A Model for Ionic Behavior in Aqueous Solution. Activity Coefficients of Electrolytes at 298.15 K

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Abstract: A model for ionic behavior in aqueous solution has been presented. It is concluded that the activity coefficients of electrolytic solutions would involve contributions from the effects of both the near neighbors (Bahe's theory) and those of the more distant ones (Debye theory) on the reference ion. This is consistent with Lietkze, Stoughton, and Fuoss's formalism of the activity coefficients of aqueous electrolyte solutions. The form of the transition function used in the Lietzke et al. stochastic expression follows as a direct consequence of the statistical mechanical treatment of the model presented here. Activity coefficients for a number of electrolytes in water calculated on the basis of this model well reproduce the experimental data in the concentration range 0.0001 to 3 M at 298.15 K. ϕ_L values for dilute 1-1 electrolytic solutions calculated according to this model also are in excellent agreement with the corresponding experimental values.

A close scrutiny[1-4] of the statistical-mechanical foundations of Debye-Hückel theory[5] has revealed that the method employed in the Debye-Hückel theory contains more elements of inexactness than had at first been realized. The quasilattice model has of course been considered for electrolytic solution before,[5-8] which leads to $c^{1/3}$ laws, and attention[9-11] has been called again to the persistent appearance of $c^{1/3}$ in the dependence on concentration of properties such as log of the activity coefficient, equivalent conductance, and diffusion coefficient.

Lietzke, Stoughton, and Fuoss[12] on the other hand maintain that as the solution is diluted, $c^{1/3}$ behavior must give way to $c^{1/2}$ properties. Consequently, they suggested that the properties of the electrolytic solution at any concentration should be expressed by the stochastic equation

$$P(c) = P(0)f(c) + P(\infty)[1 - f(c)] \qquad (1)$$

where $P(0)$ is the Debye-Hückel description of that property, $P(\infty)$ is the cell model description in which the leading term is $c^{1/3}$, and $f(c) = \bar{e}^{a\phi}$ satisfies the relation $f(0) = 1$ and $f(\infty) = 0$, where a is a constant and ϕ is the volume fraction of solute.

In another approach Bahe[13] considered a model for ions in solution which leads to an expression for the activity coefficient of electrolytic solutions that represent fairly well[13-15] the activity coefficient of 1-1, 1-2 electrolytes. A close examination of this theory reveals that the structured concept may be a reasonable description for moderate to concentrated solutions while in the limit of infinite dilution the ion cloud concept of Debye-Hückel would prevail. Since in the limit of infinite dilution most of the experimental data on the electrolytic solution support the Debye-Hückel theory, a reasonable formalism of these types of solution would be expression 1. The present work enunciates a model for ionic behavior in solution, expression 1, and the form of the function $f(c)$ follows as a direct consequence of the statistical mechanical treatment of such a model.

A Model for Ionic Behavior in Solution

In a dilute solution where the coulombic interaction is the only important interaction between any two ions, the interaction energy is $\ll kT$ so that an ion leads more or less an independent existence. However, due to Brownian motion, at any instance there is a greater probability of finding an oppositely charged ion around any other ion so that the time average population density around any ion in dilute solution is an ion cloud of oppositely charged ions. However, according to Barrow[16] the ionic distribution in a dilute solution may be looked on as an expanded and loosely held ionic crystal. The free ions in a dilute solution thus may be considered to have a certain degree of immobility. Further in a dilute solution of an electrolyte in water the intensity of the field close to any ion is extremely high so that a portion of the solvent which is in contact with it is subjected to the intense field of the ionic charge and is thus greatly modified.[17] Each ion is thus surrounded in its own cosphere,[18] while the remainder of the solvent between the ions does not differ in any way from the pure solvent. Bahe[13] has an essentially similar type of model for ions in solution; an ion is a spherical charge surrounded by a sea of dielectric gradient which extends over a small region in the solvent and which interacts with the electric field from another ion. This gives rise to a repulsive field-dielectric-gradient force in addition to the usual coulombic force between that ion pair. According to Bahe the coulombic force drops off inversily as R^2, while the field-dielectric-gradient force drops off as the inverse of R^4. In dilute solution, since R, the distance between any two ions, is large, the repulsive field-dielectric-gradient force is negligible as compared to the coulombic force while the opposite is the case for concentrated solutions. In the intermediate range of concentration both these forces are appreciable and must always be taken into consideration. Thus the difference between a dilute and a concentrated solution appears to be of degree rather than of kind. Moreover, the concept of field-dielectric-gradient force and that of coulombic force between an ion pair is quite analogous to the forces that characterize solids[19,20] and this led Bahe[13-15] to state that 1-1, 1-2 electrolytes in solution assume a loose lattice structure. Bahe also suggests[13] that for 1-1 electrolytes in solution the ions near a central ion would assume positions corresponding to a face-centered-cubic lattice but the regularity of the structure would disappear as the distance from the central ion is increased. The x-ray diffraction pattern from this loose face-centered-cubic structure would not be exactly that expected from a well-defined face-centered-cubic solid but would have elements of a dispersion curve of a liquid with the near neighbor distance corresponding to the near sites in a face-centered-cubic structure.[13] This would then mean that although the ions in solution tend to assume a loose lattice structure around a central ion, they still have a certain degree of mobility.

