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# Empirical Equations for Activity and Osmotic Coefficients

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Empirical Equations For Activity And Osmotic Coefficients.

\_\_\_\_\_  
(TITLE)

BY

N. Rangunathan

**THESIS**

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF

Master of Science, Department of Chemistry.

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY  
CHARLESTON, ILLINOIS

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YEAR

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## Abstract

Title of thesis: Empirical Equations for Activity and Osmotic Coefficients.

By N. Rangunathan.

Thesis Directed by Dr David W. Ebdon, Professor of Chemistry.

A system of equations for fitting the experimental activity and osmotic coefficients of single and mixed electrolytes in aqueous solutions has been empirically developed in the present research. The results obtained through the equations developed here are comparable to the Pitzer equations in terms of accuracy and range of fitting. The equation for activity coefficient developed in the present research compared to the Pitzer activity coefficient equation has a form which is convenient for computational purposes. The equation for activity coefficients is

$$\ln g = -|Z_m Z_x| A_D [I^{1/2} / (1 + bI^{1/2})] + E I \ln(I) + J_1 I + J_2 I^{3/2}$$

where,  $b$  is fixed parameter having a value of 1.8;  $E$ ,  $J_1$ , and  $J_2$  are floating parameters. The corresponding equation for osmotic coefficients is obtained through the Gibbs-Duhem equation. The parameters have been evaluated by a nonlinear least squares computer program. This program weights all the data points equally. Parameters for both the coefficients are presented. In most of the cases data recommended by Robinson and Stokes is used. In the case of

the 2-2 electrolytes one additional parameter is included to obtain acceptable results instead of two by Pitzer. Representing the 2-2 electrolytes in this manner ignores association constants, and thereby simplifying the treatment of these electrolytes at higher solution concentrations. Treatment of mixed electrolytes involves, in addition to pure electrolyte terms, parameters to account for the mixing effects is utilised. Only a few mixed electrolytes involving osmotic coefficients as experimental data has been treated here, and the results obtained are comparable to Pitzer's.

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## Glossary of Symbols:

$g$	mean activity coefficient of the electrolyte
$d$	rational osmotic coefficient
$\phi$	practical osmotic coefficient
$m$	molality of the solute ( when not a subscript)
$v$	moles of ions obtained on dissociation of 1M of electrolyte
$n_i$	concentration of a given ionic species
$\rho$	charge density
$D$	dielectric constant
$e$	charge of an electron
$K$	Debye-Huckel distance
$k$	Boltzmann constant
$a$	distance of closest approach
$g_{ij}(r)$	radial distribution function
$T$	temperature (deg K)
$G^{ex}$	excess Gibbs free energy per mole
$L_{ij}$	two ion interaction parameter
$u_{ij}$	three ion interaction parameter
$n$	mole of the solvent
$B^w$	second virial coefficient
$C^{mx}$	third virial coefficient
$b^{mx}$	fixed parameter (1.2 or 1.8)
$b(0)$	Pitzer parameter for second virial coeff
$b(1)$	" " " " " "
$b(2)$	" " " " " "
$b$	Pitzer 2-2 electrolyte additional parameter
$a^1$	Pitzer fixed parameter (2.0)
$a^2$	Pitzer fixed parameter (12.0)
$E$	coefficient of the logarithmic term
$J_1$	coefficient of the linear term
$J_2$	coefficient of the $1.5$ term

## Introduction

Thermodynamic properties of nonideal solutions can be accounted for by obtaining theoretical expression for the chemical potentials or activity coefficients. To obtain a theoretical expression the chemical potential or activity coefficient can be expressed as a function of temperature, composition, pressure, solvent properties or any other relevant variable. For computational purposes activity coefficients rather than chemical potentials are utilized to express the nonideal portion of solution behavior. This approach is utilized due to the nature of the relationship between the chemical potential and the activity coefficient. As the solute concentration approaches zero the chemical potential of the solute approaches negative infinity whereas the activity coefficient of the solute tends to unity. Correspondingly the solvent activity approaches unity and hence the solvent chemical potential to its standard value. The reason for not utilizing solvent chemical potential to express thermodynamic properties is due its poor sensitivity at low to moderate concentrations. In addition one is generally more interested in the behavior of different solutes in a given solvent. Physically what this means is that addition of an infinitesimal amount of solute to an infinitely dilute solution is a spontaneous process. The fundamental difference between the properties of an ideal

solution and a nonideal solution is the existence of interparticle interactions in the latter. The concept of an ideal solution is hypothetical, but it helps to form a basis in the treatment of nonideal solutions. The degree or extent of deviation from ideality is given by the activity coefficient. Different thermodynamic properties of a solution can be interrelated if one knows the degree of departure from ideality or the activity coefficient. For an aqueous solutions solutes can be classified into electrolytes or nonelectrolytes. Electrolytes are substances which on dissolution in an aqueous media dissociates into charged species known as ions, as was first proved by Arrhenius<sup>1</sup>. For any solution whether electrolytic or nonelectrolytic there exist interactions between various component particles. In the case of a nonelectrolytic solution, interactions are limited to short range forces between solute particles, and the between solute and solvent. The nature of these forces are such that they fall off with increasing distance rapidly. In ionic solutions such interactions exist in addition one has to account for long range or coulombic interactions between ions due to the presence of charge on the ions to explain the thermodynamic properties. The latter interactions do not fall off with increasing distance as rapidly as the short range interactions and are responsible for the observed deviations from ideality under dilute conditions. Under dilute

conditions the short range forces make negligible contribution to nonideality even though at higher concentrations such short range forces begin to predominate over the coulombic forces and have to be accounted for. In any theoretical treatment the relationship between chemical potential and activity coefficient of a solute is expressed as

$$\bar{G}_B = \bar{G}_B^0 + vRT \ln (g m) \quad (1)$$

where,  $\bar{G}_B$  is the chemical potential of the solute b,  $\bar{G}_B^0$  is the standard chemical potential; g is the mean activity coefficient and m the mean molality.

For the solvent

$$\bar{G}_A = \bar{G}_A^0 + RT \ln a_A \quad (2)$$

where the  $\bar{G}_A$  and  $\bar{G}_A^0$  are solvent and standard solvent chemical potential, and  $a_A$  is the activity of the solvent.

Changes in solvent activity with changes in concentration of the solute at a low to moderate concentration does not provide a sensitive measure of solvent activity. Hence Bjerrum<sup>2</sup> introduced the concept of osmotic coefficient. The rational osmotic coefficient is defined as follows

$$\bar{G}_A = \bar{G}_A^0 + dRT \ln N_A \quad (3)$$

where, d is the rational osmotic coefficient and  $N_A$  the mole fraction of the solvent. The practical osmotic coefficient is defined as

$$\begin{aligned} \ln a_A &= -d [ (vmM_A/1000) - .5*(vmM_A/1000)^2 + \dots ] \\ &= - (vmM_A/1000) \phi \end{aligned} \quad (4)$$

where  $\phi$  is the practical osmotic coefficient. This is the coefficient that is used for practical thermodynamic calculations and hence will be simply termed the "osmotic coefficient".

The activity coefficient of a solute and the osmotic coefficient of a solvent are related by the Gibbs-Duhem equation as shown in the following equations.

$$\sum n_i d\bar{G} = 0 \quad (5a)$$

$$n_A d\bar{G}_A + n_B d\bar{G}_B = 0 \quad (5b)$$

$$(1000/M_A) d \ln a_A + v_m d \ln g_m = 0 \quad (5c)$$

$$- d(m\phi) + m d \ln g_m = 0 \quad (5d)$$

$$d[m(\phi - 1)] = m d \ln g_m \quad (5e)$$

$$\phi = 1 + (1./m) \int m d \ln g_m \quad (5f)$$

Equation (5f) relates the two coefficients and will henceforth be termed as the Gibbs-Duhem relation. Thus when a theoretical or an empirical equation for activity coefficients is known the corresponding equation for osmotic coefficients can be obtained using the above relation. Furthermore, data for one of the coefficients can be computed graphically or numerically from the experimental data of the other by utilizing the above relation.



## Debye-Huckel Theory

In 1923 Debye and Huckel<sup>3</sup> were the first to present a simple theory of interionic attraction in aqueous solutions. This theory allows one to predict activity or osmotic coefficients of an electrolyte in dilute solutions. A fundamental assumption of the theory is the complete dissociation of electrolytes in aqueous solutions with ions considered to be hard spheres in a dielectric continuum. With the assumption of a hard sphere or hard core model, effects of short range interaction on thermodynamic properties are considered. Due to the dilute nature of the solution, effects of such short range interactions are negligible. The deviation from ideality are ascribed to the coulombic or long range electrostatic interactions between ions. Mathematically, the potential between two ions in aqueous solution is represented as

$$U_{1,j}(r) = U_{1,j}(r)^* + Z_1 Z_2 e^2 / D^* r \quad (6)$$

where,  $U_{1,j}(r)^*$  is the short range potential and  $Z_1 Z_2 e^2 / D^* r$  is the electrostatic potential.

$$U_{1,j}(r)^* = \begin{cases} \infty & \text{for } r < a, \text{ where } a \text{ is the radius of} \\ & \text{the ion} \\ 0 & \text{for } r > a \end{cases}$$

Debye and Huckel in order to obtain the potential,  $W$ , at a point in an ionic solution, utilize the Poisson equation of electrostatic theory and the Boltzmann distribution law of statistical mechanics. An ionic

solution on the whole is electrically neutral, but in the vicinity of a given ion this is not true. The Boltzmann distribution law for ions around a given "central" ion is

$$n_i' = n_i \exp(-Z_i e W_j / kT) \quad (7)$$

where  $Z_i e W$  is equal to the average electrical potential energy of the  $i$ -th ion.  $W_j$  is the potential at the point where the  $i$ -th ion is and the subscript  $j$  denotes that the potential is measured with respect to the  $j$ -th ion as the "central" ion.

