An Equation for the Activity Coefficient of the Ions of Strong Electrolytes for Concentrations up to $0.1 N$

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It has been shown that the Debye Hückel equation for the activity coefficient of the ions of strong electrolytes requires modification. The modification consists in replacing $(\Sigma n)^{\frac{1}{2}}$ in the expression for Kappa by $(\Sigma n)^{\frac{3}{2}}/(2\pi a)^{\frac{1}{2}}$ where $a = [(a_+)(a_-)]^{\frac{1}{2}}$, a_+ and a_- representing the "effective diameter" of the positive and negative ions of a symmetrical electrolyte and Σn the sum of the number of positive and negative ions per cc of the solution. The volume of the composite cell in the phase space containing a pair of oppositely charged ions has been defined. The modified equation has been subjected to test using the data available in the literature on HCl, NaCl, KCl and CuSO₄ and ZnSO₄ and has been found satisfactory.

TAKING into consideration interionic attraction and applying Boltzmann distribution formula and Poisson's equation, Debye and Hückel[1,2], deduced the following equations for the activity coefficient of the ions of a strong electrolyte in solution

$$-\log f_i = \frac{Ne^2 Z_i^2}{2.303(2DRT)}\left[\chi\right] \quad (1)$$

$$-\log f_i = \frac{Ne^2 Z_i^2}{4.606(DRT)}\left[\frac{4\pi e^2 \Sigma n_i Z_i^2}{DkT}\right]^{1/2} \quad (1a)$$

$$= 0.487 Z_i^2(\mu)^{1/2} \text{ at } 0°C \quad (1b)$$

$$= 0.505 Z_i^2(\mu)^{1/2} \text{ at } 25°C \quad (1c)$$

$$-\log f_i = \frac{Ne^2 Z_i^2}{4.606[DRT]}\left[\frac{\chi}{1+\chi a}\right] \quad (2)$$

$$= \frac{Z_i^2 A(\mu)^{1/2}}{1+aB(\mu)^{1/2}} \quad (2a)$$

The equations† (1) and (1a) have been deduced on the assumption that ions can be treated as point charges. In equation† (2) the finite size of the ions has been taken into consideration and 'a', denotes the average "effective diameter" of the ions and A and B are constants which can be calculated from theory.

Hückel[3] has proposed further modification of equation (2) by taking into consideration the effect of the electric field of an ion on the orientation of the solvent molecules around it and has deduced the following equation :

$$-\log f_i = \frac{Z_i^2 A(\mu)^{1/2}}{1+aB(\mu)^{1/2}} - c\mu \quad (3)$$

The aforesaid equations give f_i the activity coefficient, of a particular ion. For the mean activity coefficient f of an electrolyte dissociating into ν_+ and ν_- ions having valencies Z_+ and Z_- the following expression should be used.

$$-\log f = \frac{\nu_+(Z_+)^2 + \nu_-(Z_-)^2}{(\nu_+ + \nu_-)}\left[\frac{Ne^2}{4.606(DRT)}\right]$$
$$\frac{\chi}{1+\chi a} \quad (4)$$

The equations have been subjected to test by many investigators[4,5] and deviation from equation (1a) has been noticed for uni-univalent electrolytes such as NaCl at concentrations about $0.0005 M$ and above it. Deviations from equation ( ) or (2a) have also been noticed for bi-bivalent electrolytes such as ZnSO₄ at fairly low concentrations. Such deviations have been attributed by some authors to the neglect of terms beyond the first two in the expansion of the series

$$\exp(Z_i e\psi/kT) - \exp(-Z_i e\psi/kT)$$

for the evaluation of the charge density near the central ion. Grownwall, La Mer and Sandved[6] have used the expansion of the series up to the 5th or 6th term and also carried out approximate integration of the Poisson equation in the form of a power series. Their equation for the activity coefficient, of a symmetrical electrolyte such as

ZnSO₄ may be written as follows

$$-\ln f = \frac{NZ^2 e^2}{2DRT}\left[\frac{\chi}{1+\chi a}\right] - \sum_{m=1}^{\infty}\left[\frac{NZ^2 e^2}{DRTA}\right]^{2m+1}$$
$$\left[\frac{1}{2}X_{2m+1}(\chi a) - 2mY_{2m+1}(\chi a)\right] \quad (5)$$

Where X (χa) and Y (χa) are known functions of (χa) which have been evaluted and recorded in tables.

