The research undertaken in this study deals with three topics related to the prediction of thermodynamic properties of electrolytes in aqueous solutions.

In the first, Pitzer ion interaction parameters for 304 single electrolytes were evaluated from recently published osmotic coefficient data at 25°C by using multiple regression analysis to fit model equations for osmotic coefficients. The Pitzer ion interaction model for electrolyte solutions, which has gained acceptance recently, was used in this study. The maximum molality fitted by this evaluation was the saturation concentration when data were available. The better agreement with experimental values were observed when using parameters which were obtained at higher concentration than those used by Pitzer.

In the second, Pitzer ternary mixing parameters for 49 ternary mixture electrolytes with common ion at 25°C have been obtained by fitting all experimental data of \( \ln \eta_+ \) or \( \phi \) to the model equations. The effects of the higher order
electrostatic term were considered for all asymmetrical systems. A comparison between the values of $\ln \tau_\pm$ or $\phi -1$ calculated from the results of this study and experimental values for several systems shows the good agreement within $\pm 1\%$.

The third study deals with the development of correlations between the ion interaction parameters and ionic properties (entropy, charge, and radius) to provide a method of estimating ion interaction parameters. A close relationship between two of the binary interaction parameters, $\beta(0)$ and $\beta(1)$, was observed. The correlation obtained between $\beta(0)$ and $\beta(1)$ could be used to predict the activity coefficients of various types of electrolytes where no experimental data are available. The resulting correlations were evaluated by comparing their estimates of activity coefficients with measured values. For 1-1 type of electrolytes, the correlations predicted the activity coefficients within 10% of the mean absolute values of the relative deviation for activity coefficients up to maximum molality 6.0 M. For higher valence electrolytes, however, the mean values of the relative deviation for activity coefficients are higher than for 1-1 electrolytes. The main reason is that the plot of $\beta(0)$ versus $\beta(1)$ is more scattered than with 1-1 electrolytes. For ternary mixture, the results from using correlation fit the experimental values within $\pm 1\%$ for system of HCl-MgCl$_2$-H$_2$O at 25°C.
PREDICTION OF THERMODYNAMIC PROPERTIES
OF AQUEOUS ELECTROLYTE SOLUTIONS

by

Hee-Taik Kim

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"You may make your plans, but God directs your actions." (Prov 16.9)

I wish to express my deep appreciation to my major professor, Dr. William J. Frederick, Jr., for his support, encouragement, and guidance that allow me to finish this work. His integrity, compassion, and warmth will serve as models for me. I am also grateful to all of my graduate committee members for their reviews on my thesis and their participation on the graduate committee.

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PREDICTION OF THERMODYNAMIC PROPERTIES
OF AQUEOUS ELECTROLYTE SOLUTIONS

GENERAL INTRODUCTION

In recent years, there has been a growing interest, within industry, in the prediction of thermodynamic properties of aqueous multicomponent or mixed electrolyte solutions. Much of this interest arises from their importance in areas such as sea water desalination, oil recovery, hydrometallurgical processes and general-purpose property packages for process simulator.

These thermodynamic properties for aqueous solutions of single electrolytes, determined experimentally, have been reported extensively in the thermodynamic literature. However, experimental determination of these properties for mixed electrolyte solutions have received attention only relatively recently. One of the important thermodynamic properties of mixed electrolyte solutions is the activity coefficient. The activity coefficient gives a measure of the deviation of real solutions from ideality and include the magnitudes of all effects that lead to these deviations.

The development of accurate estimators for activity coefficients of ions also has made the use of equilibrium calculations a useful tool in process design and analysis. Historically, the development of computational tools in ionic equilibria has lagged that for nonionic solutions,
mainly because of lack of adequate methods to predict activity coefficients in aqueous electrolyte solutions of moderate to high ionic strength.

HISTORY OF ACTIVITY COEFFICIENT MODEL

In 1923, P. Debye and E. Hückel (1,2) developed the theory for activity coefficient of very dilute electrolyte solutions by assuming that ions are point charges and considering the long range electrical (Coulombic) forces. But these assumptions hold only at low concentrations \(I<0.001 \text{ M}\).

\[
\ln \gamma_{\pm} = - \frac{|z_+z_-| A}{I} \tag{1}
\]

which is called the Debye-Hückel limiting law.

The primary extension, recognizing that ions are in fact not point charge, was also given by Debye and Hückel:

\[
\ln \gamma_{\pm} = - \frac{|z_+z_-| A}{I(1+Bs/I)} \tag{2}
\]

where \(I\), the ionic strength, is defined as \(I = \frac{1}{2} \sum m_i z_i^2\) and \(A\) and \(B\) are Debye-Hückel constants which are functions of the properties of pure water only. \(z_+\) and \(z_-\) are the charge of the cation and anion respectively. \(s\) is an ion size parameter which accounts for the distance of closest
approach. It is assumed to be the same for all ions in the system. Although this is a considerable improvement over the limiting law, applications are nevertheless limited to solutions with concentration \((I<0.05 \text{ M})\).

E. Hückel (3) later modified equation (2) by adding an additional linear term which account for short range (van der Waals' forces) interaction.

\[
\ln r_\pm = - \frac{|z_+z_-|A/I}{1 + Bs/I} + CI \tag{3}
\]

Güntelberg (4) proposed the approximation form of equation (2) by setting a standard value for \(s = 3.04 \text{ Å}\) so that the Bs product becomes unity.

\[
\ln r_\pm = - \frac{|z_+z_-|A/I}{1+\sqrt{I}} \tag{4}
\]

This simplified equation of the Debye-Hückel equation represents activity coefficient for electrolyte solutions quite well up to \(I = 0.1 \text{ M}\).

In 1935, Guggenheim (5) introduced another form of above equation based on the mole fractions scale.

\[
\ln r_\pm = - \frac{|z_+z_-|A/I}{1 + \sqrt{I}} + 2\bar{\nu}\beta m \tag{5}
\]
where $\bar{V} = 2v_+/v_-/(v_+/v_-)$ and $m$ is the molality of the electrolyte. $\beta$ is a interaction parameter which was tabulated by Guggenheim and Turgeon (6) based on experimental data. Davies proposed a value of $2\bar{V}\beta = 0.1|z_+z_-|$ in 1938 (7) and revised this value to $0.15|z_+z_-|$ in 1962 (8) respectively. This method is relatively in good agreement with experiment up to about $I = 0.1 \text{ M}$.

Among more recently developed models for predicting activity coefficient of aqueous electrolyte solutions, four methods are commonly used. Their attributes are listed in Table G.1. These methods are reviewed in detail by Zemaitis and co-workers (9). Of the four methods for estimating activity coefficients, Pitzer ion interaction model (10-13) generally is the most accurate method. Pitzer's method used a virial expansion for the excess Gibbs energy to extend the Debye-Hückel equation to higher ionic strengths. Three or four ion interaction parameters are required for single salt solutions, depending on the valences of the ions involved. For multicomponent solutions, an additional parameter is required for each pair of anions or each pair of cations and another for each three ions, i.e., two different cations and an anion or two different anions and a cation. Pitzer's method was developed for strong electrolytes, but it has been applied successfully to solutions where ion association occurs and molecular species are present (14, 15).

The Pitzer method has been applied to many different
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<td>Generalized</td>
<td>Ion interactions</td>
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<tr>
<td><strong>Number of parameters for:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single salt solutions</td>
<td>1 per cation/anion pair</td>
<td>2 per cation/anion pair</td>
<td>3 per cation/anion pair if both monovalent, 4 if both ions are multivalent</td>
<td>2 per cation/anion pair</td>
</tr>
<tr>
<td>Additional parameters</td>
<td>None</td>
<td>None</td>
<td></td>
<td>None</td>
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<tr>
<td>for multicomponent</td>
<td></td>
<td></td>
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<tr>
<td>Estimation method</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
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<td>for parameters?</td>
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chemical systems (16-21), and has been shown to provide accurate estimate of activity coefficients at relatively high ionic strengths. The main limitations to the Pitzer method, however, is the amount of data required to obtain the ion interaction parameters. The total number of ion interaction parameters required is between $2N^3 + N^2$ and $2N^3 + 4N^2 + 2N$ for a solution containing $N$ cations and $N$ anions (18). The total number of parameters needed to simulate industrial process streams is large, usually in the 100-1000 range. The availability of a procedure to estimate Pitzer ion interaction parameters would increase its utility.

OBJECTIVE

The purpose of the studies presented in this thesis is to provide and evaluate a method for the accurate estimation of thermodynamic properties of aqueous mixed electrolyte solutions.

The specific objectives are:

1. to evaluate Pitzer ion interaction parameters, $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and $c^\phi$ from osmotic coefficient data for single salts at concentrations up to nearly saturation.

2. to obtain Pitzer mixing ion interaction parameters, $\theta_{ij}$ and $\psi_{ijk}$ from experimental data on aqueous mixed electrolyte solutions with a common ion.
3. to correlate Pitzer ion interaction parameters with ionic properties (such as entropy, charge and radius) to obtain equations for evaluating the ion interaction parameters, and
4. to evaluate the correlations by comparing their estimates of activity coefficients with measured values.

The result of this thesis work can be used in chemical equilibrium modeling for steady state process simulation.

ORGANIZATION OF THESIS

This thesis is divided into three major parts. Following this part, the next two parts are reproduction of papers prepared by the author and in cooperation with Dr. W. J. Frederick who is author's advisor.

The first paper, "EVALUATION OF PITZER ION INTERACTION PARAMETERS OF AQUEOUS ELECTROLYTES AT 25°C. 1. SINGLE SALT PARAMETERS" was accepted for publication in J. Chem. Eng. Data and is presented in chapter 1. The paper, "EVALUATION OF PITZER ION INTERACTION PARAMETERS OF AQUEOUS MIXED ELECTROLYTE SOLUTIONS AT 25°C. 2. TERNARY MIXING PARAMETERS" was also accepted for publication in same journal. This second paper is presented in chapter 2. The last part titled, "CORRELATION OF PITZER ION INTERACTION PARAMETERS" deals with the correlation between Pitzer parameters and
ionic properties to expand the availability of Pitzer method for calculating activity coefficients for ions in aqueous electrolyte solutions.
REFERENCES


CHAPTER 1

EVALUATION OF Pitzer Ion Interaction Parameters
of Aqueous Electrolytes at 25°C

1. SINGLE SALT PARAMETERS

by

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ABSTRACT

Ion interaction parameters for 304 single salts in aqueous solution have been obtained for Pitzer's equations. For most of the cases we evaluated, the range of molality extended up to saturation when data are available. The calculated activity coefficients of HCl, LiBr, CaBr₂, Pr(NO₃)₃ and MgSO₄ from our results and Pitzer's were compared to available smoothed experimental data. The comparisons show the better agreement with experimental data when using the values of our parameters which were evaluated at higher concentrations than those used by Pitzer.
INTRODUCTION

The principal thermodynamic properties of interest for predicting solubilities are activity and osmotic coefficients. Therefore the lack of accurate activity coefficients can result in large errors when predicting the solubility in aqueous multicomponent ionic solutions of high ionic strength even when few chemical species are present.

Ionic interaction models provide the simplest and most coherent procedures for the calculating the properties of electrolyte components. They use a single set of equations to describe the osmotic and activity coefficients of the components of single salts and mixtures with common ions. An ion interaction model for electrolyte activity coefficients was developed by Pitzer and coworkers (1-4) in the early 1970's. The Pitzer model extended the Debye-Hückel method, using a virial expansion to account for the ionic strength dependence of the short range forces in binary and ternary ion interaction. The model is applicable to solutions of high ionic strength. Moreover, these equations can be used in iterative calculations since the ion interaction parameters are expressed as explicit functions of ionic strength and need very few parameters to estimate properties of both single and mixed electrolytes. Many publications (5-11) have shown that the Pitzer model results in excellent solubility predictions.
The purpose of this work is to obtain Pitzer ion interaction parameters from osmotic coefficient data on single electrolytes at high concentration, up to nearly saturation. We used a form of the Pitzer ionic interaction model which was developed by Harvie and Weare (5) to predict the solubility of minerals in concentrated mixed salt solutions. The ionic interaction model was fit to published osmotic coefficient data at 25°C to obtain ion interaction parameters for solution of single salts. The ion interaction parameters from our results are stored on the file in a computer as a database, and activity and osmotic coefficients can be calculated simply by identifying the salt and defining the appropriate ionic strength.

GENERAL EQUATIONS

Recently, Harvie and Weare (5) developed a chemical equilibrium model for calculating mineral solubilities in the Na-K-Mg-Ca-Cl-SO₄-H₂O system at 25°C. This model was based on the Pitzer equations (1,2) for aqueous electrolyte solutions. Their equations for calculating the osmotic and mean ionic activity coefficients for single electrolyte solutions can be written as follows:

\[
\phi = 1 + \frac{2}{(m_m^{+}m_x^{-})} \left( \frac{-A^\phi I^{3/2}}{1+b/I} + m_m^{+}m_x^{-}(B^\phi Ma+2C Ma) \right) \]  \hspace{1cm} (1)
In eqs 1 and 2, \( m \) is the molality (mol/kg solvent) of a cation with charge \( z_M \) corresponding to stoichiometric coefficient \( v_M \). Similarly, the subscript \( X \) refers to anion. Also \( v = v_M + v_X \), and \( I = 0.5 \sum v_M z_M^2 \) is the ionic strength. The function \( Z \) is defined by \( Z = \sum v_M z_M = 2(\sum m v_M) = 2(\sum m z_M) \) and \( A^0 \) is the Debye-Hückel coefficient for the osmotic coefficient and is given by

\[
A^0 = \frac{1}{2} \left( \frac{2\pi No e^2}{1000} \right)^{1/2} \left( \frac{2m \Delta}{D} \right)^{3/2}
\]

where \( No \) is Avogadro's number, \( d_w \) is the density of water, and \( D \) is the static dielectric constant of water at temperature \( T \). Also, \( k \) is Boltzman's constant and \( e \) is the electronic charge. The value of \( A^0 \) at 25°C is 0.392 and the term \( b \) in eqs 1 and 2 is an empirical parameter equal to 1.2 at 25°C (2). The parameters \( B^0 M_X \), \( B_X \), and \( B'_X \) which describe the interaction of pairs of oppositely charged ions represent measurable combinations of the second virial coefficients. They are defined as explicit functions of ionic strength using the following equations.
\[ B'_{\text{MX}} = \beta_{\text{MX}}(0) + \beta_{\text{MX}}(1) e^{-\alpha_1/I} + \beta_{\text{MX}}(2) e^{-\alpha_2/I} \]  

(4)  

\[ B_{\text{MX}} = \beta_{\text{MX}}(0) + \beta_{\text{MX}}(1)f(\alpha_1/I) + \beta_{\text{MX}}(2)f(\alpha_2/I) \]  

(5)  

\[ B'_{\text{MX}} = \beta_{\text{MX}}(1)f'(\alpha_1/I)/I + \beta_{\text{MX}}(2)f'(\alpha_2/I)/I \]  

(6)  

where

\[ f(x) = 2[1-(1+x)e^{-x}]/x^2 \]  

(7)  

\[ f'(x) = -2[1-(1+x+0.5x^2)e^{-x}]/x^2 \]  

(8)  

For one or both ions univalent type electrolytes the first two terms of eqs 4 and 5, and only the first term of eq 6 are considered where \( \alpha_1 = 2 \) (2). For higher valence type, such as 2-2 electrolytes, the full eqs 4, 5, and 6 are used and \( \alpha_1 = 1.4 \) and \( \alpha_2 = 12 \) (3).  

The single electrolyte third virial coefficients, \( C_{\text{MX}} \) account for short-range interaction of ion triplets and are important only at high concentration. They are independent of ionic strength. The parameters, \( C_{\text{MX}} \) and \( \phi_{\text{MX}} \), the corresponding coefficients for calculating the osmotic coefficient, are related by the following eq 9 (2):

\[ C_{\text{MX}} = \phi_{\text{MX}}/2\sqrt{|z_{\text{MX}}|} \]  

(9)
EVALUATION OF ION Interaction PARAMETERS

The ion interaction parameters for single electrolytes were evaluated from recently published osmotic coefficient data by using multiple regression analysis to fit eq 1 to the data at 25°C. We used the computer program SIPS (Statistical Interactive Programming System), which was developed at Oregon State University, for this purpose. The best values of these fitting parameters are given in Tables 1.1 to 1.6. Tables 1.1 through 1.6 also contain the maximum molality for which data are available, frequently up to saturation. Thus the maximum molalities for most cases in our evaluation go beyond that of Pitzer's evaluation (2).

The standard deviation of fit (SD) for the osmotic coefficient data and the multiple correlation coefficient, R, which is a measure of the closeness of linear relationship, are also listed in Table 1.1 to 1.6. The sources of the osmotic coefficient data are listed in the last column in the tables.

In most cases where one or both ions are univalent, we used the experimental osmotic coefficient data evaluated by Hamer and Wu (12) for 1-1 electrolytes, Goldberg (13) for 1-2 electrolytes, Goldberg and Nuttall (14-17) for 2-1 electrolytes, and Spedding et al. (18-21) for 3-1 electrolytes.

For 2-2 type electrolytes, we used osmotic coefficient
data from Robinson and Stokes (22) and Pitzer (23) who provided the data below 0.1 molality, except for UO$_2$SO$_4$, for which data are available only over concentration range of 0.1 to 6.0 molality.

The positive value of the coefficients $B^{\phi}_{Mx}$ from eq 4 indicates the net predominance of repulsive short-range interaction forces according to Pitzer and Mayorga M.

For pure electrolytes, the two ion interaction parameters, $\beta_{Mx}^{(0)}$ and $\beta_{Mx}^{(1)}$ define the second virial coefficients which describe the interaction of pairs of oppositely charged ions. However, for 2-2 and higher valence electrolytes, one additional term, $\beta_{Mx}^{(2)}$, which reproduces the irregular behavior in the range below 0.1 molality, is added (3). From the eqs 5 and 6, one finds that the $\beta_{Mx}^{(2)}$ term is equal to 0.00005 $\beta_{Mx}^{(2)}$ at 0.1 M and negligible above 0.1 M because of the large value of $\alpha_2 = 12.0$. For the case of UO$_2$SO$_4$, there are no osmotic coefficient data below 0.1 M; hence the $\beta_{Mx}^{(2)}$ value does not affect the relative values of osmotic and activity coefficients in given concentration range and has no meaningful value. In the cases of CaSO$_4$ and CoSO$_4$, where available data are limited to dilute solutions (below 0.1 M), we omitted the coefficients, $C^{\phi}_{Mx}$ and chose the value of $\beta_{Mx}^{(2)} = 2.0$ which was proposed by Pitzer and Mayorga (2).