Charge density,  $\rho$ , in the vicinity of the central ion is equal to

$$\rho = \sum n_i' Z_i e \quad (8)$$

The Poisson equation relates charge density to the potential and is the most generalized form of Coulomb's law.

$$\nabla^2 W_j = - 4 \pi \rho / D$$

$$\nabla^2 = (1/r^2) d/dr [ r^2 dW_j/dr ] , \text{ for a spherical symmetry.}$$

The Poisson equation is based on the principle of linear superposition of potentials; i.e. the potential at a point due to two independently charged particles is equal to the sum of the potentials due to each at that point. To satisfy this condition Debye and Huckel expanded the exponential term and dropped terms beyond the linear. Application to dilute solution makes this approximation of linearizing the Boltzmann distribution law possible. Also in dilute



solutions,  $Z_j e W \ll kT$ . Thus terms beyond the linear are negligible. Substitution of the radial distribution function in the charge density equation, followed by expansion leads to

$$\rho = \sum n_i Z_i e - \sum n_i Z_i (Z_i e W_j / kT) + \dots \quad (10)$$

The first term vanishes due to the electrical neutrality condition in the solution. Substitution of the charge density in the Poisson equation and solution of the linear differential equation in  $W_j$  and  $r$  gives the potential,  $W_j$ , at a point in the solution with  $j$ -th ion as the center of the coordinate system.

$$W_j = Z_j \exp(-K(r-a)) / Dr(1+Ka)$$

where,  $K = 4 e^2 \sum n_i Z_i^2 / DkT$

$1/K$  is the Debye Huckel distance and  $k$  is the Boltzmann constant Using the principle of linear superposition of potential, the potential due to all the ions except the  $j$ -th ion at  $r$  equals

$$W_j' = W_j - Z_j e / Dr \quad (12a)$$

$$\text{or, } W_j' = (Z_j e / Dr) [ \exp(-K(r-a)) / (1+Ka) - 1 ] \quad (12b)$$

Debye and Huckel regarded ions as hard inelastic spheres carrying a point charge at its center. Hence the Poisson equation is applicable only for  $r > a$ . For  $r < a$  the right hand side of the Poisson equation vanishes. Due to continuity of the potential and its derivative, solution of the Poisson equation for  $r < a$  gives the electric potential due to ion

atmosphere at  $r < a$

$$W_j' = - Z_j e K/D(1+Ka) \quad (13)$$

Excess free energy due to electrical interactions is obtained by the "charging process". Guntelberg<sup>4</sup> was the first to propose this method, which is much simpler than the original Debye-Huckel method. Here, a hypothetical ion with zero charge is introduced in the solution and then charged to its original value,  $Ze$ , against the ion atmospheric potential. Mathematically, this is represented as

$$\begin{aligned} G_{ex}/N &= -K/D(1+Ka) \int_0^Q Q \, dQ \\ &= - (Z_j e)^2 K/2DkT(1+Ka), \quad (14) \end{aligned}$$

$$\text{or, } \ln g = |Z_1 Z_2| e^2 / 2DkT * K/(1+Ka) \quad (15)$$

where  $g$  = the mean activity coefficient. Replacing  $K$  by its definition, one obtains for  $\ln g$  :

$$\ln g = -A_D |Z_1 Z_2| I^{.5} / (1+BI^{.5}) \quad (16)$$

where,  $I = .5 \sum Z_i^2 m_i$ , the ionic strength

$$A_D = (2 \pi N/1000)^{1/2} e^3 / (kDT)^{3/2} (L/mole)^{1/2} (\text{deg K})^{3/2}$$

$$B = (8 \pi N e^2 / 1000 D k T)^{1/2} (\text{cm})^{-1} (L \text{ deg K/mole})^{1/2}$$

This is the Debye-Huckel equation for activity coefficients in dilute ionic solutions. For sufficiently dilute solutions prediction of activity coefficients using the equation is in agreement with experimental data. As concentration is increased, deviation from experimental activity coefficients increases. Thus, application of the equation to higher

concentrations yields poor results.

In the case of dilute solutions, the numerator relates to the effects of long range electrostatic force and the denominator relates to the partial effects of short range forces on thermodynamic properties. For an extremely dilute solution,  $Ka \ll 1$ , therefore deviation from ideality is solely ascribed to the presence of long range electrostatic forces between ions and the effects of short range forces is neglected. At higher concentrations effects of short range forces are too large to be ignored, and theoretical representation of short range forces by Debye and Huckel with the simplest possible model fails at higher concentrations.

Extension of the Debye Huckel theory is limited by mathematical complications since the above method outlined takes care of only long range electrostatic forces. Empirical extension is made possible by addition of terms in concentration to fit activity or osmotic coefficient data. Most of the extensions are limited to addition of a single term. The Davis<sup>5</sup> equation is suitable for 1-1 and 1-2 electrolytes; the Guggenheim<sup>6</sup> equation treats 1-1 electrolytes. Both equations are not valid for concentrations higher than 0.1 M and hence have limited applications.

## Statement of the Problem

The primary objective of this research is to develop empirically a system of equations for fitting experimental activity and osmotic coefficients of pure and mixed electrolytes in aqueous solutions to an ionic strength of 6M. A system of equations obtained in a semiempirical manner for these coefficients has been developed by Pitzer<sup>7-14</sup>. The equation for activity coefficients proposed by Pitzer is in an inconvenient form for computational purposes. The extent of nonideality of a solution is expressed in terms of activity coefficients. Hence a simple equation for activity coefficients reduces to an easier treatment of nonideality. The Pitzer equation is the most recent semiempirical extension of the Debye-Huckel theory. Pitzer's equations fit experimental activity and osmotic coefficients of pure and mixed electrolyte solutions to 6 M ionic strength. The present research involves developing equations which are empirical extensions of the Debye-Huckel theory with similar capabilities to those of Pitzer's equations but in a simpler form. The ability of the equation developed in this research to fit experimental activity and osmotic coefficients of single and mixed electrolytes will then be assessed relative to the Pitzer equations.

## Pitzer Equations

Fundamentally, the Debye-Huckel theory fails at higher concentrations due to lack of proper representation of short range forces between ions. Advances in the theory of liquid mixtures has made it possible to apply newer ideas to ionic solutions. An advanced statistical mechanical treatment by Mayer<sup>15</sup> leads to a better representation of both long and short range forces. Other theoretical approaches based on statistical mechanics by Kirkwood<sup>16</sup>, Poirier<sup>17</sup>, and Friedman<sup>18</sup> has made it possible to predict activity or osmotic coefficients in the 1 to 2M range accurately for 1-1 electrolytes. Most of the recent theoretical methods require numerical techniques such as the Monte Carlo<sup>19</sup> method for computation of thermodynamic properties.

Statistical theory is extremely complex even for 1-1 electrolyte systems. Hence it is difficult to obtain working equations which are simpler to handle mathematically. A semiempirical extension of the Debye-Huckel theory using statistical mechanics as guidance has been made by Pitzer<sup>7</sup>.

Pitzer utilizes a method similar to the virial expansion for the nonideal behavior of gases and modifies these equations to account for coulombic interactions in ionic solutions. Virial expansions for gases are generally power series in pressure or volume, and coefficients of pressure or volume are termed virial coefficients. In the case of real gases, virial coefficients represent the short



range forces between molecules involved in binary, ternary ..etc interactions. Representing the behavior of ionic solutions with such expansions leads to difficulties which are peculiar to ionic solutions due to the presence of electrostatic forces between ions. The problem is solved by assuming that one can combine the electrostatic term with a virial expansion in ionic strength or concentration terms. In such an approach the behavior of virial coefficients with concentration must be determined. This problem can be overcome by an improved analysis of the Debye-Huckel theory using statistical mechanics as a guide.

Pitzer's approach utilizes the Debye-Huckel model for the interionic potential.

$$U_{ij}(r) = U_{ij}^*(r) + Z_1 Z_2 e^2 / Dr \quad (17)$$

where,  $U_{ij}^*(r)$  is the potential of mean force<sup>22</sup>.

Here, the short range potential includes all the effects which the long range potential by itself is unable to account for. The electrostatic term accounts for interaction between ions when  $r$  is large. Effects related to solvation, the assumption of dielectric continuum, dispersion forces between ions and direct repulsion due to electron cloud overlap when ions come into contact or in close proximity are combined in  $U_{ij}^*(r)$ . In order to obtain the direct effect of short range forces on the thermodynamic properties, Pitzer abandons the traditional "charging" process and instead uses the "pressure"<sup>20</sup> equation which

yields the pressure of a pure fluid or in the case of a dilute solution its osmotic pressure. Macmillan and Mayer<sup>21</sup> were the first to show that equations applicable to molecules in imperfect fluids could be extended to solutes in dilute solutions where pressure is equated to osmotic pressure of the solution. The interionic potential of mean force and the radial distribution of ions are required to solve the "pressure" equation.

$$\phi - 1 = -(6ckT)^{-1} \sum_i \sum_j c_i c_j \int_0^\infty r \frac{dU_{ij}(r)}{dr} g_{ij}(r) (4\pi r^2) dr \quad (18)$$

$$U_{ij} = \begin{cases} + \infty & \text{for } r < a \\ Z_i Z_j e^2 / Dr & \text{for } r > a \end{cases}$$

where  $dU_{ij}(r)/dr$  is the mean force on the ions,  $g_{ij}(r)$  is the radial distribution function,  $c_i, c_j$  are the concentration of species  $i$  and  $j$  respectively, and  $c$  is the total concentration. Introducing the potential of mean force, the derivative of which gives the force on a ion or particle averaged over the motion of other ions or particles constituting the dielectric, the integral reduces to two parts, one relating to the effects of long range forces and the other to the effects of short range forces.

$$\begin{aligned} \phi - 1 = & -(1/6ckT) \sum_i \sum_j c_i c_j \int_0^\infty r \frac{d}{dr} (Z_i Z_j e^2 / Dr) \\ & g_{ij}(r) (4\pi r^2) dr - (1/6ckT) \sum_i \sum_j c_i c_j \\ & \int_0^\infty r \frac{d}{dr} (U_{ij}^*) g_{ij}(r) (4\pi r^2) dr \end{aligned} \quad (19)$$

To solve the first integral, Pitzer uses the potential,  $W_j$ , at a point in a solution as derived in the Debye-Huckel

theory. He substitutes this into the Boltzmann distribution law and expands the exponential in the Boltzmann distribution function to three terms. The third term in the expanded form for charge density has a zero value in the case of symmetrical electrolytes.

$$g_{ij}(r) = \exp(-Z_i e W_j / KT) = \exp(-q_{ij}) \quad (20a)$$

$$\text{or, } g_{ij}(r) = 1 - q_{ij} + (1/2)q_{ij}^2 \quad (20b)$$

$$\text{where, } q_{ij} = Z_i Z_j e^2 \exp(-K(r-a)) / DkT(1+Ka)r$$

Comparison of the three term form and the two term Debye-Huckel radial distribution approximations with exact Monte Carlo calculations shows a better approximation in the case of the three term extended Debye-Huckel radial distribution function. The exponential form is not used directly since only a numerical solution to the integral is possible. With substitution of the coulombic potential between two ions and the expanded radial distribution function one observes the effects of electrostatic interactions on the thermodynamic properties in the first integral.

$$I_1 = -K^3 / [6Dkt(1 + Ka)] \quad (21)$$

The first and third terms are zero in the charge density equation. This is the Debye-Huckel electrostatic term obtained using the pressure equation and reduces to the limiting law at low concentrations. Solution<sup>23</sup> to the second integral, which represents effects of short range forces, equals

$$I_2 = -(2 \pi a^3 / 3c) \sum \sum c_i c_j g_{ij}(a)$$



Thus, the osmotic pressure of a solution after substitution for  $g_{ij}(a)$ , is

$$\phi - 1 = -K^3 / (6DkT(1+Ka)) + c[2 \pi a^3 / 3 + K^4 / (48 \pi c^2 (1+Ka)^2)] \quad (23)$$

The first term is the electrostatic term. Comparison with the Debye-Huckel electrostatic term for osmotic coefficients, which is obtained by converting the activity coefficient equation using the Gibbs-Duhem equation, is inconvenient to use. Both of them, however, can be applied through the same concentration range. The first term in the short range interaction term represents the interaction at contact between ions in the absence of any electrical effects.

Pitzer labels this as the "kinetic effect of hard core".

This term is equivalent to the second virial coefficient of a nonideal fluid. In addition one has the second term which is due to increased repulsive hard-core electrical interactions between ions. Application of the above equation to electrolytes is valid to about 1 M, thus, an improvement over the Debye-Huckel theory is achieved in a very simple manner.

Approximations involved in deriving the equation here are similar to those of Debye and Huckel since the potential,  $W$ , at a point in the solution is derived using the linearized Boltzmann distribution law. To obtain thermodynamic properties a three term expansion is used and the derivation is further simplified by utilizing the property of symmetrical electrolytes.