Gronwall, La Mer equation (5) is definitely better than equation (2a) of Debye and Hückel since, for an electrolyte like $ZnSO_4$, it requires a constant value of the "ionic diameter" a, to give values of $-\log f$ which agree with the observed ones up to the concentration $0.01M$, while equation (2a) requires impossible negative values of a. This will be evident from the data recorded in page 67, Table 2.6 of L. I. Antropov's "Theoretical Electrochemistry", 1972 (English translation).

Improvement of the Debye Hückel theory adopting a different mode of approach, has been attempted by Dutta and Bagchi[7] and by Eigen and Wicke[8]. They have tried to replace Boltzmann's formula for the distribution of ions in the ion atmosphere by a new distribution formula developed by them.

Besides, those mentioned above, the following way of modifying Debye-Hückal theory may also be considered. Boltzmann's distribution law is meant for a perfect gas in which the activity coefficient of the molecules is unity. In applying it to ions in solution their activity coefficient 'f' should be taken into consideration and for an uni-univalent electrolyte the equations should be written as follows :

$$(n_+)fdv = n_o f_o \exp(-e\psi/kT)dv \qquad \dots \quad (6)$$

$$(n_-)fdv = n_o f_o \exp(e\psi/kT)dv \qquad \dots \quad (6a)$$

In the equations (6) and (6a) $(n_+)f$ and $(n_-)f$ represent the activity, per unit volume of the positive and negative ions in the volume element dv close to the central positive ion where the potential due to it is ψ and $n_o f_o$ represents the activity of the positive and negative ions in a unit volume of the solution where ψ is zero. Therefore, the expression for χ should contain f_o/f and should be written as follows :

$$\chi = \left[\frac{4\pi e^2 \Sigma n'}{DkT} f_o/f\right]^{1/2} \qquad \dots \quad (6b)$$

According to Donnan's theory of membrane equilibria we may write :—

$(n_o f_o)^2 = (n_+)(n_-)f^2$ or $(f_o/f)^2 = (n_+)(n_-)/n_o^2 = [n'/n_o]^2$ or $(f_o/f) = (n'/n_o)$ where $[(n_+)(n_-)]$ has been put equal to $(n')^2$.

It is to be noted that n' is greater than n_o and the higher the value of ψ, the greater is the ratio n'/n_o. It may be looked upon as the ratio of the negative charge density in the neighbourhood of the central positive ion to that in the bulk phase where $\psi = 0$, and it may be large in a dilute solution.

In the case of colloidal electrolytes[9] somewhat similar ratio has been found to be quite large. In a palmitic acid sol the ratio $(a)_\infty/(H)_\sigma$, denoted by $-(Pa)_\infty + (PH)_\sigma, = 10^{1.3} = 20$, where $(Pa)_\infty$ and $(PH)_\sigma$ represent PH close to the surface of the colloidal particle and that of the bulk phase at colloid concentration $C = 40$, respectively and in a clay acid sol the ratio [denoted by $-(PH)_\infty + (PH)_o$],

i.e. $\left[\frac{(H)_\infty}{(H)_o}\right] = 10^{2.18} = 135$ nearly. Similar results

have also been obtained with a gum arabic acid sol[10].

Replacing (f_o/f) by (n'/n_o) in equation (6b) and substituting it in the expression for χ in equation (1a) we get, for a uni-univalent electrolyte, the following expression :

$$-\log f = \frac{Ne^2}{2.303(2DRT)}\left[\frac{4\pi e^2 \Sigma n}{DkT}(n' n_o)\right]^{1/2} \qquad \dots \quad (7)$$

where Σn represents the sum of n positive and n negative ions and is, therefore, equal to 2n.

Assuming uniform distribution of the ions in the solution the average distance L between their centres may be represented by the following expression :

$$L = (1/2n)^{1/3} \qquad \dots \quad (8)$$

Therefore, $(1/2n)^{1/3} = L (L)^{1/2} \qquad \dots \quad (8a)$

Since L has the dimension of length so $(L)^{1/2}$ may be expressed as follows

$$(L)^{1/2} = (2\pi ax)^{1/2} \qquad \dots \quad (8b)$$

where a represents the ionic diameter and x, a dimensionless variable. Substituting the aforesaid values of L and $(L)^{1/2}$ in equation (8a) it may be written as follows :

$$(1/2n)^{1/2} = [(1/2n)^{1/3}][(2\pi ax)^{1/2}] \qquad \dots \quad (8c)$$

or $(2n)^{1/2} = (2n)^{1/3}/(2\pi ax)^{1/2} \qquad (8d)$

Replacing $(\Sigma n)^{1/2}$ in equation (6b) by $(2n)^{1/3}/(2\pi ax)^{1/2}$ we may write

$$\chi = \left(\frac{4\pi e^2}{DkT}\right)^{1/2}\left[(2n)^{1/3}\Big/(2\pi a)^{1/2}\right]\left[\frac{(n'/n_o)}{(x)}\right]^{1/2} \dots \quad (9)$$

