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A New Model to Evaluate Activity Coefficients of Strong Electrolytes in Aqueous Solutions

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A simple model to calculate the mean activity coefficient based on the Debye-Hückel model is introduced. An empirical formula is given for the calculation of the distance of closest approach for simple salts in aqueous medium. The mean activity coefficients for several salts are calculated in the range 0.001–7.0 m. Good agreement with experimental values is observed.

INTRODUCTION

Interaction between ions has been widely investigated using both experimental and theoretical approaches[1–20]. Theoretical models for the interpretation of properties of strong electrolytes in dilute solutions have been based on the Debye-Hückel (DH) law[1–3]. However, in the high concentration range of practical importance, ions cannot be treated as point charges and their size in solution has to be considered. Little theoretical progress has been made in this area. Furthermore, the available models for calculation of activity coefficients at high concentrations have many limitations[4, 5, 8–11]

Bennetto and Spitzer[11] developed a model for ionic interactions at high concentrations. This model allows for mutual polarization of the ions in order to explain the characteristic shape of the activity coefficient curves at high concentrations. For ionic strengths not exceeding 1 m, Meier[12] proposed a two parameter Debye-Hückel approximation for the evaluation of mean activity coefficients of several electrolytes. Kuzhetsova[13] suggested an equation that takes into consideration the effect of concentration on the value of the activity coefficient. Munze[14] proposed an equation which yields the free energy change of complexation. This equation includes a term which allows for the calculation of the activity coefficients of ions involved in this process.

However, most of the above models did not pay sufficient attention to the effect of ionic charge and size on the value of the activity coefficient. In addition, these models tend to lack simplicity, use complex mathematical approaches and need elaborate calculations.

In the present work, a simple, easy to use and flexible model for the evaluation of activity coefficients is presented. This model takes into consideration the size, charge and concentration of ions. Comparison of activity coefficients using this model with experimetnal values indicates good agreement over a wide range of concentrations.

The model

In dilute solution, the activity coefficient, γ_i, of an ion of type i is given by[21]

$$\ln \gamma_i = \frac{\Delta G_m}{RT} = \frac{W_e}{RT} \tag{1}$$

where ΔG_m, the change in the molarGgibbs function, is identified with the electrical work of charging an isolated ion, W_e. This is the work neded to transport a charge dq from infinity to a point where the electric potential is ϕ, such that

$$dW_e = \phi \, dq \tag{2}$$

The total work of charging one mole of ions is

$$W_e = L \int_0^{q_f} \phi \, dq \tag{3}$$

where L is Avogadro's number and g_f is the final charge at the point of interest, given by the ionic charge to $Z_i e$.

On the basis of the Born model[22], in which the solvent is assumed to be a continuous dielectric and the ion a conducting sphere, the coulombic potential at a distance *r* from an isolated ion of charge $Z_i e$ is

$$\phi_i(r) = \frac{Z_i e}{4\pi\varepsilon_0 \varepsilon r} \tag{4}$$

where r is the distance from the centre of the ion, ε is the dielectric constant for the solvent and ε_0 is the permittivity of vacuum. The work of charging such a sphere is then given by

$$W_e = \frac{Z_i^2 e^2 L}{8\pi\varepsilon_0 \varepsilon r} \tag{5}$$

and the activity coefficient may be expressed as

$$\ln \gamma_i = \frac{z_i^2 e^2}{8\pi\varepsilon_0 \varepsilon r k T} \tag{6}$$

However, in a solution of positive and negative ions in a solvent with high dielectric constant, the potential falls off more steeply with distance than predicted by equation (4). This is due to the effect of ions of opposite charge in the vicinity of a given ion, which shield its central charge. Since potential drops exponentially with distance, the potential in the presence of this "ionic atmosphere" is given by

