solid)} + m\ H_2O\ \text{(steam)} = X.m\ H_2O\ \text{(steam solution)} \qquad (26)$$

$$K_{ei} = [X.mW]/[X][W]^m \qquad (27)$$

where K_{ei} is a function of temperature only and m is a measure of hydration.

Eq. 24 "has been found to apply to a wide range of inorganic materials over extended ranges of pressures and temperature. Plots of log C_s vs log ρ_w are generally found to give straight lines, yielding values for m ranging from 1/2 to 10. Generally m, which can be regarded as a measure of the number of H_2O molecules associated with each solute molecule, has a low value for highly soluble materials (e.g., m = 2 for SiO_2) and a higher value for less soluble materials (e.g., m = 9 for Na_2SO_4)" [23]. Similarly, for many solutes, Eq. 25 "is obeyed over a substantial range of pressure. In general, those materials that are weak electrolytes in water -Al_2O_3, B_2O_3, SiO_2 - have high distribution coefficients and low values of m, of the order of 1 to 2. Strong electrolytes, such as NaOH and NaCl, have low distribution coefficients and high values of m of the order of 4" [23]. The large success of Eq. 25 is examplified by the results of figure 3 reproduced here and elsewhere [22-25].

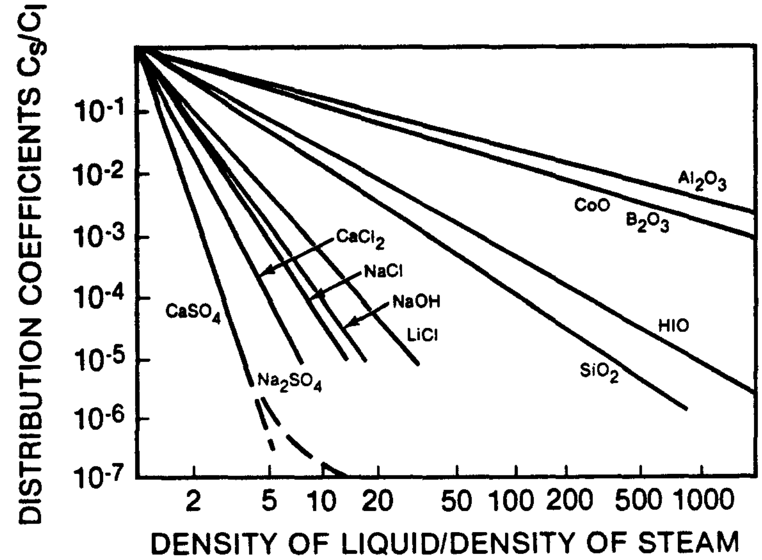

Figure 3 [22-26]. Linear dependence of the logarithm of steam to liquid distribution coefficients K_D on the logarithm of the ratio of steam to liquid densities, at high temperatures and pressures.

The derivation of Eqs. 24 and 25 was reviewed by Longton[22] and Cohen[23] with differences in detail only. Briefly, the activity of the solid is taken equal to unity and concentrations are substituted for the solute and for steam. The steam concentration is expressed as density. Rearrangement yields the solubility Eq. 24. The same steps yield the same solubilization Eq. 24 for the liquid. Assuming the same hydration number in both the liquid and steam phases, the ratio between the two solubilization equations yields Eq. 25.

II. MODEL ANALYSIS

The water concentrations are expressed as densities. These are concentration units per unit volume and, therefore, the salt concentrations must be molar, not molal, concentration units. However, molal and molar concentrations are related as follows:

$$C_{ji} = (M_w C_{jwt}/1000) m_{ji} = \rho_{j,t} m_{ji} \tag{28}$$

where M_w is the molecular weight of water (=18.016 *g/mole)*; C_{jwt} and $\rho_{j,t}$ are the actual concentration and density of the total water in phase j. Consequently, Eq. 24 should read:

$$m_{si} = K_{ei}(\rho_{s,t})^{m-1} \tag{29}$$

Eq. 29 has the same form as Eq. 24. It is seen that the exponent is lower than the hydration m by one unit [27]. The same applies to Eq. 25.

The assumption that water participates as a reactant in the solubilization process written as a hydration reaction (Eq. 26) can be justified or invalidated by comparison with facts of the consequences derivable therefrom. The large success of Eqs. 24 and 25 seems to support this assumption over a range of inorganic compounds and of parameter values.

A. Ideal Solution Properties:

1. The validity of the assumption that m is the same in the steam and liquid phases, again, is a matter of comparison with facts. The assumption seems supported over a wide range of inorganic compounds and of parameter values. As a consequence, it seems to indicate that the interaction of these solutes with the water essentially is confined to the hydration water within the hydrate complex. In other words, after formation, the hydrate complex is in ideal solution with the remaining "free water". Therefore, it may be expected that the validity of Eq. 24 could be improved by using the density of the "free " instead of the pure water.

2. Such indication is reinforced by the fact that m remains constant over a large range of temperature (Fig. 3).

3. Also the successful substitution of concentrations for activities indicates an ideal solution.

4. Another (implicit) assumption is that the equilibrium constant K_{ei} (Eqs. 24,27) is the same in the liquid and steam phases. Cohen pointed out that this assumption should limit the validity of Eq. 25 to "a restricted range of temperatures and densities not too far from the critical" [23]. However, Eq. 25 is valid over a wide range of temperature, again, indicating an ideal solution. Indeed, for an ideal solution, the quotient of activities of the reference states is equal to unity (Eq. 23) and, therefore, the equilibrium constant is the same in the steam as in the liquid phase.