The above equation, (23), is not suitable for practical

thermodynamic calculations. First, it has only one parameter,  $a$ , that can be adjusted to fit experimental data. Second, the range of prediction is limited to 1 M ionic strength. In addition to the above difficulties, approximations involved do not permit further mathematical extension of the equation to higher concentration ranges in a simplified form. Hence Pitzer utilizes the idea of virial expansion where the second virial coefficient has a behavior qualitatively similar to the short range interaction term in his "approximate" derivation. Substitution of functions which have similar mathematical behavior but also have greater flexibility enabling extension to a higher concentration range would be useful. In the virial expansion for electrolytes, the first term in concentration represents the effect of electrostatic interactions and terms beyond the first describe effects of short range interactions between two, three .. etc ions, respectively.

Thus, Pitzer defines the excess Gibbs free energy as

$$G^{\text{ex}}/n_w RT = n_w f(i) + (n_w)^{-1} \sum L_{ij} n_i n_j + (n_w)^{-2} \sum u_{ijk} n_i n_j n_k \quad (24)$$

$G^{\text{ex}}$  is the excess Gibbs free energy. This represents the departure from ideality due to additional interactions present in an ionic solution from those not present in a nonelectrolyte solution. Here  $f(i)$  is the electrostatic term,  $L_{ij}$  the two ion interaction coefficient, and which is a function of ionic strength, and  $u_{ijk}$ , the three ion

interaction coefficient which under moderate concentrations is assumed to be independent of concentration. Equations for osmotic and activity coefficients are obtained by differentiation of the excess Gibbs free energy function with respect to  $n_w$  and  $n_i$ . After proper algebraic arrangements, the osmotic and activity coefficient equations are

$$\phi - 1 = |Z_m Z_x| f^{(\phi)} + m (2v_m v_x / v) B^{(\phi)}_{mx} + m^2 [2(v_m v_x)^{3/2} / v] C^{(\phi)}_{mx} \quad (25)$$

$$\ln g_{mx} = |Z_m Z_x| f^{(g)} + m (2v_m v_x / v) B^{(g)}_{mx} + m^2 [2(v_m v_x)^{3/2} / v] C^{(g)}_{mx} \quad (26)$$

where

$$B^{(\phi)}_{mx} = (L_{mx} + I L'_{mx}) + (v_m / 2v_x) (L_{mm} + I L'_{mm}) + (v_x / 2v_m) (L_{xx} + I L'_{xx}),$$

$$C^{(\phi)}_{mx} = [3 / (v_m v_x)^{1/2}] [v_m u_{mxx} + v_x u_{mxx}],$$

$$B^{(g)}_{MX} = B^{(\phi)}_{MX} + (1/I) \int_0^1 B^{(\phi)}_{MX}(I) dI,$$

$$C^{(g)}_{mx} = 3/2 C_{mx}, \text{ and}$$

$$L'_{ij} = dL_{ij} / dI.$$

$B_{mx}$  is the second virial coefficient and  $C_{mx}$  is the third virial coefficient. The above equations are general in nature and direct application to electrolyte solutions is not possible. This is due to the equation involving a large number of variables, and these variables cannot be ascertained from experimental data. Also  $L$  and  $u$  are ion-ion

interaction parameters, and they do not take into account ion-solvent interactions directly. However such a treatment makes extrapolation to mixed electrolytes simpler. Pitzer chooses an exact form for the second virial coefficient by comparison with experimental data.

To represent properties of electrolytes accurately Pitzer tests six possible combination of  $f(1)$ , the electrostatic term and  $B_{mx}$ , the second virial coefficient. The electrostatic functions considered are: a) Debye-Huckel "charging", b) Debye Huckel osmotic derived from the "pressure" equation, c) One due to Glueckauf<sup>24</sup>. For the second virial coefficient two forms are tested

$$B^{(\phi)}(1) = b^{(0)} + b^{(1)} \exp(-a'I^{1/2}) \quad (27)$$

$$B(2) = b^0 + b^1/(1 + a'I^{1/2}) \quad (28)$$

where,  $a'$  is a fixed parameter, not related to,  $a$ , the radius of the ion. In the test the maximum concentration of each solution is limited to 2 M ionic strength. The best possible standard deviation is obtained in the case of the Debye-Huckel "osmotic" and  $B^0(1)$ . Thus, working equations for the purpose of fitting osmotic or activity coefficient data to an acceptable accuracy are

$$\begin{aligned} \phi - 1 = & -A^{(\phi)} |Z_m Z_x| [I^{1/2}/(1 + bI^{1/2})] + \\ & m(2v_m v_x/v) [b^{(0)} + b^{(1)} \exp(-a'I^{1/2})] + \\ & m^2 [2(v_m v_x)^{1.5}/v] C_{mx}^{(\phi)} \end{aligned} \quad (29)$$

$$\ln g_{mx} = -A^{(\phi)} |Z_m Z_x| [ I^{1/2} / (1 + b I^{1/2}) + (2/b) \ln (1 + b I^{1/2}) ] \\ + 2m [ b^{(0)} + (b^{(1)}) / a' I ] \{ 1 - (1 + a' I^{1/2} - (1/2) a' I) \exp(-a' I^{1/2}) \} \\ * (2v_m v_x / v) + m^2 (2(v_m v_x)^{1.5} / v) C_{mx}^{(g)} \quad (30)$$

Here,  $b$  and  $a'$  are fixed parameters with a value of 1.2 and 2.0 respectively, for all electrolytes ;  $b_0$ ,  $b_1$  and  $C_{mx}$  are the variable parameters and are different for different electrolytes. Concerning the applicability of the equations, all but the 2-2 electrolytes fit this equation. The 2-2 electrolytes, due to extensive association even at low concentrations, do not permit one to utilize these equations. Pitzer modifies the equations by inclusion of two additional parameters. Basically, these parameters fit the data at lower concentrations. Thus for 2-2 electrolytes the following additional terms are added to the second virial coefficient:

$$\text{for } B_{mx}^{(\phi)} \\ b^{(2)} \exp(a' I^{1/2})$$

$$\text{for } B_{mx}^{(g)} \\ (2 b^{(2)} / a_{(2)} I) [ 1 - (1 + a_{(2)} I^{1/2} - (1/2) a_{(2)} I) \exp(-a_{(2)} I^{1/2}) ]$$

where,  $a_{(2)}$  is a fixed parameter having a value 12.0, and  $b^{(2)}$  is a variable parameter.

The equation for the Gibbs free energy permits one easily to extend the method of interionic attraction/repulsion to mixed electrolytes. In a mixed electrolyte solution additional



interactions between cations and anions of all electrolytes is considered. The general equations for osmotic and activity coefficients of mixed electrolytes are

$$\begin{aligned} \phi - 1 = & (\sum m_i)^{-1} \{ 2I f^{(\phi)} + 2 \sum \sum m_c m_a [ B_{ca}^{(\phi)} + \\ & (\sum m Z / (Z_c Z_a)^{1/2}) C_{ca}^{(\phi)} ] + \sum \sum m_c m_{c'} [ \theta_{cc'} + I \theta'_{cc'} + \sum m_a \psi_{cc'a} ] \\ & + \sum \sum m_a m_{a'} [ \theta_{vaa'} + I \theta'_{aa'} + \sum m_c \psi_{caa'} ] \} \end{aligned} \quad (31)$$

$$\begin{aligned} \ln g_{mx} = & |Z_m Z_x| f^{(g)} + (2v_m/v) \sum \sum [ B_{Ma} + (\sum m Z) C_{Ma} + \\ & (v_x/v_m) \theta_{xa} ] + (2v_x/v) \sum m_c [ B_{cx} + (\sum m Z) C_{cx} + (v_m/v_x) \theta_{mc} ] + \\ & \sum \sum m_c m_a \{ |Z_m Z_x| B'_{ca} + v^{-1} [ 2v_m Z_m C_{ca} + v_m \psi_{mca} + v_x \psi_{cax} ] \} + \\ & (1/2) \sum \sum m_c m_{c'} [ (v_x/v) \psi_{cc'x} + |Z_m Z_x| \theta_{cc'} ] + (1/2) \sum \sum m_a m_{a'} \\ & [ (v_m/v) \psi_{maa'} + |Z_m Z_x| \theta_{aa'} ] \end{aligned} \quad (32)$$

Here, the additional parameters for mixing " $\theta$ " and " $\psi$ " represent interactions between different ions having the same charge sign and interactions between three ions, where two of the ions have the same charge sign, respectively. Interactions between three ions having the same charge is assumed to be negligible. Generally, additional terms for mixing are small or even negligible in certain cases but are often required to fit data within experimental accuracy.

Evaluation of osmotic coefficient data with a maximum ionic strength of 6 M for single electrolyte solutions is done using a least squares fit program. Coefficients for 300 single and mixed electrolytes have been evaluated.

## Present Research

Most of the extensions of the Debye Huckel theory, whether empirical or semiempirical, can be represented as a combination of electrostatic and statistical terms. A fundamental idea behind such an approach is to obtain a working equation for activity or osmotic coefficients for single electrolyte solutions. The advantage of having working equations of an empirical nature rather than a complete theoretical approach is that it allows one to fit experimental data with a minimum of adjustable parameters. In addition to fitting data the equation has to have the capability for extrapolation to multicomponent solutions.

In the simplest empirical treatment the mean ionic activity coefficient is represented as

$$g(m) = g(el)*g(stat) \quad (33)$$

where,  $g(el)$  represents the effects of long range forces,  $g(stat)$  the effects of short range forces. The equation for  $g(el)$  is theoretically derived from the behavior of dilute solutions with the assumption that  $g(stat)$  approaches unity under such circumstances. The most widely used form for the electrostatic portion is the one derived by Debye and Huckel, or other derivations<sup>15,18</sup> which reduce to the Debye-Huckel form under dilute conditions. At higher concentrations  $g(el)$  fails to represent the behavior of

ionic solutions. This is due to the presence of other forces or interactions. Also at such concentration levels one does not know whether the equation for  $g(e1)$  truly represents the nature of electrostatic forces. Thus for an empirical treatment of activity or osmotic coefficients at higher concentrations one requires additional terms, the form of which would absorb all the shortcomings in  $g(e1)$ . The  $g(\text{stat})$  term, therefore does not solely represent effects of short range forces. Factors to be included in its form, most of which are implicit, range from interdependence of short and long range force between ions, solvation of ions, solvent-ion interactions and hosts of other minor interactions. To treat statistically solutions at high concentrations with so many variables to consider is a complex task and does not provide a feasible method for routine computations.

Generally, the form adopted for representing  $g(\text{stat})$  is a power series in concentration.

$$\ln g(\text{stat}) = \sum g_i C^i \quad (34)$$

where  $g_i$ 's are general interaction parameters, the subscripts determining the number of ions involved in interaction. This definition for  $g_i$  is strictly true in the case of dilute gases where interactions are limited to short range forces, and the medium is not so dense as in the case of ionic solutions. The power series in concentration can either be in increasing integral values, half integrals or



a combination of both. Thus, the mean ionic activity coefficient is

$$\ln g(m) = \ln g(e1) + \sum g_1 C^1 \quad (35)$$

For  $n = 1$ , the Davies and the Guggenheim equations are obtained. The general interaction parameter,  $g_1$ , in these equations is different. In the Davies equation  $g_1 = .1 * |Z_m Z_x|$  and in the Guggenheim equation  $g_1 = (2v_1 v_2) * B_{12}^0$ , where  $B_{12}^0$  is a constant. For  $n = 4$  one obtains the Scatchard<sup>25</sup> equation,  $g_n = (n+1/2n) * h^n_{mx} Z_m Z_x a^{(n)}_{mx}$  where,  $h = .5 * |Z_m Z_x| v_{mx}$  and  $a^{(n)}_{mx}$  is a fitting parameter. Similarly for  $n = 2$  one obtains the Pitzer equation,  $g_1 = b^0 + b^1 * \exp(-aI^{.5})$  and  $g_2 = 3(v_1 v_2)^{3/2} C_{mx} / v$ .