$$\phi_i = \frac{Z_i e}{4\pi\varepsilon_0 \varepsilon r} e^{-r/r_a} \tag{7}$$

where r_a is the thickness of the ionic atmosphere, given by

$$r_a = \left(\frac{\varepsilon_0 \varepsilon kT}{2e^2 LI}\right)^{1/2} \tag{8}$$

in which I is the ionic strength. The potential due to the ionic atmosphere is that in the presence of the atomic atmosphere less the potential due to the isolated ion alone, *i.e.*

$$\phi_{atm}(r) = \frac{Z_i e}{4\pi\varepsilon_0\varepsilon}\left(\frac{e^{-r/r_a}}{r} - \frac{1}{r}\right) \tag{9}$$

At the centre of the ion the potential becomes

$$Q_{atm}(r = 0) = -\frac{Z_i e}{4\pi\varepsilon_0\varepsilon r_a} \tag{10}$$

and the work of charging the ionic atmosphere is thus given by

$$W_e = -\frac{Z_i^2 e^2 L}{8\pi\varepsilon_0\varepsilon r_a} \tag{11}$$

This work is a measure of deviation from ideal behaviour. The activity coefficient is then given by

$$\ln \gamma_i = -\frac{Z_i^2 e^2}{8\pi\varepsilon_0\varepsilon r_a kT} \tag{10}$$

or

$$\log \gamma_i = -Z_i^2 B\sqrt{I} \tag{11}$$

where B is a constant given by

$$B = \frac{e^3}{2.303 \times 8\pi}\left(\frac{2L}{\varepsilon_0^3\varepsilon^3 k^3 T^3}\right)^{1/2} \tag{12}$$

In an ionic solution, at least two types of ions must be present. The mean activity coefficient, $\gamma_\pm$, is what can be measured experimentally. For an ionic solution formed from M_pX_q, electric neutrality requires that $pZ_+ = q|Z_-|$ and the mean activity coefficient is then given by[21]

$$\log \gamma_\pm = \frac{1}{(p + q)}(p \log \gamma_+ + q \log \gamma_-)$$

$$= -Z_+|Z_-|B\sqrt{I} \tag{13}$$

Equation (13) is adequate at low concentrations. At high concentrations, however, the value of $\log \gamma_\pm$ is significantly less negative than predicted by equation (13), and at sufficiently high concentrations, it may actually attain positive values (Fig. 1).

An important factor that accounts for the deviation from experimental observation is the assumption that ions are point charges. Actually, ions occupy space and have definite sizes. If (a) is the closest distance the centres of the ions can approach one another, then the shielded coulomb potential falls off as[21]