B. Extension of the Ideal Solution Properties to the Dissociated Fraction

As it stands, the model is far from perfect:

1. Figure 4 [24] shows the effect of NaCl concentration on its distribution coefficient. One might argue that such departure from adherence to Eq. 25 follows the deviation from ideal solution expected to develop with the progression of ionic dissociation as the solute concentration is decreased. That argument, however, is precluded by the validation of

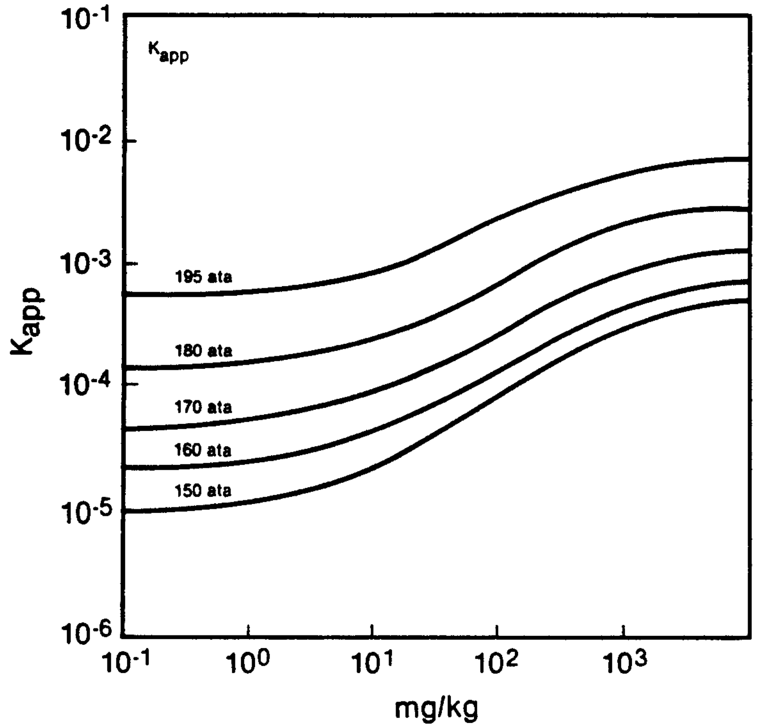

Figure 4 [24]. Effect of NaCl concentration on its steam to liquid distribution coefficient K_D, at high temperatures and pressures.

Eq. 25 at the lower concentrations where, presumably, there is more dissociation and the solution is less ideal. Then, the alternative argument is that also the ionic fraction is in ideal solution but at a higher hydration level [24] m+k. With the larger m+k exponent, the dis sociated fraction has a lower distribution coefficient than the associated fraction. On such basis, it is expected that the *average* (or apparent) distribution coefficient would increase with concentration from the value of the dissociated to that of the associated fraction over the transition range of concentration, consistent with the data (Fig.4). Figure 5 [24] illustrates the concept.

2. Figure 6 [24] shows the effect of pH on distribution coefficients. Again, the deviation from Eq. 25 is attributed to ionic dissociation and/or hydrolysis. The same argument as above applies.

C. Discussion Summary and Conclusions:

Again, no amount of criticism of the theory will make the data disappear. Therefore, here too we face the conflict: The high temperature and pressure data appear to indicate ideal solution properties for the hydration model of electrolytic solutions. Such properties are incompatible with the presence of the ion species resulting from the ionic dissociation.

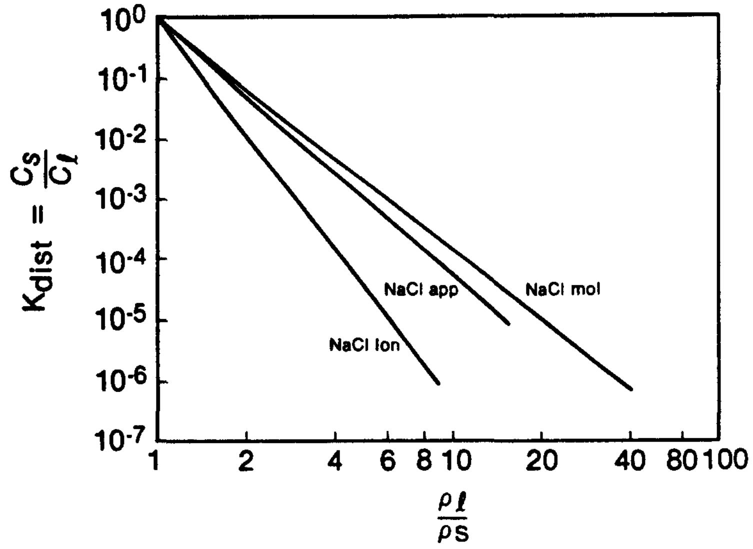

Figure 5 [23]. Illustration of different steam to liquid distribution coefficient for the associated and dissociated fractions of NaCl.

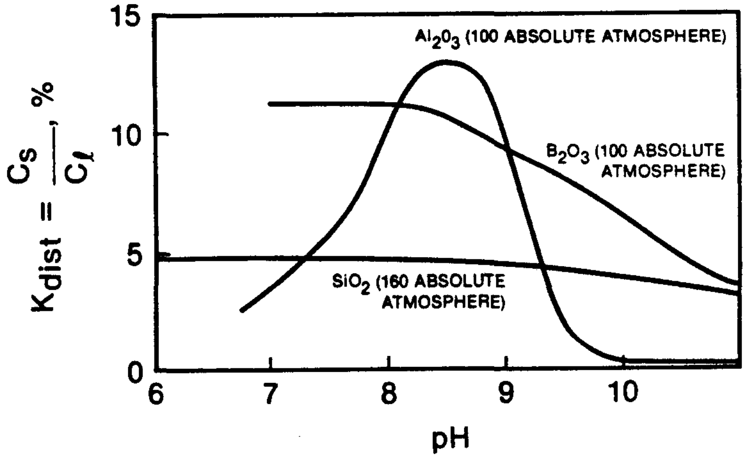

Figure 6 [23]. Effect of pH on steam to liquid distribution coefficients K_D.

SUMMARY

I. An impressive amount of data of various kinds on aqueous solutions of electrolytes at high temperatures and pressures overwhelmingly relate properties of these solutions to the polar solvent (water) densities.

II. The classical model of electrolytic solutions does not explain those relations.

III. Expansion of the classical model to include the polar solvent (water) in the dissolution and ionic dissociation processes considered as hydration reactions appears very successful except for the following:

IV. The expanded model requires ideal solution properties to explain the data and such properties are inconsistent with the dissociated ionic fraction.

The problem simply may be rephrased as an apparent conflict between the extensive available data and the classical model of ionic dissociation. Such problem may be addressed in many ways.

MAIN OPTIONS

I. Some do not see the conflict or ignore it altogether.

II. Many hope for a reconciliation in the future.

III. No one has dared disqualify the data.

IV. In the following, other shortcomings of the classical model of ionic dissociation briefly are reviewed.

ADDITIONAL DIFFICULTIES WITH THE CLASSICAL MODEL OF IONIC DISSOCIATION IN AQUEOUS SOLUTIONS

I. EXPERIMENTALLY

A. Electrochemical potentials of electrochemical reactions always are observed in combinations yielding Gibbs free energies of chemical reactions, and chemical potentials for electroneutral groupings of ion species.

B. So far, no thermodynamic measurement of any single ion species has been possible.

C. In aqueous solutions, the electroneutrality condition is very successful in solving electrochemical mass transport problems [28], indicating that ion species essentially are not located independently of each other but in electroneutral groupings.