The third virial coefficients, $C^{\phi}_{Mx}$, which account for ion triplet interactions, are usually very small and
Table 1.1 Ion interaction parameters for 1-1 electrolytes at 25°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\beta(0)$</th>
<th>$\beta(1)$</th>
<th>$C^0$</th>
<th>Max.m</th>
<th>SD</th>
<th>R</th>
<th>Ref.</th>
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<tbody>
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<td>HF</td>
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<td>0.40156</td>
<td>-0.00018</td>
<td>20.000</td>
<td>0.0031</td>
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<tr>
<td>HCl</td>
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<td>-0.00318</td>
<td>16.000</td>
<td>0.0144</td>
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<tr>
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<td>-0.00101</td>
<td>11.000</td>
<td>0.0292</td>
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<tr>
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<td>0.28351</td>
<td>0.00138</td>
<td>10.000</td>
<td>0.0159</td>
<td>0.9998 (12)</td>
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<tr>
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<td>-0.22769</td>
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<td>0.0162</td>
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<tr>
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<td>-0.00233</td>
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<td>0.0276</td>
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<td>0.0049</td>
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<tr>
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Table 1.1 (continued)

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<th>( \beta(1) )</th>
<th>( C^\phi )</th>
<th>Max. m</th>
<th>SD</th>
<th>R</th>
<th>Ref.</th>
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<tr>
<td>Compound</td>
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<td>$\beta(1)$</td>
<td>$C^\phi$</td>
<td>Max.m</td>
<td>SD</td>
<td>R</td>
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Table 1.1  (continued)

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<th>$\beta(1)$</th>
<th>$C^\phi$</th>
<th>Max.m</th>
<th>SD</th>
<th>R</th>
<th>Ref.</th>
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<td>0.0049</td>
<td>0.9822</td>
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</tr>
<tr>
<td>Et$_4$NNO$_3$</td>
<td>-0.04022</td>
<td>-0.87108</td>
<td>0.00565</td>
<td>8.000</td>
<td>0.0076</td>
<td>0.9893</td>
<td>(28)</td>
</tr>
<tr>
<td>Me$_4$NNO$_3$</td>
<td>0.01224</td>
<td>-0.32933</td>
<td>0.00090</td>
<td>7.000</td>
<td>0.0021</td>
<td>0.9991</td>
<td>(28)</td>
</tr>
<tr>
<td>MeNH$_3$ClO$_4$</td>
<td>-0.03371</td>
<td>0.00573</td>
<td>0.00345</td>
<td>4.000</td>
<td>0.0017</td>
<td>0.9980</td>
<td>(30)</td>
</tr>
<tr>
<td>Me$_2$NH$_2$ClO$_4$</td>
<td>-0.04395</td>
<td>-0.17191</td>
<td>0.00240</td>
<td>7.500</td>
<td>0.0011</td>
<td>0.9999</td>
<td>(30)</td>
</tr>
<tr>
<td>Me$_3$NHClO$_4$</td>
<td>-0.11447</td>
<td>-0.17129</td>
<td>0.01348</td>
<td>1.800</td>
<td>0.0024</td>
<td>0.9992</td>
<td>(30)</td>
</tr>
<tr>
<td>GuCl</td>
<td>-0.02855</td>
<td>-0.10997</td>
<td>0.00177</td>
<td>12.000</td>
<td>0.0068</td>
<td>0.9845</td>
<td>(31)</td>
</tr>
<tr>
<td>Li p-tol$^b$</td>
<td>0.01223</td>
<td>0.46653</td>
<td>0.00633</td>
<td>4.500</td>
<td>0.0030</td>
<td>0.9986</td>
<td>(12)</td>
</tr>
<tr>
<td>Na p-tol$^b$</td>
<td>-0.03958</td>
<td>0.47846</td>
<td>0.00571</td>
<td>4.000</td>
<td>0.0025</td>
<td>0.9951</td>
<td>(12)</td>
</tr>
<tr>
<td>Na formate</td>
<td>0.07187</td>
<td>0.32247</td>
<td>-0.00236</td>
<td>3.500</td>
<td>0.0006</td>
<td>0.9999</td>
<td>(12)</td>
</tr>
<tr>
<td>Na propionate</td>
<td>0.18813</td>
<td>0.26772</td>
<td>-0.01288</td>
<td>3.000</td>
<td>0.0005</td>
<td>1.0000</td>
<td>(12)</td>
</tr>
<tr>
<td>Na butyrate</td>
<td>0.26081</td>
<td>0.16368</td>
<td>-0.03358</td>
<td>3.500</td>
<td>0.0037</td>
<td>0.9998</td>
<td>(12)</td>
</tr>
<tr>
<td>Na valerate</td>
<td>0.33473</td>
<td>-0.11324</td>
<td>-0.07394</td>
<td>2.000</td>
<td>0.0030</td>
<td>0.9998</td>
<td>(12)</td>
</tr>
<tr>
<td>Na caprylate</td>
<td>-0.45120</td>
<td>-7.73638</td>
<td>0.05902</td>
<td>3.000</td>
<td>0.0170</td>
<td>0.9963</td>
<td>(12)</td>
</tr>
<tr>
<td>Na pelargonate</td>
<td>0.03728</td>
<td>-10.3798</td>
<td>-0.07164</td>
<td>2.500</td>
<td>0.0169</td>
<td>0.9933</td>
<td>(12)</td>
</tr>
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</table>
Table 1.1 (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\beta(0)$</th>
<th>$\beta(1)$</th>
<th>$C^\phi$</th>
<th>Max.m</th>
<th>SD</th>
<th>R</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na caprate</td>
<td>0.07992</td>
<td>-7.40138</td>
<td>-0.06028</td>
<td>1.800</td>
<td>0.0033</td>
<td>0.9987</td>
<td>(12)</td>
</tr>
<tr>
<td>NaH malonate</td>
<td>0.02166</td>
<td>0.17611</td>
<td>-0.00089</td>
<td>5.000</td>
<td>0.0005</td>
<td>0.9998</td>
<td>(12)</td>
</tr>
<tr>
<td>NaH succinate</td>
<td>0.03463</td>
<td>0.14036</td>
<td>0.00061</td>
<td>5.000</td>
<td>0.0020</td>
<td>0.9994</td>
<td>(12)</td>
</tr>
<tr>
<td>NaH adipate</td>
<td>0.04325</td>
<td>0.33988</td>
<td>-</td>
<td>0.700</td>
<td>0.0003</td>
<td>0.9999</td>
<td>(12)</td>
</tr>
<tr>
<td>K p-tol</td>
<td>0.09842</td>
<td>0.47188</td>
<td>0.01182</td>
<td>3.500</td>
<td>0.0020</td>
<td>0.9995</td>
<td>(12)</td>
</tr>
<tr>
<td>KH malonate</td>
<td>-0.00474</td>
<td>0.06128</td>
<td>0.00048</td>
<td>5.000</td>
<td>0.0027</td>
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<tr>
<td>KH succinate</td>
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<td>0.10978</td>
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<td>0.0024</td>
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<tr>
<td>KH adipate</td>
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<td>0.47595</td>
<td>0.05523</td>
<td>1.000</td>
<td>0.0007</td>
<td>0.9997</td>
<td>(12)</td>
</tr>
</tbody>
</table>

a Acetate       b Para-toluenesulfonate
Table 1.2 Ion interaction parameters for 1-2 electrolytes at 25° C

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\beta(0)$</th>
<th>$\beta(1)$</th>
<th>$C^\phi$</th>
<th>Max. m</th>
<th>SD</th>
<th>R</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{SO}_4$</td>
<td>0.14098</td>
<td>-0.56843</td>
<td>-0.00237</td>
<td>27.500</td>
<td>0.0487</td>
<td>0.9984</td>
<td>(12)</td>
</tr>
<tr>
<td>$\text{Li}_2\text{SO}_4$</td>
<td>0.14515</td>
<td>1.23001</td>
<td>-0.00643</td>
<td>3.000</td>
<td>0.0047</td>
<td>0.9995</td>
<td>(13)</td>
</tr>
<tr>
<td>$\text{Li}_2\text{C}_6\text{H}_4\text{S}_2\text{O}_6$</td>
<td>0.40862</td>
<td>1.92482</td>
<td>-0.03240</td>
<td>2.500</td>
<td>0.0031</td>
<td>0.9999</td>
<td>(13)</td>
</tr>
<tr>
<td>$\text{Li}<em>2\text{C}</em>{14}\text{H}_{12}\text{S}_2\text{O}_6$</td>
<td>0.12189</td>
<td>1.48771</td>
<td>0.03415</td>
<td>1.000</td>
<td>0.0040</td>
<td>0.9992</td>
<td>(13)</td>
</tr>
<tr>
<td>$\text{Na}_2\text{SO}_4$</td>
<td>0.04680</td>
<td>0.91406</td>
<td>-0.00520</td>
<td>1.750</td>
<td>0.0012</td>
<td>0.9996</td>
<td>(13)</td>
</tr>
<tr>
<td>$\text{Na}_2\text{SO}_3$</td>
<td>0.08015</td>
<td>1.18500</td>
<td>-0.00436</td>
<td>2.000</td>
<td>0.0019</td>
<td>0.9996</td>
<td>(13)</td>
</tr>
<tr>
<td>$\text{Na}_2\text{CO}_3$</td>
<td>0.05306</td>
<td>1.29262</td>
<td>0.00094</td>
<td>2.750</td>
<td>0.0026</td>
<td>0.9993</td>
<td>(13)</td>
</tr>
<tr>
<td>$\text{Na}_2\text{HPO}_4$</td>
<td>-0.02169</td>
<td>1.24472</td>
<td>0.00726</td>
<td>2.000</td>
<td>0.0005</td>
<td>0.9997</td>
<td>(13)</td>
</tr>
<tr>
<td>$\text{Na}_2\text{CrO}_4$</td>
<td>0.06526</td>
<td>1.63256</td>
<td>0.00884</td>
<td>4.250</td>
<td>0.0051</td>
<td>0.9997</td>
<td>(13)</td>
</tr>
<tr>
<td>$\text{Na}_2\text{S}_2\text{O}_3$</td>
<td>0.06347</td>
<td>1.32115</td>
<td>0.00475</td>
<td>4.000</td>
<td>0.0033</td>
<td>0.9997</td>
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<tr>
<td>$\text{Na}_2\text{S}_2\text{O}_6$</td>
<td>0.08526</td>
<td>1.18961</td>
<td>-</td>
<td>0.800</td>
<td>0.0027</td>
<td>0.9986</td>
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<tr>
<td>$\text{Na}_2\text{S}_2\text{O}_8$</td>
<td>0.28075</td>
<td>1.01750</td>
<td>-</td>
<td>0.090</td>
<td>0.0004</td>
<td>0.9999</td>
<td>(13)</td>
</tr>
<tr>
<td>$\text{Na}_2\text{C}_6\text{H}_4\text{S}_2\text{O}_6$</td>
<td>0.28782</td>
<td>1.31451</td>
<td>-0.04835</td>
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<td>0.0052</td>
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<tr>
<td>$\text{Na}_2\text{CrO}_4$</td>
<td>0.25277</td>
<td>2.02265</td>
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<td>3.000</td>
<td>0.0024</td>
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<tr>
<td>$\text{Na}<em>2\text{C}</em>{14}\text{H}_{12}\text{S}_2\text{O}_6$</td>
<td>0.00808</td>
<td>1.60199</td>
<td>-</td>
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<td>0.0043</td>
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<tr>
<td>$\text{Na}<em>2\text{C}</em>{14}\text{H}_{12}\text{S}_2\text{O}_8$</td>
<td>-0.36838</td>
<td>0.16958</td>
<td>-</td>
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<td>0.0098</td>
<td>0.9817</td>
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<tr>
<td>$\text{Na}_2\text{B}<em>12\text{H}</em>{12}$</td>
<td>0.51666</td>
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<tr>
<td>$\text{Na}_2\text{WO}_4$</td>
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<td>0.87616</td>
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<td>0.0028</td>
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<tr>
<td>$\text{Na}_2\text{HAsO}_4$</td>
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<td>1.70125</td>
<td>0.01202</td>
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<td>0.0006</td>
<td>0.9999</td>
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<tr>
<td>$\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$ a</td>
<td>0.23639</td>
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<td>0.0039</td>
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<tr>
<td>$\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$ b</td>
<td>0.14063</td>
<td>0.39635</td>
<td>-0.00941</td>
<td>2.750</td>
<td>0.0028</td>
<td>0.9997</td>
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<tr>
<td>$\text{K}_2\text{SO}_4$</td>
<td>0.07548</td>
<td>0.44371</td>
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<tr>
<td>$\text{K}_2\text{HPO}_4$</td>
<td>0.05307</td>
<td>1.10271</td>
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<td>0.0005</td>
<td>0.9999</td>
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</tr>
<tr>
<td>Compound</td>
<td>$\beta(0)$</td>
<td>$\beta(1)$</td>
<td>$C^0$</td>
<td>Max. m</td>
<td>SD</td>
<td>R</td>
<td>Ref.</td>
</tr>
<tr>
<td>-------------------</td>
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<td>------------</td>
<td>--------</td>
<td>--------</td>
<td>-----</td>
<td>----------</td>
<td>---------</td>
</tr>
<tr>
<td>$K_2H_2P_2O_7$</td>
<td>-0.00585</td>
<td>1.25198</td>
<td>0.00524</td>
<td>3.000</td>
<td>0.008</td>
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</tr>
<tr>
<td>$K_2HAsO_4$</td>
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<td>1.80042</td>
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<td>0.800</td>
<td>0.0022</td>
<td>0.9995</td>
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<tr>
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<td>0.07712</td>
<td>1.18413</td>
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<td>3.250</td>
<td>0.0028</td>
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<tr>
<td>$K_2Cr_2O_7$</td>
<td>-0.01111</td>
<td>2.33306</td>
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<td>0.507</td>
<td>0.0155</td>
<td>0.9144</td>
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</tr>
<tr>
<td>$K_2Pt(CN)_4$</td>
<td>0.05955</td>
<td>2.25539</td>
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<td>0.948</td>
<td>0.0042</td>
<td>0.9984</td>
<td>(13)</td>
</tr>
<tr>
<td>$Rb_2SO_4$</td>
<td>0.09232</td>
<td>0.75746</td>
<td>-0.01339</td>
<td>1.500</td>
<td>0.0010</td>
<td>0.9997</td>
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</tr>
<tr>
<td>$Rb_2S_2O_8$</td>
<td>0.20464</td>
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<td></td>
<td>0.070</td>
<td>0.0001</td>
<td>0.9999</td>
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<tr>
<td>$Cs_2SO_4$</td>
<td>0.14294</td>
<td>0.66711</td>
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<tr>
<td>$Cs_2S_2O_8$</td>
<td>0.13283</td>
<td>-0.76429</td>
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<td>0.109</td>
<td>0.0001</td>
<td>0.9999</td>
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</tr>
<tr>
<td>$(NH_4)_2SO_4$</td>
<td>0.04841</td>
<td>1.13240</td>
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<td>5.500</td>
<td>0.0018</td>
<td>0.9996</td>
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</tr>
<tr>
<td>$(NH_4)_2HPO_4$</td>
<td>-0.04259</td>
<td>-0.69871</td>
<td>0.00527</td>
<td>3.000</td>
<td>0.0015</td>
<td>0.9990</td>
<td>(13)</td>
</tr>
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<td>$(NH_4)_2B_10H_10$</td>
<td>0.15824</td>
<td>1.46202</td>
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<td>3.750</td>
<td>0.0067</td>
<td>0.9988</td>
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</tr>
<tr>
<td>$(CN_3H_6)_2CO_3$</td>
<td>-0.07420</td>
<td>0.22809</td>
<td>0.01380</td>
<td>2.500</td>
<td>0.0021</td>
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<tr>
<td>$C_2H_6S_2O_6$</td>
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<td>0.0078</td>
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<tr>
<td>$C_6H_6S_2O_6$</td>
<td>0.41381</td>
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<td>-0.02071</td>
<td>1.750</td>
<td>0.0021</td>
<td>0.9999</td>
<td>(13)</td>
</tr>
</tbody>
</table>

a Sodium fumarate.  b Sodium maleate
### Table 1.3 Ion interaction parameters for 2-1 electrolytes at 25°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\beta(0))</th>
<th>(\beta(1))</th>
<th>(C^\Phi)</th>
<th>Max.m</th>
<th>SD</th>
<th>R</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl(_2)</td>
<td>0.35573</td>
<td>1.61738</td>
<td>0.00474</td>
<td>5.750</td>
<td>0.0036</td>
<td>1.0000</td>
<td>(14)</td>
</tr>
<tr>
<td>MgBr(_2)</td>
<td>0.43469</td>
<td>1.73184</td>
<td>0.00275</td>
<td>5.610</td>
<td>0.0058</td>
<td>1.0000</td>
<td>(14)</td>
</tr>
<tr>
<td>MgI(_2)</td>
<td>0.49161</td>
<td>1.78273</td>
<td>0.00780</td>
<td>5.000</td>
<td>0.0042</td>
<td>1.0000</td>
<td>(14)</td>
</tr>
<tr>
<td>Mg(ClO(_4))(_2)</td>
<td>0.50083</td>
<td>1.94817</td>
<td>0.00848</td>
<td>4.000</td>
<td>0.0065</td>
<td>0.9999</td>
<td>(22)</td>
</tr>
<tr>
<td>Mg(NO(_3))(_2)</td>
<td>0.34284</td>
<td>2.68244</td>
<td>-0.00723</td>
<td>5.000</td>
<td>0.0076</td>
<td>0.9999</td>
<td>(22)</td>
</tr>
<tr>
<td>Mg(Ac)(_2)</td>
<td>0.20801</td>
<td>1.05448</td>
<td>-0.01286</td>
<td>4.000</td>
<td>0.0065</td>
<td>0.9998</td>
<td>(22)</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>0.32579</td>
<td>1.38412</td>
<td>-0.00174</td>
<td>6.000</td>
<td>0.0158</td>
<td>0.9998</td>
<td>(14)</td>
</tr>
<tr>
<td>CaBr(_2)</td>
<td>0.33899</td>
<td>2.04551</td>
<td>0.01067</td>
<td>6.000</td>
<td>0.0071</td>
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<tr>
<td>CaI(_2)</td>
<td>0.43225</td>
<td>1.84879</td>
<td>0.00085</td>
<td>1.915</td>
<td>0.0016</td>
<td>1.0000</td>
<td>(14)</td>
</tr>
<tr>
<td>Ca(ClO(_4))(_2)</td>
<td>0.47924</td>
<td>2.16287</td>
<td>-0.00837</td>
<td>6.000</td>
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<td>0.0134</td>
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Table 1.3 (continued)

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<th>Max.m</th>
<th>SD</th>
<th>R</th>
<th>Ref.</th>
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<td>CuCl$_2$</td>
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<td>7.840</td>
<td>0.0031</td>
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<td>0.800</td>
<td>0.0021</td>
<td>0.9995</td>
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<td>FeCl$_2$</td>
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Table 1.3  (continued)