Comparing the applicability of these equations to higher concentrations one finds that both the Davies and the Guggenheim equations do not fit experimental data beyond 0.1 M ionic strength. The Scatchard equation fits experimental data to higher concentrations limits, but its applicability is limited due to its complexity in the case of the mixed electrolytes.

In the Guggenheim equation the parameter  $g_1$  represents binary interactions between ions of the same and opposite charge types. This is basically an extension of the Bronsted<sup>40</sup> principle of specific ion interaction. The inadequacy in the Guggenheim theory, as pointed out by Pitzer, is that  $g_1$  or the first virial coefficient in  $g(\text{stat})$  is not a constant but a function of concentration, and this leads to a much improved treatment of ionic

solutions. Pitzer's treatment of ionic solutions, as discussed previously, is the best available "semi empirical" equation. The difficulty or inconvenience in the Pitzer method is that the equation for activity coefficients has a form which is not simple for computational purposes. In the relation,  $g(m) = g(el)g(stat)$  Pitzer uses an improved Debye-Huckel electrostatic term and an empirical  $g(stat)$  term. Since one is dealing with  $g(stat)$  empirically the assumption is that  $g(stat)$  would take care of fitting data at higher concentrations as well as the shortcomings in the approximations used in deriving  $g(el)$ . Therefore "slight" improvements in  $g(el)$  is not going to make much of a difference in fitting data at higher concentrations. The equation for  $g(m)$  suggested in the present research is

$$\ln g(m) = -A_D |Z_m Z_x| (I^{1/2}/1+bI^{1/2}) + E I \ln(I) + J_1 I + J_2 I^{3/2} \quad (36)$$

where,  $E, J_1, J_2$  are fitting parameters;  $b$  is a fixed parameter having a value of 1.8. The corresponding equation for the osmotic coefficient is obtained through the Gibbs-Duhem equation.

$$\phi - 1 = -[A_D |Z_m Z_x| / b^3 I] Q(bI^{1/2}) + E' I \ln(I) + J_1' I + J_2' I^{3/2}$$

where,  $Q(bI^{1/2}) = [(1+x) - (1/(1+x)) - 2 \ln(1+x)]$ ,  
 $x = bI^{.5}$

$$2 E' = E, (2 J_1' - E') = J_1, (5/3) J_2' = J_2$$

In the original Debye-Huckel theory,  $b$  was related to the

distance of closest approach or diameter of an ion. Such a definition, ascribing to  $b$  a physical description, is not always possible since different ions have different radii and in solution a given ion may have a radius different from its gaseous value due to solvation. Furthermore, there are no experimental techniques to obtain these radii for all the ions. Hence, one treats  $b$  simply as a fixed parameter in the extensions of the Debye-Huckel theory in order to fit the observed experimental data. Any deviation from the actual  $b$  "value" would be taken care of by the floating parameters. In the set of equations proposed in the present research only the electrostatic term in the osmotic coefficient is in an inconvenient form, but the statistical terms in both the cases are similar and much simpler to handle. Using these equations for 2-2 electrolytes leads to the same problem as Pitzer faced: they do not work. The problem is solved by one additional parameter instead of the two utilized by Pitzer. The equation for 2-2 electrolytes is obtained by addition of the following term,  $E'_2 I^{.5}$  in (I) to the osmotic coefficient equation. Using the Gibbs-Duhem equation one obtains the corresponding equation for the activity coefficient. Initially it was hoped in addition to  $b$  being fixed, that  $E$  could be fixed. Then one could just float  $J_1$  and  $J_2$ . This was possible in the low concentration ranges, typically under 1M ionic strength. However, as concentration increased the fit deteriorated. In the case of 2-2 electrolytes introduction of effective

ionic strength or an association constant into the Pitzer or the present equations fails at higher concentrations, probably due to triple-ion or four-ion association. In any case introduction of association constants in such empirical extensions complicates the equation rather than simplifying them. The addition of a single parameter increases the concentration range to a great extent, and one can thus ignore association.

All these mechanistic or empirical equations under very dilute conditions reduce to the Debye-Huckel limiting law. In the present case the ionic strength,  $I$ , converges to zero faster than  $\ln(I)$  approaches negative infinity. Thus the second term approaches zero as  $I$  approaches zero, and the problem of an indefinite value at  $I = 0$  does not exist. Considering the application of these equations beyond 6M ionic strength one finds that they would give acceptable results, but with slightly higher deviations.

The present set of equations can be used to fit mixed electrolyte solutions. Most of the data fitted yield acceptable results. In mixed electrolyte solutions one needs to consider additional interactions between ions of different electrolytes. Thus to obtain osmotic or activity coefficients in mixed electrolyte solutions the parameters for pure electrolytes plus the additional interaction parameters must be considered. The additional parameters are obtained by plotting or fitting by the method of least

squares differences in experimental values of these coefficients versus a function in ionic strength and the fraction of the electrolyte in the mixture. For a simple mixture of the same charge type electrolytes, the equation for osmotic coefficients is

$$\phi_{mix} = y_a \phi_a^0 + y_b \phi_b^0 + (C + D I) y_a y_b I \quad (37)$$

The above equation can be extended in treating mixtures having three or more similar electrolytes. For mixtures involving a 2-1 and 1-1 electrolytes with or without a common ion, the method suggested by Scatchard<sup>26</sup> is utilized.

The equation for such mixtures is

$$(1 + y_a) \phi_{mix} = y_a \phi_a^0 + y_b \phi_b^0 + (C + DI) y_a y_b I \quad (38)$$

Equations for activity coefficient of mixtures where the composition is not fixed have not been investigated in the present research. A direct conversion of the above osmotic equation using the Gibbs-Duhem equation is not possible. In order to estimate the parameters for single electrolyte solutions a simple nonlinear least squares fit computer program is used. The program weights all the data points equally. Before consideration of the program itself, a few points need to be mentioned. Both osmotic and activity coefficients are fitted separately, even though knowing the parameters for one of them enables computation of the other through the Gibbs-Duhem equation. This is done to compare the present set of equations with the Pitzer equations. Pitzer fits only osmotic coefficients and one uses the



parameters obtained from them to compute the activity coefficients. For electrolytes at higher concentrations experimental determinations generally involves obtaining osmotic coefficients by the isopiestic technique<sup>27</sup>. Activity coefficients are then obtained using the Gibbs-Duhem equation either numerically, i.e by fitting to a power series in  $I$ , or by plotting  $(\phi - 1)/m^{.5}$  verses  $m^{.5}$ . The isopiestic technique involves determining the osmotic coefficient of an electrolyte relative to a known electrolyte. The accuracy of this method is about 0.1%, and measurements below 0.1M are seldom done. The reason for this is due to a long equilibrium period, and the accuracy deteriorates rapidly with decreasing concentration. Hence at lower concentrations one has to resort to potentiometric or colligative properties of solutions to determine these coefficients. Hence conversions between these coefficients involve some error, and when one fits both these coefficients the parameters obtained would not be exactly related as the Gibbs-Duhem equation predicts. Most of the data on electrolytes involving these coefficients are compiled by Robinson and Stokes<sup>28</sup> in their monograph. Both osmotic and activity coefficients are given with rounded-off molalities. Pitzer uses most of the data from this source; so has the present research. If one utilizes the Pitzer parameters obtained from osmotic coefficients to determine activity coefficients, there would be a slight discrepancy from the one given by Robinson and Stokes even though they

have used the same set of osmotic coefficients to determine activity coefficients. This is mainly due to the different approaches involved; that is different computational methods. Therefore assessing which is the superior approach is very difficult.

The computer program language is Fortran 77. A flowsheet of the program is as follows:

- a) Read data from a separate file. The data file has the initial guess values for the parameters
- b) Find the difference between experimental and calculated values using the guess values.
- c) Use the difference to perform a least squares fit and obtain the differential in the parameter values.
- d) Add the differential to the initial guess value and use this as the new value for the parameters and repeat from (c)
- e) A control statement determines the condition for minimization. When the difference in standard deviation between the (n-1)th and nth cycle is less than .0001, the program terminates and prints out the final results.

Calculations using the computer program for single and mixed electrolytes for both activity and osmotic coefficients have been done. The general method is the same for all these coefficients. The only differences among the several programs are in the equations themselves.

## Results

The results for osmotic coefficients are tabulated in the following tables

Table 1 - 1-1 Electrolytes

Electrolyte	E	J <sub>1</sub>	J <sub>2</sub>	Present work		Pitzer	
				sd	Max M	sd	max M
HCl	.0297	.1282	-.0121	.002	6	.002	6
HBr	.00352	.1132	.0372	.001	3	--	3
HI	-.0201	.1451	.0453	.002	3	--	3
HClO <sub>4</sub>	.00207	.0716	.0489	.002	6	.002	5.5
HNO <sub>3</sub>	.0143	.0499	.00513	.001	3	.001	3
LiCl	.00951	.00705	.0225	.002	6	.001	6
LiBr	.0293	.1143	-.000305	.002	2.5	.002	2.5
LiI	-.0768	.00917	.1463	.003	3	.006	1.4
LiOH	.1269	.0615	-.1243	.005	4	--	4
LiClO <sub>4</sub>	-.00630	.1263	.0246	.002	4	.002	3.5
LiNO <sub>3</sub>	.0369	.1133	-.0402	.002	6	.001	6
NaF	.0473	-.0185	-.0320	.001	1	.001	1
NaCl	.0233	.0108	.00126	.001	6	.001	6
NaBr	.0222	.0346	.000306	.001	4	.001	4
NaI	.00690	.0510	.0155	.002	3.5	.001	3.5
NaOH	-.0101	-.0147	.0473	.005	6	--	6
NaClO <sub>3</sub>	.0323	-.0306	-.0121	.001	3.5	.001	3.5
NaClO <sub>4</sub>	.0259	.00164	-.0114	.001	6	.001	6
NaBrO <sub>3</sub>	.0448	-.0794	-.0105	.001	2.5	.001	2.5
NaCNS	.0101	.0498	-.00493	.001	4	.001	4
NaNO <sub>3</sub>	.0447	-.0492	-.0231	.002	6	.001	6
NaH <sub>2</sub> PO <sub>4</sub>	.0582	-.1435	.000927	.002	6	.003	6
KF	.0411	.0252	-.0175	.001	4	.001	2
KCl	.0408	-.00305	-.0228	.0004	4.5	.0005	4.5
KBr	.0398	.00962	-.0259	.001	5	.001	5.5
KI	.0376	.0372	-.0338	.001	4.5	.001	4.5
KCNS	.0392	-.00249	-.0285	.0015	5	.001	5
KNO <sub>3</sub>	.0791	-.1292	-.0384	.0015	3.5	.001	3.5
KH <sub>2</sub> PO <sub>4</sub>	.00539	-.1197	.0293	.001	1.8	.003	1.8
RbF (29)	.0266	.0864	-.0433	.001	3.5	.002	3.5
RbCl	.0549	-.00263	-.0357	.001	5	.001	5
RbBr	.0546	-.00538	-.0372	.001	5	.001	5
RbI	.0588	-.00539	-.0595	.001	5	.001	5
RbNO <sub>3</sub>	.0835	-.1415	-.0365	.001	4.5	.001	4.5