II. CONCEPTUALLY, MACROSCALE (CHEMICAL THERMODYNAMICS)

Ionic chemical potentials clearly cannot be defined because of the electrical work involved in moving, say, one mole-equivalent of an ion species into or out of a solution, since this electrical work also depends on the electrical potential of the solution. As a consequence, only electrochemical potentials conceptually can be defined for ions. While electrochemical potential differences can be, and are, defined and measured as well as related to chemical potentials, the difference between an electrochemical and a chemical potential thermodynamically cannot be uniquely defined.

III. CONCEPTUALLY, MICROSCALE

A. It is perhaps significant that the current understanding of ionic dissociation was considered with suspicion by Lewis and Randall. They considered that the time required for an ionic molecule to dissociate is comparable with the total time during which the ions remain free. Under such conditions, ions starting to dissociate cannot go very far away from each other before they start reassociating with each other or with other ions. Therefore, at any instant, there are no clear cut isolated ions and ion pairs but a distribution of distances between closest neighbor ions. Then, the degree of dissociation is ambiguous:

> "For, first, it would be necessary to know how far apart the constituent atoms of a molecule must be to warrant our calling the molecule dissociated. But such a decision would be arbitrary; and according to our choice of this limiting distance, we should find one or another degree of dissociation.
>
> "Until a problem has been logically defined it cannot be experimentally solved, and it seems evident in such a case as we are now considering that, just as we should obtain different degrees of dissociation by different choices of the limiting distance, so we should expect to find different degrees of dissociation when we come to interpret different experimental methods.
>
> "Now it is generally agreed that ionic reactions are among the most rapid of chemical processes, and it is just in such reactions that we should find difficulty in determining, either logically or experimentally, a really significant value of the degree of dissociation.
>
> "On the whole, we must conclude that the degree of dissociation and the concentration of the ions are quantities which we cannot determine by existing methods, and which perhaps cannot be defined without some degree of arbitrariness" [29].

This critical view of the clear cut dissociation concept of an electrolyte into ions as relatively free independent kinetic entities subject only to the constraint of some coulombic interactions, already published by Lewis and Randall in the first edition (1923) of their book, is still valid today [30].

B. It may be useful to pursue Lewis and Randall's critique of the ionic dissociation concept in light of the hydration concept. Consider an ionic uni-univalent molecule hydrated with m water molecules in aqueous solution. Upon a suitable collision, the molecule starts dissociating. As the distance between the two ions increases, their mutual electroneutralization decreases, their interaction with the surrounding water molecules increases and their total hydration increases from m to $m+k$ water molecules. As a result of the increase in hydration they do not go too far apart but, with the increase in mass and distance, vibration modes and frequencies are changed. On the above basis, a reasonable picture emerges. The hydrated anion/cation pair may have two *average* equilibrium distances about which the hydrated ions vibrate:

1. The shorter average equilibrium distance corresponds to the associated fraction with the lower hydration m.

2. The longer average equilibrium distance corresponds to the dissociated fraction with the higher hydration $m+k$.

The above emerging picture amounts to a reinterpretation of the dissociation concept: Upon dissociation the distance between the ions increases, but they do not become kinetically independent, they continue to vibrate at the larger (average) distance. Such description may be possible at the higher temperatures and/or lower water densities because of the related lower dielectric constant and the corresponding stronger interionic bonding. Figure 7 illustrates the dissociation concept as herein reinterpreted.

In their associated state, because of their close proximity, the mutual electroneutralization between the ions is strong and their interaction reaches out to only m water molecules which bind to the ion pair forming a hydrate complex. Beyond those m water molecules of hydration the "free" water molecules interact with the outer atoms of the hydrate complex same as with the outer atoms of water molecule clusters. Thus, the hydrate complex is in ideal solution with the "free" water.

In their dissociated state, because of their lesser proximity, the mutual electroneutalization between the ions is decreased and their interaction reaches out to a larger number m+k of water molecules which bind to the ion pair forming a larger hydrate complex. Beyond those m+k water molecules of hydration, however, the "free" water molecules interact with the outer atoms of the hydrate complex same as with the outer atoms of water molecule clusters. Thus, as with the associated hydrate complex, also the dissociated one is in ideal solution with the "free" water, it only is larger.

In the next section the above picture will form the basis of a hydration model of aqueous solutions of electrolytes, at high temperature and pressure, which provides a relatively simple thermodynamic treatment.

NEW HYDRATION MODEL OF AQUEOUS SOLUTIONS OF ELECTROLYTES AT HIGH TEMPERATURE AND PRESSURE

PROPOSED MODEL

I. DESCRIPTION

Consider an aqueous solution of an electrolyte AB, as an example, in equilibrium at temperature T and pressure P with the same substance AB in a reservoir permeable only to temperature, pressure and AB.

A. In the solution, AB exists in two forms in equilibrium with AB in the reservoir and, therefore, with each other.

B. The dissolution process is considered to consist of hydration reactions:

$$\text{AB (reservoir)} + m\text{W} = \text{AB}.m\text{W} \tag{30}$$

$$\text{AB (reservoir)} + (m+k)\text{W} = \text{AB}.(m+k)\text{W} \tag{31}$$

C. The degree of dissociation α then is:

$$\alpha = C_d/(C_d + C_a) = C_d/C \tag{32}$$

D. The free water concentration C_w then is:

$$C_w = C_{w,t} - (m + \alpha k)\ C \tag{33}$$

E. Ideal solution properties are assumed for <u>the selected components</u> at high temperature and pressure.

II. CONSEQUENCES

A. From Eqs. 30 and 31 :

$$AB.mW + kW = AB.(m + k)W \tag{34}$$

B. The equilibrium constant K^{oo} (different from K^{o}) for reaction 34 then is:

$$K^{oo} = [AB.(m + k)W]/[AB.mW][W]^k \tag{35}$$

and since it is an ideal solution:

$$K^{oo} = C_d/C_a(C_w)^k = \alpha/(1 - \alpha)(C_w)^k \tag{36}$$

C. From Eq. 36:

$$\alpha = K^{oo}\ (C_w)^k/\{K^{oo}\ (C_w)^k + 1\} \tag{37}$$

1. Eq. 37 shows that as the solute concentration increases, leading to the decrease of the free water concentration C_w (Eq. 33), then the degree of dissociation α decreases too, which is the correct trend.