$$\phi(r) = A\frac{1}{r}e^{-(r-a)/r_a} \qquad r \geq a \tag{14}$$

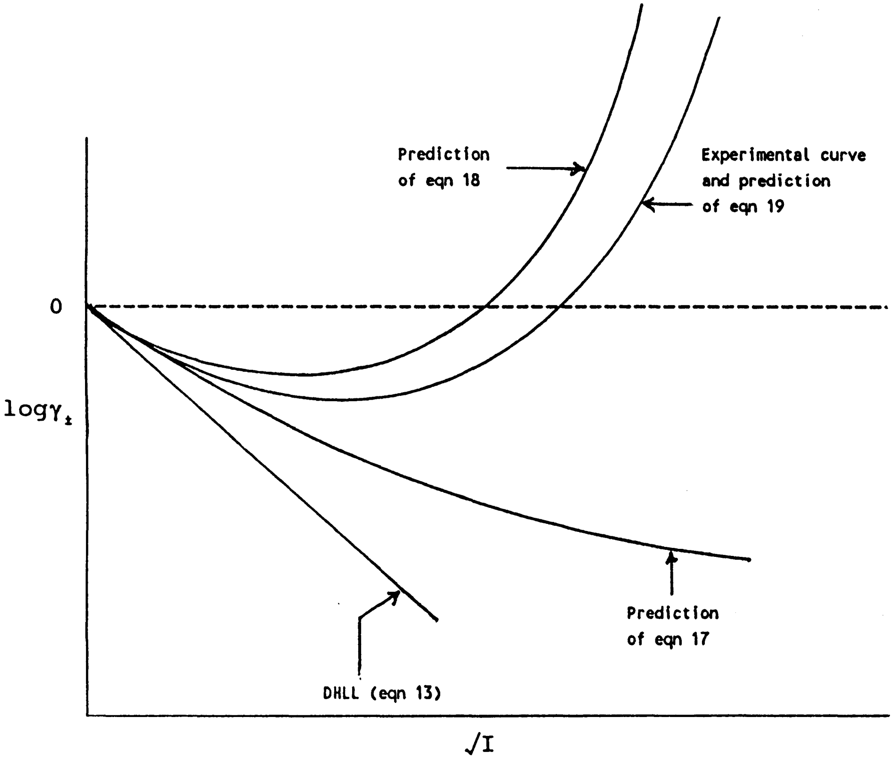

Fig. 1 Variation of log $\gamma_\pm$ with $\sqrt{I}$

where A is a constant given by

$$A = \frac{Z_i e}{4\pi\varepsilon_0\varepsilon}\frac{1}{1 + (a/r_a)} \tag{15}$$

The potential at the site of the central ion due to the ionic atmosphere is obtained from equations (4) and (14) by setting r = a. The work associated with this potential is

$$W_e = -\frac{Z_i^2 e^2 L}{8\pi\varepsilon_0\varepsilon r_a}\frac{1}{1 + (a/r_a)} \tag{16}$$

and the corresponding mean activity coefficient is

$$\log\gamma_\pm = -Z_+|Z_-|B\sqrt{I}\frac{1}{1 + (a/r_a)} \tag{17}$$

Comparing this equation with equation (13) shows that the effect of considering the ionic size on the activity coefficient is the factor $1/[1 + (a/r_a)]$.

Equation (17) shows better agreement with experimental values of the activity coefficient (Fig. 1). However, it cannot explain the reversal in the concentration dependence of log $\gamma_\pm$. To explain this behaviour, the removal of some solvent from effective parking in the ionic solution's activity needs to be considered. The work in this process is then added to the work done in building up the ionic atmosphere. This was considered by Hückel[23], who showed that it gives a term linear with the ionic strength in the expression of $\log \gamma_\pm$, such that

$$\log \gamma_\pm = -Z_+|Z_-|B\sqrt{I}\frac{1}{1 + (a/r_a)} + CI \tag{18}$$

This equation gives a better agreement with the experimental values, but it overestimates the amount of work needed for solvent removal. Activity coefficients calculated from equation (18) are usually larger than the experimental values (Fig. 1).

In the present work, a correction factor is introduced to account for the work needed to remove the solvent molecules from the effective parking of the ionic solution's activity. It yields an additional third term, to the right-hand side of equation (18), which depends negatively on the square root of the ionic strength, such that

$$\log \gamma_\pm = -Z_+|Z_-|B\frac{1}{1 + (a/r_a)} + CI - D\sqrt{I} \tag{19}$$

The prediction of this equation for the activity coefficient agrees very well with experimental values as shown in Fig. 1.

RESULTS AND DISCUSSION

Equation (18) was used to calculate the mean activity coefficient for a large number of solutions of simple salts in aqueous medium at 25°C. Calculations were performed for uni-, di- and trivalent cations in halide salts. The parameters a, C, and D were determined by the procedures outlined before.

(i) Distance of closest approach, (a)

Due to the solvation effect, the distance of closest approach between two ions in solution is expected to be larger than the sum of the crystallographic radii. However, the sum of the solvated radii may not correspond to the distance of closest approach due to the possibility that the hydration shells may "crush" to some extent when two solvated ions collide. Thus the value of (a) is expected to be larger than the sum of the crystallographic radii but less than that of the solvated radii.

