AN ABSTRACT OF THE THESIS OF

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William J. Frederick, Jr.

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 $\ln\gamma_{\pm}$ or ϕ to the model equations. The effects of the higher order

electrostatic term were considered for all asymmetrical systems. A comparison between the values of $\ln\gamma_{\pm}$ or $\phi-1$ calculated from the results of this study and experimental values for several systems shows the good agreement within ±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 ±1% for system of $HCl-MgCl_2-H_2O$ at 25°C.

PREDICTION OF THERMODYNAMIC PROPERTIES OF AQUEOUS ELECTROLYTE SOLUTIONS

by

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

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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, hydrometallurigical 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 ($I<0.001$ M).

$$\ln\gamma_{\pm} = -\ |z_{+}z_{-}|A\sqrt{I} \qquad (1)$$

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:

$$\ln\gamma_{\pm} = -\ |z_{+}z_{-}|A\sqrt{I}\ /\ (1+Bs\sqrt{I}) \qquad (2)$$

where I, the ionic strength, is defined as $I = \frac{1}{2}\ \Sigma\ m_i z_i^2$ 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 ($I<0.05$ M).

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

$$\ln\tau_{\pm} = - \frac{|z_{+}z_{-}|A\sqrt{I}}{1 + Bs\sqrt{I}} + CI \tag{3}$$

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

$$\ln\tau_{\pm} = - |z_{+}z_{-}|A\sqrt{I} \;/\; 1+\sqrt{I} \tag{4}$$

This simplified equation of the Debye-Hückel equation represents activity coefficient for electrolyte solutions quite well up to I =0.1 M.

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

$$\ln\tau_{\pm} = - \frac{|z_{+}z_{-}|A\sqrt{I}}{1 + \sqrt{I}} + 2\overline{v}\beta m \tag{5}$$

where $\bar{v} = 2v_+v_-/(v_++v_-)$ and m is the molality of the electrolyte. β 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 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

Table G.1 A comparison of activity coefficient estimation methods

Method	Bromley	Meissner	Pitzer	Chen
Approach	Ion interactions	Generalized	Ion interactions	Ion interactions
Number of parameters for: Single salt solutions	1 per cation/anion pair	2 per cation/anion pair	3 per cation/anion pair if both monovalent, 4 if both ions are multivalent	2 per cation/anion pair
Additional parameters for multicomponent	None	None	1 for each ion pair with same valence charge, different magnitude; 1 for each 3 ions with one of different valence sign	None
Estimation method for parameters?	Yes	Yes	No	No
Temperature effects by	Meissner's method	Non-ion specific equation	Debye-Huckel constant temperature dependence	Debye-Huckel constant temperature dependence

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^{ϕ} from osmotic coefficient data for single salts at concentrations up to nearly saturation.
2. to obtain Pitzer mixing ion interaction parameters, θ_{ij} and ψ_{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

1. Debye, D., and Hückel, E., Theory of Electrolytes. I Lowering of Freezing Point and Related Phenomena., Physik. Z., 24, 185-206 (1923).

2. Debye, D., and Hückel, E., Theory of Electrolytes. II The Limiting Law of Electrical Conductivity., Physik. Z., 24, 305-325 (1923).

3. Hückel, E., The Theory of Concentrated Aqueous Solutions of Strong Electrolytes., Physik. Z., 26, 93-147 (1924).

4. Güntelberg, E., Interaction of Ions, Z. Physik. Chem., 123, 199-247 (1926).

5. Guggenheim, E.A., The Specific Thermodynamic Properties of Aqueous Solutions of Strong Electrolytes, Phil. Mag. 19, 588-643 (1935).

6. Guggenheim, E.A., and Turgeon, J.C., Specific Interaction of Ions, Trans. Faraday Soc., 51, 747-761 (1955).

7. Davies, C.W., The Extent of Dissociation of Salts in Water. Part VIII An Equation for the Mean Ionic Activity Coefficient of an Electrolyte in Water, and a Revision of the Dissociation Constants of Some Sulphates, J. Chem. Soc., 2093 (1938).

8. Davies, C.W., Ion Association, Butterworths Scientific Publications, London (1962).

9. Zemaitis, J.F., Jr., Clark, D.M., Rafal, M., and Scrivner, N.C., Handbook of Aqueous Electrolyte Thermodynamics, AIChE, New York (1986).

10. Pitzer, K.S., Thermodynamics of Electrolytes. I: Theoretical Basis and General Equations, J. Phys. Chem. 77, 268-277 (1973).

11. Pitzer, K.S., and Mayorga, G., Thermodynamics of Electrolytes. II: Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent., J. Phys. Chem., 77, 2300-2308 (1973).

12. Pitzer, K.S., and Mayorga, G., Thermodynamics of Electrolytes. III: Activity and Osmotic Coefficients for 2-2 electrolytes., J. Solution Chem., 3, 539-546 (1974).

13. Pitzer, K.S., and Kim, J., Thermodynamics of Electrolytes. IV: Actiivty and Osmotic Coefficients for Mixed Electrolytes. J. Am. Chem. Soc., 96, 5701-5707 (1974).

14. Edward, T.J., Maurer, G., Newman, J., and Prausnitz, J. M., Vapor-Liquid Equilibria in multicomponent Aqueous Solutions of Volatile Weak Electrolytes., AIChE J., 24, 966-976 (1978).

15. Buetier, D., and Renon, H., Representation of NH_3-H_2S-H_2O, NH_3-CO_2-H_2O and NH_3-SO_2-H_2O Vapor-Liquid Equilibria., Ind. Eng. Chem. Process Des. Dev., 17(3), 220-230 (1978).

16. Chen, C-C, Britt, H.I., Boston, J.F., and Evans, L.B., Extension and Application of the Pitzer Equation for Vapor-Liquid Equilibrium of Aqueous Electrolyte Systems with Molecular Solutes., AIChE J., 25, 820-831 (1979).

17. Felmey, A.R., and Weare, J.H., The Prediction of Borate Mineral Equilibria in Natural Waters: Application to Searles Lake, California., Geochimica et Cosmochimica Acta, 50, 2771-2783 (1986).

18. Frederick, W.J., Jr., Kelly, B., Kim, H.C., and McIntyre, M.J., Modeling Electrolyte Behavior in Pulp and Paper Processes., AIChE National Summer Meeting, Minneapolis (August 16-19, 1987).

19. Kelly, B., and Frederick, W.J., Jr., Application of Chemical Engineering Principle in the Forest Products and Related Industries., Kayihan, F., and Krieger-Brackett, B., Editors. AIChE Forest Products Division, Seattle, 1986.

20. Harvie, C.E., and Weare, J.H., The Prediction of Mineral Solubilities in Natural Waters: the Na-K-Mg-Ca-SO_4-H_2O System from Zero to High Concentration at 25°C Geochimica et Cosmochimica Acta, 44, 981-997 (1980).

21. Harvie, C.E., Møller, N., and Weare, J.H., The Prediction of Mineral Solubilities in Natural Water: the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O System to High Ionic Strengths at 25°C., Geochimica et Cosmochimica Acta, 48, 723-751 (1984).

CHAPTER 1

EVALUATION OF PITZER ION INTERACTION PARAMETERS OF AQUEOUS ELECTROLYTES AT 25°C

1. SINGLE SALT PARAMETERS

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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, $CaBr_2$, $Pr(NO_3)_3$ and $MgSO_4$ 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-SO_4-H_2O 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:

$$\phi = 1 + \frac{2}{(m_M+m_X)} \{ \frac{-A^{\phi} I^{3/2}}{1+b\sqrt{I}} + m_M m_X (B^{\phi}_{Ma} + Z C_{Ma}) \} \qquad (1)$$

$$\ln\gamma_{MX} = -|z_M z_X| A^{\phi} \left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b}\ln(1+b\sqrt{I})\right]$$

$$+ 4m\left(\frac{v_M v_X}{v}\right)\left(B_{MX} + \frac{I}{2}B'_{MX}\right) + 6m^2\left(\frac{v_M v_X}{v}\right) v_M z_M C_{MX} \qquad (2)$$

In eqs 1 and 2, m_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 $I = 0.5 \sum_i m_i z_i^2$ is the ionic strength. The function Z is defined by $Z = \sum_i m_i |z_i| = 2(\sum_i m_M z_M) = 2(\sum_i m_X |z_X|)$ and A^{ϕ} is the Debye-Hückel coefficient for the osmotic coefficient and is given by

$$A^{\phi} = \frac{1}{3}\left(\frac{2\pi N_o d_w}{1000}\right)^{1/2}\left(\frac{e^2}{DkT}\right)^{3/2} \qquad (3)$$

where N_o 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^{ϕ} 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^{ϕ}_{MX}, 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.

$$B^{\phi}_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}\ e^{-\alpha_1\sqrt{I}} + \beta_{MX}^{(2)}\ e^{-\alpha_2\sqrt{I}} \tag{4}$$

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

$$B'_{MX} = \beta_{MX}^{(1)} f'(\alpha_1\sqrt{I})/I + \beta_{MX}^{(2)} f'(\alpha_2\sqrt{I})/I \tag{6}$$

where

$$f(x) = 2[1-(1+x)e^{-x}]/x^2 \tag{7}$$

$$f'(x) = -2[1-(1+x+0.5x^2)e^{-x}]/x^2 \tag{8}$$

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_{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_{MX} and C^{ϕ}_{MX}, the corresponding coefficients for calculating the osmotic coefficient, are related by the following eq 9 (2):

$$C_{MX} = C^{\phi}_{MX}/2\sqrt{|z_M z_X|} \tag{9}$$

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_2SO_4, for which data are available only over concentration range of 0.1 to 6.0 molality.

The positive value of the coefficients B^{ϕ}_{MX} from eq 4 indicates the net predominance of repulsive short-range interaction forces according to Pitzer and Mayorga (2).

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_2SO_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^{ϕ}_{MX} and chose the value of $\beta_{MX}^{(2)} = 2.0$ which was proposed by Pitzer and Mayorga (3).

The third virial coefficients, C^{ϕ}_{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

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref.
HF	0.02212	0.40156	-0.00018	20.000	0.0031	0.9996	(12)
HCl	0.20332	-0.01668	-0.00318	16.000	0.0144	0.9999	(12)
HBr	0.24153	-0.16119	-0.00101	11.000	0.0292	0.9994	(12)
HI	0.23993	0.28351	0.00138	10.000	0.0159	0.9998	(12)
$HClO_4$	0.21617	-0.22769	0.00192	16.000	0.0362	0.9996	(12)
HNO_3	0.08830	0.48338	-0.00233	28.000	0.0276	0.9960	(12)
LiCl	0.20972	-0.34380	-0.00433	19.219	0.0534	0.9982	(12)
LiBr	0.24554	-0.44244	-0.00293	20.000	0.0939	0.9974	(12)
LiI	0.14661	0.75394	0.02126	3.000	0.0016	0.9999	(12)
LiOH	0.05085	-0.07247	-0.00337	5.000	0.0049	0.9959	(12)
$LiClO_4$	0.20400	0.32251	-0.00118	4.500	0.0016	1.0000	(12)
$LiNO_3$	0.13008	0.40957	-0.00382	20.000	0.0064	0.9999	(12)
$LiNO_2$	0.12147	0.45734	-0.00383	19.900	0.0109	0.9997	(25)
$LiClO_3$	0.17049	0.22944	-0.00524	4.200	0.0018	0.9999	(26)
$LiBrO_3$	0.08928	0.21573	-0.00005	5.000	0.0009	1.0000	(26)
LiAc[a]	0.11215	0.20243	-0.00519	4.000	0.0012	0.9999	(12)
NaF	0.03183	0.18697	-0.00840	1.000	0.0003	0.9999	(12)
NaCl	0.07722	0.25183	0.00106	6.144	0.0006	1.0000	(12)
NaBr	0.11077	0.13760	-0.00153	9.000	0.0045	0.9999	(12)
NaI	0.13463	0.19479	-0.00117	12.000	0.0092	0.9998	(12)
NaOH	0.17067	-0.08411	-0.00342	29.000	0.0859	0.9950	(12)
$NaClO_3$	0.01908	0.27932	0.00181	3.000	0.0003	0.9999	(12)

Table 1.1 (continued)

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref.
$NaClO_4$	0.05446	0.27569	−0.00102	6.000	0.0010	0.9999	(12)
$NaBrO_3$	−0.02154	0.18207	0.00633	2.167	0.0009	0.9773	(12)
$NaNO_3$	0.00388	0.21151	−0.00006	10.830	0.0007	0.9985	(41)
$NaNO_2$	0.04793	0.22465	−0.00226	12.340	0.0064	0.9980	(25)
NaH_2PO_4	−0.04746	−0.07586	0.00659	6.500	0.0041	0.9910	(12)
NaH_2AsO_4	−0.07997	0.35866	0.02267	1.300	0.0003	0.9998	(12)
NaCNS	0.12373	0.08385	−0.00382	18.000	0.0286	0.9973	(12)
$NaBO_2$	−0.05289	−0.10888	0.01497	4.000	0.0022	0.9998	(27)
$NaBF_4$	−0.02603	−0.10084	0.00171	9.000	0.0035	0.9948	(27)
NaAc[a]	0.13723	0.34195	−0.00474	3.500	0.0009	1.0000	(12)
KF	0.10013	−0.02175	−0.00159	17.500	0.0209	0.9989	(12)
KCl	0.04661	0.22341	−0.00044	4.803	0.0004	1.0000	(12)
KBr	0.05592	0.22094	−0.00162	5.500	0.0004	1.0000	(12)
KI	0.07253	0.27710	−0.00381	4.500	0.0006	0.9999	(12)
KOH	0.17501	−0.01634	−0.00267	20.000	0.0265	0.9995	(12)
$KClO_3$	−0.09193	0.23343	-	0.700	0.0002	0.9999	(12)
$KBrO_3$	−0.11426	0.20414	-	0.500	0.0002	0.9999	(12)
KNO_3	−0.08511	0.10518	0.00773	3.500	0.0004	1.0000	(12)
KNO_2	0.00349	0.15708	−0.00025	34.120	0.0119	0.9776	(25)
KH_2PO_4	−0.11411	0.06898	0.02069	1.800	0.0002	1.0000	(12)
KH_2AsO_4	−0.12614	0.25457	0.04002	1.300	0.0003	0.9999	(12)
KCNS	0.03891	0.25361	−0.00192	5.000	0.0006	0.9999	(12)
KPF_6	−0.13710	−0.42785	-	0.500	0.0014	0.9996	(12)
KAc[a]	0.15283	0.35513	−0.00432	3.500	0.0009	1.0000	(12)

Table 1.1 (continued)

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref.
RbF	0.10872	0.39804	-0.00874	3.500	0.0019	0.9998	(12)
RbCl	0.04660	0.12983	-0.00163	7.800	0.0013	0.9999	(12)
RbBr	0.03868	0.16723	-0.00123	5.000	0.0005	0.9999	(12)
RbI	0.03902	0.15224	-0.00095	5.000	0.0004	1.0000	(12)
$RbNO_3$	-0.08174	-0.03175	0.00624	4.500	0.0023	0.9996	(12)
$RbNO_2$	-0.00303	0.05130	-0.00014	62.300	0.0194	0.9736	(25)
RbAc[a]	0.16296	0.32918	-0.00561	3.500	0.0006	1.0000	(12)
CsF	0.13644	0.14166	-0.00674	3.500	0.0017	0.9999	(12)
CsCl	0.03643	-0.01169	-0.00096	11.000	0.0036	0.9993	(12)
CsBr	0.02311	0.04587	0.00092	5.000	0.0014	0.9995	(12)
CsI	0.02121	0.07307	-0.00307	3.000	0.0004	0.9997	(12)
$CsNO_3$	-0.13004	0.08169	0.03018	1.500	0.0006	0.9999	(12)
$CsNO_2$	0.00926	0.32052	-0.00036	36.000	0.0179	0.9330	(25)
CsOH	0.16439	0.32693	0.00788	1.200	0.0003	1.0000	(12)
CsAc	0.17144	0.32896	-0.00793	3.500	0.0006	1.0000	(12)
$AgNO_3$	-0.07102	-0.16793	0.00322	13.000	0.0082	0.9984	(12)
TlCl	-3.16406	-2.43821	-	0.010	0.0002	0.9996	(12)
$TlClO_4$	-0.11111	0.07553	-	0.500	0.0004	0.9999	(12)
$TlNO_3$	-0.12518	-0.30145	-	0.400	0.0004	0.9999	(12)
$TlNO_2$	-0.65041	-0.11038	0.37782	1.400	0.0003	1.0000	(12)
TlAc[a]	0.00878	-0.04105	-0.00153	6.000	0.0022	0.8848	(12)
NH_4Cl	0.05191	0.17937	-0.00301	7.405	0.0009	0.9999	(12)
NH_4I	0.05701	0.31566	-0.00308	7.500	0.0017	0.9998	(28)
NH_4ClO_4	-0.00697	-0.05618	-0.00071	2.100	0.0002	0.9995	(12)

Table 1.1 (continued)

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref.
NH_4NO_3	-0.01476	0.13826	0.00029	25.954	0.0054	0.9977	(12)
NH_4SCN	0.00528	-0.34080	-0.00036	23.431	0.0049	0.9822	(29)
Et_4NNO_3	-0.04022	-0.87108	0.00565	8.000	0.0076	0.9893	(28)
Me_4NNO_3	0.01224	-0.32933	0.00090	7.000	0.0021	0.9991	(28)
$MeNH_3ClO_4$	-0.03371	0.00573	0.00345	4.000	0.0017	0.9980	(30)
$Me_2NH_2ClO_4$	-0.04395	-0.17191	0.00240	7.500	0.0011	0.9999	(30)
Me_3NHClO_4	-0.11447	-0.17129	0.01348	1.800	0.0024	0.9992	(30)
GuCl	-0.02855	-0.10997	0.00177	12.000	0.0068	0.9845	(31)
Li p-tol^{b}	0.01223	0.46653	0.00633	4.500	0.0030	0.9986	(12)
Na p-tol^{b}	-0.03958	0.47846	0.00571	4.000	0.0025	0.9951	(12)
Na formate	0.07187	0.32247	-0.00236	3.500	0.0006	0.9999	(12)
Na propionate	0.18813	0.26772	-0.01288	3.000	0.0005	1.0000	(12)
Na butyrate	0.26081	0.16368	-0.03358	3.500	0.0037	0.9998	(12)
Na valerate	0.33473	-0.11324	-0.07394	2.000	0.0030	0.9998	(12)
Na caprylate	-0.45120	-7.73638	0.05902	3.000	0.0170	0.9963	(12)
Na pelargonate	0.03728	-10.3798	-0.07164	2.500	0.0169	0.9933	(12)

Table 1.1 (continued)

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref.
Na caprate	0.07992	-7.40138	-0.06028	1.800	0.0033	0.9987	(12)
NaH malonate	0.02166	0.17611	-0.00089	5.000	0.0005	0.9998	(12)
NaH succinate	0.03463	0.14036	0.00061	5.000	0.0020	0.9994	(12)
NaH adipate	0.04325	0.33988	-	0.700	0.0003	0.9999	(12)
K p-tol[b]	-0.09842	0.47188	0.01182	3.500	0.0020	0.9995	(12)
KH malonate	-0.00474	0.06128	0.00048	5.000	0.0027	0.8707	(12)
KH succinate	0.01309	0.10978	0.00215	4.500	0.0024	0.9972	(12)
KH adipate	-0.03998	0.47595	0.05523	1.000	0.0007	0.9997	(12)