2. a. For strong electrolytes, α must be nearly unity. Therefore from Eq. 37, the following must hold for strong electrolytes:

$$K^{oo}\ (C_w)^k \gg 1 \tag{38}$$

   b. For non electrolytes, α must be nearly zero. Therefore, from Eq. 37, the following must hold for non-electrolytes:

$$K^{oo}\ (C_w)^k \ll 1 \tag{39}$$

   c. Weak electrolytes are in between

3. At the infinite dilution limit, Eq. 37 becomes:

$$\alpha \rightarrow K^{oo}\ (C_{w,t})^k/\{K^{oo}\ (C_{w,t})^k + 1\} = \alpha_o \tag{40}$$

   According to Eq. 40, weak electrolytes <u>do not necessarily</u> dissociate completely at the infinite dilution limit. Some might and others might not.

4. Further, Eq. 37 predicts that as the concentration of water is decreased by mixing with an inert diluent or by lowering the pressure (at supercritical conditions) strong electrolytes will gradually weaken through the whole range of electrolytic strength all the way to non-electrolytes for sufficiently low water densities, consistent with observed trends.

5. It also explains the same different behavior of electrolytes in liquid and steam at subcritical conditions.

DISCUSSION

Notwithstanding its merits, it is necessary (not sufficient) to show that the proposed model is consistent with the existing data. Such consistency next is derived. Also, it is found that the relations derived from the proposed model are of greater generality than existing relations, and are expected to apply to a wider range of parameter values. The derivation also indicates the need for a reinterpretation of the data in terms of the proposed model.

I. CONDUCTIVITY

The conventional and expanded models consider that the ratio of the equivalent conductance Λ to the limiting equivalent conductance Λ_o tends to the degree of dissociation α (which tends to unity) in the limit of infinite dilution, from which the Ostwald dilution law derives:

$$K = (\Lambda/\Lambda_o)^2 C/(1 - \Lambda/\Lambda_o) \rightarrow \alpha^2 C/(1 - \alpha) = K1(T,P) \qquad \text{(limit)} \qquad (41)$$

Often, the measurements cannot be pursued at sufficient dilution and more elaborate relations are used to extrapolate the data from the practical concentrations to dilutions where Eq. 41 would apply and, then, further to infinite dilution. The infinite dilution limit of Log K experimentally is found to vary linearly with Log C_w. On the basis of these data on of Eq. 41, it may be concluded that K1(T,P) is linear with Log C_w. However, for the present purpose, it is necessary and sufficient to interpret K in light of the proposed model. Since, according to the proposed model, the infinite dilution limit of the degree of dissociation is not necessarily unity, the ratio Λ/Λ_o tends to α/α_o and, in this light, the Ostwald quotient is then expressed as:

$$K = (\Lambda/\Lambda_o)^2 C/(1-\Lambda/\Lambda_o) \rightarrow \alpha_o C/(\alpha_o - \alpha) \qquad \text{(infinite dilution limit)} \qquad (42)$$

The last expression is the indeterminate ratio of expressions each tending to zero and is, therefore, equal to the ratio of their differentials:

$$K \rightarrow - \alpha_o (dC/d\alpha) \qquad \text{(infinite dilution limit)} \qquad (43)$$

The derivative is evaluated by derivation of Eqs. 33 and 36 and eliminating $dC_w/d\alpha$ between the two results. Derivation of Eq. 33 relative to α:

$$(dC_w/d\alpha) = - kC - (m + k\alpha)(dC/d\alpha) \qquad (44)$$

Taking the logarithm and then the derivative, with respect to α, on each side of Eq. 36 then rearranging, yields:

$$(dC_w/d\alpha) = C_w/k\alpha(1 - \alpha) \qquad (45)$$

Equating the right sides of Eqs. 44 and 45, then extracting $dC/d\alpha$ yields:

$$(dC/d\alpha) = -\{kC + C_w/k\alpha(1 - \alpha)\}/(m + k\alpha) \qquad (46)$$

Substituting this expression into Eq. 43 and taking the limit at infinite dilution, now yields:

$$K \rightarrow C_{w,t}/k(1 - \alpha_o)(m + k\alpha_o) \qquad \text{(infinite dilution limit)} \qquad (47)$$

From Eq. 40: $$(1 - \alpha_o) = 1/\{1 + K^{oo}(C_{w,t})^k\} \qquad (48)$$

Substituting for this expression in Eq. 47, yields:

$$K = C_{w,t}\{1 + K^{oo}(C_{w,t})^{k}\}/k(m + k\alpha_{o}) \qquad \text{(infinite dilution limit)} \qquad (49)$$

For a weak electrolyte that does dissociate nearly to completion, condition 38 applies and Eq. 49 becomes:

$$K = K_{oo}(C_{w,t})^{k+1}/k(m + k) \qquad \text{(infinite dilution limit)} \qquad (50)$$

and in logarithmic form:

$$\text{Log } K = \{\text{Log } K_{oo} - \text{Log } k(k + m)\} + (k + 1) \text{ Log } C_{w,t} \qquad \text{(limit)} \qquad (51)$$

According to Eq. 51, Log K should vary linearly with Log $C_{w,t}$ and, therefore, with the logarithm of the water density. QED.

It is seen that Marshall's relation is a particular case of the more general treatment based on the proposed model which should apply over a wider range of conditions. Also, the experimental data must be reinterpreted in accordance with Eq. 51 where the slope (k + 1) is one unit larger than the increased hydration upon dissociation, and the intercept is Log K^{oo} - Log k(k + m).

II. SOLUBILITY IN STEAM

The equilibrium constants for Eqs. 30 and 31, respectively, can be written as follows, (remembering these are ideal solutions):

$$K_{ea} = [AB.mW]/[AB][W]^{m} = C_{a}/(C_{w})^{m} \qquad (52)$$

$$K_{ed} = [AB.(m + k)W]/[AB][W]^{m+k} = C_{d}/(C_{w})^{m+k} \qquad (53)$$

from which the solubility is:

$$C = C_{a} + C_{d} = \{K_{ea} + K_{ed}(C_{w})^{k}\}(C_{w})^{m} \qquad (54)$$

with the concentration C_w given by Eq. 33.

At constant supercritical temperature and <u>low steam densities</u>,

$$K_{ed}(C_{w})^{k} \quad << \quad K_{ea} \qquad (55)$$

and: $$C = K_{ea}(C_{w,t})^{m} = K_{ea}(1000/M_{w})^{m}(\rho_{s})^{m} \qquad \text{(low steam density)} \qquad (56)$$

from which: $$m = K_{ea}(1000/M_{w})^{m}(\rho_{s})^{m-1} \qquad \text{(low steam density)} \qquad (56\text{-a})$$

where the total water concentration and the pure water density are justified by the low solubility C at low steam densities.