The value of the parameter (a) depends on ionic charge and size. The larger the charge and the smaller the size of the ion the larger the possibility that more solvent molecules are introduced between the cation and the anion. For a fixed anion size, usually larger than that of the cation, the value of (a) should increase with decreasing cation radius.

For the aqueous solutions, water molecules orient themselves around cations and anions as shown in Fig. 2a. Assuming that only one water molecule is present between a cation and an anion (Fig. 2b), the two ions will be 1.10 Å, *i.e.* the sum

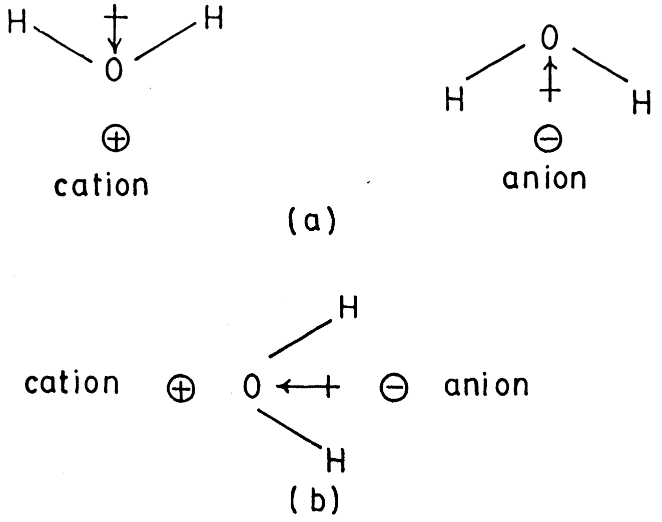

Fig. 2 Orientation of water molecules around ions

of the covalent diameters of oxygen and hydrogen. In general, the separation between ions should be a multiple or a fraction of the 1.10 Å distance, depending on their charges and sizes. Based on this, the following equation is proposed to calculate the distance of closest approach

$$a = r_{ac} + \frac{1.10|\Delta r|Z_c}{r_c^{0.7(2 - Z_c)}} \times \text{CFa} \tag{20}$$

where r_{ac} is the sum of Pauling ionic radii of the cation and the anion, Δr is the difference in the ionic radii of the ions, Z_c is the charge of the cation, r_c is the radius of the cation and CFa is a correction factor, such that

$$\text{CFa} = 1 \text{ for salts with uni-and divalent cations}$$

$$= \left(\frac{1}{Z_c} - 0.04\right)^{r_{ac}r_c^{-0.7}} \quad \text{for salts with tri- and tetravalent cations}$$

Table 1 lists values of (a) as calculated from equation (20) as well as those obtained experimentally[13, 24]. The agreement is good for a wide range of various salts.

(ii) The parameters C and D

The two parameters C and D were treated as empirical constants. Their values, for a specific ion in aqueous medium, were convoluted by fitting equation (19) to experimental values of activity coefficients at some concentration. Their values were then adjusted so that they can be used to calculate the activity coefficient over a large range of concentrations: from 0.001 m to as high as 7.0 m solutions.

Since the values of C and D represent the magnitude of deviation from DHLL,

TABLE 1
VALUES OF THE DISTANCE OF CLOSEST APPROACH, a, IN AQUEOUS SOLUTIONS IN Å

Uni-univalent, di-univalent, tri-univalent and tetra-univalent electrolytes:

Salt	a_{calc}	a_{expr} [24]	Salt	a_{calc}	a_{exp} [13, 24]
LiCl	4.31	4.32	$SrCl_2$	4.44	4.61
NaCl	3.74	3.97	$SrBr_2$	4.88	4.89
KCl	3.57	3.63	SrI_2	5.56	5.58
LiBr	4.68	4.56	$BaCl_2$	4.17	4.45
NaBr	4.04	4.24	$BaBr_2$	4.62	4.68
KBr	3.84	3.85	BaI_2	5.29	5.44
LiI	5.22	5.60	$MnCl_2$	4.83	4.74
NaI	4.49	4.47	$CoCl_2$	4.90	4.81
KI	4.24	4.16	$NiCl_2$	4.93	4.86
$MgCl_2$	5.01	5.02	$FeCl_2$	4.88	4.80
$MgBr_2$	5.46	5.46	$AlCl_3$	5.20	5.43
MgI_2	6.13	6.18	$CrCl_3$	5.18	5.16
$CaCl_2$	4.60	4.73	$ScCl_3$	5.13	5.02
$CaBr_2$	5.05	5.02	$LaCl_3$	4.83	4.70
CaI_2	5.72	5.69	$ThCl_4$	4.88	4.90

one would expect different C's and D's for different ions. The constants C and D were obtained by fitting the experimental values of the activity coefficient for the salt to equation 19, as shown below:

(1) *Salts of univalent cations:* The experimental values of the activity coefficient for NaCl[25] were fitted to equation (19) at moderate concentrations. The equation was solved for C and D and the obtained values were adjusted to fit a wide range of concentrations. For all other salts with uni-univalent electrolytes, a correction factor is introduced to account for the size of the ion, as given by

$$CF1 = \left(\frac{r_{Na^+}}{r^+}\right)^3 \left(\frac{r^-}{r_{Cl}^-}\right)^3 \qquad (21)$$

where r_{Na^+} is the ionic radius of Na^+, r_{Cl^-} is the ionic radius of Cl^-, r^+ and r^- are the ionic radii of the salt's cation and the anion, respectively.

The values of C and D used in the calculation of the activity coefficient of a salt are then given by

$$C_{salt} = C_{NaCl} \times CF1$$

$$D_{salt} = D_{NaCl} \times CF1 \qquad (22)$$

(2) *Salts of divalent cations:* The experimental data for $MgCl_2$ [13] were fitted

to equation (19). The values obtained for C and D were adjusted to fit a wider range of concentrations. For all other di-univalent electrolytes, the following correction factor was used

$$CF2 = \left(\frac{R_{Mg^{2+}}}{r^{2+}}\right)^{0.47} \left(\frac{r^-}{r_{Cl^-}}\right)^{2.3} \tag{23}$$

The values of C and D for a salt are then given by

$$C = C_{MgCl_2} \times CF2$$

$$D = D_{MgCl_2} \times CF2 \tag{24}$$

(3) *Salts of trivalent cations:* The experimental data for $AlCl_3$[26] were fitted to equation (19). Again, a correction factor was introduced for all other chlorides containing trivalent cations, such that

$$C = C_{AlCl_3} \times CF3$$

$$D = D_{AlCl_2} \times CF3 \tag{25}$$

where

$$CF3 = \left(\frac{r_{Al^{3+}}}{r^{3+}}\right)^{XCF}$$

and

$$XCF = \frac{r^{3+} - r_{Al^{3+}}}{r^{3+} + r_{Al^{3+}}} \tag{26}$$

values of C and D for NaCl, $MgCl_2$ and $AlCl_3$ are given in Table 2.

TABLE 2
VALUES OF C AND D, IN SI UNITS, FOR UNI-UNIVALENT, DI-UNIVALENT, AND TRI-UNIVALENT ELECTROLYTES AT 25°C

Salt	$C(m^3)$	$D(m^{3/2})$
NaCl	4.30×10^{-5}	2.60×10^{-5}
$MgCl_2$	1.30×10^{-4}	3.10×10^{-3}
$AlCl_3$	1.02×10^{-4}	2.33×10^{-3}

A computer program has been prepared that uses equations (19) through (26). Only the charge and the radius of the ions, and the temperature of the solution, are needed to evaluate the activity coefficient at a given concentration. The values of the calculated activity coefficients for various salts along with experimental values are shown in Table 3.