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<th>β(1)</th>
<th>Cφ</th>
<th>Max.m</th>
<th>SD</th>
<th>R</th>
<th>Ref.</th>
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<td>0.0101</td>
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<td>Zn(NO₃)₂</td>
<td>0.32587</td>
<td>1.90781</td>
<td>-0.00842</td>
<td>6.750</td>
<td>0.0028</td>
<td>1.0000</td>
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<td>Zn(C₇H₇O₃S)</td>
<td>0.11840</td>
<td>1.67138</td>
<td>-</td>
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<td>0.9999</td>
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<tr>
<td>CdCl₂</td>
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<td>Cd(C₇H₇O₃S)₂</td>
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<td>Pb(ClO₄)₂</td>
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<td>Pb(NO₃)₂</td>
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<tr>
<td>Compound</td>
<td>$\beta(0)$</td>
<td>$\beta(1)$</td>
<td>$C^\phi$</td>
<td>Max.m</td>
<td>SD</td>
<td>R</td>
<td>Ref.</td>
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<tr>
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<td>0.0042</td>
<td>0.9857</td>
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<td>$[\text{Co(NH}_3\text{)}_5\text{CH}_2\text{COO}]\text{(NO}_3\text{)}_2$</td>
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<td>0.35251</td>
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<td>0.9844</td>
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<td>0.0025</td>
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<td>0.0037</td>
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Table 1.4  Ion interaction parameters for 3-1, 1-3 electrolytes at 25 C

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<th>Compound</th>
<th>$\beta^{(0)}$</th>
<th>$\beta^{(1)}$</th>
<th>$C^\phi$</th>
<th>Max.m</th>
<th>SD</th>
<th>R</th>
<th>Ref</th>
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<td>3.800</td>
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<td>$\beta^{(1)}$</td>
<td>$C^o$</td>
<td>Max.m</td>
<td>SD</td>
<td>R</td>
<td>Ref</td>
</tr>
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<td>$g(1)$</td>
<td>$C^\phi$</td>
<td>Max. m</td>
<td>SD</td>
<td>R</td>
<td>Ref.</td>
</tr>
<tr>
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<td>5.5849</td>
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<td>0.0247</td>
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<td>Co(en)$_3$Cl$_3$</td>
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<td>Co(en)$_3$(NO$_3$)$_3$</td>
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<td>0.261</td>
<td>0.0036</td>
<td>0.9973</td>
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Table 1.5  Ion interaction parameters for 4-1,1-4 electrolytes at 25 C

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<th>Compound</th>
<th>$\beta^{(o)}$</th>
<th>$\beta^{(1)}$</th>
<th>C$^0$</th>
<th>Max.m</th>
<th>SD</th>
<th>R</th>
<th>Ref.</th>
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<td>0.00575</td>
<td>-7.4744</td>
<td>0.01015</td>
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<td>0.0132</td>
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<td>$K_4Fe(CN)_6$</td>
<td>-0.00638</td>
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<td>-</td>
<td>0.900</td>
<td>0.0155</td>
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<td>-9.2939</td>
<td>0.01591</td>
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<td>0.0099</td>
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<tr>
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<td>0.0093</td>
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<td>0.47146</td>
<td>-9.4843</td>
<td>-0.00078</td>
<td>1.800</td>
<td>0.0179</td>
<td>0.9994</td>
<td>(22)</td>
</tr>
<tr>
<td>$Th(NO_3)_4$</td>
<td>0.35392</td>
<td>-7.6453</td>
<td>-0.01869</td>
<td>5.000</td>
<td>0.0126</td>
<td>0.9997</td>
<td>(22)</td>
</tr>
<tr>
<td>$Pt(pn)_3Cl_4$</td>
<td>0.28756</td>
<td>10.7131</td>
<td>-</td>
<td>0.100</td>
<td>0.0063</td>
<td>0.9983</td>
<td>(38)</td>
</tr>
<tr>
<td>$[N(Me)_4]_4^-$</td>
<td>0.53495</td>
<td>9.6607</td>
<td>0.08620</td>
<td>1.440</td>
<td>0.0120</td>
<td>0.9988</td>
<td>(38)</td>
</tr>
</tbody>
</table>

$ATPa$ (adenosine-5'-triphosphate)
Table 1.6  Ion interaction parameters for 2-2 electrolytes at 25 C

<table>
<thead>
<tr>
<th>Compound</th>
<th>$g^{(0)}$</th>
<th>$g^{(1)}$</th>
<th>$g^{(2)}$</th>
<th>$C^*$</th>
<th>Max.m</th>
<th>SD</th>
<th>R</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO$_4$</td>
<td>0.20458</td>
<td>2.7490</td>
<td>-42.038</td>
<td>0.01886</td>
<td>1.400</td>
<td>0.00175</td>
<td>0.9999</td>
<td>(22,23)</td>
</tr>
<tr>
<td>ZnSO$_4$</td>
<td>0.18404</td>
<td>3.0310</td>
<td>-27.709</td>
<td>0.03286</td>
<td>3.500</td>
<td>0.00212</td>
<td>1.0000</td>
<td>(22,23)</td>
</tr>
<tr>
<td>CdSO$_4$</td>
<td>0.20948</td>
<td>2.6474</td>
<td>-44.473</td>
<td>0.01021</td>
<td>3.500</td>
<td>0.00265</td>
<td>0.9999</td>
<td>(22,23)</td>
</tr>
<tr>
<td>NiSO$_4$</td>
<td>0.15471</td>
<td>3.0769</td>
<td>-37.593</td>
<td>0.04301</td>
<td>2.500</td>
<td>0.00310</td>
<td>0.9999</td>
<td>(22,23)</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>0.22438</td>
<td>3.3067</td>
<td>-40.493</td>
<td>0.02512</td>
<td>3.000</td>
<td>0.00346</td>
<td>0.9999</td>
<td>(22,23)</td>
</tr>
<tr>
<td>MnSO$_4$</td>
<td>0.20563</td>
<td>2.9362</td>
<td>-38.931</td>
<td>0.01650</td>
<td>4.000</td>
<td>0.00470</td>
<td>0.9999</td>
<td>(22,23)</td>
</tr>
<tr>
<td>BeSO$_4$</td>
<td>0.31982</td>
<td>3.0540</td>
<td>-77.689</td>
<td>0.00598</td>
<td>4.000</td>
<td>0.00421</td>
<td>0.9999</td>
<td>(22,23)</td>
</tr>
<tr>
<td>UO$_2$SO$_4$</td>
<td>0.33190</td>
<td>2.4208</td>
<td>98.958</td>
<td>-0.01789</td>
<td>6.000</td>
<td>0.00224</td>
<td>1.0000</td>
<td>(22)</td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>0.20000</td>
<td>3.7762</td>
<td>-58.388</td>
<td>-</td>
<td>0.020</td>
<td>0.00460</td>
<td>0.9863</td>
<td>(23)</td>
</tr>
<tr>
<td>CoSO$_4$</td>
<td>0.20000</td>
<td>2.9709</td>
<td>-28.752</td>
<td>-</td>
<td>0.100</td>
<td>0.00248</td>
<td>0.9992</td>
<td>(23)</td>
</tr>
</tbody>
</table>
sometimes negligible. Therefore $C^{\phi}_{MX}$ is omitted in cases where the experimental data exist only in the range below 1.0 molality.

In some cases these coefficients, $C^{\phi}_{MX}$ are negative, suggesting some tendency to ion-pair formation (2). This trend appeared in most aqueous rare earth electrolyte solutions at 25°C.

For the cases of aqueous solutions of rare earth chlorides, nitrates and perchlorates, the importance of differences in the parameters $\beta_{MX}^{(1)}$ was already considered by Pitzer and colleagues (24). Thus, in this calculation, we used the values of 7.7, 8.4, and 9.8 for $(3/2) \beta_{MX}^{(1)}$ for nitrates, chlorides, and perchlorates, respectively, following Pitzer et al. (24).

**COMPARISON WITH PREVIOUSLY PUBLISHED ION INTERACTION PARAMETERS**

The ion interaction parameters for various single electrolytes were evaluated by a multiple regression method. The maximum molality fitted by our evaluation was the saturation concentration when data for saturated solutions were available. The standard deviations in fitting the osmotic coefficient for many salts, for instance, HCl, LiBr, CaBr$_2$, and Pr(NO$_3$)$_3$, seem larger than Pitzer's result (2). It is important to recognize, however, that the maximum molalities for these salts are beyond those of Pitzer's
evaluation.

The calculated mean activity coefficients for various single electrolytes from our results are shown in Figures 1.1-1.5 to give good agreement with available smoothed experimental data at high concentration. For example, the activity coefficient of HCl can be predicted with a standard deviation of 0.0285 in $\ln(\gamma_{\text{HCl}})$ over the entire concentration range up to 16.0 M in the experimental smoothed data by using our evaluation parameters in Table 1.1. However, using Pitzer's values (2) for this salt, the standard deviation is 0.2203 when the maximum molality is 16.0. These results are given in Table 1.7. Also Figure 1.1 shows the comparison of experimental smoothed mean activity coefficients of HCl as $\ln(\gamma_{\text{HCl}})$ with values calculated from Pitzer and our work. It should be noted that the fit at lower concentrations is better using the ion interaction parameters reported by Pitzer. His parameters were obtained over a more limited range of concentration (0-6 M) than ours were.

Similar results are observed in all of the cases for which the maximum molalities go beyond that of Pitzer's evaluation. That is, the Pitzer's fit gives accurate results at low concentration but poor agreements with experimental data at high concentration.

Figures 1.2 to 1.5 are the same kind of comparison plots of $\ln(\gamma_{\text{MX}})$ as a function of the molality for LiBr,
Table 1.7 Comparison of standard deviations for estimated versus experimental activity coefficients in Figures 1.1-1.5

<table>
<thead>
<tr>
<th>Salt</th>
<th>Maximum Molality</th>
<th>Standard Deviation&lt;sup&gt;1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>16.00</td>
<td>0.02854 (0.22031)</td>
</tr>
<tr>
<td></td>
<td>6.00</td>
<td>0.02956 (0.00311)</td>
</tr>
<tr>
<td>LiBr</td>
<td>20.00</td>
<td>0.07224 (0.060991)</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>0.06780 (0.00286)</td>
</tr>
<tr>
<td>CaBr&lt;sub&gt;2&lt;/sub&gt;</td>
<td>7.66</td>
<td>0.08760 (0.46557)</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>0.00732 (0.00773)</td>
</tr>
<tr>
<td>Pr(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>6.20</td>
<td>0.17827 (1.78436)</td>
</tr>
<tr>
<td></td>
<td>1.10</td>
<td>0.07117 (0.00623)</td>
</tr>
<tr>
<td>MgSO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>3.62</td>
<td>0.00574 (0.00794)</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>0.00385 (0.00317)</td>
</tr>
</tbody>
</table>

<sup>1</sup>Standard deviations in parentheses are for salts using Pitzer's ion interaction parameter values (2) which were obtained from data up to the lower concentration given in the table for each compound. The other standard deviations are based on our evaluation of ion interaction parameters from data up to the higher concentrations reported here.
CaBr$_2$, Pr(NO$_3$)$_3$, and MgSO$_4$. In all of these comparisons, the parameters we evaluated using data at high concentrations give as good or better fit to the experimental data over the entire concentration range than do Pitzer's parameters. Pitzer's parameters give a better fit over the more limited range of concentrations for which his parameter values were obtained, however. Standard deviations for the estimated versus experimental activity coefficients in Figures 1-5 (as $\ln y_{MX}$) and the maximum concentrations corresponding to Pitzer's and our ion interaction parameter evaluations are given in Table 1.7.

Ternary ion interaction parameters for various mixture with common ion will be evaluated in a subsequent paper.

ACKNOWLEDGEMENTS

We would like to thank the following companies for their advice and financial support: Associated Pulp and Paper Mills (Australia); Crown-Zellerbach Corporation; HPD, Inc.; Union Camp Corporation; Westvaco Corporation; and Weyerhaeuser Company.
Figure 1.1

Comparison of experimental smoothed $\tau_{MX}$ with values calculated from Pitzer and present work for HCl at 25°C.
Hamer and Wu (12)  Pitzer and Mayorga (2)  

![Graph showing 
\( \ln \gamma_{\text{Mx}} \) vs MOLALITY, mol/kg solvent]

- Hamer and Wu (12)
- Pitzer and Mayorga (2)
- Our correlation
Figure 1.2

Comparison of experimental smoothed $r_{MX}$ with values calculated from Pitzer and present work for LiBr at 25°C.
Hamer and Wu (12)
○ Pitzer and Mayorga (2)
▼ Our correlation

Figure 1.2

\[ \ln \gamma_{\text{MX}} \]

MOLALITY, \( \text{mol/kg solvent} \)
Figure 1.3

Comparison of experimental smoothed $r_{MX}$ with values calculated from Pitzer and present work for CaBr$_2$ at 25°C.
Figure 1.3

- Goldberg and Nuttall (14)
- Pitzer and Mayorga (2)
- Our correlation

\[ \ln \gamma_{MX} \]

MOLALITY, mol/kg solvent
Figure 1.4

Comparison of experimental smoothed $\tau_{MX}$ with values calculated from Pitzer and present work for Pr(NO$_3$)$_2$ at 25°C.
Our correlation

\[ \ln \gamma_{Mx} \]

MOLALITY, mol/kg solvent

- Rard and Miller (21)
- Pitzer et al. (24)
- Our correlation
Figure 1.5

Comparison of experimental smoothed $\tau_{MX}$ with values calculated from Pitzer and present work for MgSO$_4$ at 25°C.
Rard and Miller (40)

Pitzer and Mayorga (3)

Our correlation

Figure 1.5

\[ \ln \gamma_{Mx} \]

MOLALITY, mol/kg solvent
REFERENCES


CHAPTER 2

EVALUATION OF PITZER ION INTERACTION PARAMETERS OF
AQUEOUS MIXED ELECTROLYTE SOLUTIONS AT 25°C

2. TERNARY MIXING PARAMETERS

by

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The Pitzer mixing parameters $\theta_{ij}$ and $\Psi_{ijk}$ were evaluated for 49 ternary mixtures with common ions at 25°C. The Harvie and Weare model, which is based on Pitzer equations for aqueous mixed electrolyte solutions, was used for these evaluations. Evaluation of these parameters for mixed electrolyte solutions required only the single salt parameters and experimental values of $\ln(\tau_\pm)$ or $\phi$ for ternary mixtures with common ions. The effects of the higher order electrostatic terms were considered for all asymmetrical mixtures of electrolytes. The mean standard deviation for the calculated $\ln(\tau_\pm)$ or $\phi$ values is 0.0070 when compared with the experimental values used to obtain the ternary mixing parameters.
INTRODUCTION

In recent years there has been increasing interest in the thermodynamic properties of aqueous mixed electrolyte solutions, especially at high concentrations. In fields such as sea water desalination, geothermal energy recovery, chemical oceanography, hydrometallurgy, and pulp and paper chemistry, it is essential to have accurate data on the thermodynamic properties of mixed electrolyte solutions.

The nonideality of a single electrolyte solution is conventionally represented in terms of the mean activity coefficient, \( \tau_\pm \).

Activity coefficients are of primary importance in describing accurately the thermodynamic behavior of aqueous mixed electrolyte solutions. The lack of accurate activity coefficient predictions can result in large errors when calculating the solubility of inorganic species in aqueous multicomponent ionic solutions of high ionic strength even when only a few chemical species are present.

Among recently developed models of electrolyte solutions, ionic interaction models provide the simplest and most coherent procedures for calculating the thermodynamic properties of electrolyte components. They use a single set of equations to describe the activity and osmotic coefficients of the components of aqueous single and mixed electrolyte solutions. An ion interaction model for
predicting activity coefficients of mixed electrolyte solution was developed by Pitzer and co-workers (1-4) in the early 1970's. The Pitzer model extended the Debye-Hückel method, using a virial expansion to account for the ionic strength dependence of the short range forces in binary and ternary ion interaction. This virial expansion approach accurately represents the compositional dependence of the thermodynamic properties in most multicomponent electrolyte solutions to high ionic strengths. Also, these equations can be used in iterative calculations since the ion interaction parameters are expressed as explicit function of ionic strength, and only a few parameters are needed to evaluate properties of both single and mixed electrolyte solutions. Many publications (5-11) have shown that the Pitzer model results in excellent solubility prediction.

The purpose of this work is to obtain Pitzer mixing ion interaction parameters, $\theta_{ij}$ and $V_{ijk}$ from experimental data on aqueous mixed electrolyte solutions with common ions. The $\theta$-terms summarize interaction between ions of like charged sign that are independent of the common ion in a ternary mixture and the $V$-terms account for the modifying influence of the common ion on these interactions. The mixing ion interaction parameters from our results are stored in a computer as a database with single salt parameters, and activity or osmotic coefficients for mixed electrolyte solutions can be calculated simply by
identifying the salt and defining the appropriate ionic strength.

GENERAL EQUATION FOR MIXED ELECTROLYTE SOLUTIONS

Recently Harvie and Weare (5) have developed a chemical equilibrium model for calculating mineral solubilities in brines from zero to high ionic strengths at 25°C. This model was based on the semi-empirical equations of Pitzer and co-workers (1-4) for the thermodynamics of aqueous electrolyte solutions.

The following set of equations for mixed electrolytes are identical to the form used by Harvie and Weare (5) for modeling the osmotic coefficient and the activity coefficient of a neutral electrolyte.

\[
\phi - 1 = \frac{2}{\Sigma m_i} \left( \frac{-A_i^{1/2}}{1+b/I} + \Sigma a \Sigma m_i a \left( B_{ca}^{\phi} + Z_{ca} \right) \right) + \\
+ \sum_{c} \sum_{\mu} m^{\mu} c_{\mu} \left( \phi_{cc} + \sum_{a} m^{\mu} a c_{\mu} \right) \\
+ \sum_{a} \sum_{\mu} m^{\mu} a \left( \phi_{aa} + \sum_{c} m^{\mu} a c_{\mu} \right) \tag{1}
\]
\[ \ln \tau_{MX} = |z_M z_X| F + \left( \frac{2V_M}{V} \right) \sum_{a} m_a [B_{Ma} + \frac{Z}{2} C_{Ma} + (\frac{V_X}{V}) \phi_{Ma}] + \]

\[\left( \frac{2V_X}{V} \right) \sum_{c} m_c [B_{Cx} + \frac{Z}{2} C_{Cx} + (\frac{V_M}{V}) \phi_{cx}] + \]

\[v^{-1} \sum_{d} \sum_{c} m_c m_a [2V_M M_{ca} + V_M M_{ca} + V_X X_{ac}] + \]

\[\sum_{cc'} \sum_{M} \sum_{M} m_c m_{c'} (\frac{V_X}{V}) \phi_{cc',X} + \sum_{a} \sum_{a'} m_a m_{a'} (\frac{V_M}{V}) \phi_{aa',M} \quad (2) \]

The term \( F \) in eq 2 depends only on ionic strength and temperature. The defining equation for \( F \) is given by

\[ F = -A\phi \left[ \frac{\sqrt{I}}{1+b/I} + \frac{2}{b} \ln (1+b/I) \right] + \sum_{c} \sum_{a} m_c m_a B'_{ca} \]

\[\sum_{cc'} \sum_{M} \sum_{M} m_c m_{c'} \phi'_{cc',X} + \sum_{a} \sum_{a'} m_a m_{a'} \phi'_{aa',M} \quad (3) \]

where \( A\phi = 1/3 \left( 2\pi N_o \frac{d_{w}}{1000} \right)^{1/2} \left( e^2/DkT \right)^{3/2} \)

\( A\phi \) is the Debye-Hückel coefficient for the osmotic coefficient and equal to 0.392 for water at 25°C (2). \( N_o \) is Avogadro's number. \( d_{w} \) and \( D \) are the density and static dielectric constant of the solvent (water in this case) at temperature \( T \). Also \( k \) is Boltzmann's constant and \( e \) is the electronic charge. The empirical parameter \( b \) in eqs 1 and 3 is taken as 1.2 at 25°C (2).