1-1 Electrolytes (cont)

Electrolyte	E	J <sub>1</sub>	J <sub>2</sub>	Present work		Pitzer	
				sd	Max M	sd	Max M
CsF (29)	.0445	.1158	-.0551	.003	3.5	.002	3.5
CsCl	.0809	-.0123	-.0538	.001	6	.002	5
CsBr	.0839	-.0154	-.0566	.001	5	.002	5
CsI	.0939	.00818	-.0851	.001	3.0	.001	3
CsNO <sub>3</sub>	.0885	-.1545	-.0323	.001	1.4	.002	1.4
AgNO <sub>3</sub>	.0689	-.1657	-.0159	.001	6	.001	6

Table 2 - Salts of Carboxylic acids (1-1 type)

Electrolyte	E	J <sub>1</sub>	J <sub>2</sub>	Present Work		Pitzer	
				sd	Max M	sd	Max M
Li Acetate	.0400	.0797	-.0401	.0005	4	.001	4
Na acetate	.0233	.1079	-.0288	.001	3.5	.001	3.5
K acetate	.0261	.1303	-.0351	.001	3.5	.001	3.5
Rb acetate	.0191	.1231	-.0220	.001	3.5	.001	3.5
Cs acetate	.0129	.1215	-.0165	.001	3.5	.001	3.5
Tl acetate	.0828	-.0341	-.0589	.001	6	.001	6

Table 3 - Tetraalkylammonium Halides (Data from ref 30 & 31)

Electrolyte	E	J <sub>1</sub>	J <sub>2</sub>	Present work		Pitzer	
				sd	Max M	sd	Max M
Me <sub>4</sub> NF	.0375	.2111	-.0135	.002	3	.002	3
Et <sub>4</sub> NF	-.0804	.1357	.1923	.001	2	.002	2
Pr <sub>4</sub> NF	-.0423	.2434	.2095	.002	2	.002	2
Bu <sub>4</sub> NF	-.0586	.4233	.1077	.004	1.6	.005	1.7
Me <sub>4</sub> NCl	.0976	-.00935	-.0514	.001	3.5	.005	3.4
Et <sub>4</sub> NCl	.1269	.0362	-.0790	.003	3	.002	3
Pr <sub>4</sub> NCl	.1475	.0702	-.0641	.005	2.5	.002	2.5
Bu <sub>4</sub> NCl	.2360	.3883	-.3691	.005	2.5	.001	2.5
Me <sub>4</sub> NBr	.1240	-.0592	-.0690	.005	3.5	.004	3.5
Et <sub>4</sub> NBr	.1572	-.0997	-.0691	.002	4	.001	4
Pr <sub>4</sub> NBr	.2513	-.0029	-.1661	.005	3	.003	3
Bu <sub>4</sub> NBr	.1860	-.0634	-.1482	.009	4.5	.007	4.5

Table 4 - Inorganic Compounds of 2-1 type

Electrolyte	E	J <sub>1</sub>	J <sub>2</sub>	Present work		Pitzer	
				sd	Max M	sd	Max M
MgCl <sub>2</sub>	.00838	.0297	.0257	.003	3	.003	4.5
MgBr <sub>2</sub>	.00912	.0734	.0207	.002	3.5	.004	5
MgI <sub>2</sub>	-.00722	.0825	.0424	.004	2	.003	5
Mg(C <sub>10</sub> ) <sub>2</sub>	-.0324	.0752	.0660	.003	2	.002	2
Mg(NO <sub>3</sub> ) <sub>2</sub>	.0235	.0597	-.00781	.002	2	.003	2
CaCl <sub>2</sub>	.00970	.0156	.0207	.002	3	.003	2.5
CaBr <sub>2</sub>	.0113	.0446	.0191	.001	2	.002	2
CaI <sub>2</sub>	-.00526	.0671	.0333	.002	2	.001	2
Ca(C <sub>10</sub> ) <sub>2</sub>	-.0185	.0619	.0451	.001	2	.005	2
Ca(NO <sub>3</sub> ) <sub>2</sub>	.0406	-.00634	-.0218	.002	2	.002	2
SrCl <sub>2</sub>	.0251	.0179	.00282	.005?	4	.003	4
SrBr <sub>2</sub>	.00164	.0179	.0299	.0015	2	.001	2
SrI <sub>2</sub>	-.0127	.0452	.0429	.002	2	.001	2
Sr(C <sub>10</sub> ) <sub>2</sub>	.0263	.0852	-.00632	.0014	2.5	.003	2.5
Sr(NO <sub>3</sub> ) <sub>2</sub>	.0393	-.0447	-.0186	.002	2	.002	2
BaCl <sub>2</sub>	.0314	.0134	-.0132	.001	1.8	.001	1.8
BaBr <sub>2</sub>	.0241	.0330	-.00469	.002	2	.001	2
BaI <sub>2</sub>	.00849	.0737	.00956	.002	1.8	.003	1.8
Ba(C <sub>10</sub> ) <sub>2</sub>	.0289	.0683	-.0216	.001	2	.003	2
MnCl <sub>2</sub>	.0435	.0582	-.0294	.005	2.5	.003	2.5
FeCl <sub>2</sub>	.0252	.0362	.000672	.002	2	.002	2
CoCl <sub>2</sub>	.0429	.0649	-.0223	.005	3	.004	3
CoBr <sub>2</sub>	.00834	.0642	.0225	.002	2	.002	2
CoI <sub>2</sub>	.00860	.110	.0183	.01	2	.01	2
Co(NO <sub>3</sub> ) <sub>2</sub>	.0180	.0302	.00456	.001	2	.003	5.5
NiCl <sub>2</sub>	.00235	.410	.00445	.002	2.5	.002	2.5
CuCl <sub>2</sub>	.0526	.0590	-.500	.002	2	.003	2
Cu(NO <sub>3</sub> ) <sub>2</sub>	.0386	.0416	-.0216	.001	2	.002	2
ZnCl <sub>2</sub>	-.0429	-.0514	.0462	.006	2.	.006	1.2
ZnBr <sub>2</sub>	.0370	.1600	-.0817	.006	2	.007	1.6
ZnI <sub>2</sub>	-.0229	.0839	.0422	.003	.8	.002	.8
Zn(C <sub>10</sub> ) <sub>2</sub>	-.0212	.0727	.0615	.003	2	.003	2
Cd(NO <sub>3</sub> ) <sub>2</sub>	.0265	.0377	-.0186	.001	2.5	.002	2.5
Pb(C <sub>10</sub> ) <sub>2</sub>	.0177	.0436	.00230	.002	3.	.004	6
Pb(NO <sub>3</sub> ) <sub>2</sub>	.1226	-.1353	-.0620	.003	2	.002	2
UO <sub>2</sub> Cl <sub>2</sub>	.0298	.1083	-.0298	.002	2	.001	2
UO <sub>2</sub> (C <sub>10</sub> ) <sub>2</sub>	-.0394	.1220	.0790	.004	2.5	.003	2.5
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	.0306	.1183	.0258	.003	2	.002	2
Li <sub>2</sub> SO <sub>4</sub>	.0470	-.0533	-.0131	.001	3	.002	3
Na <sub>2</sub> SO <sub>4</sub>	.0509	-.1184	-.00608	.002	4	.003	4
Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	.0416	-.0944	-.00112	.0015	3.5	.002	3.5
Na <sub>2</sub> CF <sub>3</sub> O <sub>4</sub>	.0320	-.0820	.00337	.002	2	.002	3
Na <sub>2</sub> HPO <sub>4</sub>	.0155	-.1747	.0405	.001	1	.001	1
K <sub>2</sub> CrO <sub>4</sub>	.0479	-.0837	-.0107	.002	3.5	.003	3.5
K <sub>2</sub> HPO <sub>4</sub>	.00539	-.1197	.0293	.001	1	.002	1
Rb <sub>2</sub> SO <sub>4</sub>	.0577	-.0928	-.0171	.001	1.8	.001	1.8
Cs <sub>2</sub> SO <sub>4</sub>	.0609	-.0723	-.0252	.001	1.8	.001	1.8
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	.0790	-.1073	-.0312	.006	5.5	.004	5.5

Table 5 - Inorganic Compounds of Type 3-1

Electrolyte	E	J <sub>1</sub>	J <sub>2</sub>	Present work		Pitzer	
				sd	Max M	sd	Max M
AlCl <sub>3</sub>	-.0234	.00985	.0516	.005	1.8	.005	1.6
ScCl <sub>3</sub>	.0118	.0279	.0121	.006	1.8	.005	1.8
YCl <sub>3</sub>	.00527	.0111	.0194	.003	1.8	.007	1.8
LaCl <sub>3</sub>	.00616	.00780	.0154	.004	1.8	.007	1.8
CeCl <sub>3</sub>	.00372	.00761	.0175	.003	1.8	.01	1.8
PrCl <sub>3</sub>	.00826	.00425	.0153	.005	1.8	.006	2
NdCl <sub>3</sub>	.00825	.00583	.0154	.004	1.8	.007	1.8
SmCl <sub>3</sub>	.00525	.00958	.0173	.005	1.8	.01	1.8
EuCl <sub>3</sub>	.00676	.01063	.0164	.003	1.8	.007	1.8
CrCl <sub>3</sub>	.0205	.0385	.00316	.007	1.2	.005	1.2
Cr(NO <sub>3</sub> ) <sub>3</sub>							
Ga(ClO <sub>4</sub> ) <sub>3</sub>	-.0409	.0373	.0726	.01	2	.008	2
Na <sub>3</sub> PO <sub>4</sub>	.0341	-.1421	.00969	.001	.7	.003	.7
Na <sub>3</sub> AsO <sub>4</sub>	.0377	-.1167	.00280	.001	.7	.001	.7
K <sub>3</sub> PO <sub>4</sub>	.0411	-.0700	-.0117	.001	.7	.001	.7
K <sub>3</sub> AsO <sub>4</sub>	.0262	-.0292	-.0113	.001	.7	.001	.7
K <sub>3</sub> Fe(CN) <sub>6</sub>	.0217	-.0712	.00556	.003	1.4	.003	1.4

Table 6 - 4:1 electrolytes

	E	J <sub>1</sub>	J <sub>2</sub>	Present work		Pitzer	
				sd	Max M	sd	Max M
ThCl <sub>4</sub>	-.0174	.00925	.0291	.004	1	.006	1
Th(NO <sub>3</sub> ) <sub>4</sub>	.0128	-.0257	.00477	.004	1	.01	1
K <sub>4</sub> Fe(CN) <sub>6</sub>	.0294	-.0935	-.00053	.002	.9	.008	.9
K <sub>4</sub> Mo(CN) <sub>8</sub>	.0159	-.0994	.0110	.002	.8	.01	.8

Table 7 - 2:2 electrolytes (Data from ref 32 and R & S)