However, Evans[19] maintains that in an ionizing solvent the solute occurs as dispersed ions; "In the case of solution in water there is ample evidence that the ions exist co-ordinated by water molecules, to which they are relatively strongly attached

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owing to the polar character of the molecules. It is the energy of hydration of the ions which provides the work necessary to disperse them into solution." Further, nuclear magnetic relaxation studies[21] indicate that the water molecules in the first hydration sphere of certain ions like Na^+, Li^+, etc., rotate about the dipolar axis and that the mean time of rotation is about 10^{-11} s. This finding implies that for these ions the first hydration sphere is not a strictly rigid arrangement of water molecules during a time of 10^{-11} s. Moreover, recent model calculations[22] on solutions of alkali halides in dimethyl sulfoxide (DMSO) indicate that the DMSO molecules around the cation and the anion do not have a regular arrangement at all times; rather, they are in continuous thermal motion and are exchanging with each other. However, averaged over time, the cation in DMSO is in a cage[23] with the oxygen atom in direct proximity to the metal with the dipole oriented toward it.[24] The loose lattice arrangement of the ions in solution, as suggested by Bahe,[13,15] may then be considered as the time average population density of these dispersed ions around a central ion in solution.

Thus whereas in a dilute solution the effect of the thermal motion overweighs the interionic effects (as in the familiar ion cloud concept of the Debye's theory), the reverse is true for concentrated solutions (as in Bahe's theory). In the intermediate range of concentration, the actual position may lie in between these two extremes. Moreover, it is the time average population density of the ions that correspond to either the Debye model or the lattice model. We assume that the Debye and the lattice distribution of the ions in solution are not two isolated effects but that they operate at all concentrations so that the ionic behavior in solution is determined by the following two main factors: (i) interionic effects that cause the ions to be arranged on a loose lattice; (ii) effects due to thermal jostling.

This would then mean that once an ion (say) leaves the loose lattice arrangement, and before the two factors described above subsequently cause it to be rearranged on a loose lattice around another ion, it passes through an ionic distribution that corresponds closely to Debye distribution. Further while the ions are passing from the Debye arrangements to the lattice arrangements and vice versa at the intermediate concentration, the distribution shifts mainly in one direction at the two ends of the concentration scale. Each ion thus has a certain but definite probability (which changes drastically with concentration) to be in a Debye arrangement and a lattice arrangement. There would then be a large number of ions undergoing these arrangements and as both the Debye model and the Bahe model depend upon cooperative effects among a large number of ions, they (ionic distribution) would (depending on concentration) make a suitable contribution to both of them. Moreover, the fluctuation with concentration in any one of these ionic arrangements would depend on ion-solvent interactions and its magnitude (which depends on the hydration of the ions and which determines the probability that an ion is in Debye's distribution) is determined by the molal concentration of the solution. The present model would then take explicit account of ion-solvent interactions which were shown[25] to affect the dielectric constant of water and hence the activity coefficient of the solute salt. Recent IR and Raman spectral studies[26-29] of aqueous electrolytic solutions have also been interpreted in terms of ion-solvent interactions, and Zundel and Weidemann[30] maintain that these effects are of importance in explaining the concentration dependence of the activity coefficients at higher concentration. Further, while the effects due to factor (i) determine lattice contributions, those due to factor (ii) govern Debye's contribution, and the relative magnitude of these two opposing factors is governed by the molar concentration of the solution. Such a conjecture would then envisage that at any temperature each ion in solution has a certain probability to act as a "Debye ion" and as a "Bahe ion" and that each ion of the electrolyte would behave essentially like an ordinary liquid molecule. This in turn would require the x-ray diffraction pattern of the aqueous electrolyte solutions to have elements of the dispersion curve of a liquid with near distance corresponding to the near sites on a suitable lattice as has indeed been observed by Bahe.[13] Thus at any concentration, $\log \gamma_\pm$ of any aqueous electrolytic solution would involve contributions due both to "Debye" and "Bahe" ionic distribution so that