[a] Acetate [b] Para-toluenesulfonate

Table 1.2 Ion interaction parameters for 1-2 electrolytes at 25° C

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref.
H_2SO_4	0.14098	-0.56843	-0.00237	27.500	0.0487	0.9984	(32)
Li_2SO_4	0.14515	1.23001	-0.00643	3.000	0.0047	0.9995	(13)
$Li_2C_6H_4S_2O_6$	0.40862	1.92482	-0.03240	2.500	0.0031	0.9999	(13)
$Li_2C_{14}H_{12}S_2O_6$	0.12189	1.48771	0.03415	1.000	0.0040	0.9992	(13)
Na_2SO_4	0.04680	0.91406	-0.00520	1.750	0.0012	0.9996	(13)
Na_2SO_3	0.08015	1.18500	-0.00436	2.000	0.0019	0.9996	(13)
Na_2CO_3	0.05306	1.29262	0.00094	2.750	0.0026	0.9993	(13)
Na_2HPO_4	-0.02169	1.24472	0.00726	2.000	0.0005	0.9997	(13)
Na_2CrO_4	0.06526	1.63256	0.00884	4.250	0.0051	0.9997	(13)
$Na_2S_2O_3$	0.06347	1.32115	0.00475	4.000	0.0033	0.9997	(13)
$Na_2S_2O_6$	0.08526	1.18961	-	0.800	0.0027	0.9986	(13)
$Na_2S_2O_8$	0.28075	1.01750	-	0.090	0.0004	0.9999	(13)
$Na_2C_2H_4S_2O_6$	0.28782	1.31451	-0.04835	1.750	0.0052	0.9994	(13)
$Na_2C_6H_4S_2O_6$	0.25277	2.02265	-0.02132	3.000	0.0024	0.9999	(13)
$Na_2C_{14}H_{12}S_2O_6$	0.00808	1.60199	-	0.400	0.0043	0.9926	(13)
$Na_2C_{14}H_{12}S_2O_8$	-0.36838	0.16958	-	0.400	0.0098	0.9817	(13)
$Na_2B_{12}H_{12}$	0.51666	1.76589	-0.01834	1.500	0.0009	1.0000	(13)
Na_2WO_4	0.20318	0.87616	-0.01941	2.500	0.0028	0.9999	(13)
Na_2HAsO_4	0.13607	1.70125	0.01202	1.000	0.0006	0.9999	(13)
$Na_2C_4H_2O_4$ [a]	0.23639	0.82784	-0.02218	2.000	0.0039	0.9996	(13)
$Na_2C_4H_2O_4$ [b]	0.14063	0.39635	-0.00941	2.750	0.0028	0.9997	(13)
K_2SO_4	0.07548	0.44371	-	0.692	0.0014	0.9990	(13)
K_2HPO_4	0.05307	1.10271	-	0.800	0.0005	0.9999	(13)

Table 1.2 (continued)

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref.
$K_2H_2P_2O_7$	-0.00585	1.25198	0.00524	3.000	0.0008	0.9995	(13)
K_2HAsO_4	0.10466	1.80042	-	0.800	0.0022	0.9995	(13)
K_2CrO_4	0.07712	1.18413	-0.00107	3.250	0.0028	0.9996	(13)
$K_2Cr_2O_7$	-0.01111	2.33306	-	0.507	0.0155	0.9144	(13)
$K_2Pt(CN)_4$	0.05955	2.25539	-	0.948	0.0042	0.9984	(13)
Rb_2SO_4	0.09232	0.75746	-0.01339	1.500	0.0010	0.9997	(13)
$Rb_2S_2O_8$	0.20464	-0.26340	-	0.070	0.0001	0.9999	(13)
Cs_2SO_4	0.14294	0.66711	-0.02746	1.631	0.0012	0.9999	(13)
$Cs_2S_2O_8$	0.13283	-0.76429	-	0.109	0.0001	0.9999	(13)
$(NH4)_2SO_4$	0.04841	1.13240	-0.00155	5.500	0.0018	0.9996	(22)
$(NH4)_2HPO_4$	-0.04259	-0.69871	0.00527	3.000	0.0015	0.9990	(13)
$(NH4)_2B_{10}H_{10}$	0.15824	1.46202	-0.01710	3.750	0.0067	0.9988	(13)
$(CN_3H_6)_2CO_3$	-0.07420	0.22809	0.01380	2.500	0.0021	0.9983	(13)
$C_2H_6S_2O_6$	0.42897	2.00694	-0.01984	5.500	0.0078	0.9999	(13)
$C_6H_6S_2O_6$	0.41381	2.01836	-0.02071	1.750	0.0021	0.9999	(13)

[a] Sodium fumarate. [b] Sodium maleate

Table 1.3 Ion interaction parameters for 2-1 electrolytes at 25° C

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref.
$MgCl_2$	0.35573	1.61738	0.00474	5.750	0.0036	1.0000	(14)
$MgBr_2$	0.43469	1.73184	0.00275	5.610	0.0058	1.0000	(14)
MgI_2	0.49161	1.78273	0.00780	5.000	0.0042	1.0000	(14)
$Mg(ClO_4)_2$	0.50083	1.94817	0.00848	4.000	0.0065	0.9999	(22)
$Mg(NO_3)_2$	0.34284	2.68244	-0.00723	5.000	0.0076	0.9999	(22)
$Mg(Ac)_2$	0.20801	1.05448	-0.01286	4.000	0.0065	0.9998	(22)
$CaCl_2$	0.32579	1.38412	-0.00174	6.000	0.0158	0.9998	(14)
$CaBr_2$	0.33899	2.04551	0.01067	6.000	0.0071	1.0000	(14)
CaI_2	0.43225	1.84879	0.00085	1.915	0.0016	1.0000	(14)
$Ca(ClO_4)_2$	0.47924	2.16287	-0.00837	6.000	0.0173	0.9999	(22)
$Ca(NO_3)_2$	0.17030	2.02106	-0.00690	6.000	0.0134	0.9987	(22)
$SrCl_2$	0.28170	1.61666	-0.00071	3.500	0.0039	0.9999	(14)
$SrBr_2$	0.32410	1.78223	0.00344	2.100	0.0008	1.0000	(14)
SrI_2	0.39394	1.92536	0.00474	1.970	0.0009	1.0000	(14)
$Sr(ClO_4)_2$	0.44138	2.00236	-0.01454	6.000	0.0064	0.9999	(22)
$Sr(NO_3)_2$	0.10196	1.65662	-0.00719	4.000	0.0071	0.9991	(22)
$BaCl_2$	0.29073	1.24998	-0.03046	1.785	0.0015	0.9999	(14)
$BaBr_2$	0.31552	1.57056	-0.01610	2.300	0.0027	0.9999	(14)
BaI_2	0.40227	1.90862	-0.00936	1.998	0.0017	1.0000	(14)
$Ba(ClO_4)_2$	0.32673	2.53859	-0.01576	5.500	0.0101	0.9998	(22)
$Ba(NO_3)_2$	-0.03356	0.80934	-	0.400	0.0017	0.9987	(22)
$Ba(Ac)_2$	0.22541	1.50143	-0.03306	3.500	0.0066	0.9994	(22)

Table 1.3 (continued)

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref.
$MnCl_2$	0.29486	2.01251	-0.01528	7.500	0.0243	0.9990	(16)
$MnBr_2$	0.44655	1.34477	-0.02269	5.640	0.0055	0.9999	(16)
$Mn(ClO_4)_2$	0.50957	2.16209	0.01144	3.456	0.0032	1.0000	(16)
$NiCl_2$	0.39304	0.99773	-0.01658	5.500	0.0138	0.9998	(15)
$NiBr_2$	0.44305	1.48323	-0.00590	4.500	0.0087	0.9999	(15)
$Ni(ClO_4)_2$	0.49285	1.98517	0.01679	3.500	0.0024	1.0000	(15)
$Ni(NO_3)_2$	0.30978	2.10644	-0.00394	4.500	0.0102	0.9999	(15)
$CoCl_2$	0.37351	1.25999	-0.01803	4.000	0.0071	0.9999	(15)
$CoBr_2$	0.47172	0.98425	-0.01716	5.750	0.0216	0.9997	(15)
CoI_2	0.51953	1.71266	-0.00101	4.000	0.0157	0.9999	(15)
$Co(NO_3)_2$	0.30654	1.80197	-0.00649	5.500	0.0049	0.9999	(15)
$Co(ClO_4)_2$	0.50409	1.96664	0.01349	3.500	0.0032	1.0000	(15)
$CuCl_2$	0.23052	2.20897	-0.01639	5.750	0.0066	0.9976	(16)
$CuBr_2$	0.41247	1.66270	-0.04262	3.606	0.0059	0.9999	(16)
$Cu(ClO_4)_2$	0.48984	1.90361	0.00839	3.500	0.0017	1.0000	(16)
$Cu(NO_3)_2$	0.28124	1.72906	-0.00842	7.840	0.0031	1.0000	(16)
$Cu(C_7H_7O_3S)_2$	0.08473	1.79523	-	0.800	0.0021	0.9995	(16)
$FeCl_2$	0.35011	1.40092	-0.01412	2.000	0.0018	1.0000	(15)
ZnF_2	0.00144	-0.08746	-	0.142	0.0006	0.9327	(17)
$ZnCl_2$	0.08887	2.94869	0.00095	10.000	0.0144	0.9995	(17)
$ZnBr_2$	0.18728	4.34674	-0.00911	6.000	0.0458	0.9888	(17)
ZnI_2	0.28596	5.08037	-0.02004	6.000	0.0726	0.9813	(17)

Table 1.3 (continued)

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref.
$Zn(ClO_4)_2$	0.52365	1.46269	0.00748	4.300	0.0101	0.9999	(17)
$Zn(NO_3)_2$	0.32587	1.90781	-0.00842	6.750	0.0028	1.0000	(17)
$Zn(C_7H_7O_3S)$	0.11840	1.67138	-	0.300	0.0004	0.9999	(17)
$CdCl_2$	0.01624	0.43945	0.00109	6.000	0.0011	0.9998	(22)
$CdBr_2$	0.02087	-0.86302	0.00284	4.000	0.0037	0.9989	(22)
CdI_2	0.14916	0.55935	-0.01117	2.500	0.0034	0.9995	(22)
$Cd(ClO_4)_2$	0.38986	1.99610	0.02075	1.750	0.0012	1.0000	(17)
$Cd(NO_2)_2$	0.00265	-2.15854	0.00302	7.840	0.0190	0.9917	(17)
$Cd(NO_3)_2$	0.28764	1.68468	-0.02587	2.500	0.0032	0.9999	(17)
$Cd(C_7H_7O_3S)_2$	0.07161	1.75817	-	0.600	0.0028	0.9999	(17)
$PbCl_2$	0.08010	-2.57126	-	0.039	0.0037	0.9833	(16)
$Pb(ClO_4)_2$	0.33500	1.61813	-0.00904	10.830	0.0046	1.0000	(16)
$Pb(NO_3)_2$	0.01506	-0.27095	-0.01330	1.830	0.0048	0.9410	(16)
UO_2Cl_2	0.40951	1.74913	-0.02949	3.174	0.0054	0.9999	(16)
$UO_2(ClO_4)_2$	0.66563	1.42853	0.00699	4.000	0.0130	0.9999	(16)
$UO_2(NO_3)_2$	0.47803	1.59530	-0.03971	5.500	0.0144	0.9997	(16)
$C_8H_{22}N_2Cl_2$	0.10390	-0.10568	0.00165	4.400	0.0045	0.9998	(17)
$C_8H_{22}N_2I_2$	-0.07160	-0.85778	0.01156	4.000	0.0094	0.9792	(17)
$[Co(NH_3)_5NO_2]Cl_2$	-2.71103	6.03902	-	0.100	0.0032	0.9958	(15)
$[Co(NH_3)_5Cl]Cl_2$	1.44407	0.63074	-	0.008	0.0003	0.9991	(15)

Table 1.3 (continued)

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref.
$[Co(NH_3)_5F]Cl_2$	0.03945	0.64984	-0.00976	1.000	0.0004	0.9999	(15)
$[Co(NH_3)_5Cl](ClO_4)_2$	0.03550	0.61167	-	0.100	0.0015	0.9914	(15)
$[Co(NH_3)_5CH_3CH_2COO](NO_3)_2$	-0.01298	0.46747	-	0.400	0.0008	0.9950	(15)
$[Co(NH_3)_5CH_3CH_2COO]I_2$	0.02342	0.55520	-	0.500	0.0030	0.9833	(15)
$[Co(NH_3)_5CH_3CH_2COO]Br_2$	0.05240	0.48711	-0.00539	1.200	0.0006	0.9998	(15)
$[Co(NH_3)_5CH_3CH_2COO]Cl_2$	0.11194	0.34489	-0.01339	2.400	0.0019	0.9997	(15)
$[Co(NH_3)_5CH_3COO](NO_3)_2$	0.38956	-0.41144	-	0.050	0.0001	0.9998	(15)
$[Co(NH_3)_5CH_3COO]I_2$	0.40728	-0.31106	-	0.100	0.0004	0.9996	(15)
$[Co(NH_3)_5CH_3COO]Br_2$	0.04621	0.52415	-	0.600	0.0012	0.9986	(15)
$[Co(NH_3)_5CH_3COO]Cl_2$	0.07197	0.39910	-	0.600	0.0042	0.9857	(15)
$[Co(NH_3)_5(CH_3)_2CHCOO](NO_3)_2$	-0.01831	0.35251	0.00279	2.500	0.0020	0.9844	(15)
$[Co(NH_3)_5(CH_3)_2CHCOO]I_2$	0.00203	0.58539	-	0.800	0.0025	0.9832	(15)
$[Co(NH_3)_5(CH_3)_2CHCOO]Br_2$	0.05108	0.36726	-	0.800	0.0037	0.9880	(15)
$[Co(NH_3)_5(CH_3)_2CHCOO]Cl_2$	0.10966	0.35157	-0.01293	2.500	0.0020	0.9997	(15)

Table 1.4 Ion interaction parameters for 3-1, 1-3 electrolytes at 25 C

Compound	$\beta^{(o)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref
$LaCl_3$	0.59625	5.6000	-0.02464	3.800	0.0083	0.9999	(18)
$La(ClO_4)_3$	0.83815	6.5333	-0.01288	4.500	0.0269	0.9998	(33)
$La(NO_3)_3$	0.30507	5.1333	-0.01750	4.000	0.0314	0.9963	(21)
$La(C_2H_5SO_4)_3$	0.80506	5.2315	-0.10389	1.100	0.0003	1.0000	(34)
$PrCl_3$	0.58804	5.6000	-0.02060	3.800	0.0108	0.9999	(18)
$Pr(ClO_4)_3$	0.82454	6.5333	-0.00914	4.500	0.0240	0.9999	(33)
$Pr(NO_3)_3$	0.32615	5.1333	-0.01851	4.000	0.0290	0.9973	(21)
$Pr(C_2H_5SO_4)_3$	0.80996	5.3111	-0.09972	0.800	0.0003	1.0000	(34)
$NdCl_3$	0.58674	5.6000	-0.01882	3.800	0.0102	0.9999	(18)
$Nd(ClO_4)_3$	0.81468	6.5333	-0.00677	4.500	0.0209	0.9999	(33)
$Nd(NO_3)_3$	0.33927	5.1333	-0.01945	4.000	0.0277	0.9977	(21)
$Nd(C_2H_5SO_4)_3$	0.79101	5.4928	-0.09135	1.100	0.0003	1.0000	(34)
$SmCl_3$	0.59361	5.6000	-0.01914	3.600	0.0095	0.9999	(18)
$Sm(ClO_4)_3$	0.82673	6.5333	-0.00487	4.500	0.0211	0.9999	(33)
$Sm(NO_3)_3$	0.35802	5.1333	-0.01884	4.200	0.0235	0.9987	(20)
$Sm(C_2H_5SO_4)_3$	0.84486	5.8016	-0.10039	0.800	0.0002	1.0000	(34)
$EuCl_3$	0.60135	5.6000	-0.01926	3.400	0.0089	0.9999	(18)
$Eu(C_2H_5SO_4)_3$	0.80148	5.6723	-0.08613	1.100	0.0003	1.0000	(34)
$Ga(ClO_4)_3$	0.78535	5.2055	0.04202	2.000	0.0072	0.9999	(22)
$GdCl_3$	0.61142	5.6000	-0.01924	3.400	0.0084	0.9999	(18)
$Gd(ClO_4)_3$	0.84832	6.5333	-0.00792	4.500	0.0197	0.9999	(33)
$Gd(NO_3)_3$	0.37841	5.1333	-0.01960	4.200	0.0283	0.9986	(20)
$Gd(C_2H_5SO_4)_3$	0.85152	5.4619	-0.10224	0.800	0.0004	1.0000	(34)
$TbCl_3$	0.62231	5.6000	-0.01923	3.400	0.0088	0.9999	(18)

Table 1.4 (continued)

Compound	$\beta^{(o)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref
$Tb(ClO_4)_3$	0.88329	6.5333	−0.01112	4.600	0.0290	0.9998	(19)
$Tb(NO_3)_3$	0.36850	5.1333	−0.01794	4.400	0.0291	0.9983	(20)
$Tb(C_2H_5SO_4)_3$	0.84999	5.6688	−0.09676	1.100	0.0004	1.0000	(34)
$DyCl_3$	0.62826	5.6000	−0.01895	3.600	0.0108	0.9999	(18)
$Dy(ClO_4)_3$	0.88021	6.5333	−0.00947	4.500	0.0297	0.9998	(33)
$Dy(C_2H_5SO_4)_3$	0.85138	5.9023	−0.09248	1.100	0.0003	1.0000	(34)
$HoCl_3$	0.62346	5.6000	−0.01675	3.600	0.0111	0.9999	(18)
$Ho(ClO_4)_3$	0.87129	6.5333	−0.00699	4.500	0.0346	0.9998	(33)
$Ho(C_2H_5SO_4)_3$	0.84317	5.4972	−0.09396	1.100	0.0003	1.0000	(34)
$ErCl_3$	0.62158	5.6000	−0.01524	3.600	0.0109	0.9999	(18)
$Er(ClO_4)_3$	0.87506	6.5333	−0.00671	4.500	0.0348	0.9998	(33)
$Er(NO_3)_3$	0.43114	5.1333	−0.02587	4.000	0.0289	0.9983	(20)
$Er(C_2H_5SO_4)_3$	0.85345	5.6291	−0.09371	1.100	0.0004	1.0000	(34)
$TmCl_3$	0.62640	5.6000	−0.01513	3.800	0.0120	0.9999	(18)
$Tm(ClO_4)_3$	0.87513	6.5333	−0.00617	4.500	0.0342	0.9998	(33)
$Tm(NO_3)_3$	0.45394	5.1333	−0.02776	4.000	0.0277	0.9986	(20)
$Tm(C_2H_5SO_4)_3$	0.84589	5.6167	−0.09279	1.100	0.0003	1.0000	(34)
$YbCl_3$	0.62580	5.6000	−0.01453	4.000	0.0120	0.9999	(18)
$Yb(ClO_4)_3$	0.88116	6.5333	−0.00664	4.500	0.0315	0.9998	(33)
$Yb(NO_3)_3$	0.46744	5.1333	−0.02812	4.000	0.0242	0.9990	(20)
$Yb(C_2H_5SO_4)_3$	0.85915	5.6640	−0.09078	1.200	0.0002	1.0000	(34)
$LuCl_3$	0.62106	5.6000	−0.01356	4.000	0.0113	0.9999	(18)
$Lu(ClO_4)_3$	0.86883	6.5333	−0.00188	4.000	0.0291	0.9998	(33)

Table 1.4 (continued)

Compound	$\beta^{(o)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref.
$Lu(C_2H_5SO_4)_3$	0.86256	5.7210	−0.09167	1.200	0.0003	1.0000	(34)
$AlCl_3$	0.68627	6.0203	0.00810	1.800	0.0088	0.9999	(22)
$ScCl_3$	0.72087	6.5317	0.03367	1.800	0.0044	0.9999	(22)
$CrCl_3$	0.69081	2.7849	−0.04390	1.200	0.0033	0.9999	(22)
$Cr(NO_3)_3$	0.72490	6.3169	−0.05993	1.400	0.0035	0.9999	(22)
YCl_3	0.62570	5.6000	−0.01571	3.800	0.0117	0.9999	(18)
$Y(C_2H_5SO_4)_3$	0.85187	5.6577	−0.09322	1.200	0.0003	1.0000	(34)
$CeCl_3$	0.63509	7.4991	−0.03001	2.000	0.0127	0.9996	(22)
$FeCl_3$	0.23617	−5.3975	−0.00796	10.000	0.0087	0.9999	(35)
Na_3PO_4	0.13514	5.4136	-	0.700	0.0063	0.9401	(22)
Na_3AsO_4	0.20193	5.5366	-	0.700	0.0048	0.9932	(22)
K_3PO_4	0.31668	7.4659	-	0.700	0.0079	0.9942	(22)
K_3AsO_4	0.42291	9.9809	-	0.011	0.0111	0.9934	(22)
$K_3Fe(cn)_6$	0.34915	5.5849	−0.04508	1.400	0.0034	0.9995	(22)
$K_3Co(cn)_6$	0.36592	1.6190	−0.06946	1.311	0.0247	0.9890	(36)
$Co(en)_3Cl_3$	0.18592	3.8000	−0.02783	1.000	0.0009	0.9997	(22)
$Co(en)_3(NO_3)_3$	0.10340	3.5513	-	0.275	0.0013	0.9997	(36)
$Co(pn)_3(ClO_4)_3$	0.14854	2.9504	-	0.261	0.0036	0.9973	(36)

Table 1.5 Ion interaction parameters for 4-1,1-4 electrolytes at 25 C

Compound	$\beta^{(o)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R	Ref.
$K_4Mo(CN)_8$	0.00575	-7.4744	0.01015	1.400	0.0132	0.9878	(22)
$K_4Fe(CN)_6$	-0.00638	-10.6019	-	0.900	0.0155	0.9799	(22)
$K_4P_2O_7$	0.05939	-9.2939	0.01591	2.300	0.0099	0.9989	(37)
$K_4W(CN)_8$	0.38299	6.1624	-0.05810	1.500	0.0192	0.9948	(38)
K_4ATP^a	0.08619	-4.8045	0.01494	2.400	0.0080	0.9994	(39)
Na_4ATP^a	-0.04154	-6.0631	0.03044	2.000	0.0093	0.9974	(39)
$Na_4P_2O_7$	0.06250	-11.1364	-	0.230	0.0038	0.9929	(37)
$ThCl_4$	0.47146	-9.4843	-0.00078	1.800	0.0179	0.9994	(22)
$Th(NO_3)_4$	0.35392	-7.6453	-0.01869	5.000	0.0126	0.9997	(22)
$Pt(pn)_3Cl_4$	0.28756	10.7131	-	0.100	0.0063	0.9983	(38)
$[N(Me)_4]_4$-$Mo(CN)_8$	0.53495	9.6607	0.08620	1.440	0.0120	0.9988	(38)

---

[a] ATP (adenosine-5'-triphosphate)

Table 1.6 Ion interaction parameters for 2-2 electrolytes at 25 C

Compound	$\beta^{(o)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	Max.m	SD	R	Ref.
$CuSO_4$	0.20458	2.7490	-42.038	0.01886	1.400	0.00175	0.9999	(22,23)
$ZnSO_4$	0.18404	3.0310	-27.709	0.03286	3.500	0.00212	1.0000	(22,23)
$CdSO_4$	0.20948	2.6474	-44.473	0.01021	3.500	0.00265	0.9999	(22,23)
$NiSO_4$	0.15471	3.0769	-37.593	0.04301	2.500	0.00310	0.9999	(22,23)
$MgSO_4$	0.22438	3.3067	-40.493	0.02512	3.000	0.00346	0.9999	(22,23)
$MnSO_4$	0.20563	2.9362	-38.931	0.01650	4.000	0.00470	0.9999	(22,23)
$BeSO_4$	0.31982	3.0540	-77.689	0.00598	4.000	0.00421	0.9999	(22,23)
UO_2SO_4	0.33190	2.4208	98.958	-0.01789	6.000	0.00224	1.0000	(22)
$CaSO_4$	0.20000	3.7762	-58.388	-	0.020	0.00460	0.9863	(23)
$CoSO_4$	0.20000	2.9709	-28.752	-	0.100	0.00248	0.9992	(23)

sometimes negligible. Therefore C^{ϕ}_{MX} is omitted in cases where the experimental data exist only in the range below 1.0 molality.