	E <sub>1</sub>	E <sub>2</sub>	J <sub>1</sub>	J <sub>2</sub>	Present work		Pitzer	
					sd	Range	sd	Range
MgSO <sub>4</sub>	.0475	.114	-.255	.0170	.002	.005-3	.004	.006-3
NiSO <sub>4</sub>	.0593	.116	-.287	.0158	.003	.001-2.5	.005	.005-2.5
CuSO <sub>4</sub>	.0798	.127	-.277	-.00661	.002	.001-1.4	.003	.005-1.4
ZnSO <sub>4</sub>	.0626	.110	-.275	.0115	.004	.001-3.5	.004	.005-3.5
CdSO <sub>4</sub>	.0790	.126	-.280	-.00547	.003	.001-3.5	.002	.005-3.5
BeSO <sub>4</sub>	.0712	.118	-.236	-.00389	.003	.1-4	.004	.1-4
MnSO <sub>4</sub>	.0716	.107	-.261	-2.95E-3	.003	.001-3	.003	.1-4
UO <sub>2</sub> SO <sub>4</sub>	.1076	.155	-.280	-.0305	.002	.1-5	.003	.1-5

Table 8 - Mixed Electrolyte Solution

Electrolyte Mixture	C	D	Present work		Pitzer		Ref
			Max I	sd	Max I	sd	
NaCl-LiCl	.00770	-.00187	6	.0014	6	.001	33
Na-Li acetate	.0287	-.00990	4	.001	3.5	.002	33
K-Na nitrate	-.0140	-.00132	3.7	.001	3.3	.001	34
Na-Li "	.00567	-.00568	6	.002	6	.002	33
Na-K sulphate	-.116	.0235	3.6	.004	3.6	.004	35
NaCl-NaNO3	.0234	-.00764	5.7	.002	5	.001	34
KCl-KNO3	-.0659	-.00732	4	.002	4	.002	34
KCl-NaNO3	-.0659	.00370	4	.002	4	.002	34
Na-K-Ba-Cl	.279	-.113	4.5	.003	4.5	.003	36
Na-Li-Ba-Cl	.262	-.0410	3.3	.002	3.3	.001	36
Li-Na-K-Cl	-1.505	.433	3	.001	3	.004	36
Li-Na-Cs-Cl	-.307	-.0699	5.2	.002	5.2	.004	36
Li-Ba-Cl	-.0764	-.000343	4.3	.002	4.3	.002	37
Cs-Ba-Cl	-.000357	-.0210	4	.003	4	.003	37
K-Ca-Cl	.0314	-.00988	5	.002	5	.003	38
Na-Mn-Cl	.0437	-.124	5	.002	5.5	.003	39
NaCl-K sulph	-.146	.00891	3.3	.003	3.6	.003	35
KCl-K "	-.0509	.00839	2.3	.002	2.3	.002	35
KCl-Na "	-.0798	.0118	3	.005	3.6	.003	35



The results for activity coefficients are tabulated in the following tables

Table 9 - 1-1 Electrolytes

Electrolyte	E	J <sub>1</sub>	J <sub>2</sub>	sd	Max M
HCl	.0548	.2223	-.0147	.003	6
HBr	.00675	.2158	.0652	.001	3
HI	-.0305	.3133	.0679	.003	3
HClO <sub>4</sub>	.00424	.1383	.0892	.004	6
HNO <sub>3</sub>	.0281	.0885	.00783	.001	3
LiCl	.0344	.1382	.0224	.003	4.5
LiBr	.0485	.1904	-.0121	.002	2.5
LiI	-.0987	.1471	.1757	.005	3
LiOH	.2949	.0259	-.2527	.004	4
LiClO <sub>4</sub>	-.0296	.2343	.0668	.001	3.5
LiNO <sub>3</sub>	.0721	.1863	-.0645	.002	6
NaF	.0842	-.1068	-.0297	.001	1
NaCl	.0502	3.7E-5	-.00141	.001	6
NaBr	.0541	.0552	-.0106	.001	4
NaI	.0392	.1125	-.00198	.002	3.5
NaOH	-.0393	-.00389	.0264	.007	6
NaClO <sub>4</sub>	.0542	-.0217	-.0211	.001	6
NaBrO <sub>3</sub>	.0826	-.0210	-.00863	.001	2.5
NaCNS	.0303	.0959	-.0188	.002	4
NaNO <sub>3</sub>	.0903	-.1419	-.0396	.001	6
NaH <sub>2</sub> PO <sub>4</sub>	.1087	-.3486	.00907	.001	6
KF	.0821	.00934	-.0291	.001	4
KCl	.0825	-.0456	-.0393	.0004	4.5
KBr	.0794	-.0207	-.0430	.0005	5
KI	.0682	.0305	-.0482	.001	4.5
KCNS	.0844	-.0414	-.0534	.001	5
KNO <sub>3</sub>	.1429	-.3481	-.0470	.001	3.5
KH <sub>2</sub> PO <sub>4</sub>	.1239	-.4892	.0446	.001	1.8
RbF (29)	.1539	.2047	-.1736	.005	3.5
RbCl	.1095	-.0599	-.0595	.001	5
RbBr	.1106	-.0651	-.0632	.001	5
RbI	.1160	-.0698	-.0645	.0005	5
RbNO <sub>3</sub>	.1582	-.3720	-.0514	.001	4.5
CsF (29)	.0890	.1501	-.0665	.008	3.5
CsCl	.1492	-.1096	-.0782	.001	6
CsBr	.1493	-.1208	-.0772	.001	5
CsI	.1571	.1061	-.1036	.001	3.0
CsNO <sub>3</sub>	.1299	-.4670	-.0235	.001	1.4
AgNO <sub>3</sub>	.1388	-.3999	-.0273	.0005	6

Table 10 - Salts of Carboxylic acids (1-1 type)

Electrolyte	E	J <sub>1</sub>	J <sub>2</sub>	sd	Max M
Li Acetate	.0737	.1036	-.0551	.001	4
Na acetate	.0586	.2014	-.0616	.001	3.5
K acetate	.0490	.2272	-.0516	.001	3.5
Rb acetate	.0544	.2305	-.0439	.001	3.5
Cs acetate	.0351	.2390	-.0388	.001	3.5
Tl acetate	.1551	-.1536	-.0890	.001	6

Table 11 - Inorganic Compounds of 2-1 type

Electrolyte	E	J <sub>1</sub>	J <sub>2</sub>	sd	Max M
MgCl <sub>2</sub>	.0216	.0514	.0391	.003	3
MgBr <sub>2</sub>	.0195	.1364	.0344	.003	2.5
MgI <sub>2</sub>	-.0413	.1701	.0929	.005	2
Mg(C <sub>10</sub> ) <sub>2</sub>	-.0712	.1826	.1151	.005	2
Mg(NO <sub>3</sub> ) <sub>2</sub>	.0600	.0974	-.0235	.001	2
CaCl <sub>2</sub>	.0335	.0201	.0240	.002	3
CaBr <sub>2</sub>	.0285	.0795	.0267	.001	2
CaI <sub>2</sub>	-.0139	.1360	.0600	.002	2
Ca(C <sub>10</sub> ) <sub>2</sub>	-.0321	.1421	.0714	.001	2
Ca(NO <sub>3</sub> ) <sub>2</sub>	.1016	-.0496	-.0537	.001	2
SrCl <sub>2</sub>	.0425	.00722	.01182	.002	3
SrBr <sub>2</sub>	.0159	.0350	.0400	.001	2
SrI <sub>2</sub>	-.0214	.1034	.0685	.002	2
Sr(C <sub>10</sub> ) <sub>2</sub>	.0673	.1454	-.0226	.001	2
Sr(NO <sub>3</sub> ) <sub>2</sub>	.0989	-.1241	-.0488	.001	2
BaCl <sub>2</sub>	.0683	-.00239	-.0271	.001	1.8
BaBr <sub>2</sub>	.0548	.0441	-.0137	.001	2
BaI <sub>2</sub>	.0381	.1463	-.0035	.002	1.8
Ba(C <sub>10</sub> ) <sub>2</sub>	.0608	.1060	-.0377	.002	2
FeCl <sub>2</sub>	.0502	.0456	.0019	.002	2
CoCl <sub>2</sub>	.0522	.0666	-.0029	.002	2
CoBr <sub>2</sub>	.0224	.1224	.0321	.002	2
Co(NO <sub>3</sub> ) <sub>2</sub>	.0487	.0493	-.0048	.001	3
NiCl <sub>2</sub>	.0433	.0521	.0129	.001	2
CuCl <sub>2</sub>	.0961	.0656	-.0763	.001	2
Cu(NO <sub>3</sub> ) <sub>2</sub>	.0780	.0463	-.0372	.001	2
ZnCl <sub>2</sub>	-.0424	-.0528	.0404	.003	2.
ZnBr <sub>2</sub>	.0596	.2800	-.1240	.003	2
ZnI <sub>2</sub>	-.126	.484	-.216	.007	2
Zn(C <sub>10</sub> ) <sub>2</sub>	-.0479	.1618	.1090	.003	1.8
Cd(NO <sub>3</sub> ) <sub>2</sub>	.0530	.0493	-.0312	.001	2
Pb(C <sub>10</sub> ) <sub>2</sub>	.0342	.0655	.0064	.001	2
Pb(NO <sub>3</sub> ) <sub>2</sub>	.2900	-.3866	-.142	.002	2



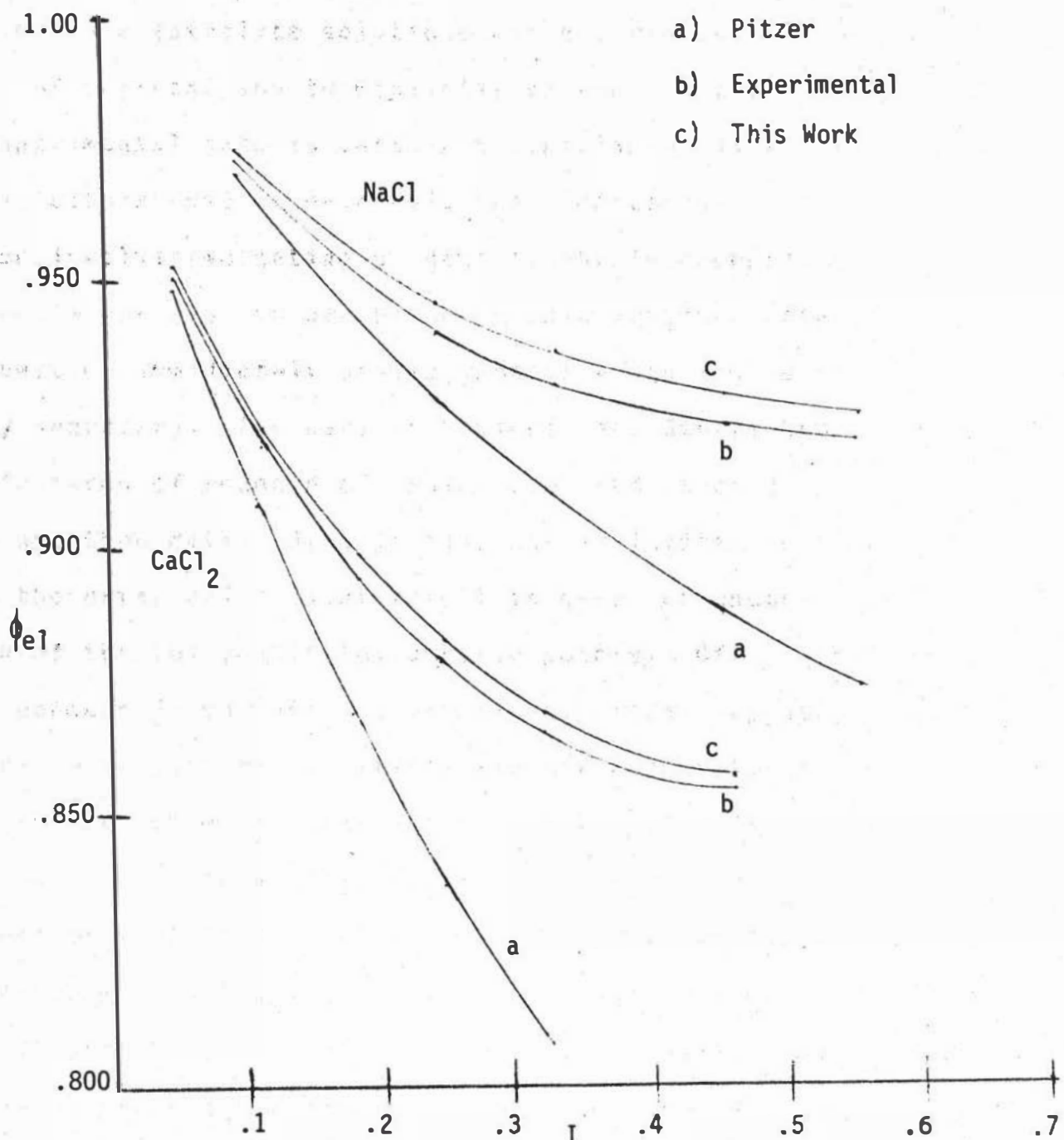
2-1 Electrolytes (cont)