Therefore, Eqs. 56 explain both the success of Styrikhovich's solubility Eq.24 and its failure at the higher steam densities for some substances. Also, it shows that Eq. 24 is a particular case of the more general Eq. 54 (together with Eq. 33) which should apply over a wider range of parameter values.

III. STEAM TO LIQUID DISTRIBUTION COEFFICIENTS

Eqs. 30,31,52-54 are valid in liquid as well as in steam. Therefore, applying Eq.54 to the steam and to the liquid, and forming the ratio of the two expressions so obtained yields an expression for the distribution coefficient:

$$K_D = C_{sx}/C_{lx} = \{(K_{ea} + K_{ed}C_{sw}^k)/(K_{ea} + K_{ed}C_{lw}^k)\}(C_{sw}/C_{lw})^m \qquad (57)$$

where subscript x stands for an inorganic solute, and subscripts s and l indicate in steam and liquid phase, respectively.

The same reasoning applies to the distribution of associated and dissociated fractions. Expressing the concentration C_a from Eq. 52, applying it to the steam and to the liquid then forming their ratio:

$$K_{Da} = C_{sa}/C_{la} = (C_{sw}/C_{lw})^m \qquad (58)$$

Similarly for the dissociated fraction, using Eq. 53:

$$K_{Dd} = C_{sd}/C_{ld} = (C_{sw}/C_{lw})^{m+k} \qquad (59)$$

from which: $$K_{Dd}/K_{Da} = (C_{sw}/C_{lw})^k \qquad (60)$$

At conditions of large density difference (away from the critical point):

A. According to Eq. 60, the volatility of the dissociated fraction is negligible compared to that of the associated fraction, consistent with all observations.

B. Therefore, at conditions where $K_{ed}(C_{lw})^k << K_{ea}$ then, from Eq. 57:

$$K_D = (C_{sw}/C_{lw})^m = (C_{swt}/C_{lwt})^m = (\rho_s/\rho_l)^m \qquad (61)$$

C. Similarly, at conditions where $K_{ea} << K_{ed}(C_{sw})^k$, then:

$$K_D = (\rho_s/\rho_l)^{m+k} \qquad (62)$$

Eq. 61 is identical with Martynova's Eq. 25 which, thus, is established (except that the exponent should be decreased to m-1 for the molal ratio). Together with Eq. 62, they explain the kind of data of fig 4. Both equations are particular cases of the general Eq. 57 which is expected to apply over a much wider range of conditions than Martynova's equation.

IV. AQUEOUS SOLUTIONS OF INORGANIC ELECTROLYTES
AT HIGH TEMPERATURE AND PRESSURE

With the ideal solution properties of the hydrate complexes solution in the free water, the calculations are expected to be much simpler:

A. The activity coefficients are expected to remain equal to unity up to practical concentrations. The corresponding ranges of concentration need to be experimentally determined.

B. At still higher concentrations, the variation of the activity coefficients for the hydrate complexes and the free water should be slow and more easily amenable to tabulation and analytical expression.

Obviously, there is much work to be done. To encourage the readers in undertaking such tasks, the simplicity and power of the proposed model is illustrated in the following relatively simple application.

EXAMPLE: APPLICATION TO THE NaCl-H_2O SYSTEM

To illustrate the relative simplicity and power of the proposed model, the NaCl-H_2O system is worked out. The solution is considered in equilibrium with its vapor and, in the absence of data, it is assumed that NaCl hydrolysis, if any, is negligible. First, the constants k, m and K^{oo} at 285°C will be determined from the combination of:

A. Experimental data of Marshall on NaCl limiting equivalent conductance in aqueous solutions at high temperature and pressure[3,9], reinterpreted in light of the proposed model.

B. Experimental data of Styrikhovich and Martynova on the steam/liquid distribution of NaCl, also at high temperature and pressure[27], reinterpreted in light of the proposed model.

C. Available steam table data.

Second, the chemistry in the liquid phase and the distribution between the two phases will be calculated as a function of the steam quality. Such determinations are of importance in the electric power generation industry.

I. PROCEDURE TO DETERMINE THE CONSTANTS k, m and K^{oo}

A. At 285°C, Marshall's straight line slope and intercept for NaCl are 10 and -16, respectively. Applying Eq. 51 to these data yields:

$$10 = (k + 1) \quad \text{i.e.} \quad k = 9 \tag{63}$$

and: $-16 = \text{Log } K^{oo} - \text{Log } 9 - \text{Log } (9 + m)$

$$\text{from which:} \quad K^{oo} = (9 + m)\ 10^{-15.05} \tag{64}$$

B. From fig. 3, the slope of the molal distribution coefficient of NaCl is about 4.4, i.e.:

$$K_D \text{ (molal ratio)} = m_{sx}/m_{lx} = (\rho_s/\rho_l)^{4.4} \tag{65}$$

C. Marshall's data show that at 285°C NaCl in the liquid solution is already a weak electrolyte. Since at that temperature, the steam/liquid density ratio for pure water is about 0.0484, it follows (Eq. 60) that the dissociated fraction of NaCl in the steam is negligible. Therefore, the distribution coefficient K_{Da} for the associated fraction can be expressed as:

$K_{Da} \text{ (molal ratio)} = m_{sx}/(1 - \alpha)m_{lx} = (\rho_s/\rho_l)^{m-1}$

from which: $K_D = (1 - \alpha)K_{Da} = (1 - \alpha)(\rho_s/\rho_l)^{m-1}$

and combining with Eq. 65 yields: $(1 - \alpha) = (0.0484)^{5.4-m}$

$$\text{from which:} \quad \text{Log } (1 - \alpha) = -1.315\ (5.4 - m) = 1.315\ m - 7.1 \tag{66}$$

Substituting for α from Eq. 37, noting that $k = 9$:

$$\text{Log}\ \{1 + K^{oo}(C_{\ell w})^{9}\} = 7.1 - 1.315\ m \tag{67}$$

D. Since Marshall's linear graph is for infinite dilution data, the water concentration in Eq. 67 is that of pure water which is calculated for 285°C, again, from steam tables:

$$C_{\ell w,t} = 1000\ \rho_{\ell}/M_{w} = 41.2$$

and substituting in Eq. 67 and rearranging, yields:

$$K^{oo} = 2.95\{(1.26 * 10^{7}\ (20.65)^{-m} - 1\}\ 10^{-15} \tag{68}$$

E. Eliminating K^{oo} between Eqs. 64 and 68 yields:

$$1.26 * 10^{7}\ (20.65)^{-m} - 0.3\ m - 3.7 = 0$$

and numerical solution of this equation yields: $m = 5$ (69)