In some cases these coefficients, C^{ϕ}_{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 $\ln(\tau_{HCl})$ 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 $\ln(\tau_{HCl})$ 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 $\ln(\tau_{MX})$ 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

Salt	Maximum Molality	Standard Deviation[1]
HCl	16.00	0.02854 (0.22031)
	6.00	0.02956 (0.00311)
LiBr	20.00	0.07224 (0.060991)
	2.50	0.06780 (0.00286)
$CaBr_2$	7.66	0.08760 (0.46557)
	2.00	0.00732 (0.00773)
$Pr(NO_3)_3$	6.20	0.17827 (1.78436)
	1.10	0.07117 (0.00623)
$MgSO_4$	3.62	0.00574 (0.00794)
	3.00	0.00385 (0.00317)

---

[1] 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 $\ln\gamma_{MX}$) 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.

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Figure 1.1

Comparison of experimental smoothed τ_{MX} with values calculated from Pitzer and present work for HCl at 25°C.

Figure 1.1

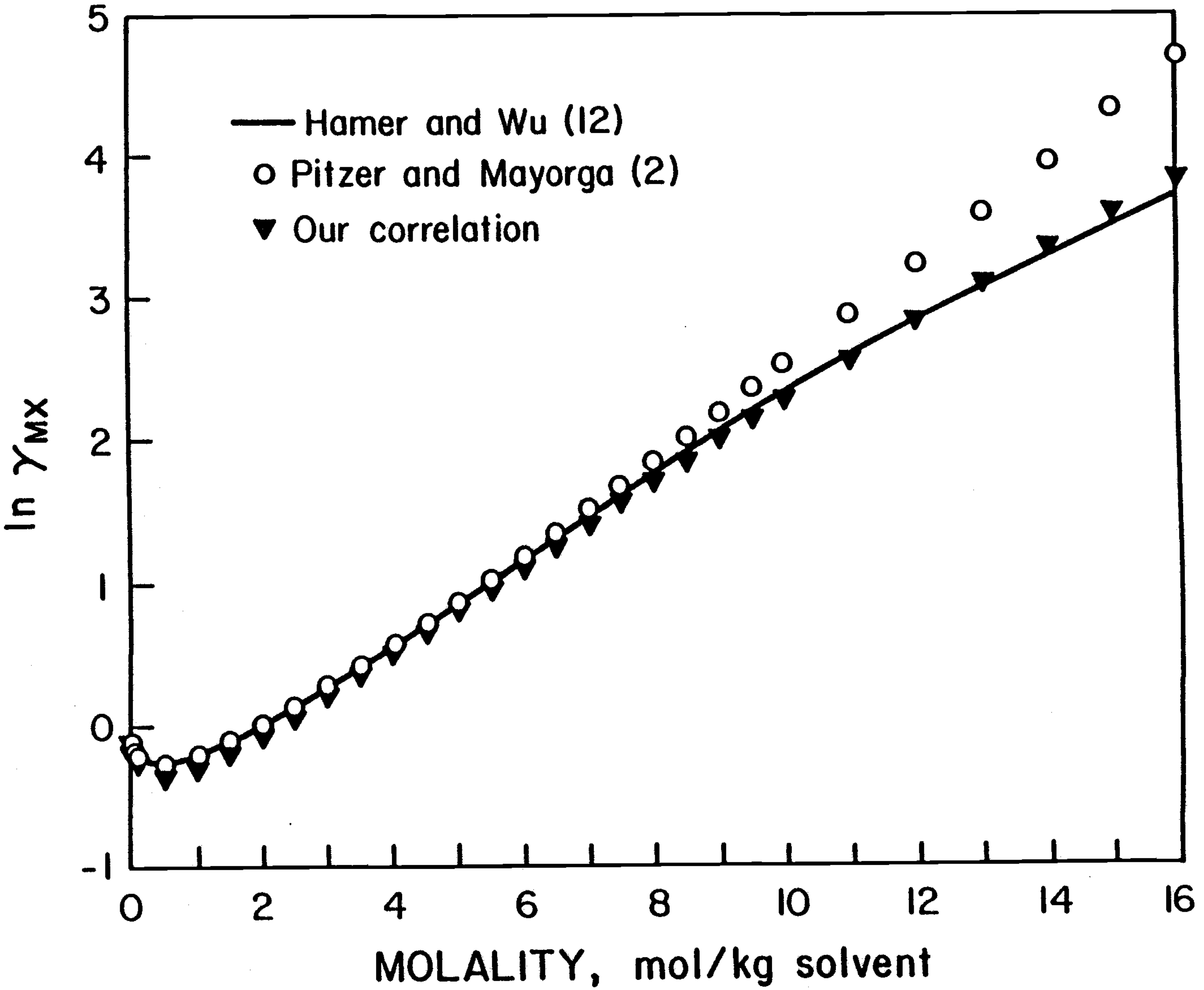
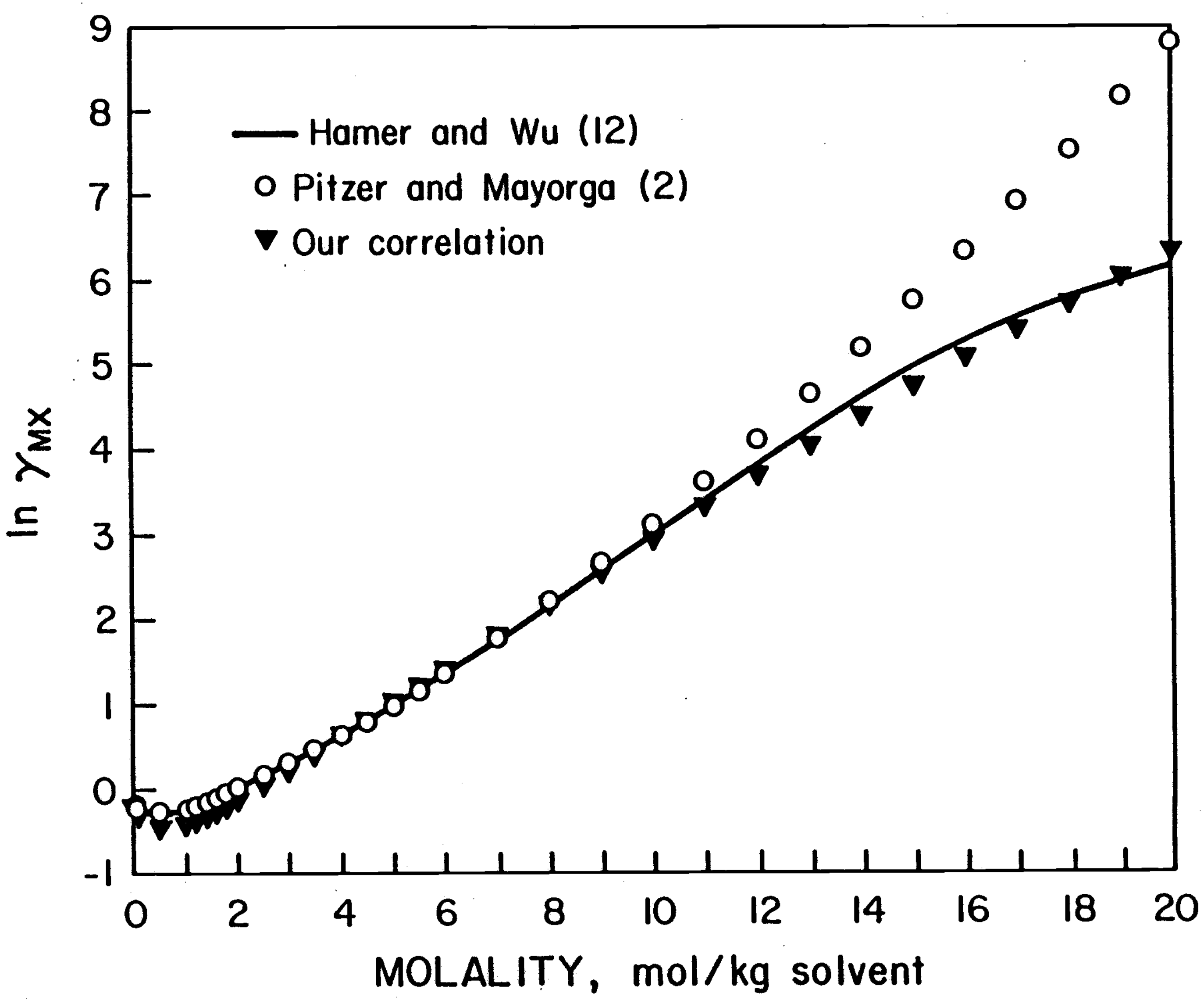

Hamer and Wu (12)
Pitzer and Mayorga (2)
Our correlation
$\ln \gamma_{MX}$
5
4
3
2
1
0
-1
0
2
4
6
8
10
12
14
16
MOLALITY, mol/kg solvent

Figure 1.2

Comparison of experimental smoothed τ_{MX} with values calculated from Pitzer and present work for LiBr at 25°C.



Hamer and Wu (12)
Pitzer and Mayorga (2)
Our correlation
$\ln \gamma_{MX}$
9
8
7
6
5
4
3
2
1
0
-1
0
2
4
6
8
10
12
14
16
18
20
MOLALITY, mol/kg solvent

Figure 1.2

Figure 1.3

Comparison of experimental smoothed τ_{MX} with values calculated from Pitzer and present work for $CaBr_2$ at 25°C.

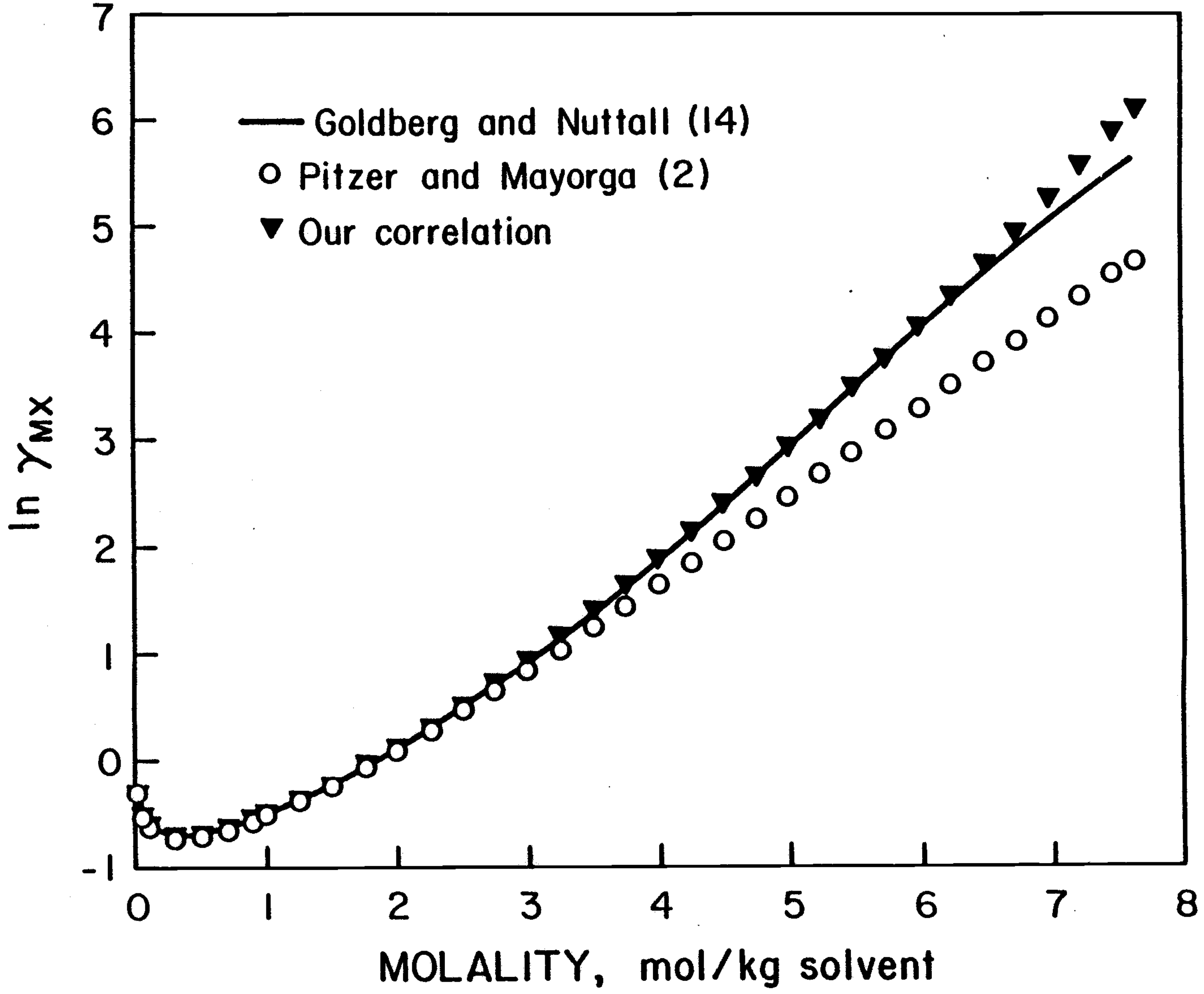

Goldberg and Nuttall (14)
○ Pitzer and Mayorga (2)
▼ Our correlation
ln γ_{MX}
MOLALITY, mol/kg solvent
7
6
5
4
3
2
1
0
-1
0
1
2
3
4
5
6
7
8

Figure 1.3

Figure 1.4

Comparison of experimental smoothed τ_{MX} with values calculated from Pitzer and present work for $Pr(NO_3)_2$ at 25°C.

Figure 1.4

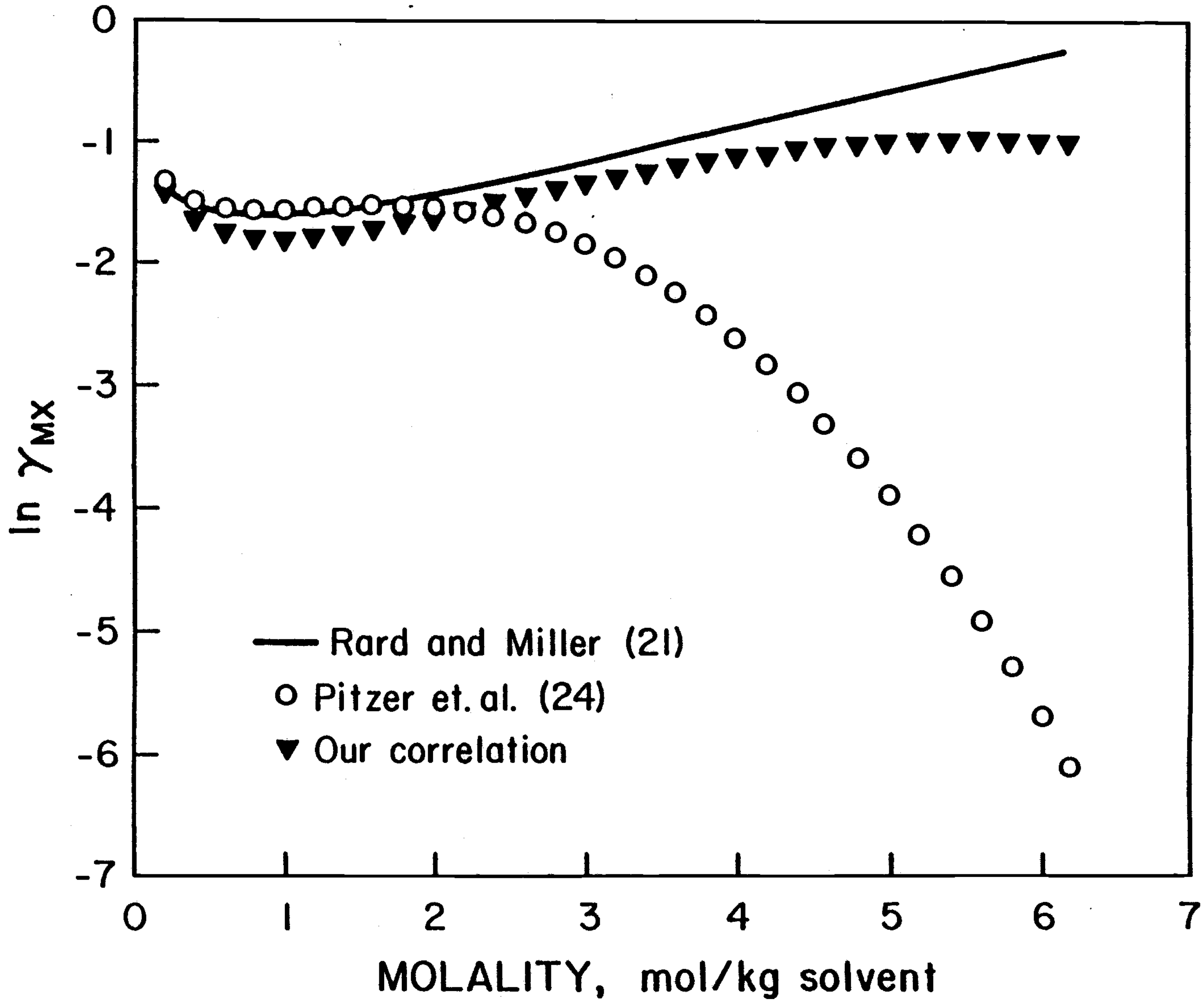
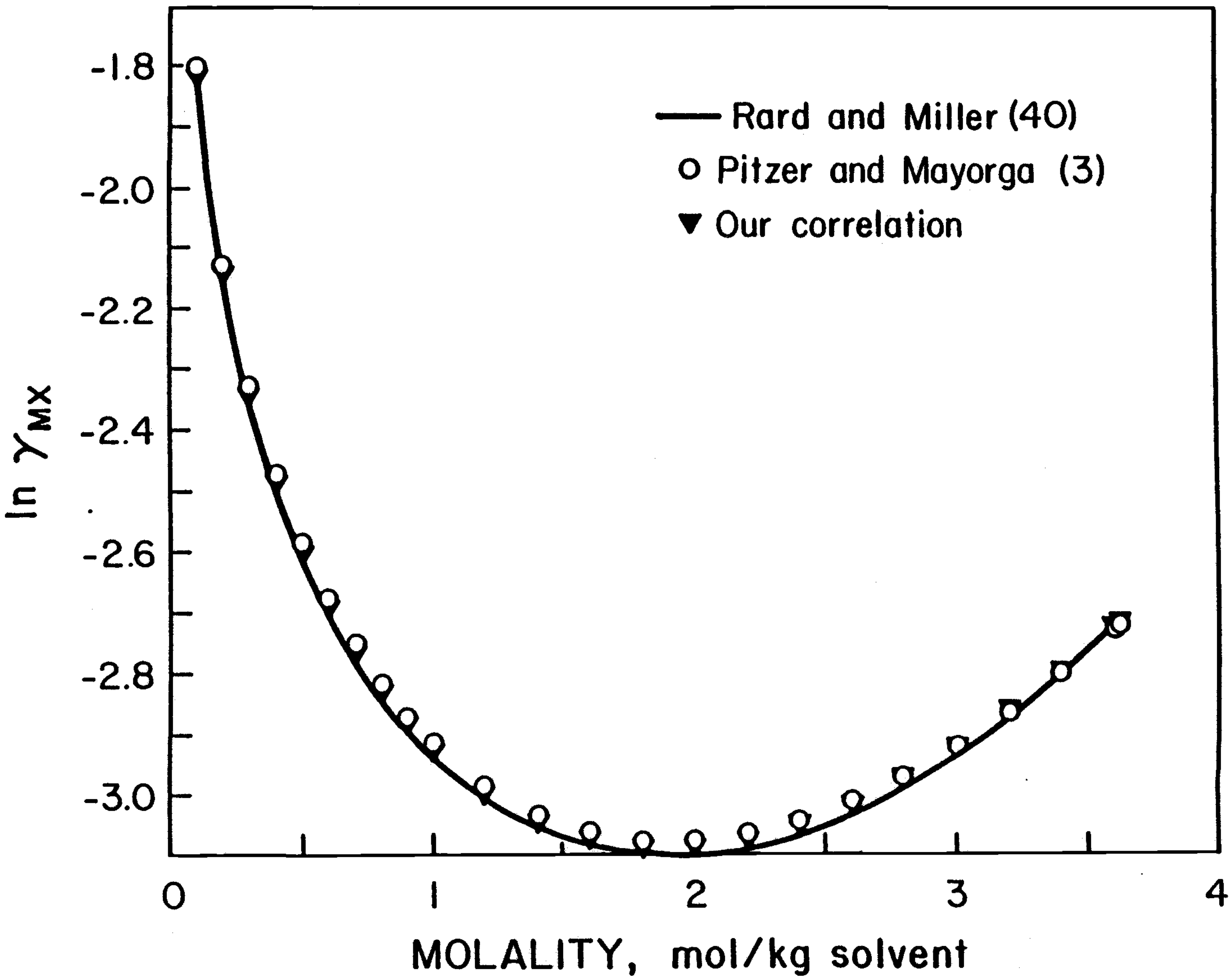

0
-1
-2
-3
-4
-5
-6
-7
ln γ_{MX}
0
1
2
3
4
5
6
7
MOLALITY, mol/kg solvent
Rard and Miller (21)
○ Pitzer et. al. (24)
▼ Our correlation

Figure 1.5

Comparison of experimental smoothed τ_{MX} with values calculated from Pitzer and present work for $MgSO_4$ at 25°C.