Electrolyte	E	J <sub>1</sub>	J <sub>2</sub>	sd	Max M
UO <sub>2</sub> C1 <sub>2</sub>	.0535	.1858	-.0446	.002	2
UO <sub>2</sub> (C1 <sub>0</sub> ) <sub>2</sub>	-.103	.270	.156	.005	2
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	.0508	.2027	-.0340	.005	2
Li <sub>2</sub> SO <sub>4</sub>	.1026	-.1546	-.0282	.001	3
Na <sub>2</sub> SO <sub>4</sub>	.1184	-.2960	-.0203	.002	4
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	.1089	-.2238	-.0247	.001	2
Na <sub>2</sub> C1 <sub>0</sub> <sub>4</sub>	.0702	-.1965	8.3E-3	.001	2
Rb <sub>2</sub> SO <sub>4</sub>	.1269	-.2408	-.0385	.001	1.6
Cs <sub>2</sub> SO <sub>4</sub>	.0609	-.0302	.0428	.004	1.6
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	.2083	-.311	-.0848	.004	4

Table 12 - Inorganic Compounds of Type 3-1

Electrolyte	E	J <sub>1</sub>	J <sub>2</sub>	sd	Max M	sd	Max M
AlCl <sub>3</sub>	-.0143	.0264	.0663	.002	1.8		
ScCl <sub>3</sub>	.0524	.0307	.00238	.001	1.8		
YCl <sub>3</sub>	.0467	-.00207	.0105	.001	1.8		
LaCl <sub>3</sub>	.0461	-.00726	.0510	.001	1.8		
CeCl <sub>3</sub>	.0525	-.00972	.00132	.002	1.8		
PrCl <sub>3</sub>	.0499	-.0161	.00497	.001	1.8		
NdCl <sub>3</sub>	.0523	-.0149	.00401	.001	1.8		
SmCl <sub>3</sub>	.0446	-.00297	.00802	.001	1.8		
EuCl <sub>3</sub>	.0344	-.00224	.0150	.001	1.8		
CrCl <sub>3</sub>	.0298	.0504	.0159	.003	1.2		
Cr(NO <sub>3</sub> ) <sub>3</sub>	.0546	.0385	-.00927	.001	1.4		

Figure 1



Plot of osmotic coefficient versus  $I$  for NaCl and CaCl<sub>2</sub>  
(for the electrostatic term only)

## Discussion

The fundamental idea behind proposing an equation containing a logarithmic term is the simplicity with which single or mixed electrolyte solutions can be treated. Comparison of our equation to Pitzer's, on the basis of fitting experimental data is certainly important, but a few additional factors need to be considered. Pitzer's computation involves weighting of data to obtain acceptable results, while our results are based on an unweighted data. Now the question immediately arises whether weighting is absolutely necessary. The data in Robinson and Stokes book is given in terms of rounded off molalities and hence is partially smoothed data. By weighting one is further smoothing the data, which might result in over- or under-estimation of the reliability of certain points. Of immediate concern is whether the equations proposed by us are comparable to Pitzer's equations and yield acceptable results. If one compares Pitzer's weighted results and ours, one observes his results for 2-1 electrolytes are slightly better than ours, the 1-1's are comparable, but higher electrolytes are certainly better in our case. In most of the cases the differences in standard deviation of the calculated osmotic coefficient do not exceed .002. In any case, whether one uses the Pitzer equation unweighted or ours weighted, the overall result should not change by a

significant magnitude. Results for mixtures were computed by our equations using parameters obtained for pure electrolytes and are comparable to Pitzer's results for the ones treated here. Only a few mixtures were examined, mostly mixtures consisting of 1-1 electrolytes or 1-2 and 1-1 mixtures either having a common ion or no common ion. Treatment of mixtures involving 3-1 and 1-1 electrolytes or other systems with no common ion or with common ion requires consideration of additional unsymmetrical mixing effects.

Comparison of the electrostatic term with a  $b$  value of 1.8 yields an excellent approximation of the Debye-Huckel equation, and the results obtained are closer to the experimental values. A plot of  $(\epsilon)$  versus  $I^{1/2}$  for NaCl and  $\text{CaCl}_2$  is shown in figure 1. Thus treating  $b$  as a parameter leads to a reasonable result. Statistical terms on the other hand are difficult to assess and compare. The reason, in simple terms, is that these terms are fitting functions for higher concentrations, and the numerical accuracy achieved distinguishes the different statistical terms. Basically one can interchange different statistical terms with the electrostatic terms and obtain reasonable results; that is one can use the Pitzer statistical terms with the Debye-Huckel equation or our statistical terms with the Pitzer electrostatic terms and get similar results provided one adjusts the  $b$  value.

An example of future applications of our equation is the

very simple form required for obtaining a relationship between activity coefficients and partial molal heat content, or heat capacity. In the Pitzer approach one would surely have problems in using the activity coefficient equation. Instead one has to utilize the expression for the excess Gibbs free energy. The electrostatic term is similar to ours but the statistical term is inconvenient to use. Thus, the equations for the above thermodynamic properties represent an improvement in ease of use and in devising a scale of single ion activities for use in computer modeling of natural water systems.



APPENDIX

00100C THIS PROGRAM PERFORMS A LEAST SQUARES  
 00150C FIT TO DETERMINE PARAMETERS FOR ACTIVITY  
 00200C OR OSMOTIC COEFFICIENTS FOR EQUATIONS  
 00250C DEVELOPED IN THE PRESENT RESEARCH.

00300C EQUATIONS FOR ACTIVITY AND OSMOTIC COEFFICIENTS  
 00350C ARE AS FOLLOWS:

00400C  
 00450C  
 00500C  $(\text{GAMMA}) = - [(Z_1 \cdot Z_2) \cdot \text{AD} \cdot I^{.5} / (1 + B \cdot I^{.5})]$   
 00550C  $+ E \cdot I \cdot (I) + J_1 \cdot I + J_2 \cdot I^{1.5}$

00600C  
 00650C  
 00700C  $Q-1 = - [(Z_1 \cdot Z_2) \cdot \text{AD} \cdot (1/B^{3 \cdot I}) \cdot ((1 + B \cdot I^{.5})$   
 00750C  $(1/(1 + B \cdot I^{.5})) - 2 \cdot \text{LN}(1 + B \cdot I^{.5}))]$   
 00800C  $+ E' \cdot I \cdot \text{LN}(I) + J_1' \cdot I + J_2' \cdot I^{1.5}$

00850C WHERE, Z1 AND Z2 ARE CHARGES ON THE IONS.  
 00900C AD : THE DEBYE-HUCKEL CONSTANT WHICH HAS A VALUE OF  
 00950C 1.176.  
 01000C B : A FIXED PARAMETER HAVING A VALUE OF 1.8.  
 01050C I : EQUALS TO THE IONIC STRENGTH OF THE SOLUTION.  
 01100C LN : THE NATURAL LOGARITHM. (=ALOG)  
 01150C E, J1, J2 ARE PARAMETERS FOR THE COEFFICIENT.  
 01200C PARAMETERS FOR THE ACTIVITY AND OSMOTIC  
 01250C COEFFICIENTS ARE RELATED THROUGH THE GIBBS-DUHEM  
 01300C RELATIONSHIP, AND HENCE THEY DO NOT HAVE SAME  
 01350C VALUES.  
 01400C GAMMA IS THE ACTIVITY COEFFICIENT, AND Q THE  
 01450C OSMOTIC COEFFICIENT.  
 01500C THE TERM IN BRACKETS [...] REPRESENTS THE  
 01550C ELECTROSTATIC TERM.  
 01600C NONBRACKETED T S REPRESENT STATISTICAL  
 01650C TERMS.

01700C  
 01750C DATA FOR THESE COEFFICIENTS HAVE TO BE READ  
 01800C THROUGH A SEPARATE FILE. BEFORE RUNNING THE  
 01850C PROGRAM ONE SHOULD CALL THE DATA FILE.  
 01900C DATA FILES DO NOT HAVE Z AND A VALUES  
 01950C HENCE BEFORE RUNNING THE PROGRAM USE APPROPRIATE  
 02000C VALUES IN LINE NUMBERS .....  
 02050C A1 AND A2 ARE THE NUMBER OF MOLES OF CATION AND  
 02100C ANIONS OBTAINED ON DISSOCIATION OF ONE MOLE OF  
 02150C THE ELECTROLYTE.

02200C  
 02250C  
 02300C PROGRAM CMR (INPUT, OUTPUT, QKCL, TAPE5=INPUT,  
 02350C TAPE6=OUTPUT, TAPE7=QKCL)