In eqs 1, 2 and 3, the subscripts \( M, c \) and \( c' \) represent
cations. Similarly, the subscripts $X$, $a$ and $a'$ refer to anions. The designation $\sum_{<j=\bar{a}}$ and $\sum_{\bar{a}<j}$ in eqs 1, 2 and 3 means the sum over all distinguishable pairs of dissimilar anions or cations ($\bar{a}$). $m_M$ is molality (mol/kg solvent) of a cation with charge $z_M$ corresponding to stoichiometric coefficient $v_M$, and $v = v_M + v_X$. The function $Z$ is defined by

$$Z = \sum_i m_i |z_i| = 2(\sum_M m_M z_M^2) = 2(\sum_X m_X |z_X|)$$

and

$$I = 1/2 \sum_i m_i z_i^2$$

is the total ionic strength of given system.

The parameters $B_{MX}^\phi$, $B_{MX}$ and $B'_{MX}$ which describe the interaction of pairs of oppositely charged ions represent measurable combinations of the second virial coefficients. They are defined as explicit functions of ionic strength using the following equations.

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha_1 I} + \beta_{MX}^{(2)} e^{-\alpha_2 I} \quad (4)$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} f(\alpha_1 I) + \beta_{MX}^{(2)} f(\alpha_2 I) \quad (5)$$

$$B'_{MX} = \beta_{MX}^{(1)} f'(\alpha_1 I)/I + \beta_{MX}^{(2)} f'(\alpha_2 I)/I \quad (6)$$
For one or both ions univalent type electrolytes, the first two terms of eqs 4 and 5, and only the first term of eq 6 are considered, and $\alpha_1 = 2$ (2). For higher valence type, such as 2-2 electrolytes, the full eqs 4, 5 and 6 are used, and $\alpha_1 = 1.4$ and $\alpha_2 = 12$ (3).

The single electrolyte third virial coefficients, $C_{MX}$, account for short range interaction of ion triplets and are important only at high concentration. These terms are independent of ionic strength. The parameters $C_{MX}$ and $C^{\phi}_{MX}$, the corresponding coefficients for calculating the osmotic coefficient, are related by the following eq 9 (2).

$$C_{MX} = C^{\phi}_{MX}/2\sqrt{\frac{Z_M Z_M}{}}$$

(9)

The mixed electrolyte second virial coefficients, $\phi_{ij}$, account for interactions between ions of the same signs, and are defined by eqs 10-12.

$$\phi_{ij} = \theta_{ij} + E\theta_{ij}(I) + IE\theta'_{ij}(I)$$

(10)
\[ \phi_{ij} = \theta_{ij} + E\theta_{ij}(I) \]  

(11)

\[ \phi'_{ij} = E\theta'_{ij} \]  

(12)

\( \theta_{ij} \) is a adjustable parameter for each pair of anions or cations. The third virial coefficients, \( \varphi_{ijk} \) in eqs 1 and 2 are mixed electrolyte parameters for each cation-cation-anion and anion-anion-cation triplet in mixed electrolyte solutions. These parameters are also assumed to be independent of ionic strength.

HIGHER ORDER ELECTROSTATIC TERMS

The terms \( E\theta_{ij}(I) \) and \( E\theta'_{ij}(I) \) from eqs 10, 11, and 12 account for electrostatic unsymmetric mixing effects. Friedman (12) predicted the existence of these significant effects for unsymmetrical mixtures when ions of the same sign, but different charges, are mixed. Pitzer (13) derived equations for calculating these effects and Harvie and Weare (5) summarized Pitzer's equations in a convenient form as follows:

\[ E\theta_{MN}(I) = \frac{Z_MZ_N}{4I} \left[ J_0(X_{MN}) - \frac{1}{2} J_0(X_{MM}) - \frac{1}{2} J_0(X_{NN}) \right] \]  

(13)
where $X_{MN} = 6 z_M z_N \Phi / I$, for cations $M$ and $N$. $E_{\theta_{ij}(I)}$ and $E'_{\theta_{ij}(I)}$ are zero when $z_M = z_N$ and are functions of ionic strength, the electrolyte pair type, and temperature. For anion pairs, equations similar to eqs 13 and 14 are defined. The terms $J_0(X)$ and $J_1(X)$ are given by the following integrals.

$$J_0(X) = \frac{1}{4} X - \frac{1}{X} \int_0^\infty [1 - \exp\left(-\frac{X}{Y} e^{-Y}\right)] Y^2 \, dY$$

$$J_1(X) = \frac{1}{4} X - \frac{1}{X} \int_0^\infty [\exp(-1+\frac{X}{Y} e^{-Y})\exp(-\frac{X}{Y} e^{-Y})] Y^2 \, dY$$

These terms $J_0(X)$ and $J_1(X)$ are equal to $J(X)$ and $XJ'(X)$, respectively, which are given by Pitzer (13). Pitzer has given convenient forms (13) for evaluating approximate values of his expressions, $J(X)$ and $J'(X)$. However, we chose to evaluate the integrals $J_0(X)$ and $J_1(X)$ directly using the IMSL library subroutine DMLIN (14). We have included values of $J_0(X)$ and $J_1(X)$, calculated by our method for various $X$ values, in Table 2.1. Also, the values of $J_0(X_{MN})$, $J_1(X_{MN})$, $J_0(X_{MM})$, $J_1(X_{MM})$, $J_0(X_{NN})$, $J_1(X_{NN})$, $E_{\theta_{MN}}$, and $E'_{\theta_{MN}}$ for $MX-NX_2-H_2O$ systems where $M$ and $N$ denote the different cations.
and X denotes anion as a common ion at constant total ionic strength at 25°C are shown in Table 2.2.

EVALUATION OF MIXING ION INTERACTION PARAMETERS

The set of parameters defining the model for calculating the thermodynamic properties of mixed electrolyte solutions is $\beta_{\text{MX}}(0)$, $\beta_{\text{MX}}(1)$, $\beta_{\text{MX}}(2)$, $\text{C}^\circ_{\text{MX}}$, $\Theta_{ij}$, and $\Psi_{ijk}$. Among these parameters, $\beta_{\text{MX}}(0)$, $\beta_{\text{MX}}(1)$, $\beta_{\text{MX}}(2)$, and $\text{C}^\circ_{\text{MX}}$ are readily obtained from single salt data as shown in our earlier tabulation (15). However, for many salts, experimental data for mixtures with common ions are not available at high concentrations. For example in the system HCl-NCl$_2$-H$_2$O, where N = Ba, Ca, Co, Mg, Mn, or Ni, the maximum molality of HCl for which data is reported in the literature is 5.0 M. The maximum molality in our evaluation of single salt parameters for HCl was 16.0 M. Use of the single salt parameters evaluated at a higher concentration range may result in inaccurate values of mixing parameters. In order to avoid this problem, we reevaluated the salt parameters for pure electrolyte solutions at a reduced maximum molality which corresponded to the maximum molality for the ternary mixture data. The results for single salts are shown in Table 2.3.

The functions $B'_{\text{MX}}$, $B_{\text{MX}}$, $B''_{\text{MX}}$ and $\text{C}_{\text{MX}}$ may be calculated from their defining eqs 4, 5, 6, and 9 using single salt...
<table>
<thead>
<tr>
<th>$X$</th>
<th>$J_0(X)$</th>
<th>$J_1(X)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.00005178</td>
<td>0.00013627</td>
</tr>
<tr>
<td>0.05</td>
<td>0.00113941</td>
<td>0.00192858</td>
</tr>
<tr>
<td>0.10</td>
<td>0.00360030</td>
<td>0.00586202</td>
</tr>
<tr>
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<td>0.01088057</td>
<td>0.01699179</td>
</tr>
<tr>
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<td>0.03086422</td>
</tr>
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<td>0.03131183</td>
<td>0.04655732</td>
</tr>
<tr>
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<td>0.06357538</td>
</tr>
<tr>
<td>0.60</td>
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</tr>
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</tr>
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</tr>
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<td>0.14001019</td>
</tr>
<tr>
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<td>0.116437</td>
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</tr>
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</tr>
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</tr>
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<td>0.702924</td>
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<td>1.843571</td>
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<tr>
<td>9.00</td>
<td>1.829861</td>
<td>2.092624</td>
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<td>2.342115</td>
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<tr>
<td>20.00</td>
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<td>4.846403</td>
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<tr>
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</tr>
<tr>
<td>40.00</td>
<td>9.352336</td>
<td>9.861749</td>
</tr>
<tr>
<td>(X)</td>
<td>(J_0(X))</td>
<td>(J_1(X))</td>
</tr>
<tr>
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<td>--------</td>
<td>--------</td>
</tr>
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<td>50.00</td>
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<td>12.368340</td>
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<td>49.195521</td>
<td>49.915589</td>
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<td>149.948642</td>
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</tr>
<tr>
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<td>249.960644</td>
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<td>5000.00</td>
<td>1249.024371</td>
<td>1249.984829</td>
</tr>
<tr>
<td>10000.00</td>
<td>2499.015087</td>
<td>2499.990364</td>
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</tbody>
</table>
Table 2.2 High order electrostatic functions at constant total ionic strength for MX-NX\(_2\)-H\(_2\)O systems at 25°C

<table>
<thead>
<tr>
<th>I</th>
<th>J(_0)(X(_MN))</th>
<th>J(_1)(X(_MN))</th>
<th>J(_0)(X(_MM))</th>
<th>J(_1)(X(_MM))</th>
<th>J(_0)(X(_NN))</th>
<th>J(_1)(X(_NN))</th>
<th>E(_0)(MN)</th>
<th>E(_1)(MN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.19940</td>
<td>0.26539</td>
<td>0.07701</td>
<td>0.10892</td>
<td>0.48777</td>
<td>0.61005</td>
<td>-0.41477</td>
<td>1.79542</td>
</tr>
<tr>
<td>0.50</td>
<td>0.56037</td>
<td>0.69411</td>
<td>0.23115</td>
<td>0.30458</td>
<td>1.29014</td>
<td>1.50897</td>
<td>-0.20028</td>
<td>0.18791</td>
</tr>
<tr>
<td>1.00</td>
<td>0.85538</td>
<td>1.02870</td>
<td>0.36238</td>
<td>0.46284</td>
<td>1.92487</td>
<td>2.19437</td>
<td>-0.14413</td>
<td>0.06915</td>
</tr>
<tr>
<td>1.50</td>
<td>1.08934</td>
<td>1.28860</td>
<td>0.46839</td>
<td>0.58755</td>
<td>2.42142</td>
<td>2.72253</td>
<td>-0.11852</td>
<td>0.03830</td>
</tr>
<tr>
<td>2.00</td>
<td>1.29014</td>
<td>1.50897</td>
<td>0.56037</td>
<td>0.69411</td>
<td>2.84431</td>
<td>3.16855</td>
<td>-0.10305</td>
<td>0.02513</td>
</tr>
<tr>
<td>2.50</td>
<td>1.46915</td>
<td>1.70378</td>
<td>0.64298</td>
<td>0.78879</td>
<td>3.21934</td>
<td>3.56185</td>
<td>-0.09240</td>
<td>0.01810</td>
</tr>
<tr>
<td>3.00</td>
<td>1.63239</td>
<td>1.88029</td>
<td>0.71875</td>
<td>0.87490</td>
<td>3.55999</td>
<td>3.91760</td>
<td>-0.08450</td>
<td>0.01383</td>
</tr>
<tr>
<td>3.50</td>
<td>1.78349</td>
<td>2.04287</td>
<td>0.78920</td>
<td>0.95442</td>
<td>3.87437</td>
<td>4.24486</td>
<td>-0.07833</td>
<td>0.01102</td>
</tr>
<tr>
<td>4.00</td>
<td>1.92487</td>
<td>2.19437</td>
<td>0.85538</td>
<td>1.02870</td>
<td>4.16781</td>
<td>4.54953</td>
<td>-0.07334</td>
<td>0.00904</td>
</tr>
<tr>
<td>4.50</td>
<td>2.05825</td>
<td>2.33679</td>
<td>0.91799</td>
<td>1.09864</td>
<td>4.44407</td>
<td>4.83572</td>
<td>-0.06920</td>
<td>0.00760</td>
</tr>
<tr>
<td>5.00</td>
<td>2.18486</td>
<td>2.47160</td>
<td>0.97760</td>
<td>1.16495</td>
<td>4.70586</td>
<td>5.10643</td>
<td>-0.06569</td>
<td>0.00650</td>
</tr>
</tbody>
</table>
parameter values which are given in Table 2.3 and our earlier paper (15). Mixed electrolyte terms $\phi_{ij}$, $\phi_{ij}$, and $\phi'_{ij}$ were obtained from $E_{ij}$ and $E_{ij}'$ values, calculated from eqs 13 and 14. The remaining terms in eqs 1, 2, and 3 contain $\Theta_{ij}$ and $\Psi_{ijk}$ which are the adjustable parameters in our evaluation for mixed electrolyte solutions with common ions.

Pitzer (4) suggested simplified equations and a simple graphical procedure for evaluation of $\Theta_{ij}$ and $\Psi_{ijk}$. For the activity and osmotic coefficients of an MX-NX mixture, he obtained

$$\Delta \phi \left( \frac{\sum m_i}{2m_Mm_N} \right) = \Theta_{MN} + m_X\Psi_{MNX}$$  \hspace{1cm} (18)$$

and

$$\Delta \ln \tau_{MX} \left( \frac{v}{Z_MZ_N} \right) = \Theta_{MN} + \frac{1}{2} (m_X + m_M\left|\frac{Z_M}{Z_X}\right|) \Psi_{MNX}$$  \hspace{1cm} (19)$$

The terms $\Delta \phi$ and $\Delta \ln \tau_{MX}$ are the difference between the experimental values of $\phi$ or $\ln \tau_{MX}$ and the calculated values of $\phi$ or $\ln \tau_{MX}$ with the appropriate single salt parameters values for the pure single electrolyte terms, but with $\Theta_{MX} = \Psi_{MNX} = 0$ in eqs 1 and 2.

The quantity on the left-hand side of eq 18 or 19 is plotted against the coefficients of on the right-hand side.
Table 2.3 Ion interaction parameters for single salts at 25°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\beta^{(0)}$</th>
<th>$\beta^{(1)}$</th>
<th>$C^\phi$</th>
<th>Max.m</th>
<th>$SD^a$</th>
<th>$R^b$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>0.18024</td>
<td>0.27154</td>
<td>0.00006</td>
<td>6.00</td>
<td>0.0013</td>
<td>1.000</td>
<td>(16)</td>
</tr>
<tr>
<td>HBr</td>
<td>0.19622</td>
<td>0.34529</td>
<td>0.00762</td>
<td>4.00</td>
<td>0.0006</td>
<td>1.000</td>
<td>(16)</td>
</tr>
<tr>
<td>HClO$_4$</td>
<td>0.17238</td>
<td>0.31708</td>
<td>0.00855</td>
<td>6.00</td>
<td>0.0019</td>
<td>1.000</td>
<td>(16)</td>
</tr>
<tr>
<td>LiCl</td>
<td>0.14667</td>
<td>0.33703</td>
<td>0.00393</td>
<td>6.00</td>
<td>0.0020</td>
<td>1.000</td>
<td>(16)</td>
</tr>
<tr>
<td>LiBr</td>
<td>0.17362</td>
<td>0.25976</td>
<td>0.00556</td>
<td>4.50</td>
<td>0.0016</td>
<td>1.000</td>
<td>(16)</td>
</tr>
<tr>
<td>LiNO$_3$</td>
<td>0.14060</td>
<td>0.28894</td>
<td>-0.00547</td>
<td>6.00</td>
<td>0.0012</td>
<td>1.000</td>
<td>(16)</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.09934</td>
<td>0.26202</td>
<td>0.00097</td>
<td>5.00</td>
<td>0.0010</td>
<td>1.000</td>
<td>(16)</td>
</tr>
<tr>
<td>NaN$_3$</td>
<td>0.00479</td>
<td>0.20241</td>
<td>-0.00027</td>
<td>6.00</td>
<td>0.0005</td>
<td>0.999</td>
<td>(17)</td>
</tr>
<tr>
<td>NaH$_2$PO$_4$</td>
<td>-0.06509</td>
<td>0.09100</td>
<td>0.01138</td>
<td>4.00</td>
<td>0.0023</td>
<td>0.998</td>
<td>(16)</td>
</tr>
<tr>
<td>NaClO$_4$</td>
<td>0.05621</td>
<td>0.27177</td>
<td>-0.00143</td>
<td>5.00</td>
<td>0.0005</td>
<td>1.000</td>
<td>(16)</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>0.07185</td>
<td>1.15645</td>
<td>-0.00835</td>
<td>1.50</td>
<td>0.0007</td>
<td>0.999</td>
<td>(18)</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>0.02800</td>
<td>0.04400</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>(19)</td>
</tr>
<tr>
<td>KCl</td>
<td>0.04680</td>
<td>0.22096</td>
<td>-0.00050</td>
<td>4.00</td>
<td>0.0003</td>
<td>1.000</td>
<td>(16)</td>
</tr>
<tr>
<td>KH$_2$PO$_4$</td>
<td>-0.11280</td>
<td>0.06058</td>
<td>0.02012</td>
<td>1.80</td>
<td>0.0003</td>
<td>1.000</td>
<td>(16)</td>
</tr>
<tr>
<td>CsCl</td>
<td>0.02995</td>
<td>0.06367</td>
<td>0.00027</td>
<td>6.00</td>
<td>0.0007</td>
<td>0.999</td>
<td>(16)</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>0.30654</td>
<td>1.64278</td>
<td>0.00222</td>
<td>3.50</td>
<td>0.0028</td>
<td>1.000</td>
<td>(20)</td>
</tr>
<tr>
<td>CaBr$_2$</td>
<td>0.36272</td>
<td>1.81585</td>
<td>0.00349</td>
<td>2.50</td>
<td>0.0016</td>
<td>1.000</td>
<td>(20)</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$</td>
<td>0.18472</td>
<td>1.64500</td>
<td>-0.01069</td>
<td>4.00</td>
<td>0.0074</td>
<td>0.999</td>
<td>(21)</td>
</tr>
<tr>
<td>CoCl$_2$</td>
<td>0.35623</td>
<td>1.54019</td>
<td>-0.01251</td>
<td>3.00</td>
<td>0.0039</td>
<td>0.999</td>
<td>(22)</td>
</tr>
<tr>
<td>CuCl$_2$</td>
<td>0.31373</td>
<td>1.24607</td>
<td>-0.04222</td>
<td>2.00</td>
<td>0.0021</td>
<td>0.999</td>
<td>(23)</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>0.35372</td>
<td>1.70054</td>
<td>0.00524</td>
<td>5.00</td>
<td>0.0029</td>
<td>1.000</td>
<td>(20)</td>
</tr>
<tr>
<td>Mg(NO$_3$)$_2$</td>
<td>0.36516</td>
<td>1.59563</td>
<td>-0.01971</td>
<td>2.00</td>
<td>0.0023</td>
<td>1.000</td>
<td>(21)</td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>0.34657</td>
<td>1.58940</td>
<td>-0.00326</td>
<td>2.50</td>
<td>0.0020</td>
<td>1.000</td>
<td>(22)</td>
</tr>
<tr>
<td>MnCl$_2$</td>
<td>0.33547</td>
<td>1.46033</td>
<td>-0.02324</td>
<td>3.50</td>
<td>0.0012</td>
<td>1.000</td>
<td>(23)</td>
</tr>
</tbody>
</table>
Table 2.3  (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\beta(0)$</th>
<th>$\beta(1)$</th>
<th>$c^d$</th>
<th>Max.m</th>
<th>SD$^a$</th>
<th>R$^b$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$(ClO$_4$)$_2$</td>
<td>0.62346</td>
<td>1.97357</td>
<td>0.02084</td>
<td>2.50</td>
<td>0.0030</td>
<td>1.000</td>
<td>(23)</td>
</tr>
<tr>
<td>La(C1O$_4$)$_3$</td>
<td>0.76485</td>
<td>6.53333</td>
<td>0.00275</td>
<td>3.00</td>
<td>0.0007</td>
<td>0.999</td>
<td>(24)</td>
</tr>
</tbody>
</table>

$^a$ SD; standard deviation of fit for the osmotic coefficient data
$^b$ R; multiple correlation coefficient which is a measure of the closeness of linear relationship
$^c$ used the values of Peiper and Pitzer [see ref.(19)]
The values of $\theta_{MN}$ and $\psi_{MNX}$ are obtained from the linear plot as the intercept, $\theta_{MN}$ and the slope, $\psi_{MNX}$ respectively.