Figure 1.5


-1.8
-2.0
-2.2
-2.4
-2.6
-2.8
-3.0
ln γ_{MX}
0
1
2
3
4
MOLALITY, mol/kg solvent
Rard and Miller (40)
○ Pitzer and Mayorga (3)
▼ Our correlation

REFERENCES

1. Pitzer, K.S., Thermodynamics of Electrolytes I: Theoretical basis and general equations., J. Phys. Chem., 77, 268-277 (1973).

2. Pitzer, K.S., and Mayorga, G., Thermodynamics of Electrolytes II: Activity and osmotic coefficients for strong electrolytes with one or both ions univalent., J. Phys. Chem., 77, 2300-2308 (1973).

3. Pitzer. K.S., and Mayorga, G., Thermodynamics of Electrolytes III: Activity and osmotic coefficients for 2-2 electrolytes., J. Solution Chem., 3, 539-546 (1974).

4. Pitzer, K.S., and Kim, J.J., Thermodynamics of Electrolytes IV: Activity and osmotic coefficients for mixed electrolytes., J. Am. Chem. Soc., 96, 5701-5707 (1974).

5. Harvie, C.E., and Weare, J.H., The Prediction of Mineral Solubilities in Natural Waters: the Na-K-Mg-Ca-SO_4-H_2O System from Zero to High Concentration at 25°C., Geochim. Cosmochim. Acta.,44, 981-997 (1980).

6. Harvie, C.E., Eugster, H.P., and Weare, J.H., Mineral Equilibria in the Six-Component Seawater System, Na-K-Mg-Ca-SO_4-Cl-H_2O at 25°C, II: Compositions of the Saturated Solutions., Geochim. Cosmochim. Acta., 46, 1603-1618 (1982).

7. Harvie, C.E., Moller, N., and Weare, J.H., The Prediction of Mineral Solubilities in Natural Water: the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O System to High Ionic Strengths at 25°C., Geochim. Cosmochim. Acta.,48, 723-751 (1984).

8. Kelly, B., and Frederick, W.J. Jr., Application of Chemical Engineering Principle in the Forest Products and Related Industries., F. Kayihan and B. Krieger-Brackett, Editors. AIChE Forest Products Division, Seattle, 1986.

9. Chen, C.C., Britt, H.I., Boston, J.F., and Evans, L.B., Extension and Application of the Pitzer Equation for Vapor-Liquid Equilibrium of Aqueous Electrolyte Systems with Molecular Solutes., AIChE J., 25, 820-831 (1979).

10. Whitfield, M., An Improved Specific Interaction Model for Seawater at 25°C and 1 Atmosphere Total Pressure., Mar. Chem., 3, 197-213 (1975).

11. Whitfield, M., The Extension of Chemical Models for Sea Water to Include Trace Components at 25°C and 1 atm Pressure., Geochim. Cosmochim. Acta., 39, 1545-1557 (1975).

12. Hamer, W.J., and Wu, Y.C., Osmotic Coefficients and Mean Activity Coefficients of Uni-Univalent Electrolytes in Water at 25°C., J. Phys. Chem. Ref. Data, 1, 1047 -1099 (1972).

13. Goldberg, R.N., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Thirty-Six Uni-Bivalent Electrolytes., J. Phys. Chem. Ref. Data, 10, 671-764 (1981).

14. Goldberg, R.N., and Nuttall, R.L., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: The Alkaline Earth Metal Halides., J. Phys. Chem. Ref. Data, 7, 263-310 (1978).

15. Goldberg, R.N., Nuttall, R.L., and Staples, B.R., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Iron Chloride and the Bi-Univalent Compounds of Nickel and Cobalt., J. Phys. Chem. Ref. Data, 8, 923 -1003 (1979).

16. Goldberg, R.N., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-Univalent Compounds of Lead, Copper, Manganese, and Uranium., J. Phys. Chem. Ref. Data , 8, 1005-1050 (1979).

17. Goldberg, R.N., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-Univalent Compounds of Zinc, Cadmium, and Ethylene Bis (Trimethylammonium) Chloride and Iodie., J. Phys. Chem. Ref. Data , 10, 1-55 (1981).

18. Spedding, F.H., Weber, H.O., Saeger, V.W., Petheram, H.H., Rard, J.A., and Habenschuss, A.J., Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25°C. 1. The Rare Earth Chlorides., Chem. Eng. Data, 21, 341 -360 (1976).

19. Rard, J.A., Weber, H.O., and Spedding, F.H., Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25°C. 2. The Rare Earth Perchlorates., J. Chem. Eng. Data, 22, 187-201 (1977).

20. Rard, J.A., Shiers, L.E., Heiser, D.J., and Spedding, F.H., Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25°C. 3. The Rare Earth Nitrates., J. Chem. Eng. Data, 22, 337-347 (1977).

21. Rard, J.A., and Miller, D.C., Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25°C. 4. $La(NO_3)_3$, $Pr(NO_3)_3$, and $Nd(NO_3)_3$., J. Chem. Eng. Data, 24, 348-354 (1979).

22. Robinson, R.A., and Stokes, R.H., Electrolyte Solutions, 2nd ed., Butterworths: London, 1959.

23. Pitzer, K.S., Thermodynamic Properties of Aqueous Solutions of Bivalent Sulfates., J. Chem. Soc., Faraday Trans., 68, 101-113 (1972).

24. Pitzer, K.S., Peterson, J.R., and Silvester, L.F., Thermodynamics of Electrolytes. IX. Rare Earth Chlorides, Nitrates, and Perchlorates., J. Solution Chem., 7, 45-56 (1978).

25. Staples, B.R., Activity and Osmotic Coefficients of Aqueous Alkali Metal Nitrites., J. Phys. Chem. Ref., 10, 765-777 (1981).

26. Bonner, O.D., Osmotic and Activity Coefficients of Lithium Chlorate and Lithium Bromate., J. Chem. Eng. Data, 24, 210-211 (1979).

27. Platford, R.A., Osmotic and Activity Coefficients of Some Simple Borates in Aqueous Solution at 25°C., Can. J. Chem., 47, 2771-2773 (1969).

28. Bonner, O.D., The Osmotic and Activity Coefficients of Some Salts Having Relatively Large Molar Volumes., J. Chem. Eng. Data, 21, 498-499 (1976).

29. Kalman, E., and Schwabe, K., Osmotic and Activity Coefficients of Ammonium Thiocyanate in Aqueous Solutions at 25°C., J. Solution Chem., 8, 1-4 (1979).

30. Bonner, O.D., Osmotic and Activity Coefficients of Methyl-Substituted Ammonium Perchlorates at 298,15 K., J. Chem. Eng. Data, 27, 62-64 (1982).

31. Macaskill, J.B., Robinson, R.A., and Bates, R.G., Osmotic and Activity Coefficients of Guanidinium Chloride in Concentrated Aqueous Solutions at 25°C., J. Chem. Eng. Data, 22, 411-412 (1977).

32. Staples, B.R., Activity and Osmotic Coefficients of Aqueous Sulfuric Acid at 298.15 K., J. Phys. Chem. Ref. Data, 10, 779-798 (1981).

33. Libus, Z., Sadowaska, T., and Trzaskowski, J., Osmotic Coefficients of Aqueous Rare-Earth Perchlorates and Nitrates., J. Chem. Thermodynamics, 11, 1151-1161 (1979).

34. Libus, Z., Zak, E., and Sadowaska, T., Osmotic Coefficients of Aqueous Rare-Earth Ethylsulphates., J. Chem. Thermodynamics, 16, 257-266 (1984).

35. Kangro, W., and Groeneveld, A., Concentrated Aqueous Solutions I., Z. Phys. Chem. (Frankfurt am Main), 32, 110-126 (1962).

36. Wynveen, R.A., Dye, J.L., and Brubaker, C.H. Jr., Activity Coefficient and Conductivity Measurements of High-Charge (3-1, 1-3, 3-2) Electrolytes, I., J. Am. Chem. Soc., 82, 4441-4445 (1960).

37. Bonner, O.D., The Osmotic and Activity Coefficients of Some Pyrophosphates., J. Chem. Thermodynamics, 11, 559-562 (1979).

38. Groves, K.O., Dye, J.L., and Brubaker, C.H. Jr., Activity Coefficients and Conductances of High-Charge (4-1, 1-4, 1-2) Electrolytes, II., J. Am. Chem. Soc., 82, 4445-4448 (1960).

39. Bonner, O.D., The Osmotic and Activity Coefficients of Tetrasodium and tetrapotassium Adenosine-5'-Triphosphate., J. Chem. Thermodynamics, 11, 563-565 (1979).

40. Rard, J.A., and Miller, D.G., Isopiestic Ditermination of the Osmotic Coefficients of Aqueous Na_2So_4, $MgSO_4$, and Na_2SO_4-$MgSO_4$ at 25°C. J. Chem. Eng. Data, 26, 33-38 (1981).

41. Wu, Y.C., and Hamer, W.J., Revised Values of the Osmotic Coefficients and Mean Activity Coefficients of Sodium Nitrate in Water at 25°C., J. Phys. Chem. Ref. Data, 9, 513.-518 (1980).

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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ABSTRACT

The Pitzer mixing parameters θ_{ij} and $¥_{ijk}$ 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 ϕ 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 ϕ 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, $\gamma_{\pm}$.

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, θ_{ij} and ψ_{ijk} from experimental data on aqueous mixed electrolyte solutions with common ions. The θ-terms summarize interaction between ions of like charged sign that are independent of the common ion in a ternary mixture and the ψ-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.

$$\phi - 1 = \frac{2}{\sum_i m_i} \{ \frac{-A^{\phi} I^{3/2}}{1+b\sqrt{I}} + \sum_c \sum_a m_c m_a (B^{\phi}_{ca} + Z C_{ca}) +$$

$$+ \sum_{c<} \sum_{c'} m_c m_{c'} (\Phi^{\phi}_{cc'} + \sum_a m_a \psi_{cc'a})$$

$$+ \sum_{a<} \sum_{a'} m_a m_{a'} (\Phi^{\phi}_{aa'} + \sum_c m_c \psi_{aa'c}) \} \qquad (1)$$

$$\ln\gamma_{MX} = |z_M z_X| F + \left(\frac{2v_M}{v}\right) \sum_a m_a [B_{Ma} + \frac{Z}{2} C_{Ma} + \left(\frac{v_X}{v_M}\right) \Phi_{Ma}] +$$

$$\left(\frac{2v_X}{v}\right) \sum_c m_c [B_{cX} + \frac{Z}{2} C_{cX} + \left(\frac{v_M}{v_X}\right) \Phi_{cX}] +$$

$$v^{-1} \sum_c \sum_a m_c m_a [2v_M z_M C_{ca} + v_M \psi_{Mca} + v_X \psi_{Xac}] +$$

$$\sum_{c<}\sum_{c'} m_c m_{c'} \left(\frac{v_X}{v}\right) \psi_{cc'X} + \sum_{a<}\sum_{a'} m_a m_{a'} \left(\frac{v_M}{v}\right) \psi_{aa'M} \qquad (2)$$

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

$$F = -A^{\phi}[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b} \ln (1+b\sqrt{I})] + \sum_c \sum_a m_c m_a B'_{ca} +$$

$$\sum_{c<}\sum_{c'} m_c m_{c'} \Phi'_{cc'} + \sum_{a<}\sum_{a'} m_a m_{a'} \Phi'_{aa'} \qquad (3)$$

where $A^{\phi} = 1/3 \ (2\pi \ N_o \ d_w/1000)^{1/2} \ (e^2/DkT)^{3/2}$

A^{ϕ} 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 $\sum_{c<}\sum_{c'}$, and $\sum_{a<}\sum_{a'}$, in eqs 1, 2 and 3 means the sum over all distinguishable pairs of dissimilar anions or cations (5). 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

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

and

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

is the total ionic strength of given system.

The parameters B^{ϕ}_{MX}, 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.

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

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

$$B'_{MX} = \beta_{MX}^{(1)} f'(\alpha_1\sqrt{I})/I + \beta M_X^{(2)} f'(\alpha_2\sqrt{I})/I \quad (6)$$

where

$$f(x) = 2[1-(1+x)e^{-x}]/x^2 \tag{7}$$

$$f'(x) = -2[1-(1+x+\tfrac{1}{2}x^2)e^{-x}]/x^2 \tag{8}$$

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, 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^{ϕ}_{MX}, the corresponding coefficients for calculating the osmotic coefficient, are related by the following eq 9 (2).

$$C_{MX} = C^{\phi}_{MX}/2\sqrt{|z_M z_M|} \tag{9}$$

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

$$\Phi^{\phi}_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) + I\,{}^{E}\theta'_{ij}(I) \tag{10}$$

$$\Phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) \tag{11}$$

$$\Phi'_{ij} = {}^{E}\theta'_{ij} \tag{12}$$

θ_{ij} is a adjustable parameter for each pair of anions or cations. The third virial coefficients, Ψ_{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:

$${}^{E}\theta_{MN}(I) = \frac{z_M z_N}{4I}\left[J0(x_{MN}) - \frac{1}{2}J0(x_{MM}) - \frac{1}{2}J0(x_{NN})\right] \tag{13}$$

$$^{E}\theta'_{MN}(I) = \frac{z_M z_N}{8I^2}\,[J1(X_{MN}) - \frac{1}{2}J1(X_{MM}) - \frac{1}{2}J1(X_{NN})]$$

$$- \frac{^{E}\theta_{MN}}{I} \qquad (14)$$

where $X_{MX} = 6\ z_M z_N A^{\phi}\ \surd I$, 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 J0(X) and J1(X) are given by following integrals.

$$J0(X) = \frac{1}{4}X - 1 + \frac{1}{X}\int_0^{\infty} [1 - \exp(-\frac{X}{Y}e^{-Y})]\ Y^2\ dY \qquad (15)$$

$$J1(x) = \frac{1}{4}X - \frac{1}{X}\int_0^{\infty} [1-(1+\frac{X}{Y}e^{-Y})\exp(-\frac{X}{Y}e^{-Y}))Y^2 dY \qquad (16)$$

These terms J0(X) and J1(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 value of his expressions, J(X) and J'(X). However we chose to evaluate the integrals J0(X) and J1(X) directly using the IMSL library subroutine DMLIN (14). We have included values of J0(X) and J1(X), calculated by our method for various X values, in Table 2.1. Also. the values of $J0(X_{MN})$, $J1(X_{MN})$, $J0(X_{MM})$, $J1(X_{MM})$, $J0(X_{NN})$, $J1(X_{NN})$, $^{E}\theta_{MN}$, 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 $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, C^{ϕ}_{MX}, θ_{ij} and ¥$_{ijk}$. Among these parameters, $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, and C^{ϕ}_{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 $HCl-NCl_2-H_2O$, 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^{ϕ}_{MX}, B_{MX}, B'_{MX} and C_{MX} may be calculated from their defining eqs 4, 5, 6, and 9 using single salt

Table 2.1 Values of the integrals J0(X) and J1(X)

X	J0(X)	J1(X)
0.01	0.00005178	0.00013627
0.05	0.00113941	0.00192858
0.10	0.00360030	0.00586202
0.20	0.01088057	0.01699179
0.30	0.02032005	0.03086422
0.40	0.03131183	0.04655732
0.50	0.04350765	0.06357538
0.60	0.05667930	0.08161027
0.70	0.07066533	0.10045379
0.80	0.08534549	0.11995732
0.90	0.10062710	0.14001019
1.00	0.116437	0.160528
2.00	0.294158	0.381213
3.00	0.492823	0.615992
4.00	0.702924	0.856962
5.00	0.920340	1.101259
6.00	1.142862	1.347551
7.00	1.369157	1.595127
8.00	1.598356	1.843571
9.00	1.829861	2.092624
10.00	2.063238	2.342115
20.00	4.454392	4.846403
30.00	6.893411	7.354296
40.00	9.352336	9.861749

Table 2.1 (continued)

X	J0(X)	J1(X)
50.00	11.822009	12.368340
60.00	14.298329	14.874126
70.00	16.779125	17.379234
80.00	19.263116	19.883775
90.00	21.749488	22.387845
100.00	24.237693	24.891520
200.00	49.195521	49.915589
400.00	99.117123	99.937508
600.00	149.093071	149.948642
800.00	199.078617	199.955682
1000.00	249.068759	249.960644
5000.00	1249.024371	1249.984829
10000.00	2499.015087	2499.990364

Table 2.2 High order electrostatic functions at constant total ionic strength for $MX-NX_2-H_2O$ systems at 25°C

I	$J0(X_{MN})$	$J1(X_{MN})$	$J0(X_{MM})$	$J1(X_{MM})$	$J0(X_{NN})$	$J1(X_{NN})$	${}^{E}\theta_{MN}$	${}^{E}\theta'_{MN}$
0.10	0.19940	0.26539	0.07701	0.10892	0.48777	0.61005	-0.41477	1.79542
0.50	0.56037	0.69411	0.23115	0.30458	1.29014	1.50897	-0.20028	0.18791
1.00	0.85538	1.02870	0.36238	0.46284	1.92487	2.19437	-0.14413	0.06915
1.50	1.08934	1.28860	0.46839	0.58755	2.42142	2.72253	-0.11852	0.03830
2.00	1.29014	1.50897	0.56037	0.69411	2.84431	3.16855	-0.10305	0.02513
2.50	1.46915	1.70378	0.64298	0.78879	3.21934	3.56185	-0.09240	0.01810
3.00	1.63239	1.88029	0.71875	0.87490	3.55999	3.91760	-0.08450	0.01383
3.50	1.78349	2.04287	0.78920	0.95442	3.87437	4.24486	-0.07833	0.01102
4.00	1.92487	2.19437	0.85538	1.02870	4.16781	4.54953	-0.07334	0.00904
4.50	2.05825	2.33679	0.91799	1.09864	4.44407	4.83572	-0.06920	0.00760
5.00	2.18486	2.47160	0.97760	1.16495	4.70586	5.10643	-0.06569	0.00650

parameter values which are given in Table 2.3 and our earlier paper (15). Mixed electrolyte terms Φ^{ϕ}_{ij}, Φ_{ij}, and Φ'_{ij} were obtained from $^{E}\theta_{ij}$ and $^{E}\theta'_{ij}$ values, calculated from eqs 13 and 14. The remaining terms in eqs 1, 2, and 3 contain θ_{ij} and ψ_{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 θ_{ij} and ψ_{ijk}. For the activity and osmotic coefficients of an MX-NX mixture, he obtained

$$\Delta\phi \left(\frac{\sum_{i} m_i}{2m_M m_N}\right) = \theta_{MN} + m_X \psi_{MNX} \tag{18}$$

and

$$\Delta \ln\gamma_{MX} \left(\frac{\nu}{2\nu_M m_N}\right) = \theta_{MN} + \frac{1}{2}\left(m_X + m_M\left|\frac{z_M}{z_X}\right|\right)\psi_{MNX} \tag{19}$$