$$\begin{aligned}\log \gamma_\pm = {} & \left[\frac{-A_\gamma Z_+ Z_- \left(\tfrac{1}{2}\sum_i C_i Z_i^2\right)^{1/2}}{1 + ab\left(\tfrac{1}{2}\sum_i C_i Z_i^2\right)^{1/2}}\right] \\ & \times \text{probability that an ion behaves as a Debye ion} \\ & + \left[-A\sqrt[3]{C} + \beta C + \delta\right] \\ & \times \text{probability that an ion behaves as a lattice ion} \\ & - \log\left(1 + \nu m M_1/1000\right) \qquad (2)\end{aligned}$$

where $\nu = \nu_+ + \nu_-$, M_1 is the molecular weight of the solvent, and β and δ are the slopes and intercepts of Bahe plots.[13] The quantity ab in Debye's expression has values[31] between 1.3 and 1.5 and for the present calculations we take $ab = 1.4$. The introduction of δ in Bahe's original expression[13]

$$\log f_\pm = -A\sqrt[3]{C} + \beta C$$

corrects all the activity coefficients calculated according to this theory to the standard state where Debye-Hückel limiting laws were obeyed at infinite dilution. Even Bahe notes:[13] "At the ultimate limit of zero concentration, the field-dielectric-gradient repulsion must become insignificant compared to the coulombic effects and at concentration very close to zero Debye-Hückel theory will apply".

Statistical Mechanical Treatment of the Model

Assuming that the ions in solution behave as postulated above, let us consider a small part of a solution and let it contain N_1 solute particles and a constant number N_0 of solvent molecules. Since each "ion" in solution is postulated to have a certain probability to act as a "Debye ion" and as a "Bahe ion", the probability that an ion acts as a "Debye ion" is governed by the fluctuation in the number of solute particles N_1 contained in a small part of this solution.

If ΔN_1 is the change in N_1 particles contained in a small part of the solution, then the minimum work required to bring about this change is given by

$$w_{\min} = \Delta E - T\Delta S + p\Delta V - \mu_1 \Delta N_1 \qquad (3)$$

Expanding ΔE in powers of ΔS, ΔV, and ΔN_1 we get

$$\begin{aligned}\Delta E = T\Delta S - p\Delta V + \left(\frac{\partial \mu_1}{\partial N_1}\right)\Delta N_1 + \tfrac{1}{2}\Bigg\{&\left(\frac{\partial^2 E}{\partial S^2}\right)(\Delta S)^2 \\ & + \left(\frac{\partial^2 E}{\partial V^2}\right)(\Delta V)^2 + \left(\frac{\partial^2 E}{\partial N_1^2}\right)(\Delta N_1)^2 \\ & + 2\left(\frac{\partial^2 E}{\partial S \partial V}\right)\Delta S \Delta V + 2\left(\frac{\partial^2 E}{\partial S \partial N_1}\right)\Delta S \Delta N_1 \\ & + 2\left(\frac{\partial^2 E}{\partial V \partial N_1}\right)\Delta V \Delta N_1\Bigg\} \qquad (4)\end{aligned}$$

We also know that

$$\begin{aligned}\Delta T = \Delta\left(\frac{\partial E}{\partial S}\right) = {} & \left(\frac{\partial^2 E}{\partial S^2}\right)\Delta S \\ & + \left(\frac{\partial^2 E}{\partial V \partial S}\right)\Delta V + \left(\frac{\partial^2 E}{\partial S \partial N_1}\right)\Delta N_1 \qquad (5)\end{aligned}$$

Table I. Values of the Coefficients and of σ_f^2 Obtained Using Equation 12 at 298.15 K

	β	δ	$\sigma_f^2 \times 10^6$	Max dev in log $\gamma_\pm$
HCl	0.194	0.02	1.27	0.0008
HBr	0.228	0.022	1.10	−0.0013
NaCl	0.100	0.019	1.87	0.0010
NaBr	0.123	0.018	0.90	0.0017
NaI	0.154	0.019	10.60	−0.0013
KCl	0.070	0.013	2.70	0.0010
KBr	0.0785	0.020	9.52	0.0010
LiCl	0.1734	0.025	2.34	−0.0018
$CaCl_2$	0.3900	−0.0237	10.20	0.0020
$BaCl_2$	0.284	−0.0287	17.9	−0.0018

$$-\Delta P = \Delta\left(\frac{\partial E}{\partial V}\right) = \left(\frac{\partial^2 E}{\partial V^2}\right)\Delta V + \left(\frac{\partial^2 E}{\partial S \partial V}\right)\Delta S + \left(\frac{\partial^2 E}{\partial S \partial N_1}\right)\Delta N_1 \quad (6)$$

and

$$\Delta\mu_1 = \Delta\left(\frac{\partial E}{\partial N_1}\right) = \left(\frac{\partial^2 E}{\partial N_1^2}\right)\Delta N_1 + \left(\frac{\partial^2 E}{\partial S \partial N_1}\right)\Delta S + \left(\frac{\partial^2 E}{\partial V \partial N_1}\right)\Delta N_1 \quad (7)$$