However Khoo (53) pointed out the disadvantage of this procedure. According to Khoo, eqs 18 and 19 represent a nonlinear plot particularly at low molality of the solute $NX$. That is, the uncertainties in $\Delta \phi$ and $\Delta \ln r_{MX}$ are greatly magnified at low values of the coefficients of $\psi_{MNX}$ in eqs 18 and 19, so that one must observe the least square fitting carefully. The validity of Khoo's indication was clearly represented in Figures 2.1 and 2.2, which show plots of $\ln r_A/m_B$ versus $\frac{1}{2}(m_{H^+} + m_{Cl^-})$ from eq 19 for the $HCl(A)-BaCl_2(B)-H_2O$ system (35) and the $HCl(A)-CaCl_2(B)-H_2O$ system (37), respectively.

Our method of obtaining $\theta_{ij}$ and $\psi_{ijk}$ considered all experimental points in a fitting to eq 1 or 2 using multiple regression. We used the regression package in Number Cruncher Statistical System (NCSS) (54). The resulting values of mixing parameters, $\theta_{ij}$ and $\psi_{ijk}$, for 49 ternary mixtures with common ions at 25°C are listed in Table 2.4.

It was suggested that the same pair of cations or anions should have the same value of $\theta_{ij}$ but different values of $\psi_{ijk}$ in ternary or multicomponent mixtures. For example, the value of $\theta_{HNa}=0.0368$ in the present study was selected by considering all system (HCl-NaCl-H$_2$O, HBr-NaBr-H$_2$O, and HClO$_4$-NaClO$_4$-H$_2$O) which contain both of $H^+$ and $Na^+$. 
Figure 2.1

Fits of equation 19 for HCl-BaCl₂-H₂O system at 25°C.
Figure 2.1
Figure 2.2

Fits of equation 19 for HCl-CaCl₂-H₂O system at 25°C
Figure 2.2
DISCUSSION

Although Pitzer (13) has pointed out that the higher order electrostatic effects may be ignored for several $M^{+}-N^{+2}$ systems, we included these effects for all ternary mixtures of asymmetrical electrolytes with common ions. Table 2.4 shows that the standard deviations in $\ln \gamma_\pm$ or $\phi$ are less than 0.01 in 38 systems among the total 49 sets of ternary mixtures which were considered in the present work. The mean standard deviation for the 49 data sets is 0.0070. Only for two systems, however, the standard deviations in $\phi$ are above 0.02. These latter results are due to the relatively large values of ionic strengths (Max. $I = 18.25$ mol/kg for CaCl$_2$-Ca(NO$_3$)$_2$-H$_2$O and 14.25 mol/kg for NaClO$_4$-UO$_2$(ClO$_4$)$_2$-H$_2$O) in those two systems. A comparison between the calculated values using our results and experimental values of $\ln \gamma_\pm$ or $(\phi-1)$ for several systems is shown in Figure 2.3. It is clear that $\ln \gamma_\pm$ or $\phi$ for mixed electrolyte solutions with common ions can be predicted accurately by using our evaluated values of ternary mixing parameters.

In order to compare our results with previously published mixing parameter values, we chose HX-CaX systems with $X = \text{Cl}$ and Br. The activity coefficients of these systems have been measured and interpreted, based on the Pitzer equations, by various methods. Khoo et. al. (38, 55)
<table>
<thead>
<tr>
<th>System</th>
<th>Exptl</th>
<th>θ</th>
<th>Ψ</th>
<th>SD (θ &amp; Ψ)</th>
<th>SD (θ=Ψ=0)</th>
<th>Max.I</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC1-KCl</td>
<td>lnY</td>
<td>0.0067</td>
<td>-0.0081</td>
<td>0.0128</td>
<td>0.0177</td>
<td>3.51</td>
<td>(25)</td>
</tr>
<tr>
<td>HBr-KBr</td>
<td>lnY</td>
<td>0.0067</td>
<td>-0.0215</td>
<td>0.0065</td>
<td>0.0257</td>
<td>3.01</td>
<td>(25)</td>
</tr>
<tr>
<td>HC1-NaCl</td>
<td>lnY</td>
<td>0.0368</td>
<td>-0.0033</td>
<td>0.0014</td>
<td>0.0439</td>
<td>3.01</td>
<td>(25)</td>
</tr>
<tr>
<td>HBr-NaBr</td>
<td>lnY</td>
<td>0.0368</td>
<td>-0.0107</td>
<td>0.0032</td>
<td>0.0323</td>
<td>3.01</td>
<td>(25)</td>
</tr>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;-NaClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>♦</td>
<td>0.0368</td>
<td>-0.0162</td>
<td>0.0017</td>
<td>0.0163</td>
<td>5.35</td>
<td>(26)</td>
</tr>
<tr>
<td>HC1-LiCl</td>
<td>lnY</td>
<td>0.0151</td>
<td>-0.0022</td>
<td>0.0052</td>
<td>0.0215</td>
<td>4.01</td>
<td>(25)</td>
</tr>
<tr>
<td>HClO&lt;sub&gt;4&lt;/sub&gt;-LiClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>♦</td>
<td>0.0151</td>
<td>0.0000</td>
<td>0.0028</td>
<td>0.0109</td>
<td>4.45</td>
<td>(26)</td>
</tr>
<tr>
<td>HBr-LiBr</td>
<td>lnY</td>
<td>0.0151</td>
<td>0.0101</td>
<td>0.0141</td>
<td>0.0351</td>
<td>3.01</td>
<td>(25)</td>
</tr>
<tr>
<td>HC1-CaCl</td>
<td>lnY</td>
<td>-0.0459</td>
<td>0.0040</td>
<td>0.0100</td>
<td>0.0371</td>
<td>3.00</td>
<td>(27)</td>
</tr>
<tr>
<td>NaCl-KCl</td>
<td>lnY</td>
<td>0.0070</td>
<td>-0.0098</td>
<td>0.0112</td>
<td>0.0274</td>
<td>4.30</td>
<td>(28)</td>
</tr>
<tr>
<td>NaH&lt;sub&gt;2&lt;/sub&gt;P&lt;sub&gt;4&lt;/sub&gt;-KH&lt;sub&gt;2&lt;/sub&gt;P&lt;sub&gt;4&lt;/sub&gt;</td>
<td>♦</td>
<td>0.0070</td>
<td>-0.0162</td>
<td>0.0072</td>
<td>0.0302</td>
<td>6.04</td>
<td>(29)</td>
</tr>
<tr>
<td>NaCl-LiCl</td>
<td>♦</td>
<td>0.0120</td>
<td>-0.0022</td>
<td>0.0020</td>
<td>0.0027</td>
<td>5.84</td>
<td>(30)</td>
</tr>
<tr>
<td>NaNO&lt;sub&gt;3&lt;/sub&gt;-LiNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>♦</td>
<td>0.0120</td>
<td>-0.0065</td>
<td>0.0028</td>
<td>0.0216</td>
<td>5.92</td>
<td>(30)</td>
</tr>
<tr>
<td>NaOAc-LiOAc</td>
<td>♦</td>
<td>0.0120</td>
<td>-0.065</td>
<td>0.0064</td>
<td>0.0185</td>
<td>6.05</td>
<td>(30)</td>
</tr>
<tr>
<td>NaClO&lt;sub&gt;4&lt;/sub&gt;-LiClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>♦</td>
<td>0.0120</td>
<td>-0.0061</td>
<td>0.0028</td>
<td>0.0094</td>
<td>5.82</td>
<td>(26)</td>
</tr>
<tr>
<td>KCl-KH&lt;sub&gt;2&lt;/sub&gt;P&lt;sub&gt;4&lt;/sub&gt;</td>
<td>♦</td>
<td>0.1071</td>
<td>-0.0160</td>
<td>0.0026</td>
<td>0.0243</td>
<td>2.07</td>
<td>(29)</td>
</tr>
<tr>
<td>NaCl-NaH&lt;sub&gt;2&lt;/sub&gt;P&lt;sub&gt;4&lt;/sub&gt;</td>
<td>♦</td>
<td>0.1071</td>
<td>-0.0147</td>
<td>0.0048</td>
<td>0.0335</td>
<td>2.37</td>
<td>(29)</td>
</tr>
</tbody>
</table>
Table 2.4 (continued)

<table>
<thead>
<tr>
<th>System</th>
<th>Exptl</th>
<th>$\theta$</th>
<th>$\psi$</th>
<th>SD ($\theta$ &amp; $\psi$)</th>
<th>SD ($\psi = 0$)</th>
<th>Max. I</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl-NaF</td>
<td>$\ln\gamma$</td>
<td>-0.0028</td>
<td>0.0076</td>
<td>0.0019</td>
<td>0.0021</td>
<td>1.05</td>
<td>(10,31)</td>
</tr>
<tr>
<td>NaCl-NaHCO₃</td>
<td>$\ln\gamma$</td>
<td>0.0735</td>
<td>0.0989</td>
<td>0.0135</td>
<td>0.0200</td>
<td>1.10</td>
<td>(32)</td>
</tr>
<tr>
<td>HCl-CoCl₂</td>
<td>$\ln\gamma$</td>
<td>0.0829</td>
<td>0.0075</td>
<td>0.0039</td>
<td>0.0310</td>
<td>3.00</td>
<td>(33)</td>
</tr>
<tr>
<td>HCl-MgCl₂</td>
<td>$\ln\gamma$</td>
<td>0.0895</td>
<td>0.0044</td>
<td>0.0039</td>
<td>0.0316</td>
<td>3.00</td>
<td>(34)</td>
</tr>
<tr>
<td>HCl-BaCl₂</td>
<td>$\ln\gamma$</td>
<td>0.0991</td>
<td>-0.0081</td>
<td>0.0050</td>
<td>0.0300</td>
<td>3.00</td>
<td>(35)</td>
</tr>
<tr>
<td>HBr-BaBr₂</td>
<td>$\ln\gamma$</td>
<td>0.0991</td>
<td>0.0035</td>
<td>0.0060</td>
<td>0.0268</td>
<td>2.00</td>
<td>(36)</td>
</tr>
<tr>
<td>HCl-CaCl₂</td>
<td>$\ln\gamma$</td>
<td>0.0682</td>
<td>0.0043</td>
<td>0.0046</td>
<td>0.0120</td>
<td>5.00</td>
<td>(37)</td>
</tr>
<tr>
<td>HBr-CaBr₂</td>
<td>$\ln\gamma$</td>
<td>0.0682</td>
<td>0.0285</td>
<td>0.0060</td>
<td>0.0284</td>
<td>2.00</td>
<td>(38)</td>
</tr>
<tr>
<td>HCl-MnCl₂</td>
<td>$\ln\gamma$</td>
<td>0.0899</td>
<td>-0.0092</td>
<td>0.0050</td>
<td>0.0372</td>
<td>5.00</td>
<td>(39)</td>
</tr>
<tr>
<td>HCl-MgCl₂</td>
<td>$\ln\gamma$</td>
<td>0.0891</td>
<td>-0.0066</td>
<td>0.0065</td>
<td>0.0483</td>
<td>5.00</td>
<td>(40)</td>
</tr>
<tr>
<td>HCl-SrCl₂</td>
<td>$\ln\gamma$</td>
<td>0.0728</td>
<td>0.0050</td>
<td>0.0016</td>
<td>0.0286</td>
<td>3.00</td>
<td>(41)</td>
</tr>
<tr>
<td>HBr-SrBr₂</td>
<td>$\ln\gamma$</td>
<td>0.0728</td>
<td>0.0310</td>
<td>0.0055</td>
<td>0.0197</td>
<td>2.00</td>
<td>(42)</td>
</tr>
<tr>
<td>HClO₄⁻-UO₂(ClO₄)₂</td>
<td>$\delta$</td>
<td>0.1377</td>
<td>-0.0319</td>
<td>0.0131</td>
<td>0.0603</td>
<td>10.88</td>
<td>(43)</td>
</tr>
<tr>
<td>KCl-SrCl₂</td>
<td>$\delta$</td>
<td>0.0149</td>
<td>-0.0201</td>
<td>0.0018</td>
<td>0.0214</td>
<td>4.80</td>
<td>(44)</td>
</tr>
<tr>
<td>LiCl-BaCl₂</td>
<td>$\delta$</td>
<td>0.0243</td>
<td>0.0208</td>
<td>0.0057</td>
<td>0.0188</td>
<td>4.32</td>
<td>(45)</td>
</tr>
<tr>
<td>CaCl-BaCl₂</td>
<td>$\delta$</td>
<td>-0.0441</td>
<td>-0.0229</td>
<td>0.0026</td>
<td>0.0167</td>
<td>4.08</td>
<td>(45)</td>
</tr>
<tr>
<td>System</td>
<td>Exptl</td>
<td>θ</td>
<td>ψ</td>
<td>SD (θ &amp; ψ)</td>
<td>SD (θ=ψ=0)</td>
<td>Max.I</td>
<td>Ref.</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>--------</td>
<td>------</td>
<td>-------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>NaCl-MnCl₂</td>
<td>♦</td>
<td>0.0907</td>
<td>-0.0190</td>
<td>0.0019</td>
<td>0.0130</td>
<td>9.30</td>
<td>(46)</td>
</tr>
<tr>
<td>NaCl-CoCl₂</td>
<td>♦</td>
<td>0.0382</td>
<td>-0.0056</td>
<td>0.0036</td>
<td>0.0063</td>
<td>7.29</td>
<td>(47)</td>
</tr>
</tbody>
</table>
| NaCl⁺⁺⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓   


Figure 2.3

Comparison of experimental and calculated $\ln r_\pm$ or $(\phi-1)$ for various systems at 25°C.
Figure 2.3

- HCl-NaCl (ln $\gamma_\pm$)
- Na$_2$SO$_4$-MgSO$_4$ ($\phi$-1)
- Na$_2$SO$_4$-CuSO$_4$ ($\phi$-1)
- HCl-CoCl$_2$ (ln $\gamma_\pm$)

1% Coeff. of Variation
obtained the values of $\theta_{HCa}=0.0739$ and $\Psi_{HCaCl}=0.003$ for HCl-CaCl$_2$-H$_2$O and $\theta_{HCa}=0.0600$ and $\Psi_{HCaBr}=0.0009$ for HBr-CaBr$_2$-H$_2$O, respectively. Also, $\theta_{HCa}=0.0612$ and $\Psi_{HCaBr}=0.0008$ were obtained for HCl-CaCl$_2$-H$_2$O by Roy et al. (37). These values are close to, but not identical with, our result in Table 2.4. This is due to the following reasons:

1. Roy et al. (37) used a linear plot of eq 19, as suggested by Pitzer (4) to obtain $\theta_{HCa}$ and $\Psi_{HCaCl}$, while Khoo et al. (38, 55) utilized a nonlinear regression method in eq 2. We used multiple linear regression with eq 2 to obtain $\theta_{HCa}$ and $\Psi_{HCaX}$ for both systems, HCl-CaCl$_2$-H$_2$O and HBr-CaBr$_2$-H$_2$O simultaneously.

2. Khoo et al. (38, 55) covered ionic strengths only up to 3.0 mol/kg for HCl-CaCl$_2$-H$_2$O, but Roy et al. (37) and our work included data up to $I = 5.0$ mol/kg for HCl-CaCl$_2$-H$_2$O.

It can be seen from Table 2.4 that $\theta_{MN}$ values for the HX-NX$_2$-H$_2$O systems, where X = Cl Br, and N = Co, Ni, Ba, Ca, Mn, Mg, and Sr, are close to each other. This could be expected to define an average value for $\theta_{HN}$ and to characterize $H^+$ and $N^{+2}$ interactions which are not specific to the $N^{+2}$ ion. The average value of $\theta_{HN}$ is 0.0838 in the present work, whereas $\theta_{HN} = 0.078$ obtained by Khoo et al (33) for six HCl-NCl$_2$-H$_2$O systems where N = Mg, Ca, Sr, Ba, Mn and Co.
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REFERENCES


CHAPTER 3

CORRELATION OF PITZER ION INTERACTION PARAMETERS

by

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The Pitzer model equations follow from a virial expansion of the excess Gibbs free energy, but are semi-empirical rather than the theoretically suggested form. Thus the exact physical meaning and interrelationship between the ion interaction parameters are not fully understood. The application of Pitzer's method for estimating activity coefficients in aqueous solutions also is often limited by the lack of ion interaction parameters for the species of interest.