The terms $\Delta\phi$ and $\Delta\ln\gamma_{MX}$ are the difference between the experimental values of ϕ or $\ln\gamma_{MX}$ and the calculated values of ϕ or $\ln\gamma_{MX}$ 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

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD[a]	R[b]	Ref.
HCl	0.18024	0.27154	0.00006	6.00	0.0013	1.000	(16)
HBr	0.19622	0.34529	0.00762	4.00	0.0006	1.000	(16)
$HClO_4$	0.17238	0.31708	0.00855	6.00	0.0019	1.000	(16)
$LiCl$	0.14667	0.33703	0.00393	6.00	0.0020	1.000	(16)
$LiBr$	0.17362	0.25976	0.00556	4.50	0.0016	1.000	(16)
$LiNO_3$	0.14060	0.28894	−0.00547	6.00	0.0012	1.000	(16)
$NaBr$	0.09934	0.26202	0.00097	5.00	0.0010	1.000	(16)
$NaNO_3$	0.00479	0.20241	−0.00027	6.00	0.0005	0.999	(17)
NaH_2PO_4	−0.06509	0.09100	0.01138	4.00	0.0023	0.998	(16)
$NaClO_4$	0.05621	0.27177	−0.00143	5.00	0.0005	1.000	(16)
$Na2CO_3$	0.07185	1.15645	−0.00835	1.50	0.0007	0.999	(18)
$NaHCO_3$[c]	0.02800	0.04400	—	—	—	—	(19)
KCl	0.04680	0.22096	−0.00050	4.00	0.0003	1.000	(16)
KH_2PO_4	−0.11280	0.06058	0.02012	1.80	0.0003	1.000	(16)
$CsCl$	0.02995	0.06367	0.00027	6.00	0.0007	0.999	(16)
$CaCl_2$	0.30654	1.64278	0.00222	3.50	0.0028	1.000	(20)
$CaBr_2$	0.36272	1.81585	0.00349	2.50	0.0016	1.000	(20)
$Ca(NO_3)_2$	0.18472	1.64500	−0.01069	4.00	0.0074	0.999	(21)
$CoCl_2$	0.35623	1.54019	−0.01251	3.00	0.0039	0.999	(22)
$CuCl_2$	0.31373	1.24607	−0.04222	2.00	0.0021	0.999	(23)
$MgCl_2$	0.35372	1.70054	0.00524	5.00	0.0029	1.000	(20)
$Mg(NO_3)_2$	0.36516	1.59563	−0.01971	2.00	0.0023	1.000	(21)
$NiCl_2$	0.34657	1.58940	−0.00326	2.50	0.0020	1.000	(22)
$MnCl_2$	0.33547	1.46033	−0.02324	3.50	0.0012	1.000	(23)

Table 2.3 (continued)

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD[a]	R[b]	Ref.
$UO_2(ClO_4)_2$	0.62346	1.97357	0.02084	2.50	0.0030	1.000	(23)
$La(ClO_4)_3$	0.76485	6.53333	0.00275	3.00	0.0007	0.999	(24)

[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 θ_{MN} and $¥_{MNX}$ are obtained from the linear plot as the intercept, θ_{MN} and the slope, $¥_{MNX}$ 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 $\Delta\ln\tau_{MX}$ are greatly magnified at low values of the coefficients of $¥_{MNX}$ 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 $\ln\tau_A/m_B$ 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 θ_{ij} and $¥_{ijk}$ 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, θ_{ij} and $¥_{ijk}$, 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 θ_{ij} but different values of $¥_{ijk}$ in ternary or mlticomponent mixtures. For example, the value of θ_{HNa}=0.0368 in the present study was selected by considering all system (HCl-NaCl-H_2O, HBr-NaBr-H_2O, and $HClO_4$-$NaClO_4$-H_2O) which contain both of H^+ and Na^+.

Figure 2.1

Fits of equation 19 for $HCl-BaCl_2-H_2O$ system at 25°C.

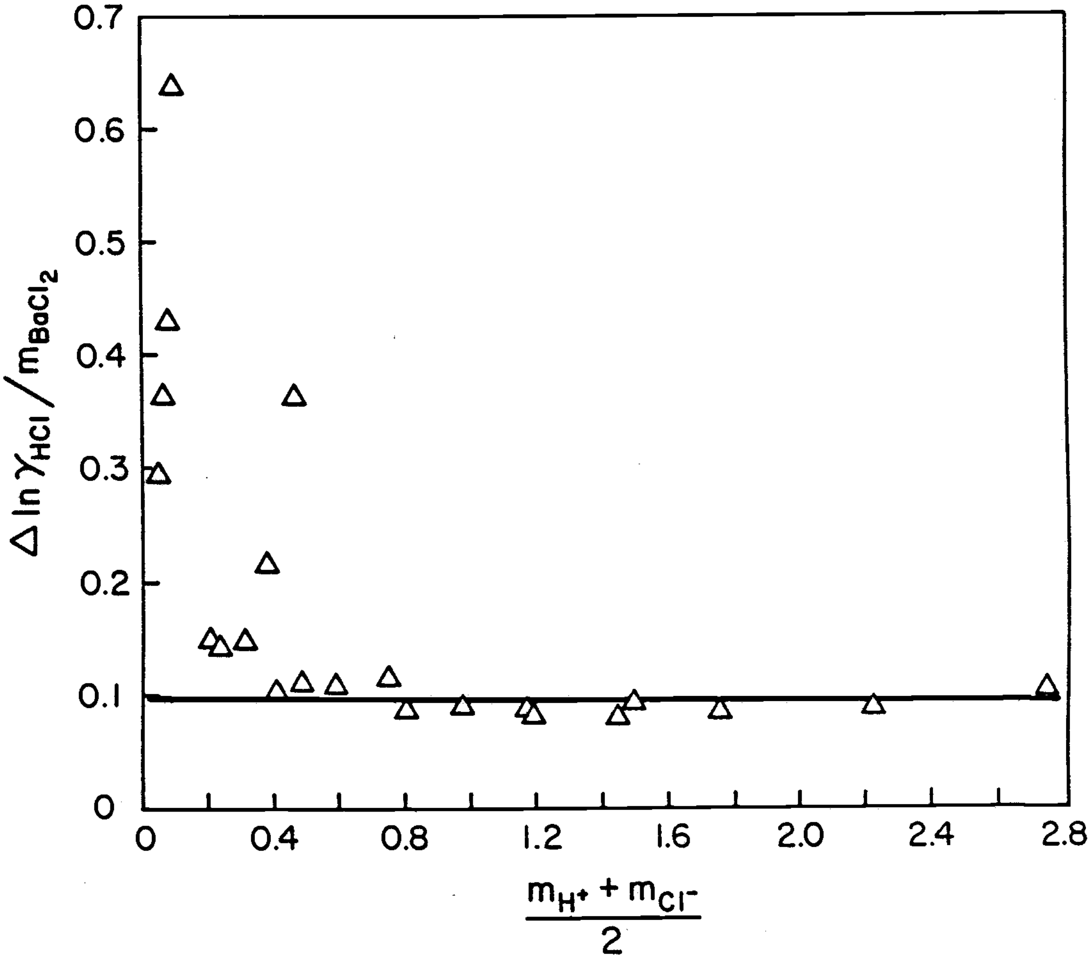
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
$\Delta \ln \gamma_{HCl} / m_{BaCl_2}$
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
$\frac{m_{H^+} + m_{Cl^-}}{2}$

Figure 2.1

Figure 2.2

Fits of equation 19 for HCl-$CaCl_2$-H_2O system at 25°C

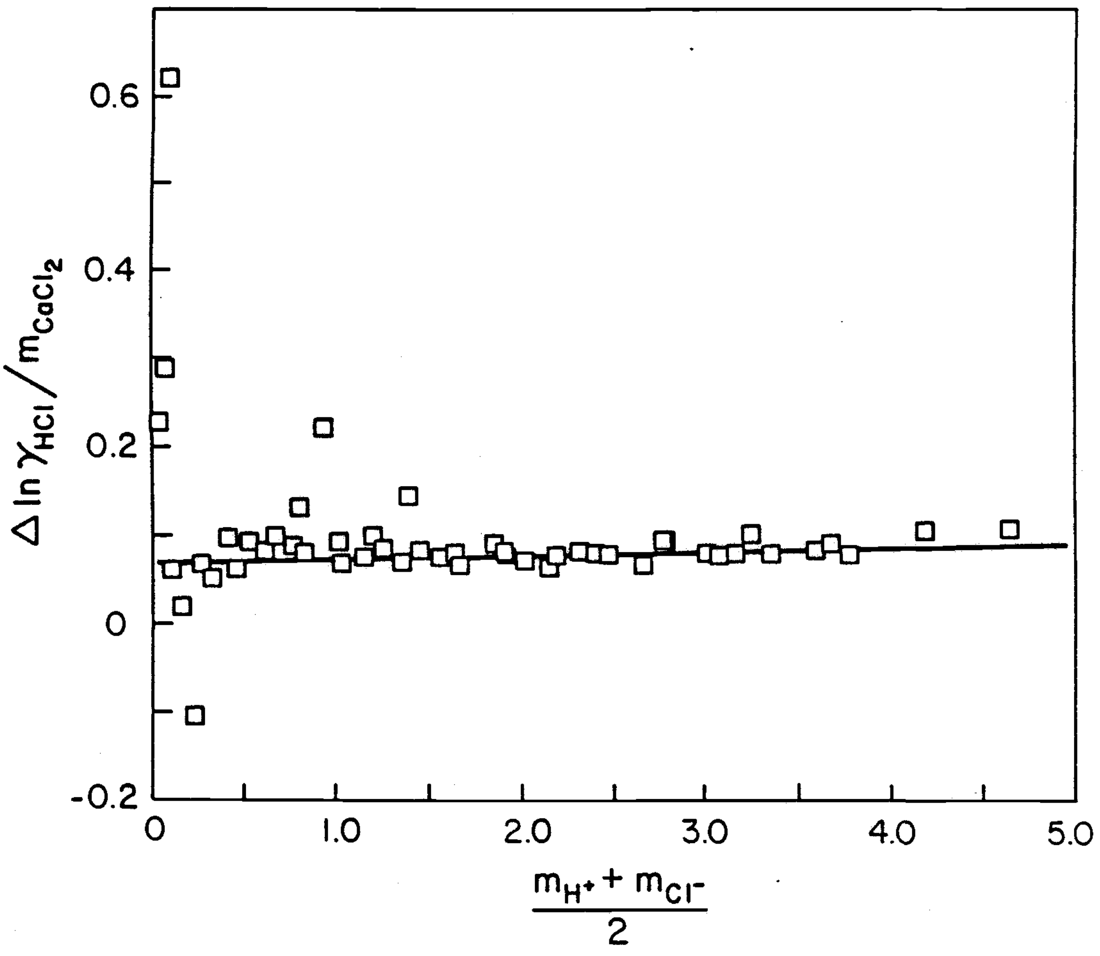
0.6
0.4
0.2
0
-0.2
$\Delta \ln \gamma_{HCl} / m_{CaCl_2}$
0
1.0
2.0
3.0
4.0
5.0
$\frac{m_{H^+} + m_{Cl^-}}{2}$

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 ϕ 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 ϕ 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_2O and 14.25 mol/kg for $NaClO_4$-$UO_2(ClO_4)_2$-H_2O) 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 ϕ 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 = 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 2.4 Pitzer's mixing parameters for mixtures with common ion

System	Exptl	θ	¥	SD (θ & ¥)	SD (θ=¥=0)	Max.I	Ref.
HCl-KCl	$\ln\gamma$	0.0067	-0.0081	0.0128	0.0177	3.51	(25)
HBr-KBr	$\ln\gamma$	0.0067	-0.0215	0.0065	0.0257	3.01	(25)
HCl-NaCl	$\ln\gamma$	0.0368	-0.0033	0.0014	0.0439	3.01	(25)
HBr-NaBr	$\ln\gamma$	0.0368	-0.0107	0.0032	0.0323	3.01	(25)
$HClO_4$-$NaClO_4$	ϕ	0.0368	-0.0162	0.0017	0.0163	5.35	(26)
HCl-LiCl	$\ln\gamma$	0.0151	-0.0022	0.0052	0.0215	4.01	(25)
$HClO_4$-$LiClO_4$	ϕ	0.0151	0.0000	0.0028	0.0109	4.45	(26)
HBr-LiBr	$\ln\gamma$	0.0151	0.0101	0.0141	0.0351	3.01	(25)
HCl-CsCl	$\ln\gamma$	-0.0459	0.0040	0.0100	0.0371	3.00	(27)
NaCl-KCl	$\ln\gamma$	0.0070	-0.0098	0.0112	0.0274	4.30	(28)
NaH_2PO_4-KH_2PO_4	ϕ	0.0070	-0.0162	0.0072	0.0302	6.04	(29)
NaCl-LiCl	ϕ	0.0120	-0.0022	0.0020	0.0027	5.84	(30)
$NaNO_3$-$LiNO_3$	ϕ	0.0120	-0.0065	0.0028	0.0216	5.92	(30)
NaOAc-LiOAc	ϕ	0.0120	-0.0065	0.0064	0.0185	6.05	(30)
$NaClO_4$-$LiClO_4$	ϕ	0.0120	-0.0061	0.0028	0.0094	5.82	(26)
KCl-KH_2PO_4	ϕ	0.1071	-0.0160	0.0026	0.0243	2.07	(29)
NaCl-NaH_2PO_4	ϕ	0.1071	-0.0147	0.0048	0.0335	2.37	(29)

Table 2.4 (continued)

System	Exptl	θ	¥	SD (θ & ¥)	SD (θ=¥=0)	Max.I	Ref.
NaCl-NaF	lnγ	-0.0028	0.0076	0.0019	0.0021	1.05	(10,31)
$NaCl-NaHCO_3$	lnγ	0.0735	0.0989	0.0135	0.0200	1.10	(32)
$HCl-CoCl_2$	lnγ	0.0829	0.0075	0.0039	0.0310	3.00	(33)
$HCl-NiCl_2$	lnγ	0.0895	0.0044	0.0039	0.0316	3.00	(34)
$HCl-BaCl_2$	lnγ	0.0991	-0.0081	0.0050	0.0300	3.00	(35)
$HBr-BaBr_2$	lnγ	0.0991	0.0035	0.0060	0.0268	2.00	(36)
$HCl-CaCl_2$	lnγ	0.0682	0.0043	0.0046	0.0120	5.00	(37)
$HBr-CaBr_2$	lnγ	0.0682	0.0285	0.0060	0.0284	2.00	(38)
$HCl-MnCl_2$	lnγ	0.0899	-0.0092	0.0050	0.0372	5.00	(39)
$HCl-MgCl_2$	lnγ	0.0891	-0.0006	0.0065	0.0483	5.00	(40)
$HCl-SrCl_2$	lnγ	0.0728	0.0050	0.0016	0.0286	3.00	(41)
$HBr-SrBr_2$	lnγ	0.0728	0.0310	0.0055	0.0197	2.00	(42)
$HClO_4-UO_2(ClO_4)_2$	φ	0.1377	-0.0319	0.0131	0.0603	10.88	(43)
$KCl-SrCl_2$	φ	0.0149	-0.0201	0.0018	0.0214	4.80	(44)
$LiCl-BaCl_2$	φ	0.0243	0.0208	0.0057	0.0188	4.32	(45)
$CsCl-BaCl_2$	φ	-0.0441	-0.0229	0.0026	0.0167	4.08	(45)

Table 2.4 (continued)

System	Exptl	θ	¥	SD (θ & ¥)	SD (θ=¥=0)	Max.I	Ref.
$NaCl-MnCl_2$	ϕ	0.0907	-0.0190	0.0019	0.0130	9.30	(46)
$NaCl-CoCl_2$	ϕ	0.0382	-0.0056	0.0036	0.0063	7.29	(47)
$NaClO_4-UO_2(ClO_4)_2$	ϕ	0.0231	-0.0437	0.0257	0.2993	14.25	(43)
$MgCl_2-Mg(NO_3)_2$	ϕ	0.0002	0.0073	0.0163	0.0353	13.70	(48)
$CaCl_2-Ca(NO_3)_2$	ϕ	0.0002	-0.0116	0.0268	0.1180	18.25	(48)
$Mg(NO_3)_2-Ca(NO_3)_2$	ϕ	-0.1844	0.0252	0.0125	0.0219	14.42	(48)
$Na_2SO_4-MgSO_4$	ϕ	0.0970	-0.0352	0.0051	0.0126	8.83	(49)
$NaCl-MgCl_2$	ϕ	0.0970	-0.0517	0.0149	0.0528	7.14	(49)
$CuCl_2-CuSO_4$	ϕ	0.0380	0.0234	0.0022	0.0253	6.90	(50)
$MgCl_2-MgSO_4$	ϕ	0.0380	-0.0062	0.0052	0.0100	7.71	(49)
$NaCl-Na_2SO_4$	ϕ	0.0380	0.0081	0.0100	0.0249	6.00	(49)
$NaCl-CuCl_2$	ϕ	0.0370	-0.0129	0.0044	0.0070	7.30	(50)
$Na_2SO_4-CuSO_4$	ϕ	0.0370	-0.0235	0.0031	0.0041	5.47	(50)
$NaCl-Na_2CO_3$	ϕ	-0.0630	0.0025	0.0076	0.0163	5.70	(51)
$NaClO_4-La(ClO_4)_3$	ϕ	0.2174	-0.0202	0.0049	0.0158	4.90	(52)
$CaCl_2-CoCl_2$	ϕ	0.1722	-0.0332	0.0144	0.0300	13.08	(47)

Figure 2.3

Comparison of experimental and calculated $\ln\gamma_{\pm}$ or $(\phi-1)$ for various systems at 25°C.