F. Substituting this value for m in Eq. 64 now yields:

$$K^{oo} = 1.25\ 10^{-14} \tag{70}$$

Thus have the three constants been determined for 285°C:

$k = 9$; $m = 5$ and $K^{oo} = 1.25\ 10^{-14}$

Since m is expected to remain constant over a wide range of temperature values (based on data such as that of fig. 3), the determination of k and K^{oo} at other temperatures should be greatly simplified. Once determined for a given temperature, the constants k, m and K^{oo} can be applied to the solution of various problems at that temperature. The general treatment of solutes distribution between steam and liquid is discussed elsewhere [31]. Here, the simplified particular case of the two component system $NaCl$-H_2O at 285°C is worked out to illustrate the power of the proposed model and its simplicity.

II. MODELING THE $NaCl$-H_2O SYSTEM AT 285°C

In the absence of data, it is assumed that at 285°C, $NaCl$ hydrolysis (if any) is negligible. When the amount of vapor in equilibrium with the steam is negligible, it is sufficient to simultaneously solve Eqs. 33 and 37 for the degree of dissociation α and the free water concentration $C_{\ell w}$ for any given salt concentration $C_{\ell x}$ in the liquid. The corresponding salt concentration C_{sx} in the steam then is calculated from Eq. 57. As the amount of steam increases with steam quality, the mass balance over the steam/liquid system must be considered.

The mass balance equation may be expressed as follows:

$$m_{\ell x} = \dot{m}^{o}/\{1 - [1 - (1 - \alpha)K_{Da}](SQ)\} \tag{71}$$

where K_{Da} expresses the steam to liquid molal ratio of the salt associated fraction and SQ represents the steam quality defined by:

$$SQ = \frac{(\text{mass of total water in the steam})}{(\text{mass of total water in both phases})} \tag{72}$$

and m^{o} is the initial salt concentration (for SQ = 0). The mass balance Eq. 71 is solved simultaneously with Eqs. 33 and 37 (converted to molal units). Then C_s is calculated from Eq. 57. The procedure is as follows:

A. The molal distribution coefficient for the associated species is evaluated from the molar coefficient (Eq. 58) by decreasing m to m-1 and substituting the values 0.0484 for the density ratio and 5 for m:

$$K_{Da}\ (\text{molal}) = (\rho_s/\rho_l)^{m-1} = 0.0484^4 \qquad (73)$$

B. The degree of dissociation is evaluated by substituting for the values of k and K^{oo} in Eq. 37 and dividing numerator and denominator by 5/4:

$$\alpha = 10_{-14}(C_{lw})^9/\{0.8 + 10^{-14}(C_{lw})^9\} \qquad (74)$$

then converting to molal concentrations:

$$\alpha = 10^{-14}(\rho_{lt}m_{lw})^9/\{0.8 + 10^{-14}(\rho_{lt}m_{lw})^9\} \qquad (75)$$

C. Converting Eq. 33 to molal concentrations, yields:

$$m_{lw} = m_{lwt} - (m + \alpha k)\, m_l \qquad (76)$$

D. Substituting for K_{Da} (molal) from Eq. 73 into Eq. 71 then simultaneously solving Eqs. 71, 75 and 76 yields the water and salt concentrations and the degree of dissociation α in the liquid for any couple of values of steam quality (SQ) and initial salt concentration m^{o} (at SQ = 0).

Results graphically are presented in figures 8-10 [31]. Figure 8 shows the calculated variation of NaCl concentration in the residual liquid as the steam quality is increased for initial concentrations (at SQ = 0) of 1 ppb and 10 ppb. In each case, that concentration reaches a limit in accordance with Eq. 71 {as SQ tends to unity, then m_{sx} *tends to* m^{o}, and m_{lx} tends to $m^{o}/(1 - \alpha)K_{Da}$}. Defining a *degree D of concentration* as,

$$D = m_{lx}/m^{o} \qquad (77)$$

a careful examination of fig. 8 discloses that as SQ tends to unity, *D* becomes larger for the smaller initial concentration. This effect, clearer shown in figure 9, results from the larger decrease in the degree of dissociation α (in the liquid) at the larger concentrations reached with the larger initial concentration m^{o}.

Figure 10 shows the calculated variation of the degree of dissociation α and of the overall (or average, or apparent) distribution coefficient K_D for NaCl as a function of its concentration in the residual liquid. It predicts a sharp increase of the salt distribution in the steam as the concentration in the liquid increases. Such increases have been observed but not understood before [33]. It is encouraging that the proposed model can predict such heretofore unexplained observations.

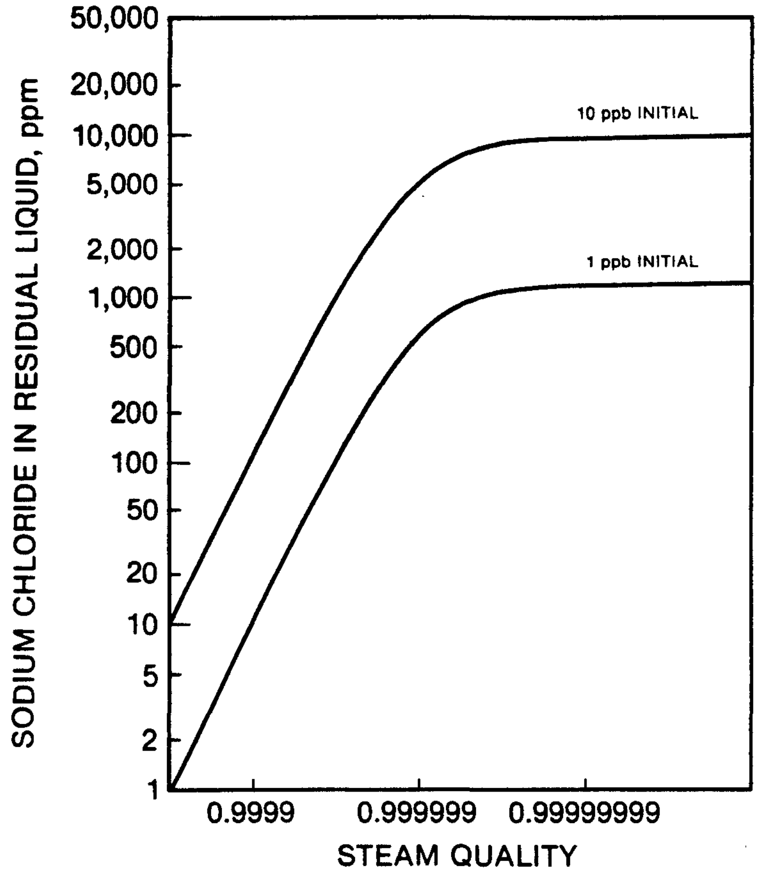

Figure 8 [32]. Modeled dependence of NaCl concentration, in the residual liquid, on steam quality.