The purposes of this part of the work are to correlate Pitzer ion interaction parameters with ionic properties, i.e., ionic charge, radius and entropy, and to use the correlations as a method of estimating the ion interaction parameters for the Pitzer equations for activity coefficients from available data. In other words, the goal of the correlation effort is to find a way to minimize the amount of experimental data required to obtain a set of ion interaction parameters. Correlations were developed for group IA and IIA compounds using available ion interaction parameters and the values of ionic properties at 25°C. Correlations were also developed for both binary and ternary parameters. The applicability of the correlations were evaluated by comparing their estimates of activity coefficients with experimental data.
Correlations of this type will make it possible to use the more accurate Pitzer method for activity coefficient estimation without the need for hundreds of experimental measurements.

ORDER OF MAGNITUDES OF ION INTERACTION PARAMETERS AND TEMPERATURE EFFECTS

The ion interaction parameters in the Pitzer equations differ in magnitude, so their contributions become important at different ionic strengths, as shown in Table 3.1.

The range of values for each of the coefficients varies by more than a factor of 10, so concentrations where each becomes important differs considerably from ion to ion. However, the $\beta$ terms obviously have the greatest influence over a large part of the range of concentrations of industrial interest. It should be also remembered that the principal effects on aqueous mixed electrolyte solutions arise from difference in the binary ion interaction parameters and that the ternary parameters, $\theta$ and $\psi$ have only a small effect, if any.

Another important consideration is the effect of temperature on activity coefficients. Pitzer noted that the dominating temperature effect on activity coefficients is the change in the dielectric constant ($1, 2$); the changes in the ion interaction parameters with temperature are small ($3$). He suggests making only the Debye-Hückel constant, $A$,
Table 3.1  Comparison of magnitudes of ion interaction parameters

<table>
<thead>
<tr>
<th>Term</th>
<th>Order of magnitude</th>
<th>Specie concentrations where terms Approch O[f(I)]</th>
<th>Exceed $\beta$ terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f(I)$</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta'$s</td>
<td>1.0</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.001</td>
<td>10.0</td>
<td>1000</td>
</tr>
<tr>
<td>$\theta$</td>
<td>0.1</td>
<td>1.0</td>
<td>10</td>
</tr>
<tr>
<td>$\psi$</td>
<td>0.01</td>
<td>2.0</td>
<td>10</td>
</tr>
</tbody>
</table>
in the activity coefficient equation temperature dependent. The ion interaction parameters can be treated as temperature independent.

THEORETICAL BASIS FOR CORRELATING ION INTERACTION PARAMETERS

Structure-making and -breaking ions

In 1933, Bernal and Fowler (4) introduced the concept of the special structure of water into the discussion of the properties of aqueous electrolyte solutions. This structure of water can be affected by the addition of salts which ionize. Blandamer (5) describes these effects as occurring in three zones of water structure around each ion. According to this approach, a charged solvated ion is surrounded by two concentric spheres: Zone I (hydration shell), between the surface of the ion and the first sphere, contains the electrostricted water molecules; Zone III (the bulk water), beyond the outer sphere, includes the water molecules which have essentially the same structure as in pure water, and whose structure is unaffected by the ion; and Zone II (the structure-broken layer), between the two concentric spheres, is subject to the competing demands of water structures associated with zone I and zone III. Generally, since the influences of zone I and zone III on zone II show differently, the water structure in zone II is broken down. In other words, water molecules in zone II
are more disoriented than bulk water. Zone I contributes negative entropy while zone II contributes positive entropy to the system. Which zone predominates depends on the size, shape and charge of the specific ions in the aqueous electrolytes.

Using this concept, ions are considered structure breaking ions, if their effect is to disorder nearby water molecules, creating a large zone II. These are the typically large diameter, monovalent ions which decrease the solution viscosity, and increase its specific volume and entropy. Structure making ions, on the other hand, have little or no disruptive influence on water molecules outside their hydration layer. These are small, high charge density ions where zone I predominates. Their influence on solution properties is opposite that of structure breaking ions. The order of monatomic ions in this scheme follows the order of the corresponding elements in the Periodic Table: that is, smaller ions of a given family are more structure making. Examples for cations and anions, in order of structure making influence are

\[
\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} > \text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+ \\
\text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^-
\]

The influence of ion pairs (i.e., single salt solutions) on activity coefficients is determined mainly by the structure making/breaking influence of the individual ions. Gurney (6) observed that the more similar the cation and
anion in structural influence, the lower will be the stoichiometric activity coefficient of the corresponding salt. Hence, for alkali bromides, where Br$^-$ is structure breaking, the order of the activity coefficients (at the same total molality) is

LiBr > KBr > RbBr > CsBr

For hydroxide (a structure-making ion) compounds, the order is CsOH > KOH > NaOH > LiOH

The ionic potential and entropy

The above is one indication of the qualitative relationship between ionic charge ($Z$), ionic radius ($r$), and solution properties. Ionic charge and radius are often used as qualitative indicators or correlation parameters for solution properties. Ionic charge and ionic radius act in opposite direction in determining the properties of substances. For examples, polarization will be increased by high charge and small size of the cation ($Z$), and oxides are increasingly acidic the higher the charge or the smaller the radius of the cation for constant charge ($\hat{8}$).

According to Cartledge ($\hat{8}, \hat{9}$), the ratio of ionic charge and radius is an important periodic property of the ions and may be made the basis of a quantitative classification. This is often expressed by the ionic potential, $P_i = \frac{Z_i}{r_i}$, where $Z_i$ is the charge and $r_i$ is the radius of $i$. The Coulombic term, $Z^2/r$, which is similar in form to the ionic
potential, is another logical correlating variable. The general relationship $Z^m/r^n$ ($m,n=1,2,...$) is often used and give similar result for different values of $m$ and $n$ (7). Wood et. al (10) demonstrated a correlation between the activity coefficient and the ionic potential ratio, $P_C/P_A$, for several salts using Pauling's crystal ionic radii.

While ionic potential (or $Z^m/r^n$) terms are the primary variable in determining solution properties, there are reasons to expect other factors will affect correlations. For example, ions with the same charge and radius may have different entropies as a result of their differing electron configurations (7). Thus the $Z/r$ functional dependence of ion properties will be different for different groups. For that reason, ion entropy may be a better correlating parameter than ionic potential for example. These two variables correlate well, which indicates that other parameters may have only secondary effects. Depending on the accuracy required when estimating the various ion interaction parameters, the effects of factors other than ion entropy or ionic potential may be negligible.

Ions may be grouped in several ways for the purpose of accounting for structural differences. For example, Beutier and Renon (11) used Harned and Owen's classification of ions as monovalent cations, halogenides, oxygenerated polyatomic anions, and proton acceptors to correlate the sum of Pitzer ion interaction parameters, $\beta(0)+\beta(1)$ versus common ion
entropy. Criss and Cobble (12) used the categories simple cations (uni- and multi-valent), simple anions and OH\textsuperscript{-}, oxy anions, and acid oxy anions to correlate solution heat capacity with ion entropy.

CORRELATION OF BINARY ION INTERACTION PARAMETERS

Very little has been published regarding the estimation of ion interaction parameters for Pitzer's method. Pitzer (3) reported a correlation between two of the binary interaction parameters, $\beta(0)$ and $\beta(1)$. Staples (13) found that $\beta(0)$ correlates well with $Z^2/r$, where $Z$ is the charge on the cation and $r$ is the ionic radius, for group IA, IIA, and 8 cations. He also found that the apparent molar heat capacity of transition metal ions correlated with $Z^2/r$ (14).

The salts to be used in this study include:
1. group IA (Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Rb\textsuperscript{+}, Cs\textsuperscript{+}) halides
2. group IA chlorates, perchlorates, nitrates, acetates, and hydroxides
3. group IA sulfates
4. group IIA (Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Sr\textsuperscript{2+}, Ba\textsuperscript{2+}) halides
5. group IIA chlorates, and nitrates

They were chosen for the following reasons:
1. these group compounds represent the typical electrolyte solutions for 1-1, 1-2, and 2-1 type,
2. groups IA, IIA, and the halides constitute
distinct and well characterized groups for correlation purposes,

3. the halides should associate minimally, especially with the group IA cations,

4. many of the compounds are of industrial importance, and

5. there are more activity and osmotic coefficient data available for compounds from these groups than for any other combination of group in the Periodic Table.

As shown in Table 3.1, $\beta$'s for single electrolyte solutions are of the order of 1, whereas $C^\phi$ is of the order of 0.001. The small value of $C^\phi$ means that the contribution of triple ion interaction to the thermodynamic properties is negligible at low concentration and is still small at high molality. The sensitivity of estimated activity coefficients to $\beta^{(0)}$ and $\beta^{(1)}$ was examined for the 1-1, 1-2, and 2-1 types of electrolytes. The results of NaCl, Na$_2$SO$_4$, and MgCl$_2$ are listed in Table 3.2. From these results, it is obvious that the predicted activity coefficients are more sensitive to $\beta^{(0)}$ than to $\beta^{(1)}$. Especially, for MgCl$_2$, if $\beta^{(0)}$ deviates 50% from the evaluated value, a large difference occurs between the experimental value and predicted value at molalities exceeding 0.1 M. Thus a correlation method must predict the $\beta^{(0)}$ accurately if it is
Table 3.2  Comparison with estimated $\tau_\pm$ for 1-1, 1-2, and 2-1 type of electrolytes

<table>
<thead>
<tr>
<th>M (mol/kg)</th>
<th>$\tau_\pm$ (exptl)</th>
<th>$\tau_\pm^a$</th>
<th>$\tau_\pm^b$</th>
<th>$\tau_\pm^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaCl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.822</td>
<td>0.820</td>
<td>0.823</td>
<td>0.828</td>
</tr>
<tr>
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<td>0.779</td>
<td>0.777</td>
<td>0.783</td>
<td>0.789</td>
</tr>
<tr>
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<td>0.681</td>
<td>0.679</td>
<td>0.706</td>
<td>0.710</td>
</tr>
<tr>
<td>1.00</td>
<td>0.657</td>
<td>0.655</td>
<td>0.708</td>
<td>0.694</td>
</tr>
<tr>
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<td>0.654</td>
<td>0.717</td>
<td>0.695</td>
</tr>
<tr>
<td>1.40</td>
<td>0.656</td>
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<td>0.729</td>
<td>0.697</td>
</tr>
<tr>
<td>1.60</td>
<td>0.658</td>
<td>0.657</td>
<td>0.743</td>
<td>0.701</td>
</tr>
<tr>
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Table 3.2 (continued)

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<tr>
<th>M (mol/kg)</th>
<th>( \tau_{\pm}(\text{exptl}) )</th>
<th>( \tau_{\pm}^{a} )</th>
<th>( \tau_{\pm}^{b} )</th>
<th>( \tau_{\pm}^{c} )</th>
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<tr>
<td>MgCl\textsubscript{2}</td>
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<tr>
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<td>0.590</td>
<td>0.584</td>
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<td>0.10</td>
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<td>0.530</td>
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<td>0.759</td>
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<td>0.893</td>
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<tr>
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<td>3.621</td>
<td>3.580</td>
<td>18.657</td>
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<td>3.75</td>
<td>4.523</td>
<td>4.471</td>
<td>26.211</td>
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<td>5.607</td>
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<tr>
<td>4.25</td>
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<td>11.324</td>
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<td>14.417</td>
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<tr>
<td>5.25</td>
<td>18.298</td>
<td>18.415</td>
<td>219.042</td>
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<tr>
<td>5.50</td>
<td>23.329</td>
<td>23.596</td>
<td>315.802</td>
<td>28.542</td>
</tr>
</tbody>
</table>

\( ^{a} \) using the original evaluated values of \( \beta^{(0)} \) and \( \beta^{(1)} \)

\( ^{b} \) using 50% deviated value of \( \beta^{(0)} \)

\( ^{c} \) using 50% deviated value of \( \beta^{(1)} \)
to provide accurate estimates of activity coefficients. Less accuracy is required for the other parameters; the accuracy requirement increases as the concentrations of the species for which calculations are increase.

A correlation can be observed between $\beta^{(0)}$ and $\beta^{(1)}$ for various valence types of electrolytes. It provides the basis for a convenient approximation as shown by Chen et. al (15). In order to get a good correlation between $\beta^{(0)}$ and $\beta^{(1)}$ for compounds which are included in this work, the binary ion interaction parameters were reevaluated at a reduced maximum molality up to 6 M. The results are included in Table 3.3. Although Beutier and Renon (11) used Pitzer's correlation between $\beta^{(0)}$ and $\beta^{(1)}$; $\beta^{(0)}/(\beta^{(0)}+\beta^{(1)})=0.3$ for 1-1 salts, it was observed that a simpler relationship which provides a first approximation can be obtained between $\beta^{(0)}$ and $\beta^{(1)}$ for various valence type of electrolytes which were covered in this work. The ratio, $\beta^{(0)}/\beta^{(1)}$ has close to the value 0.424 for 1-1 type, 0.087 for 1-2 type, and 0.200 for 2-1 type of electrolytes. The values of $\beta^{(0)}$ and $\beta^{(1)}$ for 1-1 type electrolyte solutions are plotted in Figure 3.1. Using this result, it is possible to obtain directly an approximate values of the activity coefficients for any given electrolytes if only $\beta^{(0)}$ is known. Similar figures could, of course, be obtained for higher valence types.
Table 3.3 Ion interaction parameters for single electrolytes at 25°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\beta^{(0)}$</th>
<th>$\beta^{(1)}$</th>
<th>$C\phi$</th>
<th>Max.m</th>
<th>SD</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO$_4$</td>
<td>0.1725</td>
<td>0.3158</td>
<td>0.0085</td>
<td>6.0</td>
<td>0.0019</td>
<td>1.00</td>
</tr>
<tr>
<td>LiI</td>
<td>0.2104</td>
<td>0.3730</td>
<td>-</td>
<td>1.5</td>
<td>0.0060</td>
<td>1.00</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.0768</td>
<td>0.2669</td>
<td>0.0012</td>
<td>6.0</td>
<td>0.0007</td>
<td>1.00</td>
</tr>
<tr>
<td>NaI</td>
<td>0.1253</td>
<td>0.3064</td>
<td>0.0004</td>
<td>6.0</td>
<td>0.0004</td>
<td>1.00</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.0897</td>
<td>0.2803</td>
<td>0.0034</td>
<td>6.0</td>
<td>0.0023</td>
<td>1.00</td>
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<tr>
<td>KF</td>
<td>0.0798</td>
<td>0.2148</td>
<td>0.0011</td>
<td>6.0</td>
<td>0.0004</td>
<td>1.00</td>
</tr>
<tr>
<td>KOH</td>
<td>0.1552</td>
<td>0.1709</td>
<td>-0.0006</td>
<td>6.0</td>
<td>0.0004</td>
<td>1.00</td>
</tr>
<tr>
<td>RbCl</td>
<td>0.0444</td>
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<td>-0.0012</td>
<td>6.0</td>
<td>0.0004</td>
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<tr>
<td>Mg(NO$_3$)$_2$</td>
<td>0.3272</td>
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<tr>
<td>Ca(ClO$_4$)$_2$</td>
<td>0.4664</td>
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<td>Ca(NO$_3$)$_2$</td>
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<tr>
<td>Sr(ClO$_4$)$_2$</td>
<td>0.4313</td>
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<td>1.00</td>
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<tr>
<td>Ba(ClO$_4$)$_2$</td>
<td>0.3157</td>
<td>2.0028</td>
<td>-0.0149</td>
<td>4.0</td>
<td>0.0084</td>
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</table>
Figure 3.1

The relationship of $\beta^{(0)}$ to $\beta^{(1)}$ for 1-1 type Electrolytes.
Figure 3.1
Sources of data

Pitzer ion interaction parameters for more than 300 single salts and for 49 sets of two salts with common ion were obtained in parts 1 and 2 of this study from published activity and osmotic coefficient data at 25°C.

Ion entropies are available at 25°C from Glushko (16) and Wagman et. al (17). Ionic radii are available from several sources, i.e., Morris(18) and Marcus(19). Marcus recommends using hydrated ion radius when correlating or estimating ion properties. He obtained the aqueous ionic radii of 35 ions. He used the obtained data of the average distances between the ions and the nearest water molecules from the extensive studies that have been conducted in recent years by means of neutron and X-ray diffraction and by means of computer simulation methods.

IA group compounds (1-1 type electrolytes)

It was observed that values of $\beta(0)$ can be correlated with ionic properties for alkali compounds. Figure 3.2 and 3.3 show that $\beta(0)$ for alkali halides correlated well with the standard state molar entropy, $S^0(J/mol K)$, and the standard state molar entropy of ion in aqueous solution, $S^0_+(J/mol K)$ respectively. The same kind of plots for alkali chlorates, perchlorates, nitrates, acetates, and hydroxides were given in Figure 3.4 and 3.5. From these figures, it is obvious that the trends of $\beta(0)$'s are the
Figure 3.2

Correlation between $\beta^{(0)}$ and the standard state molar entropy, $S^\circ$ (J/mol K) for alkali halides.
Figure 3.3

Correlation between $\beta^{(0)}$ and the standard state molar entropy of cation, $S^0_+$ (J/mol K) for alkali halides.
Figure 3.3
Figure 3.4

Correlation between $\beta^{(0)}$ and the standard state molar entropy, $S^0$ (J/mol K) for alkali chlorates, perchlorate (included HClO$_4$ and NH$_4$ClO$_4$), nitrates (included HNO$_3$), acetates, and hydroxides.
Figure 3.4
Figure 3.5
Correlation between $\beta(0)$ and the standard state molar entropy of cation, $S^0_\text{c}$ (J/mol K) for alkali chlorates, perchlorate (included HClO$_4$ and NH$_4$ClO$_4$), nitrates (included HNO$_3$), acetates, and hydroxides. Symbols for alkali compounds are chlorates $\square$, perchlorates $\blacksquare$, nitrates $+$, acetates $\bullet$, and hydroxides $\blacktriangle$. 
Figure 3.5
same as those of activity coefficients for alkali compounds. Therefore the trends of activity coefficients can be predicted by this kind of correlation. The different behavior of structure-making anions (F\(^-\), OH\(^-\), and CH\(_3\)COO\(^-\)) and structure-breaking anions (Cl\(^-\), Br\(^-\), I\(^-\), NO\(_3\)\(^-\), ClO\(_3\)\(^-\), and ClO\(_4\)\(^-\)) is also evident in Figure 3.2-3.5. The correlation results for each class are listed in Table 3.4. The correlation lines allow the evaluation of \(\beta^{(0)}\) for a new compound in any class.

Figure 3.6 and 3.7 show similar results for correlation between \(\beta^{(0)}\) for alkali compounds and the reciprocal of the ionic radius of anion (since the square of the ionic charge is 1 for all of these salts). The aqueous ionic radii of Marcus (19) which are given in Table 3.5 were used in this correlation work in lieu of the crystal ionic radii. Pauling's ionic (crystal) radii(20), however, may be used to get the correlation when Marcus's are not available, as recommended by Marcus. For Rb\(^+\), Pauling's value (0.0148 nm) were used as a tentative value of \(r_{aq}\). The results of this correlation are also given in Table 3.6.