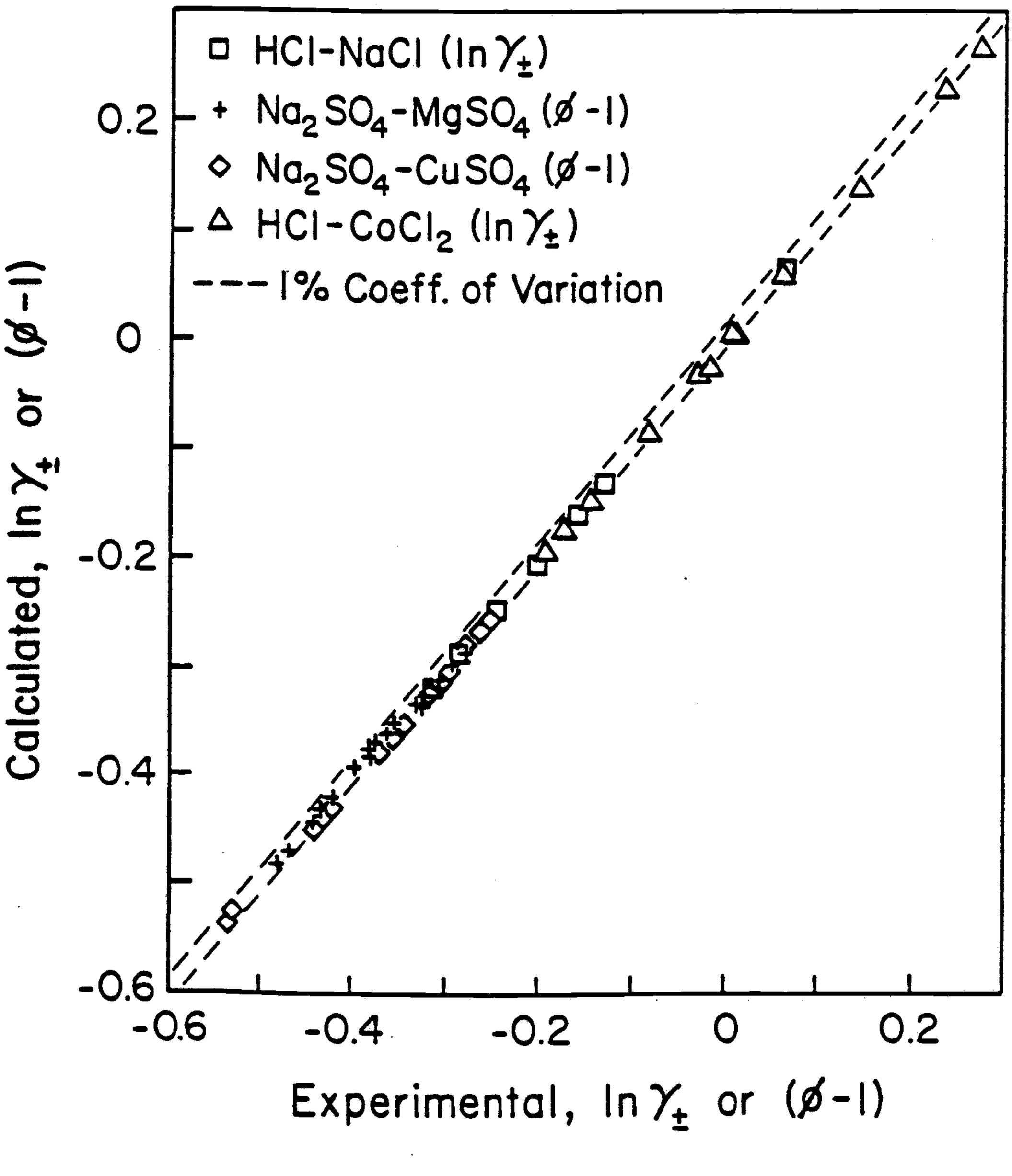
HCl-NaCl ($\ln \gamma_\pm$)
Na_2SO_4-$MgSO_4$ (ϕ-1)
Na_2SO_4-$CuSO_4$ (ϕ-1)
HCl-$CoCl_2$ ($\ln \gamma_\pm$)
1% Coeff. of Variation
Calculated, $\ln \gamma_\pm$ or (ϕ-1)
Experimental, $\ln \gamma_\pm$ or (ϕ-1)
0.2
0
-0.2
-0.4
-0.6
-0.6
-0.4
-0.2
0
0.2

Figure 2.3

obtained the values of θ_{HCa}=0.0739 and ψ_{HCaCl}=0.003 for $HClCaCl_2-H_2O$ and θ_{HCa}=0.0600 and ψ_{HCaBr}=0.0009 for $HBr-CaBr_2-H_2O$, respectively. Also, θ_{HCa}=0.0612 and ψ_{HCaBr} =0.0008 were obtained for $HCl-CaCl_2-H_2O$ 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 θ_{HCa} and ψ_{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 θ_{HCa} and ψ_{HCaX} for both systems, $HCl-CaCl_2-H_2O$ and $HBr-CaBr_2-H_2O$ simultaneously.
2. Khoo et. al. (38, 55) covered ionic strengths only up to 3.0 mol/kg for $HCl-CaCl_2-H_2O$, but Roy et. al. (37) and our work included data up to I = 5.0 mol/kg for $HCl-CaCl_2-H_2O$.

It can be seen from Table 2.4 that θ_{MN} values for the $HX-NX_2-H_2O$ 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 θ_{HN} and to characterize H^+ and N^{+2} interactions which are not specific to the N^{+2} ion. The average value of θ_{HN} is 0.0838 in the present work, whereas θ_{HN} = 0.078 obtained by Khoo et. al (33) for six $HCl-NCl_2-H_2O$ systems where N = Mg, Ca, Sr, Ba, Mn and Co.

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REFERENCES

1. Pitzer, K.S., Thermodynamics of Electrolytes I: Theoretical basis and general equations., J. Phys.Chem., 77, 268-277 (1973).

2. Pitzer, K.S., and Mayorga, G., Thermodynamics of Electrolytes II: Activity and osmotic coefficients for strong electrolytes with one or both ions univalent., J. Phys. Chem., 77, 2300-2308 (1973).

3. Pitzer. K.S., and Mayorga, G., Thermodynamics of Electrolytes III: Activity and osmotic coefficients for 2-2 electrolytes., J. Solution Chem., 3, 539-546 (1974).

4. Pitzer, K.S., and Kim, J.J., Thermodynamics of Electrolytes IV: Activity and osmotic coefficients for mixed electrolytes., J. Am. Chem. Soc., 96, 5701-5707 (1974).

5. Harvie, C.E., and Weare, J.H., The Prediction of Mineral Solubilities in Natural Waters: the Na-K-Mg-Ca-SO_4-H_2O System from Zero to High Concentration at 25°C., Geochim. Cosmochim. ACta.,44, 981-997 (1980).

6. Harvie, C.E., Eugster, H.P., and Weare, J.H., Mineral Equilibria in the Six-Component Seawater System, Na-K-Mg Ca-SO_4-Cl-H_2O at 25°C, II: Compositions of the Saturated Solutions., Geochim. Cosmochim. Acta., 46, 1603-1618 (1982).

7. Harvie, C.E., Moller, N., and Weare, J.H., The Prediction of Mineral Solubilities in Natural Water: the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O System to High Ionic Strengths at 25°C., Geochim. Cosmochim. ACta.,48, 723-751 (1984).

8. Chen, C.C., Britt, H.I., Boston, J.F., and Evans, L.B., Extension and Application of the Pitzer Equation for Vapor-Liquid Equilibrium of Aqueous Electrolyte Systems with Molecular Solutes., AIChE J., 25, 820-831 (1979).

9. Whitfield, M., An Improved Specific Interaction Model for Seawater at 25°C and 1 Atmosphere Total Pressure., Mar. Chem., 3, 197-213 (1975).

10. Whitfield, M., The Extension of Chemical Models for Sea Water to Include Trace Components at 25°C and 1 atm Pressure., Geochim. Cosmochim. Acta., 39, 1545-1557 (1975).

11. Kelly, B., and Frederick, W.J. Jr., Application of Chemical Engineering Principle in the Forest Products and Related Industries., F. Kayihan and B. Krieger-Brackett, Editors. AIChE Forest Products Division, Seattle, 1986.

12. Friedman, H.L., Ionic Solution Theory., Interscience: New York, 1962.

13. Pitzer, K.S., Thermodynamics of Electrolytes: V. Effects of Higher-Order Electrostatic Terms., J. Solution Chem., 4, 249-265 (1975).

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

15. Kim, H.T., and Frederick, W.J.,Jr., Evaluation of Pitzer Ion Interaction Parameters of Aqueous Electrolytes at 25 C. 1. Single Salt Parameters., J. Chem. Eng. Data,(in press).

16. Harmer, W.J., and Wu, Y.C., Osmotic Coefficients and Mean Activity Coefficients of Uni-Univalent Electrolytes in Water at 25°C., J. Phys. Chem. Ref. Data, 1, 1047 -1099 (1972).

17. Wu, Y.C., and Harmer, W.J., Revised Values of the Osmotic Coefficients and Mean Activity Coefficients of Sodium Nitrate in Water at 25°C., J. Phys. Chem. Ref. Data, 9, 513-518 (1980).

18. Goldberg, R.N., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Thirty-Six Uni-Bivalent Electrolytes., J. Phys. Chem. Ref. Data, 10, 671-764 (1981).

19. Peiper, J.C., and Pitzer, K.S., Thermodynamics of Aqueous Carbonate Solutions Including Mixtures of Sodium Carbonate, Bicarbonate, and Chloride., J. Chem. Thermodynamics, 14, 613-638 (1982).

20. Goldberg, R.N., and Nuttall, R.L., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: The Alkaline Earth Metal Halides., J. Phys. Chem. Ref. Data, 7, 263-310 (1978).

21. Robinson, R.A., and Stokes, R.H., Electrolyte Solutions, 2nd ed., Butterworths: London, 1959.

22. Goldberg, R.N., Nuttall, R.L., and Staples, B.R., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Iron Chloride and the Bi-Univalent Compounds of Nickel and Cobalt., J. Phys. Chem. Ref. Data, 8, 923 -1003 (1979).

23. Goldberg, R.N., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-Univalent Compounds of Lead, Copper, Manganese, and Uranium., J. Phys. Chem. Ref. Data , 8, 1005-1050 (1979).

24. Libus, Z., Sadowaska, T., and Trzaskowski, J., Osmotic Coefficients of Aqueous Rare-Earth Perchlorates and Nitrates., J. Chem. Thermodynamics, 11, 1151-1161 (1979).

25. Harned, H.S., and Owen, B.B., The Physical Chemistry of Electrolyte Solutions., 3rd ed., Reinhold: New York, N.Y., 1958.

26. Rush, R.M., and Johnson, J.S., Isopiestic Measurements of the Osmotic and Activity Coefficients for the Systems $HClO_4$-$LiClO_4$-H_2O, $HClO_4$-$NaClO_4$-H_2O, and $LiClO_4$-$NaClO_4$-H_2O., J. Phys. Chem., 72, 767-774 (1968).

27. Sanker, M., Macaskill, J.B., and Bates, R.G., Activity Coefficients of Hydrochloric Acid and Ionic Interactions in the System HCl-CsCl-H_2O from 5 to 50° C., J. Solution Chem, 10, 169-179 (1981).

28. Huston, R., and Butler, J.N., Activity Measurements in Concentrated Sodium Chloride-Potassium Chloride Electrolytes Using cation-Sensitive Glass Electrodes., Anal. Chem., 41, 1695-1698 (1969).

29. Childs, C.W., Downes, C.J., and Platford, R.F., Thermodynamics of Multicomponent Electrolyte Solutions: Aqueous Mixtures of Two Salts from Among NaCl, KCl, NaH_2PO_4, and KH_2PO_4 at 25°C., J. Solution Chem., 3, 139-147 (1974).

30. Robinson, R.A., Wood, R.H., and Reilly, P.J., Calculation of Excess Gibbs Energies and Activity Coefficients from Isopiestic Measurements on Mixtures of Lithium and Sodium Salts., J. Chem. Thermodynamics, 3, 461-471 (1971).

31. Butler, J.N., and Huston, R., Potentiometric Studies of Multicomponent Activity Coefficients Using the Lanthanum Fluoride Membrane Electrode., Anal. Chem., 42, 1308-1311 (1970).

32. Butler, J.N., and Huston, R., Activity Coefficients and Ion Pairs in the Systems Sodium Chloride-Sodium Bicarbonate-Water and Sodium Chloride-Sodium Carbonate-Water., J. Phys. Chem., 74, 2976-2983 (1970).

33. Khoo, K.H., Lim, T.K., and Chan, C.Y., Activity Coefficients for the System $HCl+CoCl_2+H_2O$ at 298.15 K., J. Chem. Soc. Faraday Trans. 1, 74, 2037-2044 (1978).

34. Khoo, K.H., Lim, T.K., and Chan, C.Y., Activity Coefficients for $HCl+NiCl_2+H_2O$ at 298.15°K and Effects of Higher-Order Electrostatic Terms., J. Solution Chem., 7, 291-301 (1978).

35. Khoo, K.H., Chan, C.Y., and Lim, T.K., Activity Coefficients for the System $HCl+BaCl_2+H_2O$ at 298.15 K., J. Chem. Soc. Faraday Trans. 1, 74, 837-845 (1978).

36. Khoo, K.H., Lim, T.K., and Chan, C.Y., Ionic Interactions in the System $HBr+BaBr_2+H_2O$ at 25°C., J. Solution Chem., 8, 277-282 (1979).

37. Roy, R.N., Gibbons, J.J., Ovens, L.K., Bliss, G.A., and Hartley, J.J., Activity Coefficients for the System $HCl+CaCl_2+H_2O$ at Various Temperatures., J. Chem. Soc. Faraday Trans. 1, 78, 1405-1422 (1981).

38. Khoo, K.H., Lim, T.K., and Chan, C.Y., Activity Coefficients for the System $HBr+CaBr_2+H_2O$ at 298.15 K., J. Chem. Soc. Faraday Trans. 1, 75, 1067-1072 (1979).

39. Roy, R.N., Gibbons, J.J., Trower, J.K., and Lee, G.A., Application of Pitzer's Equations on the System $HCl+MnCl_2+H_2O$ at Various Temperatures. V., J. Solution Chem., 9, 535-551 (1980).

40. Roy, R.N., Gibbons, J.J., Bliss, D.P., Jr., Casebolt, R.G., and Baker, B.K., Activity Coefficients for Ternary Systems: VI. The System $HCl+MgCl_2+H_2O$ at Different Temperatures; Application of Pitzer's Equations., J. Solution Chem., 9, 911-930 (1980).

41. Harned, H.S., and Paxton, T.R., The Thermodynamics of Ionized Water in Strontium Chloride Solutions from Electromotive Force Measurements., J. Phys. Chem., 57, 531-535 (1953).

42. Lim T.K., Khoo, K.H., and Chan, C.Y., Activity Coefficients for the System Hydrogen Bromide+Strontium Bromide+Water at 25°C., J. Solution Chem., 9, 785-789 (1980).

43. Rush, R.M., and Johnson, J.S., Isopiestic Measurements of the Osmotic and Activity Coefficients for the Systems $HClO_4+UO_2(ClO_4)_2+H_2O$ and $NaClO_4+UO_2(ClO_4)_2+H_2O$ at 25°C., J. Chem. Thermodynamics, 3, 779-793 (1971).

44. Downes, C.J., Osmotic and Activity Coefficients for Mixtures of Potassium Chloride and Strontium Chloride in Water at 298.15 K., J. Chem. Thermodynamics, 6, 317-323 (1974).

45. Lindenbaum, S., Rush, R.M., and Robinson, R.A., Osmotic and Activity Coefficients for Mixtures of Lithium Chloride with Barium Chloride and Cesium Chloride with barium Chloride in Water at 298.15 K., J. Chem. Thermodynamics, 4, 381-389 (1972).

46. Downes, C.J., Osmotic and Activity Coefficients for System $NaCl-MnCl_2-H_2O$ at 25°C., J. Chem. Eng. Data, 18, 412-416 (1975).

47. Downes, C.J., Thermodynamics of Mixed Electrolyte Solutions: The Systems $H_2O-NaCl-CoCl_2$ and $H_2O-CaCl_2-CoCl_2$ at 25°C., J. Solution Chem., 4, 191-204 (1975).

48. Platford, R.F., Thermodynamics of Mixed Salt Solutions: Excess Gibbs Energies of Mixing for the Six Ternary Systems Formed from Aqueous $MgCl_2$, $Mg(NO_3)_2$, $CaCl_2$, and $Ca(NO_3)_2$ at 25°C., J. Chem. Thermodynamics, 3, 319-324 (1971).

49. Wu, Y.C., Rush, R.M., and Scatchard, G., Osmotic and Activity Coefficients for Binary Mixtures of Sodium Chloride, Sodium Sulfate, Magnesium Sulfate, and Magnesium Chloride in Water at 25°C. I. Isopiestic Measurements on the Four Systems with Common Ions., J. Phys. Chem., 72, 4048-4053 (1968).

50. Downes, C.J., and Pitzer, K.S., Thermodynamics of Electrolytes. Binary Mixtures Formed from Aqueous NaCl, Na_2SO_4, $CuCl_2$, and $CuSO_4$ at 25°C., J. Solution Chem, 5, 389-398 (1976).

51. White, D.R., Jr., and Bates R.G., Osmotic Coefficients and Activity Coefficients of Aqueous Mixtures of Sodium Chloride and Sodium Carbonate at 25°C., Aust. J. Chem, 33, 1903-1908 (1980).

52. Boyd, G.E., Solute Activity Coefficients in Dilute Aqueous Electrolyte Mixtures II. The Ternary System: $NaClO_4+La(ClO_4)_3+H_2O$ at 298.15 K., J. Chem. Thermodynamics, 10, 415-424 (1978).

53. Khoo, H.K., Activity Coefficients in Mixed-Electrolyte Solutions., J. Chem. Soc., Faraday Trans. 1, 82, 1-12 (1986).

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

55. Khoo, K.H., Chan C.Y., and Lim, T.K., Thermodynamics of Electrolyte Solutions. The System $HCl+CaCl_2+H_2O$ at 298.15°K., J. Solution Chem., 6, 651-662 (1977).

56. Robinson, R.A., Roy, R.N., and Bates, R.G., System Water-Hydrochloric Acid Ammonium Chloride at 25°. Harned's Rule, J. Solution Chem., 3, 837-846 (1974).

CHAPTER 3

CORRELATION OF PITZER ION INTERACTION PARAMETERS

by

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INTRODUCTION

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 β 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, θ and ¥ 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

Term	Order of magnitude	Specie concentrations where terms	
		Approch O[$f(I)$]	Exceed β terms
$f(I)$	1.0		
β's	1.0	0.1	
C	0.001	10.0	1000
θ	0.1	1.0	10
¥	0.01	2.0	10

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

$Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Li^{+} > Na^{+} > K^{+} > Rb^{+} > Cs^{+}$

$OH^{-} > F^{-} > Cl^{-} > Br^{-} > I^{-} > ClO_4^{-}$

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 (7), and oxides are increasingly acidic the higher the charge or the smaller the radius of the cation for constant charge (8).

According to Cartledge (8,9), 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, $P_i=Z_i/r_i$, 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^-, 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^+, Na^+, K^+, Rb^+, Cs^+) halides
2. group IA chlorates, perchlorates, nitrates, acetates, and hydroxides
3. group IA sulfates
4. group IIA (Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+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, β's for single electrolyte solutions are of the order of 1, whereas C^{ϕ} is of the order of 0.001. The small value of C^{ϕ} 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_2SO_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 $\gamma_{\pm}$ for 1-1, 1-2, and 2-1 type of electrolytes

M (mol/kg)	$\gamma_{\pm}$(exptl)	$\gamma_{\pm}^{a}$	$\gamma_{\pm}^{b}$	$\gamma_{\pm}^{c}$
		NaCl		
0.05	0.822	0.820	0.823	0.828
0.10	0.779	0.777	0.783	0.789
0.50	0.681	0.679	0.706	0.710
1.00	0.657	0.655	0.708	0.694
1.20	0.655	0.654	0.717	0.695
1.40	0.656	0.654	0.729	0.697
1.60	0.658	0.657	0.743	0.701
1.80	0.662	0.661	0.759	0.707
2.00	0.668	0.667	0.778	0.714
2.50	0.688	0.687	0.832	0.736
3.00	0.714	0.713	0.897	0.764
3.50	0.746	0.744	0.974	0.799
4.00	0.783	0.781	1.062	0.838
4.50	0.826	0.824	1.164	0.884
5.00	0.874	0.872	1.280	0.935
5.50	0.928	0.925	1.412	0.993
6.00	0.986	0.985	1.562	1.057
		Na_2SO_4		
0.05	0.529	0.530	0.532	0.548
0.10	0.446	0.447	0.450	0.470
0.50	0.268	0.268	0.277	0.296
1.00	0.204	0.204	0.218	0.227
1.25	0.186	0.187	0.202	0.208
1.50	0.173	0.173	0.190	0.192
1.75	0.162	0.162	0.181	0.180
2.00	0.155	0.153	0.174	0.170
2.25	0.149	0.146	0.168	0.162
2.50	0.144	0.139	0.163	0.155

Table 3.2 (continued)

M (mol/kg)	$\gamma_{\pm}$(exptl)	$\gamma_{\pm}{}^{a}$	$\gamma_{\pm}{}^{b}$	$\gamma_{\pm}{}^{c}$
		$MgCl_2$		
0.05	0.590	0.584	0.598	0.620
0.10	0.535	0.530	0.555	0.582
0.50	0.486	0.481	0.609	0.577
1.00	0.577	0.573	0.919	0.699
1.25	0.656	0.653	1.178	0.798
1.50	0.760	0.759	1.539	0.926
1.75	0.894	0.893	2.039	1.089
2.00	1.066	1.064	2.732	1.296
2.25	1.283	1.280	3.698	1.558
2.50	1.558	1.552	5.046	1.887
2.75	1.908	1.896	6.935	2.303
3.00	2.350	2.330	9.592	2.830
3.25	2.910	2.881	13.343	3.496
3.50	3.621	3.580	18.657	4.342
3.75	4.523	4.471	26.211	5.419
4.00	5.669	5.607	39.986	6.793
4.25	7.127	7.061	52.405	8.551
4.50	8.985	8.925	74.536	10.806
4.75	11.358	11.324	106.400	13.706
5.00	14.396	14.417	152.411	17.445
5.25	18.298	18.415	219.042	22.279
5.50	23.329	23.596	315.802	28.542