In summary, this new and simple model has been shown to be fairly effective in calculating activity coefficients. A desk-top calculator, or a simple computer program, can be used to perform the operations. Though simple, the model has been demonstrated to be very accurate in predicting activity coefficients for various salts over a wide concentration range.

TABLE 3
EXPERIMENTAL AND CALCULATED (IN PARENTHESES) VALUES OF $\gamma_\pm$ FOR SOME UNI- AND BIVALENT CATION SALTS IN AQUEOUS SOLUTIONS AT 25°C.

Molality, m / Salt*	0.1	1.0	2.0	3.0	4.0	5.0	6.0	7.0
NaCl[25, 27]	0.778	0.657	0.668	0.714	0.783			
	(0.776)	(0.662)	(0.678)	(0.719)	(0.772)			
NaBr[28]	0.782	0.687	0.731	0.812	0.929			
	(0.782)	(0.691)	(0.730)	(0.796)	(0.878)			
NaI[28]	0.787	0.736	0.820					
	(0.788)	(0.733)	(0.813)					
KCl[25, 27]	0.770	0.604	0.573	0.569	0.577			
	(0.766)	(0.607)	(0.579)	(0.573)	(0.577)			
KBr[28]	0.772	0.617	0.593	0.595	0.608	0.626		
	(0.770)	(0.622)	(0.603)	(0.605)	(0.615)	(0.630)		
KI[28, 29]	0.778	0.645	0.637	0.652	0.673			
	(0.776)	(0.647)	(0.641)	(0.656)	(0.680)			
RbCl[30]	0.746	0.583	0.546	0.536	0.538	0.546		
	(0.763)	(0.594)	(0.559)	(0.547)	(0.544)	(0.545)		
RbBr[28, 30]	0.763	0.578	0.536					
	(0.764)	(0.597)	(0.566)					
$MgCl_2$[13]	0.53	0.57	1.05	2.3	5.5			
	(0.49)	(0.58)	(1.11)	(2.30)	(4.95)			
MgI_2[13]	0.57	0.88	2.39	7.8	28.6			
	(0.52)	(0.87)	(2.47)	(7.70)	(24.7)			
$CaCl_2$[13, 27]	0.523	0.50	0.79	1.48	2.93	5.89	11.11	18.28
	(0.486)	(0.50)	(0.84)	(1.51)	(2.81)	(5.30)	(10.22)	(19.79)
$SrBr_2$[13]	0.53	0.58	0.91	1.79	3.9			
	(0.49)	(0.54)	(0.97)	(1.89)	(3.8)			
SrI_2[13]	0.55	0.68	1.40	3.30	9.0			
	(0.51)	(0.68)	(1.48)	(3.50)	(8.6)			

*Reference from which experimental data were obtained.

TABLE 4
EXPERIMENTAL AND CALCULATED (IN PARENTHESES) VALUES OF $\gamma_\pm$ FOR SOME TRIVALENT CATION SALTS IN AQUEOUS SOLUTIONS AT 25°C

Molality, m / Salt*	0.2	0.5	1.0	1.2	1.6
$AlCl_3$[26]	0.305	0.331	0.539	0.701	
	(0.298)	(0.340)	(0.543)	(0.673)	
$CrCl_3$[31]	0.298	0.315	0.481	0.584	
	(0.284)	(0.314)	(0.481)	(0.584)	
$ScCl_3$[27]	0.288	0.298	0.443	0.544	0.786
	(0.276)	(0.297)	(0.439)	(0.529)	(0.853)
YCl_3[26]	0.278	0.278	0.385	0.462	0.701
	(0.271)	(0.285)	(0.406)	(0.481)	(0.693)
$LaCl_3$[26, 32]	0.274	0.266	0.342	0.398	0.561
	(0.256)	(0.257)	(0.338)	(0.390)	(0.530)

*Reference from which experimental data were obtained.

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