In equation (9) the ratio of $(n'/n_o)^{1/2}$ to $(x)^{1/2}$ may remain constant and close to unity* over a certain range of values of n. Therefore, in that range of values of n in which the aforesaid ratio

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* This point has been considered in detail in the "discussion".

remains constant the following equation should hold good :

$$\chi = \left[\frac{4\pi e^2}{DkT}\right]^{1/2}\left[(2n)^{1/3}\Big/(2\pi a)^{1/2}\right] \qquad .. \quad (9a)$$

Substituting in equation (1) the value of χ as found in equation (9a) and putting $n = NC/1000$, we get for symmetrical electrolytes the following expression :

$$-\log f = \frac{Ne^2}{4.606(DRT)}\left[\frac{Z_+^2 + Z_-^2}{2}\right]^{3/2}$$
$$\left[\frac{4\pi e^2}{DkT(2\pi a)}\right]^{1/2}\left[\frac{N2C}{1000}\right]^{1/3} \qquad ... \quad (10)$$

In equation (10), C denotes the concentration of the electrolyte in gram moles per liter. Furthermore, if the effective diameter of the positive and negative ions are denoted by a_+ and a_- respectively then in †equation (10) $a = [(a_+)(a_-)]^{1/2}$. It is to be noted that the volume g of the composite cell containing a pair of oppositely charged ions of a symmetrical electrolyte in the phase space may be found from the following relation :

$$\left(\frac{1}{2n}\right)^{1/2}\left(\frac{1}{2n}\right)^{1/2} = \left(\frac{1}{2n}\right)^{2/3}(2\pi a)x = L^2(2\pi a)x$$
$$= L_-^3 = g \qquad ... \quad (10a)$$

It follows from equation (10) that a plot of $-\log f$ against $(c)^{1/3}$ should be linear since all the other terms in the equation are constants. This has actually been found to be the case up to $C = 0.1N$ for the symmetrical electrolytes whose data are recorded in this paper, but the straight lines cut the $(c)^{1/3}$ axis at points slightly above zero. This means that f becomes unity when C is very small, less than $0.0001\ M$ and it is in broad agreement with the accepted view.

Denoting the mean activity coefficient by f, putting $A \times 10^{-8}$ cm $= a$ and B for the constant terms in equation (10), it may be written for an uni-univalent electrolyte as follows :

$$-\log f = [B/(A)^{1/2}][(C)^{1/3} - (C_0)^{1/3}] \qquad .. \quad (11)$$
$$= [0.60/(A)^{1/2}][(C)^{1/3} - (C_0)^{1/3}]\ at\ 0°C \qquad ... \quad (11a)$$
$$= [0.624/(A)^{1/2}][(C)^{1/3} - (C_0)^{1/3}]\ at\ 25°C \qquad ... \quad (11b)$$

Similarly for a bi-bivalent electrolyte, taking the valency of the ions into consideration, we may write

$$-\log f = [8B/(A)^{1/2}][(C)^{1/3} - (C_0)^{1/3}] \qquad ... \quad (12)$$

Verification of the equations :

The equations deduced above have been subjected to test using the data available in the

† $a = (a_+ + a_-)/2$ may also be used.

literature[5,11]. The data based on freezing point measurements have been recorded in Table 1 and those on $ZnSO_4$ at 25° have been recorded in Table 2. In column 1 of the tables, under the head