[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

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Max.m	SD	R
$HClO_4$	0.1725	0.3158	0.0085	6.0	0.0019	1.00
LiI	0.2104	0.3730	-	1.5	0.0060	1.00
NaCl	0.0768	0.2669	0.0012	6.0	0.0007	1.00
NaI	0.1253	0.3064	0.0004	6.0	0.0004	1.00
NaOH	0.0897	0.2803	0.0034	6.0	0.0023	1.00
KF	0.0798	0.2148	0.0011	6.0	0.0004	1.00
KOH	0.1552	0.1709	-0.0006	6.0	0.0004	1.00
RbCl	0.0444	0.1531	-0.0012	6.0	0.0004	1.00
$Mg(NO_3)_2$	0.3272	1.9440	-0.0060	4.0	0.0076	1.00
$Ca(ClO_4)_2$	0.4664	1.5185	-0.0074	4.0	0.0081	1.00
$Ca(NO_3)_2$	0.1674	1.8737	-0.0067	4.0	0.0074	1.00
$Sr(ClO_4)_2$	0.4313	1.4929	-0.0138	4.0	0.0049	1.00
$Ba(ClO_4)_2$	0.3157	2.0028	-0.0149	4.0	0.0084	1.00

Figure 3.1

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

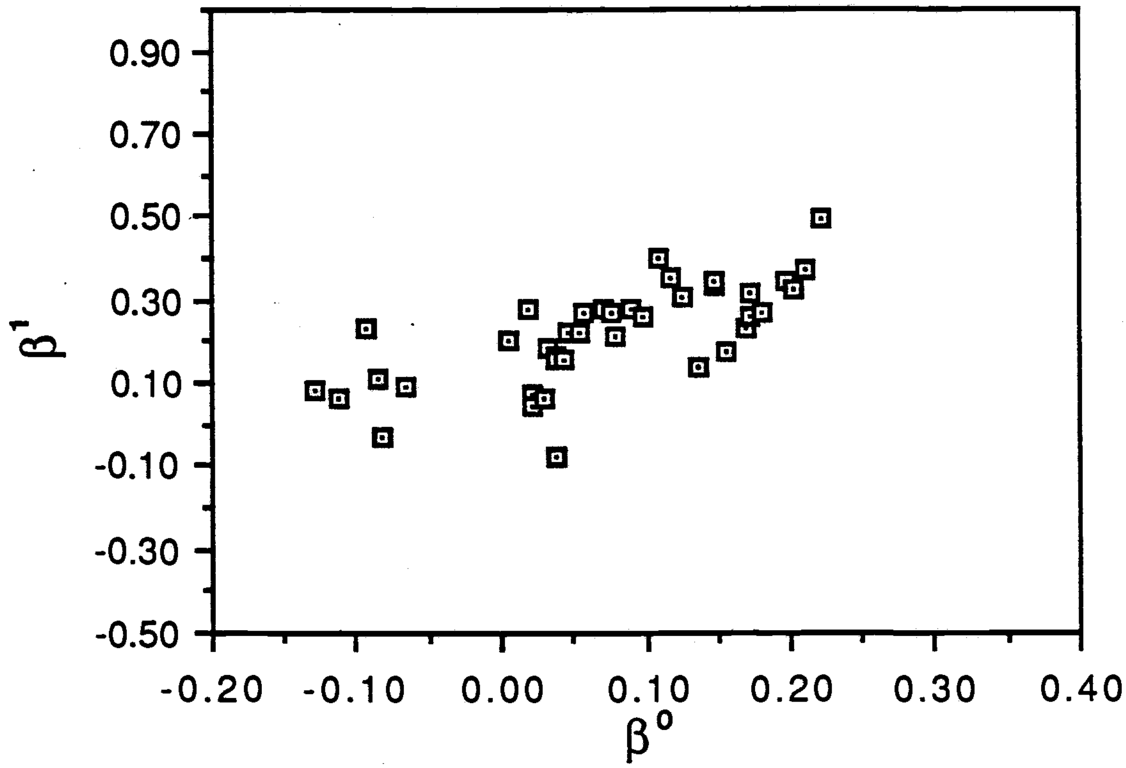

0.90
0.70
0.50
0.30
0.10
-0.10
-0.30
-0.50
β^1
-0.20
-0.10
0.00
0.10
0.20
0.30
0.40
β^0

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^o(J/mol K), and the standard state molar entropy of ion in aqueous solution, S^o_+(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^{o} (J/mol K) for alkali halides.

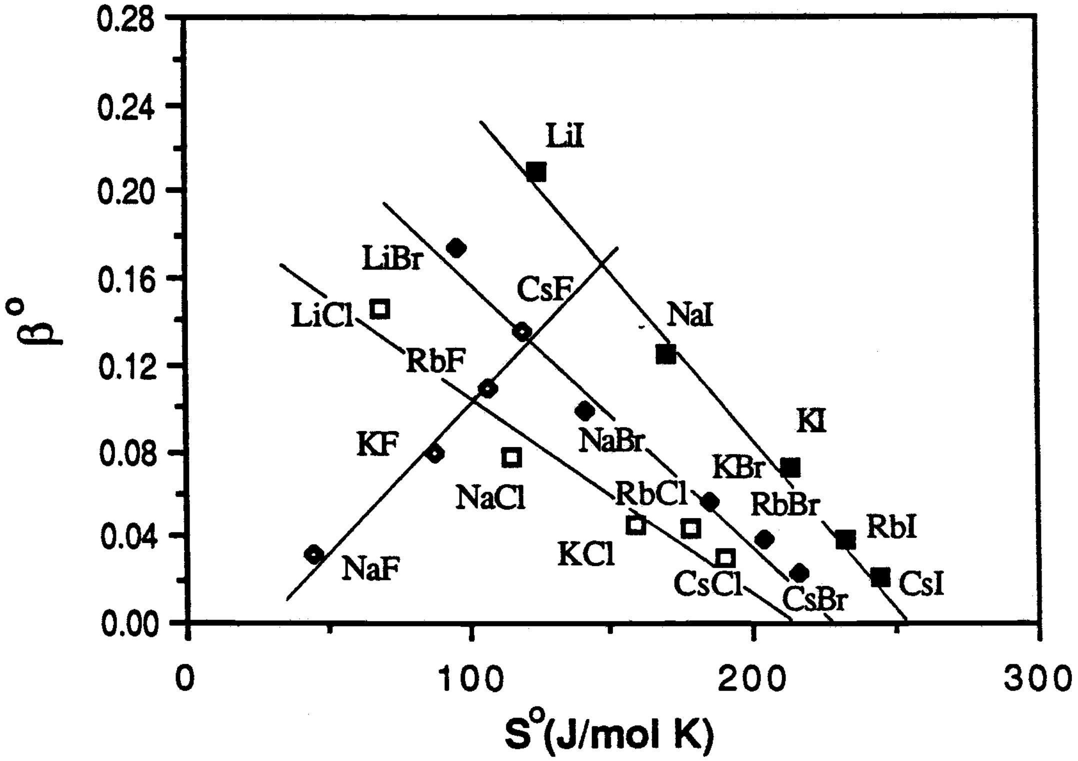

0.28
0.24
0.20
0.16
0.12
0.08
0.04
0.00
β^o
0
100
200
300
S^o(J/mol K)
LiI
LiBr
CsF
NaI
LiCl
RbF
KI
KF
NaBr
KBr
NaCl
RbCl
RbBr
RbI
KCl
NaF
CsCl
CsBr
CsI

Figure 3.2

Figure 3.3

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

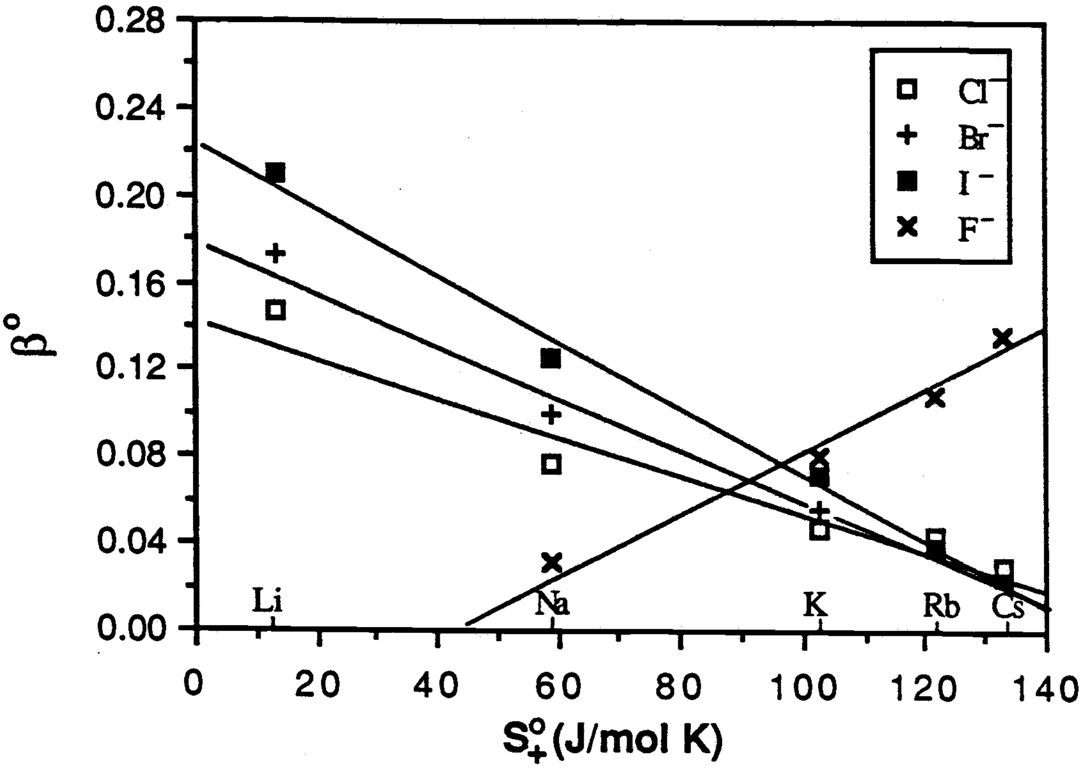

0.28
0.24
0.20
0.16
0.12
0.08
0.04
0.00
β°
0
20
40
60
80
100
120
140
S_+^o (J/mol K)
Li
Na
K
Rb
Cs
□ Cl⁻
+ Br⁻
■ I⁻
× F⁻

Figure 3.3

Figure 3.4

Correlation between $\beta^{(0)}$ and the standard state molar entropy, S^o (J/mol K) for alkali chlorates, perchlorate (included $HClO_4$ and NH_4ClO_4), nitrates (included HNO_3), acetates, and hydroxides.

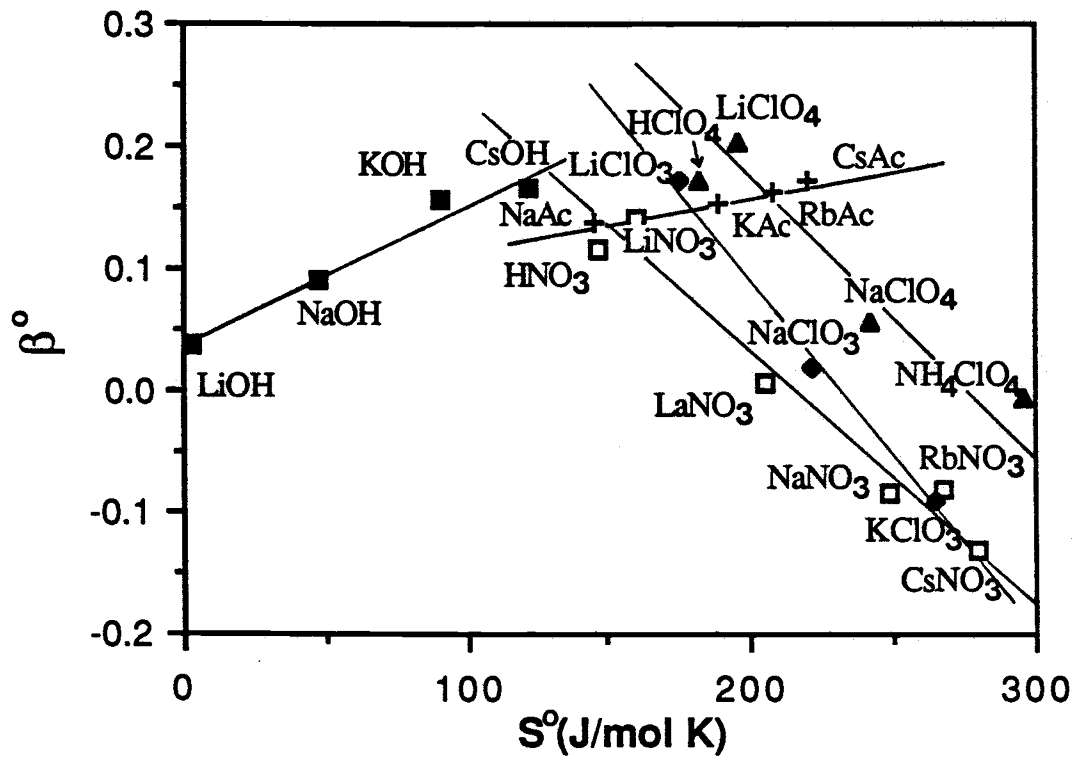

0.3
0.2
0.1
0.0
-0.1
-0.2
β°
0
100
200
300
S°(J/mol K)
KOH
CsOH
LiClO3
HClO4
LiClO4
CsAc
NaAc
KAc
RbAc
LiNO3
HNO3
NaOH
LiOH
NaClO4
NaClO3
NH4ClO4
LaNO3
RbNO3
NaNO3
KClO3
CsNO3

Figure 3.4

Figure 3.5

Correlation between $\beta^{(0)}$ and the standard state molar entropy of cation, S^{o}_{+} (J/mol K) for alkali chlorates, perchlorate (included $HClO_4$ and NH_4ClO_4), nitrates (included HNO_3), acetates, and hydroxides. Symbols for alkali compounds are chlorates □ , perchlorates ■ , nitrates + , acetates ⊡ , and hydroxides ▲ .

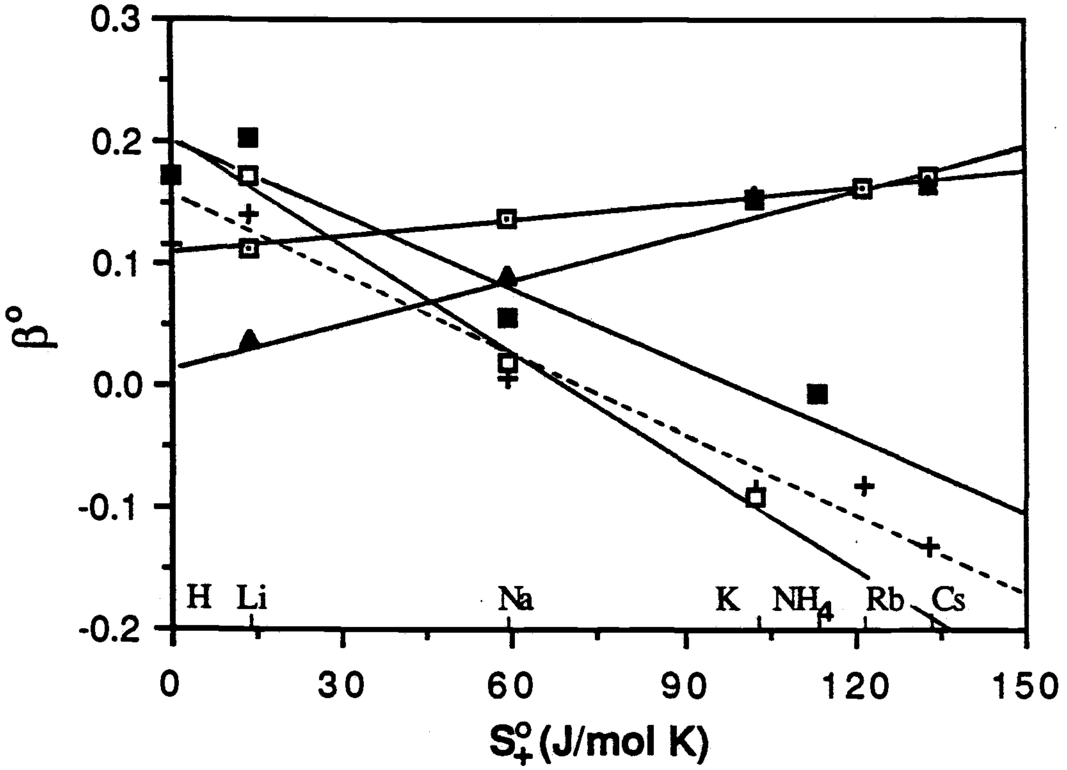


Figure 3.5

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_3COO^-) 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^o, or S^o_+ for alkali compounds

Class	Regression output	SD	R
Alkali fluorides	$\beta^{(0)}=-0.0333+0.0014*S^o$	0.008	0.99
	$\beta^{(0)}=-0.0519+0.0014*S^o_+$	0.008	0.99
Alkali chlorides	$\beta^{(0)}=0.1994-0.0009*S^o$	0.013	0.97
	$\beta^{(0)}=0.1476-0.0009*S^o_+$	0.013	0.97
Alkali bromides	$\beta^{(0)}=0.2826-0.0012*S^o$	0.008	0.99
	$\beta^{(0)}=0.1827-0.0012*S^o_+$	0.008	0.99
Alkali iodides	$\beta^{(0)}=0.3979-0.0015*S^o$	0.007	1.00
	$\beta^{(0)}=0.2261-0.0015*S^o_+$	0.007	1.00
Alkali chlorates	$\beta^{(0)}=0.6829-0.0029*S^o$	0.014	1.00
	$\beta^{(0)}=0.2044-0.0029*S^o_+$	0.014	1.00
Alkali perchlorates*	$\beta^{(0)}=0.5243-0.0018*S^o$	0.036	0.95
	$\beta^{(0)}=0.1917-0.0018*S^o_+$	0.036	0.95
Alkali nitrates**	$\beta^{(0)}=0.4241-0.0020*S^o$	0.024	0.98
	$\beta^{(0)}=0.1352-0.0020*S^o_+$	0.024	0.98
Alkali acetates	$\beta^{(0)}=0.0714+0.0005*S^o$	0.002	1.00
	$\beta^{(0)}=0.1058+0.0005*S^o_+$	0.002	1.00
Alkali hydroxides	$\beta^{(0)}=0.0474+0.0010*S^o$	0.012	0.98
	$\beta^{(0)}=0.0365+0.0010*S^o_+$	0.012	0.98

* included $HClO_4$ and NH_4ClO_4

** included HNO_3

Table 3.5 Aqueous Ionic Radii

Ion	r_{aq} (nm)	Ion	r_{aq} (nm)
Li^+	0.068±0.006	La^{3+}	0.112±0.004
Na^+	0.098±0.003	Pr^{3+}	0.115±0.005
K^+	0.134±0.004	Nd^{3+}	0.107±0.005
Cs^+	0.169±0.005	Sm^{3+}	0.106±0.004
$NH_4{}^+$	0.166±0.005	Eu^{3+}	0.106±0.004
$OH_3{}^+$	0.113±0.005	Gd^{3+}	0.100±0.004
Mg^{2+}	0.072±0.002	Tb^{3+}	0.102±0.005
Ca^{2+}	0.103±0.003	Dy^{3+}	0.101±0.005
Mn^{2+}	0.081±0.005	Er^{3+}	0.098±0.005
Fe^{2+}	0.073±0.005	Tm^{3+}	0.097±0.005
Co^{2+}	0.070±0.002	Lu^{3+}	0.095±0.005
Ni^{2+}	0.068±0.003		
Zn^{2+}	0.069±0.005	F^-	0.135±0.014
Cu^{2+}	0.059±0.005	Cl^-	0.183±0.003
Cd^{2+}	0.095±0.004	Br^-	0.194±0.003
Al^{3+}	0.049±0.002	I^-	0.222±0.002
Cr^{3+}	0.060±0.002	$NO_3{}^-$	0.206±0.006
Fe^{3+}	0.065±0.005	$SO_4{}^{2-}$	0.240±0.005

Figure 3.6

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 Rb^+, Pauling's value (=0.148 nm) were chosen.