SUMMARY AND CONCLUSIONS

Partial correlations of data on aqueous solutions of inorganic electrolytes at high temperature and pressure were reviewed. The partial correlations pertain to the following: I. Solubilities in steam. II. Steam to liquid distributions. III. Ionic dissociation constants (from conductivity measurements). The partial correlations are not explained by the classical model of electrolytic solutions. An expanded model based on the hydration of the associated solute and of its dissociated ions has met with some degree of success and of criticism. The expanded model and the critique were reviewed and discussed. In each of the three areas (solubility, distribution and ionic dissociation) the partial correlations were shown to represent ideal solution properties for the *hydrated* solutes and the *free* water species (NOT for the *pure* solutes and *total* water). The problem was shown to boil down to a conflict between those ideal solution properties and the concept of ionic dissociation as producing kinetically independent ions.

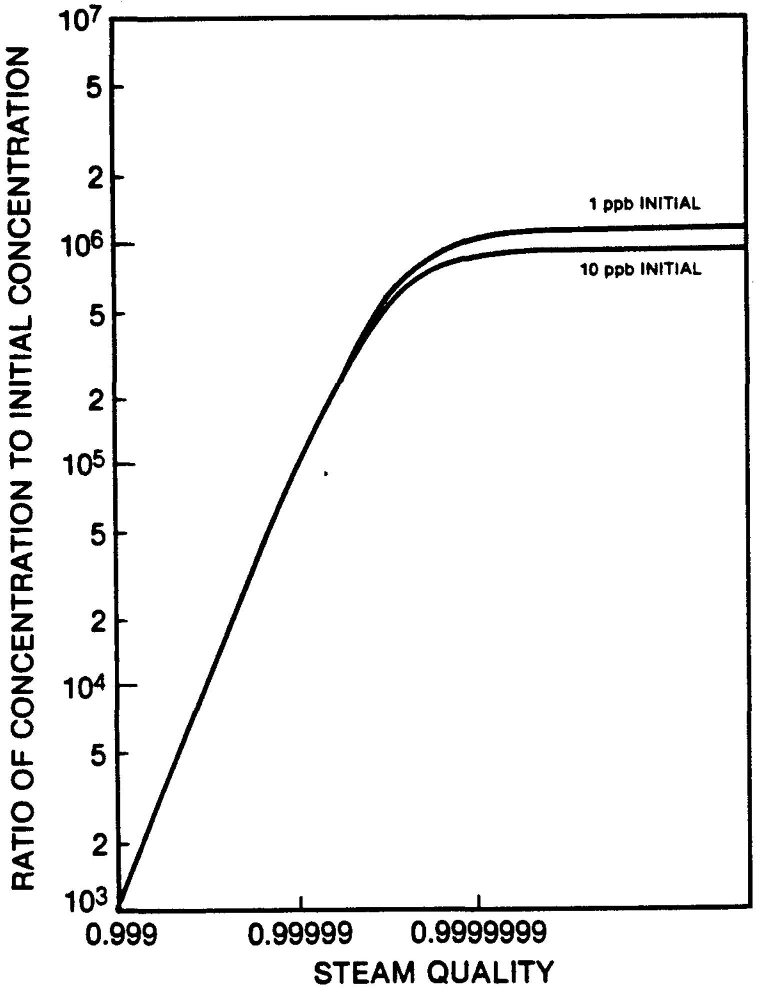

Figure 9 [32]. Modeled dependence of the ratio of concentration to initial concentration for NaCl in the residual liquid on steam quality.

The above concept of kinetic independence between anions and cations was reviewed and shown to be inconsistent with other kind of data (thermodynamic, electrochemical reactions, electrochemical transport in bulk solutions), to raise additional unresolved difficulties in chemical thermodynamic concepts and in the conceptual understanding of the situation on a microscopic scale. It was concluded that a reinterpretation of the ionic dissociation concept might be useful.

On the above basis, a new hydration model of aqueous solutions of inorganic electrolytes at high temperature and pressure was proposed. In this model, the dissociated ions still interact with each other but at a *larger average distance* and with a correspondingly larger number of hydration water molecules than the associated fraction. Such description may be possible at the higher temperatures and/or lower water densities because of the related lower dielectric constant and the corresponding stronger coulombic interactions. Also, such model may be consistent with ideal

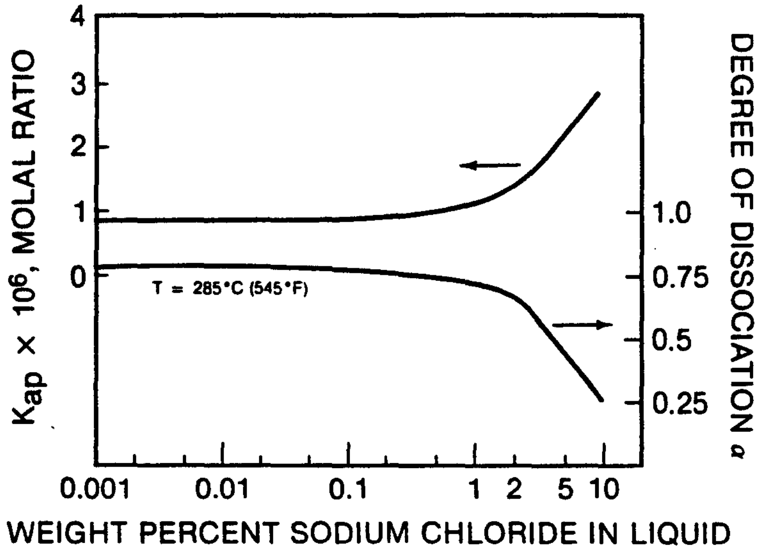

Figure 10 [31]. Modeled dependence of the degree of dissociation and of the steam to liquid distribution coefficient on NaCl concentration in the liquid.

solution properties between the *hydrated* solute species and the *free* water (NOT the *pure* solute and *total* water).