The difference between the chlorides, bromides, and iodides are eliminated when \(\beta^{(0)}\) is plotted against the ratio of the ionic potentials (defined as \(P_C/P_a\)) for the two ions (Figure 3.8). Values of \(P_C/P_a\) and the correlation results for alkali halides are given in Table 3.7 and 3.8 respectively. Wood et. al (10) proposed the ratio, \(P_C/P_a\)
Table 3.4 Results of regressions between $\beta(0)$ and $S^0$, or $S^{0+}$ for alkali compounds

<table>
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<tr>
<th>Class</th>
<th>Regression output</th>
<th>SD</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali fluorides</td>
<td>$\beta(0)=-0.0333+0.0014*S^0$</td>
<td>0.008</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>$\beta(0)=-0.0519+0.0014*S^{0+}$</td>
<td>0.008</td>
<td>0.99</td>
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<tr>
<td>Alkali chlorides</td>
<td>$\beta(0)=0.1994-0.0009*S^0$</td>
<td>0.013</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>$\beta(0)=0.1476-0.0009*S^{0+}$</td>
<td>0.013</td>
<td>0.97</td>
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<tr>
<td>Alkali bromides</td>
<td>$\beta(0)=0.2826-0.0012*S^0$</td>
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</tr>
<tr>
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<td>$\beta(0)=0.1827-0.0012*S^{0+}$</td>
<td>0.008</td>
<td>0.99</td>
</tr>
<tr>
<td>Alkali iodides</td>
<td>$\beta(0)=0.3979-0.0015*S^0$</td>
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<td>1.00</td>
</tr>
<tr>
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<td>$\beta(0)=0.2261-0.0015*S^{0+}$</td>
<td>0.007</td>
<td>1.00</td>
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<tr>
<td>Alkali chlorates</td>
<td>$\beta(0)=0.6829-0.0029*S^0$</td>
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<td>$\beta(0)=0.2044-0.0029*S^{0+}$</td>
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<tr>
<td>Alkali perchlorates*</td>
<td>$\beta(0)=0.5243-0.0018*S^0$</td>
<td>0.036</td>
<td>0.95</td>
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<tr>
<td></td>
<td>$\beta(0)=0.1917-0.0018*S^{0+}$</td>
<td>0.036</td>
<td>0.95</td>
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<tr>
<td>Alkali nitrates**</td>
<td>$\beta(0)=0.4241-0.0020*S^0$</td>
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<td>$\beta(0)=0.1352-0.0020*S^{0+}$</td>
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<td>Alkali acetates</td>
<td>$\beta(0)=0.0714+0.0005*S^0$</td>
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<td>$\beta(0)=0.1058+0.0005*S^{0+}$</td>
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<td>1.00</td>
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<tr>
<td>Alkali hydroxides</td>
<td>$\beta(0)=0.0474+0.0010*S^0$</td>
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<tr>
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<td>$\beta(0)=0.0365+0.0010*S^{0+}$</td>
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* included HClO₄ and NH₄ClO₄
** included HNO₃
Table 3.5  Aqueous Ionic Radii

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<th>raq (nm)</th>
<th>Ion</th>
<th>raq (nm)</th>
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<tr>
<td>Na⁺</td>
<td>0.098±0.003</td>
<td>Pr³⁺</td>
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<tr>
<td>K⁺</td>
<td>0.134±0.004</td>
<td>Nd³⁺</td>
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<tr>
<td>Cs⁺</td>
<td>0.169±0.005</td>
<td>Sm³⁺</td>
<td>0.106±0.004</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.166±0.005</td>
<td>Eu³⁺</td>
<td>0.106±0.004</td>
</tr>
<tr>
<td>OH³⁻</td>
<td>0.113±0.005</td>
<td>Gd³⁺</td>
<td>0.100±0.004</td>
</tr>
<tr>
<td>Mg²⁺</td>
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<td>Tb³⁺</td>
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<tr>
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<td>0.103±0.003</td>
<td>Dy³⁺</td>
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<tr>
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<td>Er³⁺</td>
<td>0.098±0.005</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.073±0.005</td>
<td>Tm³⁺</td>
<td>0.097±0.005</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>0.070±0.002</td>
<td>Lu³⁺</td>
<td>0.095±0.005</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>0.068±0.003</td>
<td>F⁻</td>
<td>0.135±0.014</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>0.069±0.005</td>
<td>Cl⁻</td>
<td>0.183±0.003</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.059±0.005</td>
<td>Br⁻</td>
<td>0.194±0.003</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>0.095±0.004</td>
<td>I⁻</td>
<td>0.222±0.002</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>0.049±0.002</td>
<td>NO₃⁻</td>
<td>0.206±0.006</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>0.060±0.002</td>
<td>SO₄²⁻</td>
<td>0.240±0.005</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.065±0.005</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Correlation between $\beta^{(0)}$ and the Coulombic term, $Z^2/r$
which is logical correlating variable for alkali
halides, where $Z$ is the charge on the cation and $r$ (nm)
is the aqueous ionic radius of cation.
For $\text{Rb}^+$, Pauling's value (=0.148 nm) were chosen.
Figure 3.6
Figure 3.7

Correlation between $\beta^{(0)}$ and the Coulombic term, $Z^2/r$ which is logical correlating variable for alkali chlorates, nitrates, hydroxides, and acetates, where $Z$ is the charge on the cation and $r(\text{nm})$ is the aqueous ionic radius of cation; Ac, Acetate($\text{CH}_3\text{COOH}$) ion.
Figure 3.7
Table 3.6 Results of regressions between $\beta^{(0)}$ and $Z*Z/r$ for alkali compounds

<table>
<thead>
<tr>
<th>Class</th>
<th>Regression output</th>
<th>SD</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali fluorides</td>
<td>$\beta^{(0)}=0.2682-0.0236*(Z*Z/r)$</td>
<td>0.009</td>
<td>0.99</td>
</tr>
<tr>
<td>Alkali chlorides</td>
<td>$\beta^{(0)}=-0.0485+0.0130*(Z*Z/r)$</td>
<td>0.005</td>
<td>0.99</td>
</tr>
<tr>
<td>Alkali bromides</td>
<td>$\beta^{(0)}=-0.0745+0.0169*(Z*Z/r)$</td>
<td>0.003</td>
<td>1.00</td>
</tr>
<tr>
<td>Alkali iodides</td>
<td>$\beta^{(0)}=-0.0980+0.0213*(Z*Z/r)$</td>
<td>0.010</td>
<td>0.99</td>
</tr>
<tr>
<td>Alkali chlorates</td>
<td>$\beta^{(0)}=-0.3556+0.0360*(Z*Z/r)$</td>
<td>0.009</td>
<td>1.00</td>
</tr>
<tr>
<td>Alkali perchlorates*</td>
<td>$\beta^{(0)}=0.0320+0.0242*(Z*Z/r)$</td>
<td>0.032</td>
<td>0.98</td>
</tr>
<tr>
<td>Alkali nitrates</td>
<td>$\beta^{(0)}=-0.3001+0.0299*(Z*Z/r)$</td>
<td>0.011</td>
<td>1.00</td>
</tr>
<tr>
<td>Alkali acetates</td>
<td>$\beta^{(0)}=0.2152-0.0078*(Z*Z/r)$</td>
<td>0.003</td>
<td>0.98</td>
</tr>
<tr>
<td>Alkali hydroxides</td>
<td>$\beta^{(0)}=0.2461-0.0137*(Z*Z/r)$</td>
<td>0.015</td>
<td>0.97</td>
</tr>
</tbody>
</table>

* include NH$_4$ClO$_4$
Figure 3.8

Plot of $\beta^{(0)}$ versus the ionic potential ratio, $P_C/P_a$ for alkali halides.
Figure 3.8
Table 3.7 Ionic potential ratios for alkali halides using ionic radii in aqueous solutions from Marcus (1983)

<table>
<thead>
<tr>
<th>Salt</th>
<th>(PC/PA = (Zc/rc)/(Za/ra))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>1.985</td>
</tr>
<tr>
<td>LiCl</td>
<td>2.691</td>
</tr>
<tr>
<td>LiBr</td>
<td>2.853</td>
</tr>
<tr>
<td>LiI</td>
<td>3.265</td>
</tr>
<tr>
<td>NaF</td>
<td>1.378</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.867</td>
</tr>
<tr>
<td>KF</td>
<td>1.980</td>
</tr>
<tr>
<td>KCl</td>
<td>1.980</td>
</tr>
<tr>
<td>KBr</td>
<td>1.448</td>
</tr>
<tr>
<td>KI</td>
<td>1.657</td>
</tr>
<tr>
<td>RbF*</td>
<td>0.912</td>
</tr>
<tr>
<td>RbCl*</td>
<td>1.237</td>
</tr>
<tr>
<td>RbBr*</td>
<td>1.311</td>
</tr>
<tr>
<td>RbI*</td>
<td>1.500</td>
</tr>
<tr>
<td>CsF</td>
<td>0.799</td>
</tr>
<tr>
<td>CsCl</td>
<td>1.083</td>
</tr>
<tr>
<td>CsBr</td>
<td>1.148</td>
</tr>
<tr>
<td>CsI</td>
<td>1.314</td>
</tr>
</tbody>
</table>

* used Pauling's ionic radius (Rb\(^+\)=0.148 nm)
Table 3.8 Results of regression between $\beta(0)$ and $P_c/P_a$ for alkali halides

<table>
<thead>
<tr>
<th>Class</th>
<th>Regression output</th>
<th>Standard error of $\beta(0)$ estimate</th>
<th>$R$ squared</th>
<th>No. of observations</th>
<th>Degree of freedom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali halides (except fluorides)</td>
<td>$\beta(0) = -0.0738 + 0.0856(P_c/P_a)$</td>
<td>0.0094</td>
<td>0.9762</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Standard error of $\beta(0)$ estimate</td>
<td>0.0094</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R$ squared</td>
<td>0.9762</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>No. of observations</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Degree of freedom</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkali fluorides</td>
<td>$\beta(0) = 0.2689 - 0.1752(P_c/P_a)$</td>
<td>0.0108</td>
<td>0.9605</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Standard error of $\beta(0)$ estimate</td>
<td>0.0108</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R$ squared</td>
<td>0.9605</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>No. of observations</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Degree of freedom</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
should approach unity for salts whose cation and anion have similar effects on the structure of water.

**IIA group compounds (2-1 type electrolytes)**

It was also observed that the values of $\beta^{(0)}$ for IIA group compounds correlated well with respect to the ionic properties as found with group IA compounds. The correlations of $\beta^{(0)}$ with $S^0$, $S^{0+}$, and $Z^+Z/r$ for alkali earth metal halides, perchlorates, and nitrates are shown in Figure 3.9, 3.10, and 3.11 respectively. The solid lines represented the regression lines which allow the prediction of $\beta^{(0)}$ for a given value of ionic properties. Marcus obtained the values of $r_{aq}$ for Mg$^{+2}$ and Ca$^{+2}$ in alkali earth metal ions, so Pauling's values for Sr$^{+2}$ and Ba$^{+2}$ were used. Table 3.9 gives the simple correlation results that fit the $\beta^{(0)}$.

**IA group compounds (1-2 type electrolytes)**

According to Figures 3.12-3.15, one finds interesting correlations between $\beta^{(0)}$ and ionic properties (charge, radius, and entropy) for alkali sulfates. A linear correlations do not exist for these compounds. However, the values of $\beta^{(0)}$ for alkali sulfates correlated well with ionic properties when a quadratic equation is used. The trends of $\beta^{(0)}$ for these compounds coincide with the trends in the calculated activity coefficients. The correlation
Figure 3.9

Correlation between $\beta^{(0)}$ and the standard state molar entropy, $S^0$ (J/mol K) for alkali earth metal halides (except fluorides), perchlorates, and nitrates.
Figure 3.9
Figure 3.10

Correlation between $\beta^{(0)}$ and the standard state molar entropy of cation, $S_{\beta}^{0+}$ (J/mol K) for alkali earth metal halides (except fluorides), perchlorates, and nitrates.
Figure 3.10
Correlation between $\beta^{(0)}$ and the Coulombic term, $Z^2/Z/r$ for alkali earth metal halides, perchlorates, and nitrates; $Z$ is the charge on the cation and $r$ (nm) is the ionic radius. For Sr$^{+2}$ and Ba$^{+2}$, Pauling's values were used (Sr$^{+2}$: 0.113 nm, Ba$^{+2}$: 0.135 nm).
Figure 3.11
Table 3.9  Results of regressions between $\beta^{(0)}$ and ionic properties ($S^0$, $S^{0+}$, and $Z*Z/r$) for alkali earth metal compounds

<table>
<thead>
<tr>
<th>Class</th>
<th>Regression output</th>
<th>SD</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali earth metal chlorates</td>
<td>$0.2873-0.00048*S^0$</td>
<td>0.018</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>$0.3426-0.00048*S^{0+}$</td>
<td>0.018</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>$0.2037+0.00276*(Z*Z/r)$</td>
<td>0.018</td>
<td>0.90</td>
</tr>
<tr>
<td>Alkali earth metal bromides</td>
<td>$0.3076-0.00085*S^0$</td>
<td>0.018</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>$0.4483-0.00085*S^{0+}$</td>
<td>0.018</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>$0.1595+0.00486*(Z*Z/r)$</td>
<td>0.012</td>
<td>0.98</td>
</tr>
<tr>
<td>Alkali earth metal iodides</td>
<td>$0.3943-0.00066*S^0$</td>
<td>0.019</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>$0.5427-0.00066*S^{0+}$</td>
<td>0.019</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>$0.2790+0.00379*(Z*Z/r)$</td>
<td>0.016</td>
<td>0.95</td>
</tr>
<tr>
<td>Alkali earth metal chlorates</td>
<td>$0.3631-0.00111*S^0$</td>
<td>0.032</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>$0.7673-0.00111*S^{0+}$</td>
<td>0.032</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>$0.1849+0.00596*(Z*Z/r)$</td>
<td>0.039</td>
<td>0.90</td>
</tr>
<tr>
<td>Alkali earth metal nitrates</td>
<td>$0.0168-0.00241*S^0$</td>
<td>0.036</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>$0.7252-0.00241*S^{0+}$</td>
<td>0.036</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>$-0.3805+0.0132*(Z*Z/r)$</td>
<td>0.057</td>
<td>0.96</td>
</tr>
</tbody>
</table>
Figure 3.12

Correlation between $\beta^{(0)}$ and the standard state molar entropy, $S^\circ$ (J/mol K) for alkali sulfates.
Figure 3.12
Figure 3.13

Correlation between $\beta^{(0)}$ and the standard state molar entropy of cation, $S_{\text{c}}^0$ (J/mol K) for alkali sulfates.
Figure 3.13
Figure 3.14

Correlation between $\beta^{(0)}$ and the Coulombic term, $Z^2Z/r$ for alkali sulfates, where $Z$ is the charge on the cation and $r$(nm) is the aqueous ionic radius of cation. For Rb$^+$, Pauling's value ($=0.148$ nm) were used.
Figure 3.14
Figure 3.15

Plot of $\beta^{(0)}$ versus the ionic potential ratio, $P_C/P_a$ for alkali sulfates.
Figure 3.15
results are represented in Table 3.10.

CORRELATION OF TERNARY ION INTERACTION PARAMETERS

Since the effect of any interaction is proportional to the concentration of the ion involved, little error will be made by omitting the values of $\theta$ and $\psi$ for ions present at low concentration even if the total ionic strength is high. As shown in Table 3.1, $\theta$ is of the order of 0.1 and $\psi$ is of the order of 0.001. According to Lim et. al (21), the Pitzer ternary ion interaction parameter, $\psi_{HNX}$ for the HX-NX$_2$-H$_2$O systems (X=Cl, Br, ..., and N=Mg, Ca, Sr,...) can be conveniently set to zero without loss in accuracy in the representation of the experimental results.

Among the available data for Pitzer ternary ion interaction parameters, HX-MX-H$_2$O systems (M=Li, Na, K, Cs, and X=Cl, Br, I, ClO$_4$) and HX-NX$_2$-H$_2$O systems (N=Ca, Mg, Sr, Ba, Ni, Co, Mn and X=Cl, Br) were chosen to examine the correlation between $\theta$ and ionic entropy. For HX-MX-H$_2$O systems, available values of $\theta_{HM}$ are plotted in Figure 3.16 as a function of ionic entropy of M$^+$. These values of $\theta_{HM}$ fall on a smooth curve with a maximum point. Table 3.11 represents the comparison of $\theta_{HM}$ for HX-MX-H$_2$O systems and curve fitting result. The same kind of procedure for HX-NX$_2$-H$_2$O systems is illustrated in Figure 3.17. The systems which included the alkali earth metal compounds and
Table 3.10 Results of regression between $\beta(0)$ and ionic properties ($S^0$, $S^{0+}$, $Z*Z/r$, and $P_c/P_a$) for alkali sulfates

<table>
<thead>
<tr>
<th>Class</th>
<th>Regression output</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali sulfates</td>
<td>$Y = 0.2378 - 0.0023X_1 + 6.812 \times 10^{-6}X_1^2$</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>$Y = 0.1935 - 0.0040X_2 + 2.716 \times 10^{-5}X_2^2$</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>$Y = 0.5739 - 0.1045X_3 + 0.0051X_3^2$</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>$Y = 0.5735 - 0.8701X_4 + 0.3558X_4^2$</td>
<td>0.99</td>
</tr>
</tbody>
</table>

dependent variable: $Y = \beta(0)$

independent " $X_1 = S^0 \ (J/mol \ K)$

$X_2 = S^{0+} \ (J/mol \ K)$

$X_3 = Z*Z/r \ (nm)$

$X_4 = P_c/P_a$
Figure 3.16

Plot of $\theta_{HM}$ versus $S^0_+ \text{ (J/mol K)}$ for HX-MX-H$_2$O systems, where M = Li, Na, K, Cs and X = Cl, Br, I, ClO$_4$. 
Figure 3.16
Table 3.11 Comparison of $\theta_{HM}$ and $S^O_{M+}$, and curve fitting result for HX-MX-H$_2$O systems

<table>
<thead>
<tr>
<th>M</th>
<th>X</th>
<th>$\theta_{HM}$</th>
<th>$S^O_{+}$(J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Cl, Br, ClO$_4$</td>
<td>0.0151</td>
<td>13.40</td>
</tr>
<tr>
<td>Na</td>
<td>Cl, Br, ClO$_4$</td>
<td>0.0368</td>
<td>59.00</td>
</tr>
<tr>
<td>K</td>
<td>Cl, Br</td>
<td>0.0067</td>
<td>102.50</td>
</tr>
<tr>
<td>Cs</td>
<td>Cl</td>
<td>-0.0459</td>
<td>133.05</td>
</tr>
</tbody>
</table>

Regression output

$$\theta_{HM} = -0.0021 + 0.0015 \times (S^O_+) - 1.341 \times 10^{-5} \times (S^O_+)^2$$

$R = 1.00$
Figure 3.17

Plot of $\theta_{HN}$ versus $S^O_{++}$ (J/mol K) for HX-NX$_2$-H$_2$O systems, where N= Ca, Mg, Sr, Ba, Ni, Co, Mn and X= Cl, Br.
Figure 3.17
transition metal compounds show the similar tendency fall on the smooth curve with a minimum value. The results for these systems are summarized in Table 3.12. These results indicate the Pitzer's ternary parameter is a function of the ionic entropy. The structure-making and -breaking characteristic of the ions appear to have an influence on the ternary parameter as Gurney observed for activity coefficients for single salt solutions.