Equation 4 reduces to

$$\Delta E = T\Delta S - p\Delta V + \mu_1 \Delta N_1 + \tfrac{1}{2}(\Delta T \Delta S - \Delta p \Delta V + \Delta\mu_1 \Delta N_1)$$

so that (3) becomes

$$w_{\min} = \tfrac{1}{2}(\Delta T \Delta S - \Delta p \Delta V + \Delta\mu_1 \Delta N_1) \quad (8)$$

Since V and μ_1 depend on T, P, and N_1, we may write

$$\Delta V = \left(\frac{\partial V}{\partial P}\right)_{T,N_1}\Delta P + \left(\frac{\partial V}{\partial T}\right)_{P,N_1}\Delta T + \left(\frac{\partial V}{\partial N_1}\right)_{T,P}(\Delta N_1)$$

and

$$\Delta\mu_1 = \left(\frac{\partial \mu_1}{\partial N_1}\right)_{T,P}\Delta N_1 + \left(\frac{\partial \mu_1}{\partial T}\right)_{P,N_1}\Delta T + \left(\frac{\partial \mu_1}{\partial P}\right)_{T,N_1}\Delta P$$

which at constant T and P reduce to

$$\Delta V = \left(\frac{\partial V}{\partial N_1}\right)_{T,P}(\Delta N_1)$$

and

$$\Delta\mu_1 = \left(\frac{\partial \mu_1}{\partial N_1}\right)_{T,P}(\Delta N_1)$$

so that expression 8 at a constant T and P becomes

$$w_{\min} = \tfrac{1}{2}\left\{\left(\frac{\partial \mu_1}{\partial N_1}\right)_{T,P}(\Delta N_1)^2\right\}$$

Now the probability distribution governing the fluctuation in N_1 is expressed as[32]

$$P(\Delta N_1) = C' \exp(-w_{\min}/kT)$$

$$\therefore P(\Delta N_1) = C' \exp\left[-\frac{1}{2kT}(\Delta N_1)^2\left(\frac{\partial \mu_1}{\partial N_1}\right)_{T,P}\right] \quad (9)$$

which yields

$$kT/(\partial\mu_1/\partial N_1)_{T,P} = \overline{(\Delta N_1)^2}$$

as the mean square fluctuation in N_1. Consequently, expression 9 may be expressed as

$$P(\Delta N_1) = C' \exp\left[-\frac{(\Delta N_1)^2}{2(\overline{(\Delta N_1)^2})}\right] \quad (10)$$

But $\overline{(\Delta N_1)^2} \propto$ solute particles or $\overline{(\Delta N_1)^2} = aN_1$ where a is a constant.

Further since $(\Delta N_1) = (N_1 - \overline{N}_1)$, $(\Delta N_1)^2/2\overline{(\Delta N_1)^2}$ depends only on the number of solute particles and not on the distance between them. Consequently $(\Delta N_1)^2/2\overline{(\Delta N_1)^2}$ is a function of the molality of the solution so that the probability that an "ion" behaves as a "Debye ion", i.e., $P(\Delta N_1)$, is given by

$$P(\Delta N_1) = C'e^{-b'm} \quad (11)$$

where C' and b' are certain constants. The molal activity coefficients of aqueous electrolytic solutions would then be expressed by

$$\log \gamma_\pm = C'e^{-b'm}\left(\frac{-A_\gamma Z_+Z_-(\tfrac{1}{2}\Sigma C_i Z_i^2)^{1/2}}{1 + 1.4(\tfrac{1}{2}\Sigma C_i Z_i^2)^{1/2}}\right) + (1 - C'e^{-b'm})(-A\sqrt[3]{C} + \beta C + \delta) - \log(1 + \nu m M_1/1000) \quad (12)$$

In order to test this expression to express the activity coefficients of electrolytes, data from the literature[33-35] have been used and the β and δ parameters of Bahe's theory reevaluated. The data necessary to change molalities to molalities were taken from Harned.[36] It was observed that the expression 12 with $C' = 1$ and $b' = 15$ well represent the activity coefficients of 1-1 electrolytes in the concentration range 0.0001 to 3.0 M. The criterion chosen to determine the effectiveness of expression 12 in describing the activity coefficient behavior of the electrolyte was the variance of the fit, σ_f^2, defined by

$$\sigma_f^2 = \Sigma_i(\log \gamma_{\pm\text{obsd}} - \log \gamma_{\pm\text{calcd}})^2/(q - p)$$

where q is the number of points used in the fit and p is the number of adjustable parameters used. In most cases about 16 concentrations were used in the range 0.0001 to 3.0 M. Table I shows the values of σ_f^2 for the various 1-1 electrolytes in water at 298.15 K.