Rigorous application of thermodynamic principles to the aqueous solutions of inorganic solutes at high temperature and pressure, based on the proposed model, yielded a simple and unifying treatment valid over the whole range of electrolytes, from the weakest to the strongest, in liquid and vapor phases as well as in cases where the polar water is mixed with an inert diluent. The treatment yielded general relations in the three areas considered here (solubility, steam to liquid distribution and conductivity) and showed that the partial correlations of Styrikhovich, Martynova and Marshall are particular cases of the more general relations derived from the proposed model. Also, the proposed model predicts the gradual change of electrolytes in aqueous solutions to non-electrolytes upon decreasing the water density by diluting with an inert solvent or by reducing the pressure (at supercritical conditions), consistent with observed trends.

The simplicity and power of the model for practical applications was demonstrated by first applying the relations to the calculation of the three constants m, k and K^{oo} from the combination of the following data: I. Martynova's data on NaCl steam to liquid distribution. II. Marshall's data on the conventional ionic dissociation (from conductivity measurements). III. Pure steam and water densities from steam tables. And then applying those values and, again, the derived relations to the modeling of the two-component system NaCl-H_2O at 285°C. The modeling results predict an observed trend not understood before.

In principle, the proposed model is not restricted to applications at infinite dilution. It is, therefore, of practical importance to determine the range of concentrations (and of temperatures) at which the model will apply.

ACKNOWLEDGMENTS

The development of the work presented here started almost ten years ago at NWT Corp. as part of a program sponsored by the Electrical Power Research Institute (EPRI) in a stimulating environment provided by management and colleagues S.G. Sawochka, W.R. Kassen and D.P. Siegwarth. The author owes a lot to C.S. Shoemaker, C.S. Welty Jr., T.O. Passel, L. Martel, J.P.N. Paine and S. Greene (all of EPRI) for their encouragements to pursue this work and for various related support. R. Mesmer (ORNL) and O. Jonas (Jonas, Inc.) have urged and encouraged the author over the years to bring this work to the public forum. Partial support by the Symposium and by Hewlett-Packard Corp. for the author's participation gratefully is acknowledged. Last but not least, the author is particularly indebted, in chronological order, to W.L. Marshall (ORNL), P. Cohen (Cohen Inc.), Professor L. Brewer (UCB), O.I. Martynova (Moscow Power Institute) and G. Bohnsack (Fa. Bayer AG) for their candid discussions of this work at various stages of its development.

While all the above contributions are acknowledged with deep gratitude, it must be made cristal clear that only the author is responsible for the views herein presented.

Nomenclature

LATIN SYMBOLS

C	Electrolyte concentration in molar units, mole/liter.
C_i	Molar concentration of species i, mole/liter.
C_{ji}	Molar concentration of species i in phase j, mole/liter.
C_{jwt}	Molar concentration of total water (including hydration water) in phase j, mole/liter.
$C_{w,o}$	Molar concentration of water in its standard state, mole/liter.
$C_{w,p}$	Molar concentration of pure water at pressure P, mole/liter.
$C_{w,t}$	Molar concentration of total water (including hydration water), mole/liter.
j	Hydration number of anion species, dimensionless.
k	Increment of solute hydration number upon dissociation, dimensionless.
K	Ostwald's expression defined by Eq. 41, dimensionless.
$K1$	Conventional equilibrium constant for the dissociation of a 1:1 electrolyte, dimensionless.
K^{o}	Marshall's complete equilibrium constant for the dissociation of a 1:1 electrolyte including hydration (see Eqs. 6-8), dimensionless.
K^{oo}	Complete equilibrium constant for the dissociation of a 1:1 electrolyte including hydration according to the proposed model (see Eqs. 34-36), dimensionless.
K_D	Steam-to-liquid distribution coefficient of a substance over all its species forms in solution, dimensionless.
K_{Di}	Steam to liquid distribution coefficient of species i, dimensionless {(mole/liter)/(mole/liter)}.
K_{Di}(molal)	Steam to liquid distribution coefficient of species i, dimensionless {(mole/Kg)/(mole/Kg)}.
K_{ei}	Equilibrium constant for the dissolution of species i, considered as a hydration reaction (see Eqs. 26,27; 30,52 and 31, 53), dimensionless.
m	Hydration number of neutral substance or species, dimensionless.
m	Stands for molal, a unit of concentration, =mole per Kg of water.
m_{ji}	Molal concentration of species i in phase j, mole/Kg of water.
m_{jwt}	Molal concentration of total water (including hydration water) in phase j, mole/Kg of water.

m^o	Initial molal concentration of water (before steaming), mole/Kg of water.
M_w	Molecular weight of water, (=18.016 *g/mole*).
p	Hydration number of cation species, dimensionless.
R	Ideal-gas constant, =8.3147 joules/^{o}K mole (where ^{o}K=degree Kelvin).
SQ	Steam quality defined by Eq. 72, dimensionless.
T	Absolute temperature, ^{o}K.
ν_i	Partial molal volume of species i, cm^3/mole.
W	Represents water.
X	Represents the electrolyte in solid state.
y_i	Activity of species i in reference state (see reference 12), dimensionless.
Y	Quotient of reference activities y_i (see Eq. 11), dimensionless.
YO	Quotient of reference activities y_i $\{=Y/(y_w)^k$, Eq. 17$\}$, dimensionless.

GREEK SYMBOLS

α	Degree of dissociation of a 1:1 electrolyte (Eq. 4), dimensionless.
γ_i	Activity coefficient of species i, liter/mole.
$\Gamma1$	Quotient of activity coefficients defined by Eq. 13, liter/mole.
Λ	Equivalent conductance, $cm^2/(ohm\ mole)$.
Λ_o	Limiting Equivalent conductance, $cm^2/(ohm\ mole)$.
ρ_j	Density of water in phase j, g/cm^3.
$\rho_{j,t}$	Density of total water (including water of hydration) in phase j, g/cm^3.

SUBSCRIPTS

+	Cation species.
-	Anion species.
a	Associated species.
d	Dissociated species.
l	Liquid phase.
s	Steam phase.
w	Water.
x	Inorganic solute.

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33. A.A. Kot, *Water and Water Treatment in Nuclear Power Plants*, Atomizdat Moskva 1964, Translated from Russian and published by Israel Program for Scientific Translations, Jerusalem, 1966, for the U.S. Atomic Energy Commission and the National Science Foundation, Washington, D.C., pp. 188-189.