**COMPARISON OF CORRELATION RESULTS WITH EXPERIMENTAL DATA**

Figure 3.18 and 3.19 show comparisons between the evaluated values using correlation results and experimental values of activity coefficients for sodium halides (NaCl, NaBr, NaI, and NaF) and other sodium compounds (NaNO\textsubscript{3}, NaClO\textsubscript{4}, NaClO\textsubscript{3}, NaOH, and NaAc) respectively. The solid lines represent the calculation values as predicted by the correlation results of $\beta^{(0)}$ versus $S^0$. The experimental data are from Hamer and Wu (22, 23).

In general, the correlation results predicted accurately the activity coefficients of these group IA compounds as 1-1 type electrolytes. The mean values of the relative deviation as the absolute values for activity coefficients are less than 5.0\% except for sodium chlorate (6.18\%) and sodium perchlorate (10.07\%). For alkali perchlorates, there are no experimental data for KClO\textsubscript{4},
Table 3.12  Comparison of $\theta_{HN}$ and $S_{N+2}^{0}$, and curve fitting result for HX-NX$_2$-H$_2$O systems

<table>
<thead>
<tr>
<th>N</th>
<th>X</th>
<th>$\theta_{HN}$</th>
<th>$S_{N+2}^{0}$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(alkali earth metal compounds)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>Cl</td>
<td>0.0891</td>
<td>-138.10</td>
</tr>
<tr>
<td>Ca</td>
<td>Cl, Br</td>
<td>0.0682</td>
<td>-53.10</td>
</tr>
<tr>
<td>Sr</td>
<td>Cl, Br</td>
<td>0.0728</td>
<td>-32.60</td>
</tr>
<tr>
<td>Ba</td>
<td>Cl, Br</td>
<td>0.0991</td>
<td>9.60</td>
</tr>
<tr>
<td>(transition metal compounds)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>Cl</td>
<td>0.0895</td>
<td>-128.90</td>
</tr>
<tr>
<td>Co</td>
<td>Cl</td>
<td>0.0829</td>
<td>-113.00</td>
</tr>
<tr>
<td>Mn</td>
<td>Cl</td>
<td>0.0899</td>
<td>-73.60</td>
</tr>
</tbody>
</table>

Regression output

1. N= Mg, Ca, Sr, Ba

\[
\theta_{HN} = 0.0916 + 7.208 \times 10^{-4} (S_{N}^{0}) + 5.093 \times 10^{-6} (S_{N}^{0})^2 \\
R = 1.00
\]

2. N= Ni, Co, Mn

\[
\theta_{HN} = 0.1921 + 0.0022 (S_{N}^{0}) + 1.072 \times 10^{-5} (S_{N}^{0})^2 \\
R = 1.00
\]
Figure 3.18
Comparison of experimental smoothed $r_\pm$ with calculated from correlation for NaCl, NaBr, NaI, and NaF at 25°C.
Figure 3.18
Figure 3.19

Comparison of experimental smoothed $r_\pm$ with calculated from correlation for NaNO$_3$, NaClO$_4$, NaClO$_3$, NaOH, and NaAc at 25°C.
Figure 3.19
RbClO₄, and CsClO₄. Thus the experimental data for HClO₄, and NH₄ClO₄ have been added to get the correlation relationship for perchlorates. It is clear that the correlation result for alkali perchlorates including HClO₄, and NH₄ClO₄ is not as good as other class.

In Figure 3.20a, 3.20b, and 3.20c, activity coefficients of alkali sulfates (1-2 type electrolytes) from experimental source and correlation results are plotted as a function of molality. The maximum mean of the absolute values of the relative deviation is 19.2% for Cs₂SO₄. For the higher valence types, the plot of β(0) versus β(1) shows more scatter than that of 1-1 type but a clear trend of β(0) with β(1) is still apparent. Especially, in the case of Cs₂SO₄, the ratio of β(0) and β(1) has a relatively large deviation from the average value of 0.09 for 1-2 type of electrolytes.

Figure 3.21a and 3.21b are the same kinds of plots as in Figure 3.20, for magnesium halides (MgCl₂, MgBr₂, and MgI₂), magnesium perchlorate, and magnesium nitrate. The mean of the absolute values of the relative deviation of these compounds also indicate the increasing tendency to the compare with 1-1 type. However, this value is within about 10%, which is very reasonable for solutions of this type at a maximum concentration of I= 9.

Figure 3.22 ia a another plot of comparisons of activity coefficients of HCl in the ternary mixture at 25°C
Figure 3.20

Comparison of experimental smoothed $r_\pm$ with calculated from correlation results; (a) for Li$_2$SO$_4$, Na$_2$SO$_4$, and K$_2$SO$_4$, (b) for Rb$_2$SO$_4$ and (c) for Cs$_2$SO$_4$ at 25°C.
Figure 3.20a
Figure 3.20b

Figure 3.20c
Comparison of experimental smoothed $r_\pm$ with calculated from correlation results: (a) for MgI$_2$, MgBr$_2$, and MgCl$_2$, (b) for Mg(ClO$_4$)$_2$ and Mg(NO$_3$)$_2$ at 25°C.
Figure 3.21a

Figure 3.21b
Figure 3.22

Comparison of experimental values of $r_{\text{HCl}}$ for HCl-MgCl$_2$-H$_2$O system with values calculated from correlation at various ionic strengths.
Figure 3.22
and various ionic strengths. The ternary ion interaction parameter, $\theta_{HMG}$ for system of HCl-MgCl$_2$-H$_2$O and binary parameters for MgCl$_2$ were evaluated by using the correlations. The results from using the correlations fit the experimental data well. The experimental points are data from Roy et. al (24).

**DISCUSSION**

Many of the trends in the calculated activity coefficients of electrolyte solutions can be explained by structure-making and -breaking correlation. It is shown that values of $\beta^{(0)}$ are the higher the more dissimilar are the ions and the lower the more similar the ions. Note that this trend of ion interaction parameter, $\beta^{(0)}$ is the same as activity coefficients at 25°C.

The alkali metal halides (chlorides, bromides, and iodides) each class have $\beta^{(0)}$ values in decreasing order for Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$, but for alkali metal fluorides, there is a increasing trend of $\beta^{(0)}$ from NaF to CsF, as shown in Figure 3.2, 3.3, and 3.6. The decrease in $\ln r_\pm$ through the series CsF > RbF > KF > NaF could be explained by the structure making character of $F^-$ together with the increasing structure breaking tendency of group IA cations from Li$^+$ through Cs$^+$. When one ion is of intermediate character, for example Na$^+$ or K$^+$, then the sequence may be
irregular. For potassium there is a smooth trend of $\beta(0)$ from KOH down through KF to KCl and then back upward for KBr and KI (Figure 3.2, and 3.4).

The alkali earth metal ions, Mg$^{2+}$, Ca$^{2+}$, and Sr$^{2+}$ each have $\beta(0)$ values in increasing order for Cl$^-$, Br$^-$, I$^-$, and ClO$_4^-$, while for Ba$^{2+}$ the values for ClO$_4^-$ drop between Br$^-$ and I$^-$ (Figure 3.10, and 3.11).

Sulfate ion appears to fall between F$^-$ and Cl$^-$. Thus its values of $\beta(0)$ for IA group compounds drop from Li$^+$ to Na$^+$ and then rise through K$^+$, Rb$^+$, and Cs$^+$, as shown in Figure 3.12-3.15. The $\beta(0)$ values for nitrates are relatively low in all cases regardless of the structure making or breaking character of the cation (Figure 3.7, 3.9, 3.10, and 3.11). This suggests some tendency toward ion pair formation as is also indicates by spectroscopic data in several cases (25, 26).

According to Pitzer and Mayorga (27), the second virial coefficient for a single electrolytes is a weighted mean of the interactions between pair of ions with signs, ++, --, and +-. Two ion interaction parameters, $\beta(0)$ and $\beta(1)$ for the short range binary interaction of a single electrolyte represent -- interactions term and, ++ and -- interactions term respectively. The relative weighting of +- interaction is greatest at low ionic strength. At high ionic strength, the ++ and -- terms become more important but never equal to the weight of the +- interaction. As discussed earlier, the
result of sensitivity test for $\beta(0)$ and $\beta(1)$ support this concept.

The second virial coefficients for electrolytes also contain the net effect of solvation, dispersion forces and any other effects (permanent dipoles or multipoles) of similar range. The contribution of each of these various types of short range forces to $++$ and $--$ interactions will not obey the same relationship as its contribution to $+-$ interactions. Thus a unique correlation does not exist for $\beta(0)$ and $\beta(1)$. But a close relationship between $\beta(0)$ and $\beta(1)$ which provides a convenient approximation was observed.

If $\beta(0)$ is predicted accurately by correlation with ionic properties and the effect of the third virial coefficient is small, the prediction of activity coefficients for a single electrolyte becomes possible using the convenient approximation for evaluating $\beta(1)$. The correlation of ion interaction parameters with ionic properties seems to work well for 1-1, 1-2, and 2-1 types of electrolytes. However, for ternary mixture, since there are limited experimental data, the available set of Pitzer mixing parameters is not sufficient to obtain a generalized correlation. More experimental work is clearly needed in this area in the future.
REFERENCES


Hintze, J.L., Number Cruncher Statistical System (4.21), Kaysville, Utah, 1986.


IMSL Library Subroutine DMLIN, ed. 9, IMSL, Inc., June 1982.


APPENDICES
APPENDIX 1

Program Pitzer

A complete listing of the program Pitzer is given. This program is used to determine the $J_0(X)$ and $J_1(X)$ values in higher order electrostatic terms of Pitzer equation.

The program makes use of the IMSL program library subroutine DMLIN, which is available on the Oregon State University CDC Cyber computer. The program is written in FORTRAN programming language.
*MAIN PROGRAM PITZER*

PROGRAM PITZER(INPUT,OUTPUT)
EXTERNAL F1,F2
COMMON RX,A
REAL J0,J1,VAL1,VAL2,A,B,AERR,RERR
INTEGER MAXFCN,N,IER

OPEN(5,FILE='OUT1')
WRITE(*,110)
110 FORMAT(//,8X,'X',11X,'J0',11X,'J1',/)

10 PRINT*, 'ENTER X VALUE'
READ(*,*,END=30) RX

*COMPUTE J0*

N=1
MAXFCN=10000
AERR=0.0
RERR=0.0000001
SUM1=0.0
CALL TARGET(A,RX)
DO 20 I=1,10
   B=10.0*I
   VAL1=DMLIN(F1,A,B,N,MAXFCN,AERR,RERR,IER)
   SUM2=VAL1-SUM1
   SUM1=VAL1
   IF(SUM2.LE.0.0000001) GO TO 25
20 CONTINUE
25 J0=(0.25*RX)-1.0+1.0/RX*SUM1

*COMPUTE J1*

SUM3=0.0
DO 40 J=1,10
   B=10.0*J
   VAL2=DMLIN(F2,A,B,N,MAXFCN,AERR,RERR,IER)
   SUM4=VAL2-SUM3
   SUM3=VAL2
   IF(SUM4.LE.0.0000001) GO TO 45
40 CONTINUE
45 J1=(0.25*RX)-1.0/RX*SUM3
WRITE(*,140) RX,J0,J1
WRITE(5,140) RX,J0,J1
140 FORMAT(1X,F15.9,2(3X,F15.9))
GO TO 10

30 STOP
END
*FUNCTION F1*

REAL FUNCTION F1(N,X)
COMMON RX
REAL X(N)
F1=(1.0-EXP(-1.0*RX/X(1)*EXP(-1.0*X(1))))*X(1)**2
RETURN
END

*FUNCTION F2*

REAL FUNCTION F2(N,X)
COMMON RX
REAL X(N)
F2=(1.0-(1.0+RX/X(1)*EXP(-1.0*X(1)))*EXP(-1.0*RX/X(1)*EXP(-1.0*X(1))))*X(1)**2
RETURN
END

*SUBROUTINE TARGET*

SUBROUTINE TARGET(A,RX)
A=0.0
Y=0.009
DO 10 I=1,150
Y=Y+0.1
C=-1.0*RX/Y*EXP(-1.0*Y)
IF(C.GT.-80.) GO TO 1
1 CONTINUE
Y=Y-0.1
DO 20 I=1,50
Y=Y+0.01
C=-1.0*RX/Y*EXP(-1.0*Y)
IF(C.GT.-80.) GO TO 2
2 CONTINUE
Y=Y-0.01
DO 30 I=1,50
Y=Y+0.001
C=-1.0*RX/Y*EXP(-1.0*Y)
IF(C.GT.-80.) GO TO 3
3 CONTINUE
Y=Y-0.001
DO 40 I=1,50
Y=Y+0.0001
C=-1.0*RX/Y*EXP(-1.0*Y)
IF(C.GT.-80) GO TO 4
4 CONTINUE
IF(C.GT.-80) GO TO 5
50 CONTINUE
5 A=Y-0.00001
RETURN
END
APPENDIX 2

Comparison of $\tau_\pm$ of single salts between experimental data and calculated values from correlation results at 25°C
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| 0.30 | 0.443 | 0.466 | 0.444 | 0.490 |
| 0.60 | 0.365 | 0.393 | 0.369 | 0.424 |
| 0.90 | 0.323 | 0.353 | 0.329 | 0.388 |
| 1.20 | 0.295 | 0.326 | 0.304 | 0.364 |
| 1.50 | 0.274 | 0.306 | 0.285 | 0.346 |
| 1.80 | 0.258 | 0.291 | 0.270 | 0.333 |
| 2.10 | 0.245 | 0.280 | 0.259 | 0.323 |
| 2.40 | 0.234 | 0.270 | 0.249 | 0.315 |
| 2.70 | 0.225 | 0.262 | 0.241 | 0.309 |
| 3.00 | 0.217 | 0.256 | 0.234 | 0.305 |
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* Calculated from correlation results
APPENDIX 3

Sensitivity analysis of activity coefficients of a single salt for solubility calculations.
In order to check how sensitive solubility calculations are to error in activity coefficients, consider the solubility of a single salt in an aqueous electrolyte solution saturated with respect to that salt. The simple dissociation reaction can be represented as:

\[ \text{A}(c) = b\text{B} + c\text{C} \]  

(1)

where A is the pure salt and B and C are the constituent ions. The thermodynamic solubility product for this reaction is defined as:

\[ K_{sp} = a_B b a_C c / a_A \]  

(2)

Assuming the salt is pure and of activity one,

\[ K_{sp} = a_B b a_C c \]  

(3)

or

\[ K_{sp} = (m_B \tau_B)^b (m_C \tau_C)^c \]  

(4)

Since charge balance shows, \( m_B = b m_A \) and \( m_C = c m_A \), and the mean activity coefficient is the thermodynamically defined:

\[ \tau_A^{(b+c)} = (\tau_B^b \tau_C^c) \]  

(5)
Finally, the solubility product is

\[ K_{sp} = (Q m_A r_A)^{b+c} \]  

(6)

where \( Q = (b^b c^c)^{1/(b+c)} \)

This \( Q \) term equals \( 1^{1/2} (=1) \) for 1-1 and 2-2 type electrolytes, \( 2^{2/3} \) for 1-2 and 2-1 type electrolytes and \( 3^{3/4} \) for 1-3 and 3-1 type electrolytes.

The calculation of an electrolyte's solubility product can therefore be based on an experimental saturation molality of a pure solution and the calculated activity coefficients.

1-1 TYPE ELECTROLYTE

For example, one of the solutions tested here is the system KCl-H\(_2\)O at 25°C. The experimental saturation concentration of a pure solution of KCl is 4.803 mol/kg and the activity coefficient at this molality is 0.589 (Hamer and Wu, 1972). Thus,

\[ K_{sp} = (m_{KCl} r_{KCl})^2 = 8.003 \]

If assuming ideal activity coefficients (\( r_{KCl} = 1 \)), the estimation value of solubility for KCl solution is 2.829 mol/kg which has a 41.1% deviation to the value given in literature of 4.803 mol/kg.
1-2 TYPE ELECTROLYTE

For: \( \text{Na}_2\text{SO}_4 (c) = 2\text{Na}^+ (aq) + \text{SO}_4^{2-} (aq) \)

\[ m = 1.957 \text{ mol/kg (saturated solution)} \]

\[ \tau_\pm = 0.1558 \text{ (Goldberg, 1981)} \]

Thus,

\[ K_{\text{sp}} = 4(m\tau_\pm)^3 = 0.1134 \]

Assuming ideal activity coefficients (\( \tau_\pm = 1 \)):

\[ m = (K_{\text{sp}}/4)^{1/3} = 0.3049 \text{ mol/kg} \]

The value of deviation as the absolute value for solubility is 84.42% when using the \( \tau_\pm = 1 \).

2-1 TYPE ELECTROLYTE

For: \( \text{MgCl}_2 (c) = \text{Mg}^{2+} (aq) + 2\text{Cl}^- (aq) \)

\[ m = 5.840 \text{ mol/kg (saturated solution)} \]

\[ \tau_\pm = 32.6458 \text{ (Goldberg and Nuttall, 1978)} \]

Thus,

\[ K_{\text{sp}} = 4(m\tau_\pm)^3 = 2.772 \times 10^7 \]

Assuming ideal activity coefficients (\( \tau_\pm = 1 \)):

\[ m = (K_{\text{sp}}/4)^{1/3} = 190.6 \text{ mol/kg} \]

The value of deviation as the absolute value for solubility is 3.16\times10^3\% when using the \( \tau_\pm = 1 \).

If using 50% deviation of \( \tau_\pm \), one get

\[ m = 3.89 \text{ mol/kg (33.4\% deviation for solubility)} \]
APPENDIX 4

Comparison of $\tau_+$ for KCl between experimental smoothed data and calculated values from various correlation results.
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Cal\(^1\): using correlation between \(\beta(0)\) and \(S^0\)
Cal\(^2\): " " " \(\beta(0)\) and \(S^0\)  
Cal\(^3\): " " " \(\beta(0)\) and \(Z^* Z/r\) 
Cal\(^4\): " " " \(\beta(0)\) and \(PC/PA\) 
*; saturated solution.