Since $P(\Delta N_1)$ depends only on the number of solute particles and not on any particular nature of the particles, expression 12 with $C' = 1$ and $b' = 15$ should be expected to describe the activity coefficients of 1-2, 2-1 electrolytic solutions. This has indeed been observed (Table I) for $CaCl_2$ and $BaCl_2$ (concentration range 0.0001 to 1 M, 12 points), the necessary data for both of which are available.[15,37-40]

The present study shows that the form of the function $f(c)$ used in Lietzke et al.[12] formalism of the electrolytic solutions follows as a direct consequence of the statistical mechanical treatment of the model presented here. Equation 12 answers Frank and Thompson's observations[4] and it also incorporates the salient features of the Debye-Hückel as well as the Bahe's concept of ionic behavior in solution.

We now examine the effectiveness of the present model to express the relative partial molal enthalpies at 298.15 K. From eq 12 it follows that the partial relative molal enthalpies of an electrolyte at any concentration would be expressed by

$$\overline{H}_2 - \overline{H}_2^0 = (\overline{H}_2 - \overline{H}_2^0)_{\text{Debye}} \times e^{-15m} + (1 - e^{-15m})(\overline{H}_2 - \overline{H}_2^0)_{\text{Bahe}} \quad (13)$$

where

$$(\overline{H}_2 - \overline{H}_2^0)_{\text{Debye}} = S_{\text{H}}(d_0 m)^{1/2} \text{ (for dilute solutions)},$$

$$(\overline{H}_2 - \overline{H}_2^0)_{\text{Bahe}^{14}} = 2(2.303)RT^2\left[\left(\frac{\partial A}{\partial T}\right)C^{1/3} - \left(\frac{\partial \beta}{\partial T}\right)C + \left(\frac{A}{3C^{1/3}} - B\right)\left(\frac{\partial C}{\partial T}\right)\right]$$

Table II. ϕ_L Values Calculated from Expression 15 and also for Debye and Bahe's Theory and Their Comparison with the Literature ϕ_L Values

	ϕ_L, cal mol^{-1}			
m	Debye	Bahe	Expression 15	Lit.[42]
0.0001	4.71	10.42	4.73	5.0
0.0002	6.66	12.72	6.67	7.0
0.0005	10.54	17.82	10.60	11.0
0.001	14.90	21.75	15.0	14.0
0.002	21.08	27.41	21.27	21.8
0.005	33.33	37.19	33.61	31.0
0.01	47.13	46.76	47.08	42.0
0.02	66.65	58.94	64.65	55.0

and the various symbols have their usual meanings.[14,41] As $\overline{H}_2 - \overline{H}_2{}^0 = \overline{L}_2 = \partial/\partial m(\phi_L m)$, consequently for dilute solutions of 1:1 electrolytes at 298.15 K

$$\phi_L = (\phi_L)_{\text{Debye}}e^{-15m} + (1 - e^{-15m})(\phi_L)_{\text{Bahe}} \quad (14)$$

But $(\phi_L)_{\text{Debye}} = \frac{2}{3} \times 708\ (d_0 m)^{1/2}$ and $(\phi_L)_{\text{Bahe}^{14}} = 217.5m^{1/3}$ for dilute 1-1 electrolytic solutions at 298.15 K and, as such, expression 14 for dilute 1-1 aqueous electrolyte solutions becomes

$$\phi_L = 471.3m^{1/2}e^{-15m} + (1 - e^{-15m})(217.5m^{1/3}) \quad (15)$$

ϕ_L values evaluated for both the Debye as well as the Bahe's theory and also from expression 15 for dilute NaCl at 298.15 are recorded in Table II. It is clear that ϕ_L values calculated from expression 15 are in good agreement with the corresponding literature values[42] and consequently the literature ϕ_L values need not be adjusted as suggested by Bahe.[14]

Acknowledgments. The patience of Professor L. G. Hepler, with whom many valuable discussions were held, is gratefully acknowledged. The author thanks the authorities of the Panjab Agricultural University, Ludhiana, India for leave of absence. This work was supported by the National Research Council of Canada.

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