02400C  
 02450C BEFORE RUNNING DIFFERENT DATA FILES. FILE NAME IN  
 02500C ABOVE STATEMENT SHOULD BE CHANGED OTHERWISE  
 02550C THE COMPUTER WOULD TERMINATE THE PROGRAM



```

02800C
02650C FOLLOWING VARIABLES ARE USED.
02750C
02800C YE: THE SUM OF THE EXPT LN(GAMMA) OR Q-1.
02850C AND THEIR RESPECTIVE ELECTROSTATIC TERM.
02900C THIS SUM EQUALS THE STATISTICAL TERMS.
02950C YC : CALCULATED VALUE OF STATISTICAL TERMS.
03000C DY: DIFFERENCE BETWEEN YE AND YC. THE
03050C PROGRAM MINIMISES DY'S VALUES BEFORE
03100C PRINTING RESULTS.
03150C SD : STANDARD DEVIATION
03200C DA : THE DIFFERENTIAL IN PARAMETER VALUE
03250C OBTAINED BY PERFORMING A LEAST SQUARES FIT
03450C DIMENSION YE(50),YC(50),AL(50),X(50),DY(50)
03500C DIMENSION SD(50),DA(50),Q(50),D(50),DH(50)
03550C DIMENSION W(50),Y(50),P(50),QC(50),XE(50)
03800C DIMENSION DS(50),AG(50),DP(50)
03850C IN FOLLOWING STATEMENTS DATA'S ARE READ
03700C FROM THE DATA FILE.
03750C KKKK, M THE NUMBER OF DATA IN THE FILE.
03800C N : THE MAXIMUM NUMBER OF CYCLE THE
03850C PROGRAM IS ALLOWED TO RUN FOR A GIVEN SET OF DATA
03900C N IS USED TO AVOID THE COMPUTER
03950C GETTING INTO AN INFINITE LOOP DUE TO INADVERTANT
04000C ERRORS IN PROGRAMMING.
04050C
04100C Q : ACTIVITY OR OSMOTIC DATA
04150C NUMBER OF DATA POINTS IS EQUAL TO M
04200C XE IS THE MOLALITY FOR THE CORRESPONDING ACTIVITY
04250C OR OSMOTIC DATA.
04300C AL(K)'S ARE INITIAL GUESS VALUES
04350C FOR PARAMETERS.
04400C AL(1) = E IN THE EQUATION
04450C AL(2) = J1 " " "
04500C AL(3) = J2 " " "
04550C
04600C
04650 READ(7,*) M
04700 READ(7,*) N
04750 READ(7,*) (Q(K),K=1,M)
04800 READ(7,*) (XE(K),K=1,M)
04850 READ(7,*)(AL(J),J=1,3)
04900C
04950C
05000C TO KEEP TRACK OF ELECTROLYTES FOR
05050C WHICH THE RESULTS ARE PRINTED OUT ONE
05100C SHOULD HAVE APPROPRIATE FORMULAE IN THE
05150C FOLLOWING WRITE STATEMENT.
05200 WRITE(8,22)"MGBR2(Q)"
05250 22 FORMAT(20X,A15)
06300 B=1.8

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05350 WRITE(6,23)('B=',B)
05400 23 FORMAT(A4,F4.2)
05450 Z1=1.
05500 Z2=1.
05550 A1=1.
05600 A2=1.
05650 SD(1)=10.
05700C THE FOLLOWING DO LOOP DETERMINES IONIC
05750C STRENGTH OF SOLUTIONS USING APPROPRIATE
05800C Z1,Z2,A1 AND A2 VALUES.
05850C
05900C
05950 DO 4 K=1,M
06000 X(K)=.5*(Z1**2*A1*XE(K)+Z2**2*A2*XE(K))
06050 4 CONTINUE
06100C
06150C
06200C YE IS DETERMINED IN THE DO LOOP 3
06250C FOR ACTIVITY CALCULATIONS USE ALOG(Q(K))
06251C INSTEAD OF (Q-1.)
06252C USE PROPER ELECTROSTATIC TERMS WHILE CALCULATING
06253C THE REQUIRED COEFFICIENT.
06300C
06350 DO 3 K=1,M
06400 YE(K)=(Q(K)-1.)+(Z1*Z2*1.176)*(1./(B**3*X(K)))
06450+ *((1.+B*X(K)**.5)-(1./(1.+B*X(K)**.5))
06500+ -2.*ALOG(1.+B*X(K)**.5))
06550 3 CONTINUE
06551C
06552C OPTIMIZATION OF PARAMETERS BEGINS:
06600 DO 10 I=2,N
06650C
06700C INITIALIZE DA,DETD,SUMA
06750C
06800 DA(1)=0.
06850 DA(2)=0.
07000 DA(3)=0.
07050 DETD=0.
07250 SUMA=0.
07251C
07252C
07253C CALCULATION OF THE STATISTICAL TERM USING
07254C GUESS VALUE OF THE PARAMETERS.
07300 DO 20 K=1,M
07350 YC(K)=AL(1)*X(K)*ALOG(X(K))+AL(2)*X(K)+
07351+ +AL(3)*X(K)**1+.5
07400 DY(K)=YE(K)-YC(K)
07450 SUMA=SUMA+DY(K)**2
07500 20 CONTINUE
07550 XM=M
07600 SD(I)=(SUMA/(XM-3.))**.5
07610C

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07620C CONTROL STATEMENT COMPARES (N-1) AND N CYCLES
07621C STANDARD DEVIATION
07650 IF(ABS(SD(I)-SD(I-1)).LT..0001) GOTO 500
07651C INITIALIZATION OF ELEMENTS IN THE DETERMINANT.
07652C THE DETERMINANT IS SYMMETRICAL HENCE A12=A21,
07653C A13=A31, A23=A32.
07700 SUM1=0.
07750 SUM2=0.
07800 SUM3=0.
07850 A11=0.
07900 A12=0.
07950 A13=0.
08000 A22=0.
08050 A23=0.
08100 A33=0.
08150 DO 40 K=1,M
08200 Y(K)=X(K)*ALOG(X(K))
08250 W(K)=X(K)
08300 P(K)=X(K)**1.5
08350 SUM1=SUM1+DY(K)*Y(K)
08400 SUM2=SUM2+DY(K)*W(K)
08450 SUM3=SUM3+DY(K)*P(K)
08500 A11=A11+Y(K)**2
08550 A12=A12+Y(K)*W(K)
08600 A13=A13+Y(K)*P(K)
08650 A22=A22+W(K)**2
08700 A23=A23+(W(K)*P(K))
08750 A33=A33+P(K)*P(K)
08800 40 CONTINUE
08850 DETD=A11*(A22*A33-A23**2)-A12*(A12*A33
08900+ -A13*A23)+A13*(A12*A23-A13*A22)
08950 DA(1)=(SUM1*(A22*A33-A23**2)-A12*(SUM2*A33
09000+ -A23*SUM3)+A13*(SUM2*A23-SUM3*A22))/DETD
09050 DA(2)=(A11*(SUM2*A33-SUM3*A23)-SUM1*(A12*A33
09100+ -A13*A23)+A13*(A12*SUM3-SUM2*A13))/DETD
09150 DA(3)=(A11*(A22*SUM3-SUM2*A23)-A12*(A12*SUM3
09200+ -A13*SUM2)+SUM1*(A12*A23-A13*A22))/DETD
09250 AL(1)=AL(1)+DA(1)
09300 AL(2)=AL(2)+DA(2)
09350 AL(3)=AL(3)+DA(3)
09400 10 CONTINUE
09450 500 SUM=0.
09500 SDI=0.
09501C
09502C CALCULATED VALUE OF OSMOTIC COEFFICIENT USING
09503C THE PARAMETERS.
09550 DO 15 K=1,M
09600 QC(K)=1.-Z1*Z2*1.176*(1./(B**3*X(K)))
09601+ *((1.+B*X(K)**.5)
09650+ -(1./(1.+B*X(K)**.5))-2.*ALOG(1.+B*X(K)**.5))
09700 D(K)=Q(K)-QC(K)
09750 SUM=SUM+D(K)**2

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09800 15 CONTINUE
09850 SDI=(SUM/(XM-3.))**.5
09900 WRIT (6,61)("MOLALITY", "EXPT OS", "CALC OS", "DIFF")
09950 61 FORMAT(A10, 6X, A6, 10X, A8, 15X, A6)
10000 WRIT (6,62)((XE(K), Q(K), QC(K), D(K)), K=1, M)
10050 62. FORMAT(2X, F7.5, 6X, F7.5, 6X, E18.10, 6X, E18.10)
10100 WRITE(6, *) "PARAMETER"
10150 WRITE(6, 63)(AL(J), J=1, 3)
10200 63 FORMAT(E18.10)
10250 WRITE(6, *) "STANDARD DEVIATION"
10300 WRIT (6, 64)SDI
10360 64 FORMAT(E18.10)
10400 STOP
10450 END
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References

- 1) Arrhenius, S., Z. Phys. Chem., 1887, 1, 631.
- 2) Bjerrum, N., Z. Electrochem., 1907, 24, 259.
- 3) Debye, P and Huckel, E., Z. Phys. Chem., 1923, 24, 185.
- 4) Guatelberg, E., Z. Phys. Chem., 1926, 123, 199.
- 5) Davies, C. W., J. Chem. Soc., 1938, 2093.
- 6) Guggenheim, E. A., Phil. Mag., 1935, 19, 588.
- 7) Pitzer, K. S., J. Phys. Chem., 1973, 77, 268.
- 8) Pitzer, K. S. and Mayorga, G., J. Phys. Chem., 1973, 77, 2300.
- 9) Pitzer, K. S. and Mayorga, G., J. Solution Chem., 1973, 3, 539.
- 10) Pitzer, K. S. and Kim, J. J., J. Am. Chem. Soc., 1974, 99, 5701.
- 11) Pitzer, K. S., J. Solution. Chem., 1975, 4, 249
- 12) Pitzer, K. S. and Silvester, L. F., J. Solution. Chem. 1976, 5, 269.
- 13) Pitzer K. S., Roy, R. N., and Silvester, L. F., J. Am. Chem. Soc. 1977, 99, 4930.
- 14) Pitzer, K. S., Acc. Chem. Res., 1977, 10, 377.
- 15) Mayer, J. E., J. Chem. Phys., 1959, 18, 1426.
- 16) Kirkwood, J. C., Chem. Rev., 1936, 19, 275.
- 17) Poirier, C. J. and Kirkwood, J. C. J. Phys. Chem., 1954, 58, 591.
- 18) Friedman, H. L., Ionic Solution Theory, Interscience, New York, 1962.
- 19) Card, D. M. and Valleau, J. P., J. Phys. Chem., 1970, 52, 6232.
- 20) Hill, T. L., An Introduction To Statistical Thermodynamics, Addison-Wesley, Reading, Mass., 1960, p.304

- 21) McMillan, W. G. and Mayer, J. E., J. Chem. Phys., 1945, 13, 276.
- 22) Reference 20, p. 313.
- 23) Barker, J. A. and Henderson, D., Rev. Mod. Phys., 1976, 48, 591.
- 24) Gluekauf, E., Proc. Roy. Soc. Ser. A., 1969, 310, 449.
- 25) Scatchard, G., Rush, R. M. and Johnson, J. S., J. Phys. Chem., 1970, 74, 3786.
- 26) Scatchard, G., J. Am. Chem. Soc., 1968, 90, 3124.
- 27) Bousfield, W. R., Isopiestic Solutions, Trans. Faraday Soc., 1917
- 28) Robinson, R. A. and Stokes, R. H., Electrolyte Solutions, Butterworths, London, 1965.
- 29) H. Ti Tien, J. Phys. Chem., 1963, 67, 532.
- 30) Wen, W. Y., Saito, S. and Lee, C., J. Phys. Chem., 1966, 70, 1244.
- 31) Lindenbaum, S. and Boyd, G. E., J. Phys. Chem., 1964, 68, 911.
- 32) Pitzer, K. S., J. Chem. Soc., Faraday Trans. 2, 1972, 68, 101.
- 33) Robinson, R. A., Wood, R. H. and Reilly, P. J., J. Chem. Thermodyn., 1971, 3, 461.
- 34) Bezboruah, C. P., Covington, A. K. and Robinson, R. A. J. Chem. Thermodyn., 1970, 2, 431.
- 35) Robinson, R. A., Platford, R. F. and Childs, C. W., J. Solution Chem., 1972, 1, 167
- 36) Reilly, R. J., Wood, R. H. and Robinson, R. A., J. Phys. Chem., 1971, 75, 1305.
- 37) Lindenbaum, S., Rush, R. M. and Robinson, R. A., J. Chem. Thermodyn., 1972, 4, 381.
- 38) Robinson, R. A. and Covington, A. K., J. Res. Nat. Bur. Stand., Sect. A., 1968, 72, 313.
- 39) Downes, C. J., J. Chem. Eng. Data., 1973, 18, 412.
- 40) Bronsted, J. N., J. Amer. Chem. Soc., 1922, 44, 877



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