TABLE 1—VARIATION OF f WITH c FROM FREEZING POINT MEASUREMENTS

Miscellaneous	2	3	4	5	6	7	8
HCl	C	0.0005	0.001	0.005	0.01	0.05	0.1
Eqn. used (11)							
B/(A)$^{1/2}$ =0.22	Obs.f	0.981	0.970	0.940	0.916	0.840	0.809
(A)$^{1/2}$ =2.7							
(C$_0$)$^{1/3}$ =0.039	Cal f	0.979	0.969	0.934	0.913	0.843	0.802
NaCl	C	0.0005	0.001	0.005	0.01	0.05	0.1
Eqn. used (11)							
B/(A)$^{1/2}$ =0.23	Obs.f	0.972	0.963	0.928	0.906	0.834	0.792
(A)$^{1/2}$ =2.6							
(C$_0$)$^{1/3}$ =0.025	Cal.f	0.972	0.961	0.926	0.904	0.834	0.792
KCl	C	0.0005	0.001	0.005	0.01	0.05	0.1
Eqn. used (11)							
B/(A)$^{1/2}$ =0.247	Obs.f	0.970	0.961	0.926	0.903	0.821	0.779
(A)$^{1/2}$ =2.4							
(C$_0$)$^{1/3}$ =0.025	Cal.f	0.970	0.959	0.921	0.903	0.826	0.780
CuSO$_4$	C	0.0005	0.001	0.005	0.05	0.05	0.1
Eqn. used (12)							
(8.0B)/(A)$^{1/2}$ =1.93	Obs.f	0.75	0.69	0.50	0.40	0.216	0.158
(A)$^{1/2}$ =2.48							
(C$_0$)$^{1/3}$ =0.017	Cal.f	0.75	0.69	0.50	0.41	0.211	0.137

TABLE 2—VARIATION OF f WITH c AT 25°C

Miscellaneous						
ZnSO$_4$	C	0.0005	0.001	0.002	0.005	0.01
Eqn. used (12)						
(8.0B)/(A)$^{1/2}$ =2.28	Obs.f	0.780	0.700	0.608	0.477	0.387
(A)$^{1/2}$ =2.19						
(C$_0$)$^{1/3}$ =0.032	Cal.f	0.780	0.700	0.611	0.482	0.381

miscellaneous, are mentioned the electrolyte and the equation used and the constants in the equation, $B/(A)^{\frac{1}{2}}$ representing the observed slope. In column 2,C denotes the concentration of the electrolyte in moles per 1000 grams of water, obs.f and cal.f represent the observed and calculated mean activity coefficient f of the ions of the electrolyte. Up to $0.1M$ no distinction has been made between a molal and a molar solution in this paper.

Discussion

It will be noticed from the data recorded in the Tables 1 and 2 that the observed values of the mean activity coefficient of the ions of the electrolytes mentioned agree satisfactorily with those calculated over the concentration range $0.0005M$ to $0.1M$ of the uni-univalent electrolytes and $0.0005\ M$ to $0.05M$ of the bi-bivalent electrolytes. This shows that the equations(11) and (12) hold good over the aforesaid range of concentrations of the electrolytes investigated.

The data recorded in the tables show that $(A)^{\frac{1}{2}}$ of HCl is greater than that of NaCl or KCL indicating that the H^+ ions in water are hydrated and exist as H_3O^+. The value of $(A)^{\frac{1}{2}}$ of $CuSO_4$ is greater than that of $ZnSO_4$ and this is in agreement with the fact that the ionic radius of Cu^{+2} is greater than that of Zn^{+2}.

It may also be mentioned that J. C. Ghosh[12] in his theory of strong electrolytes proposed that $-\log \lambda$ varies as $1/(v)^{1/3}$ where λ and v represent respectively the equivalent conductivity and volume of the solution. Although his theory fell into disrepute because some of the assumptions made were self-contradictory and doubtful, yet the cube root relationship proposed by him is significant.

It has been stated earlier in this paper that $[(n'/n_0)/x]^{1/2}$ remains constant and close to unity over a certain range of values of n. This statement may be justified in the following way.

As already mentioned the volume of the composite cell containing a pair of oppositely charged ions may be found from equation (10a) written as $g = L^2(2\pi a)x = L^3$.

Therefore, the density of negative charge in this cell is equal to $e/L^2(2\pi a)x = d_1$ say. The volume $L^2(2\pi a)$ surrounding the central positive ion will very probably contain the same negative change e. However, let us assume that it contains 0.96e. Then d_2 the density of negative charge in this volume element is $0.96e/(2\pi a)L^2$. Now d_2/d_1 may be put equal to n'/n_0 and we may write

$$n'/n_0 = d_2/d_1 = 0.96x \qquad \dots (13)$$

Therefore, $(n'/n_0)^{1/2} = 0.98x^{1/2}$ and hence $[n'/n_0)/x]^{1/2}$ is equal to 0.98 which is very close to unity and is a constant. It is to be noted that according to equation (8b), $x = L/(2\pi a)$ and that the aforesaid relation sholud hold good so long as x is greater than or equal to unity.

Acknowledgement

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