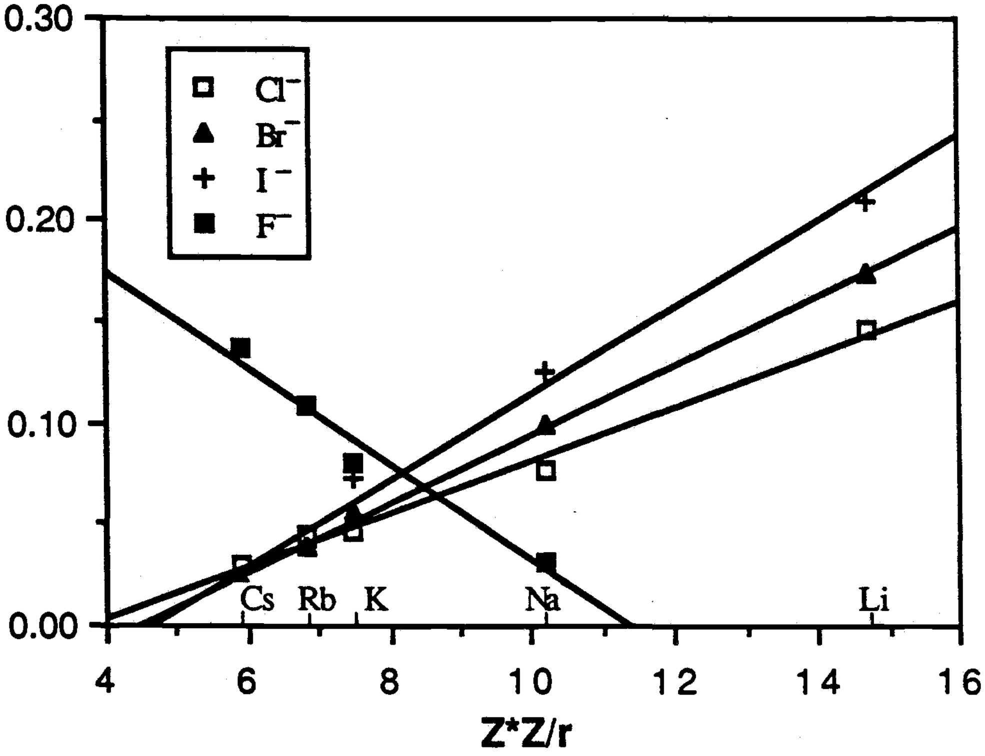


Figure 3.6

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(nm) is the aqueous ionic radius of cation; Ac, Acetate(CH_3COOH) ion.

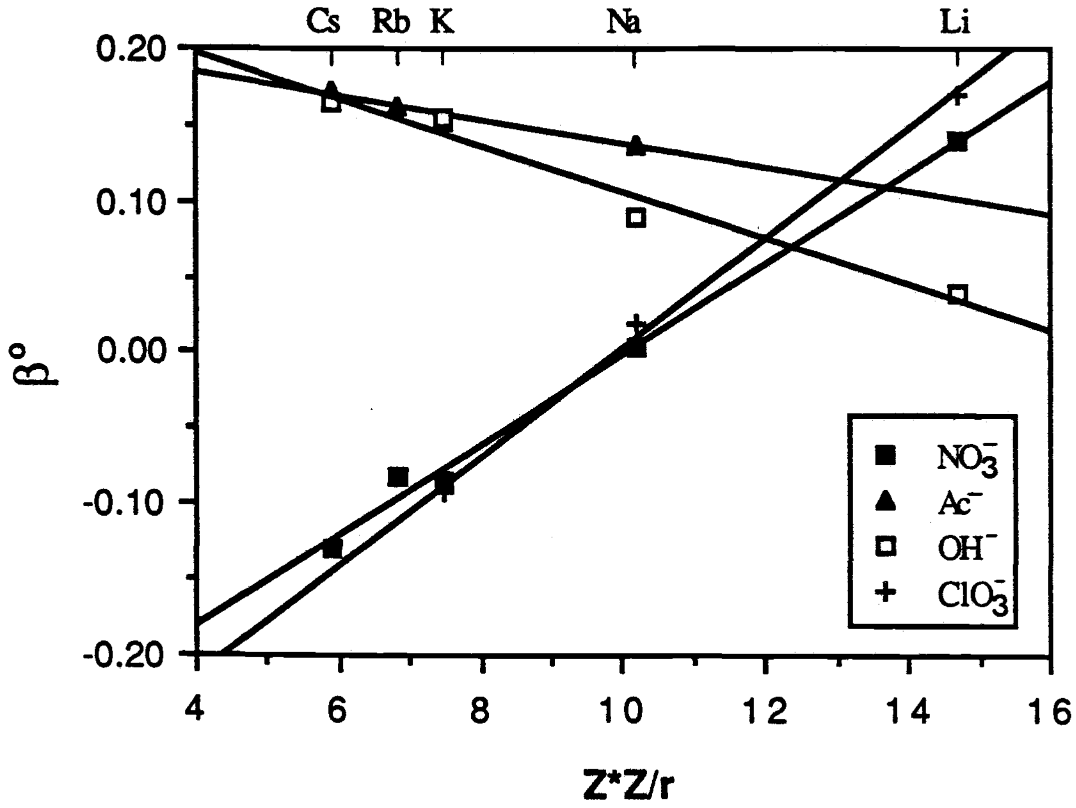

Cs
Rb
K
Na
Li
0.20
0.10
0.00
-0.10
-0.20
β°
4
6
8
10
12
14
16
Z*Z/r
■ NO_3^-
▲ Ac^-
□ OH^-
+ ClO_3^-

Figure 3.7

Table 3.6 Results of regressions between $\beta^{(0)}$ and Z*Z/r for alkali compounds

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

* include NH_4ClO_4

Figure 3.8

Plot of $\beta^{(0)}$ versus the ionic potential ratio, P_C/Pa for alkali halides.

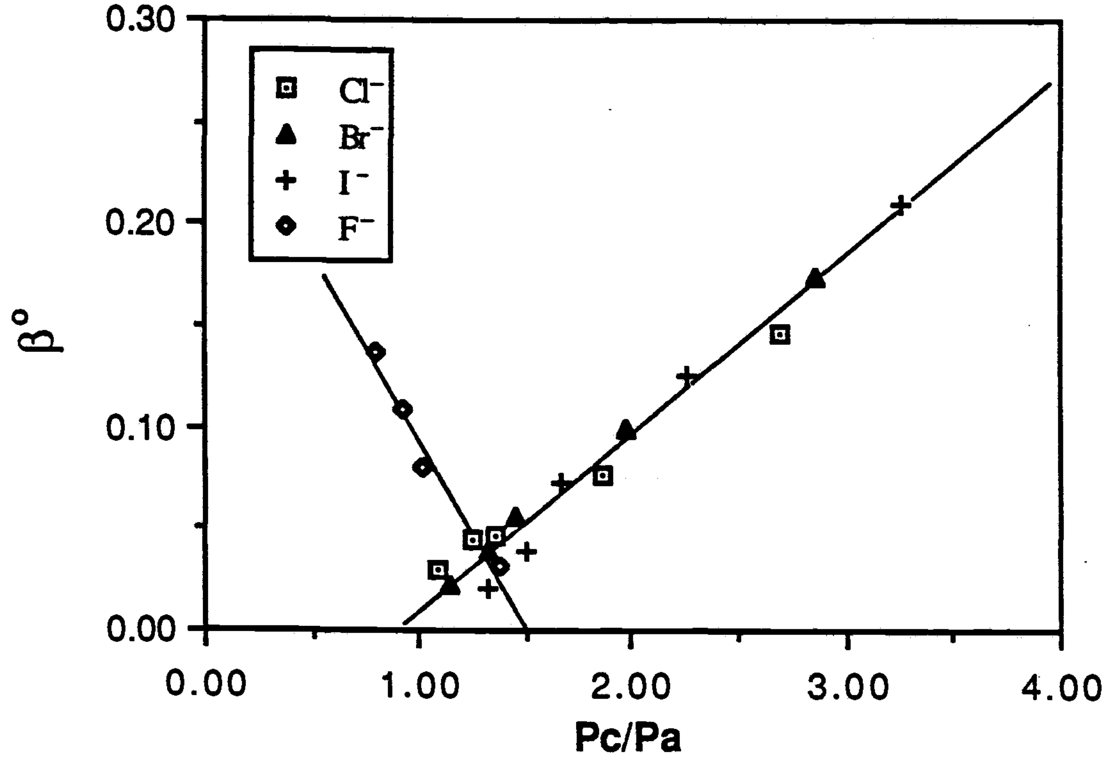


Figure 3.8

Table 3.7 Ionic potential ratios for alkali halides using ionic radii in aqueous solutions from Marcus (1983)

	$P_c/P_a = (Z_c/r_c)/(Z_a/r_a)$
Salt	P_c/P_a
LiF	1.985
LiCl	2.691
LiBr	2.853
LiI	3.265
NaF	1.378
NaCl	1.867
NaBr	1.980
NaI	2.265
KF	1.007
KCl	1.366
KBr	1.448
KI	1.657
RbF*	0.912
RbCl*	1.237
RbBr *	1.311
RbI*	1.500
CsF	0.799
CsCl	1.083
CsBr	1.148
CsI	1.314

* 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

Class	Regression output	
Alkali halides (except fluorides)	$\beta^{(0)}=-0.0738+0.0856*(P_c/P_a)$	
	Standard error of $\beta^{(0)}$ estimate	0.0094
	R squared	0.9762
	No. of observations	15
	Degree of freedom	13
Alkali fluorides	$\beta^{(0)}=0.2689-0.1752*(P_c/P_a)$	
	Standard error of $\beta^{(0)}$ estimate	0.0108
	R squared	0.9605
	No. of observations	4
	Degree of freedom	2

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^o, S^o_{++}, 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^{o} (J/mol K) for alkali earth metal halides (except fluorides), perchlorates, and nitrates.

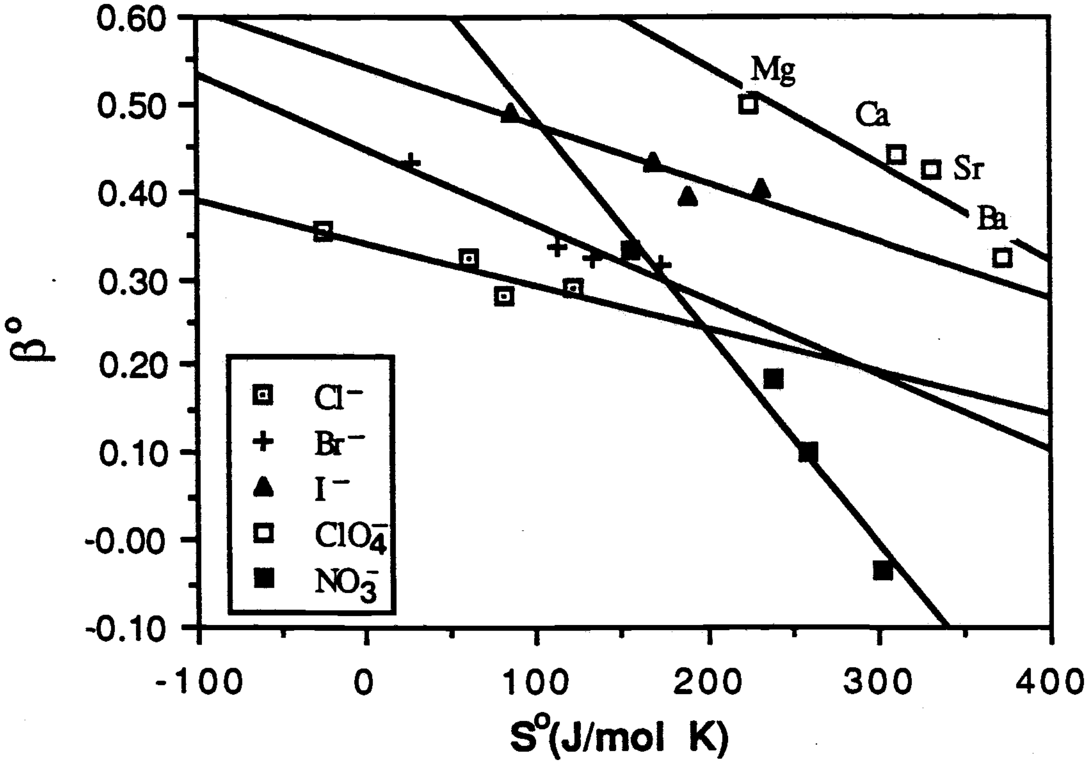

0.60
0.50
0.40
0.30
0.20
0.10
-0.00
-0.10
β°
-100
0
100
200
300
400
S°(J/mol K)
Mg
Ca
Sr
Ba
Cl⁻
Br⁻
I⁻
ClO₄⁻
NO₃⁻

Figure 3.9

Figure 3.10

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

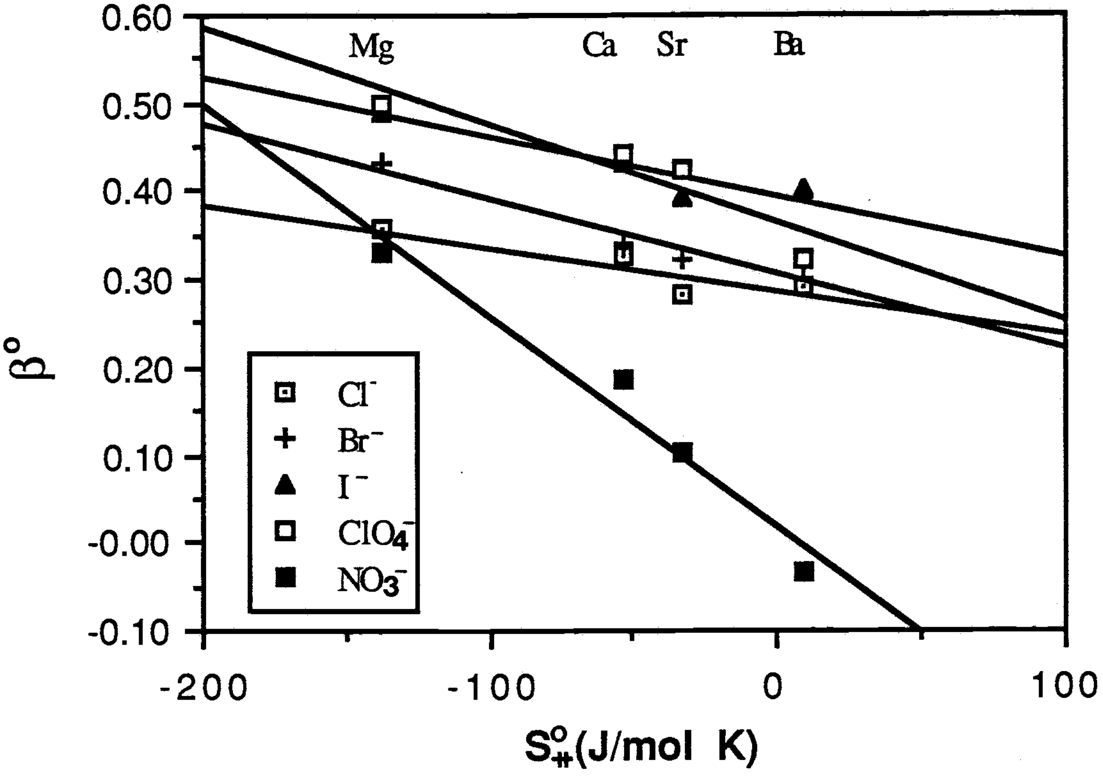

Mg
Ca
Sr
Ba
0.60
0.50
0.40
0.30
0.20
0.10
-0.00
-0.10
β°
-200
-100
0
100
S°_+(J/mol K)
Cl^-
Br^-
I^-
ClO_4^-
NO_3^-

Figure 3.10

Figure 3.11

Correlation between $\beta^{(0)}$ and the Coulombic term, Z*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).

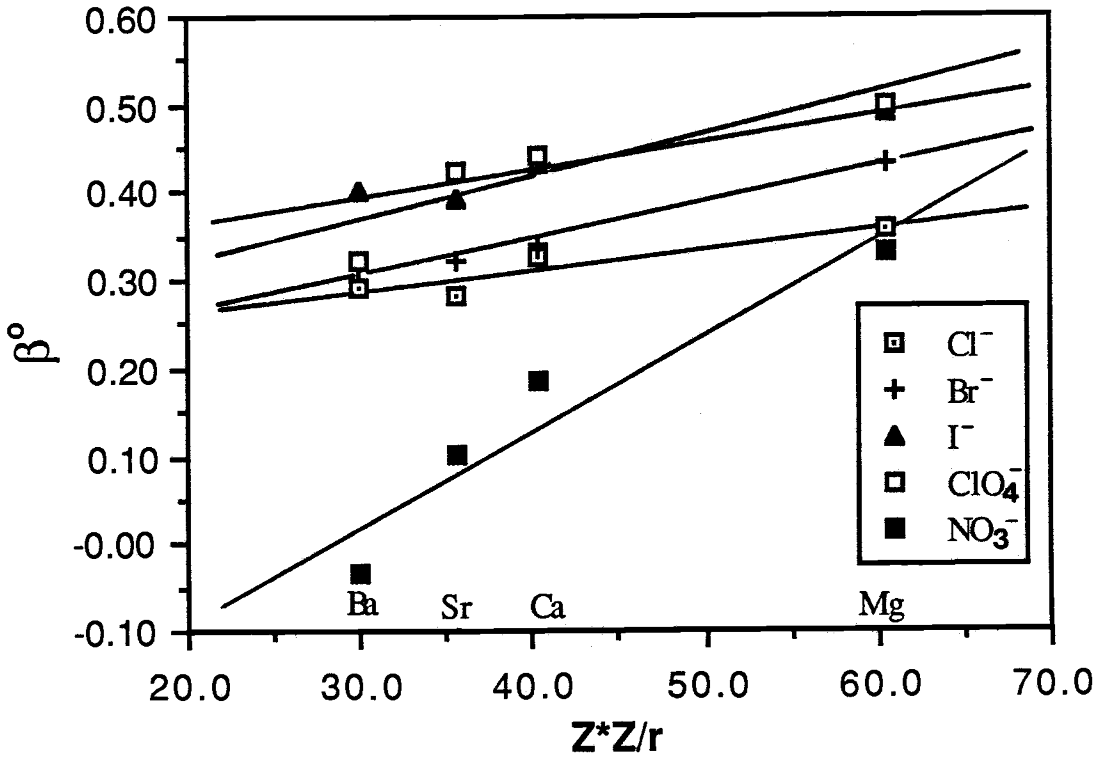

0.60
0.50
0.40
0.30
0.20
0.10
-0.00
-0.10
β°
20.0
30.0
40.0
50.0
60.0
70.0
Z*Z/r
Ba
Sr
Ca
Mg
Cl^-
Br^-
I^-
ClO_4^-
NO_3^-

Figure 3.11

Table 3.9 Results of regressions between $\beta^{(0)}$ and ionic properties (S^o, S^o_{++}, and Z*Z/r) for alkali earth metal compounds

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

Figure 3.12

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

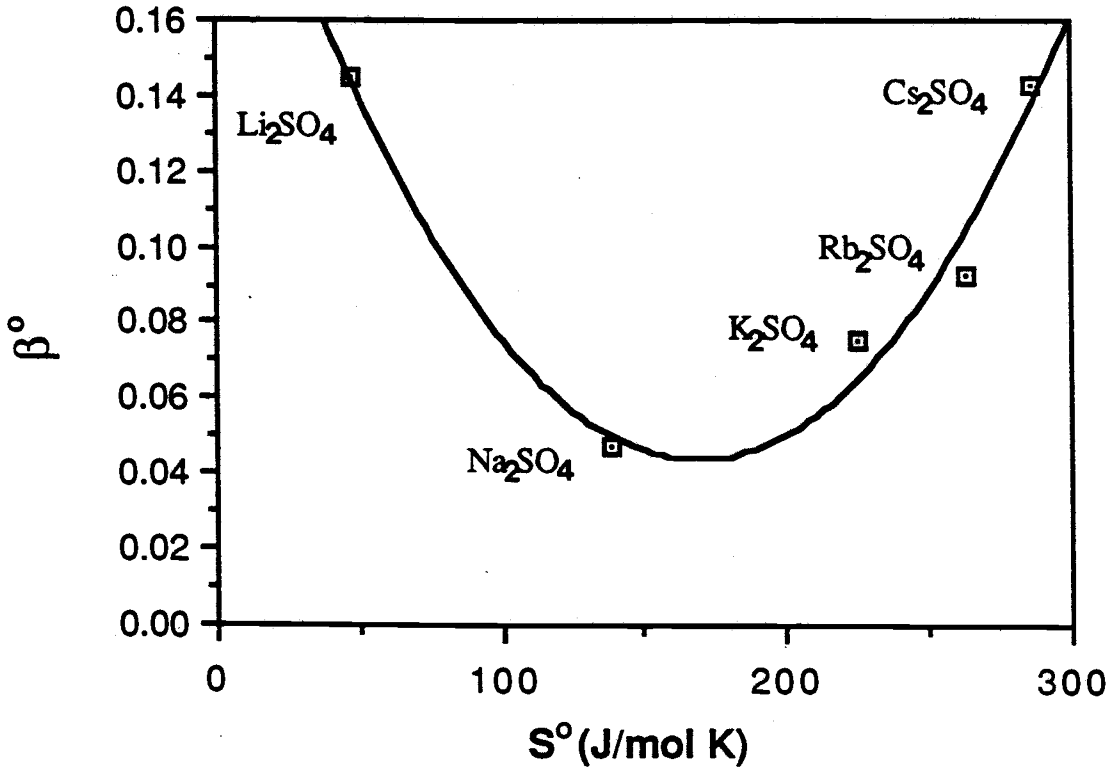

0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
β°
0
100
200
300
S° (J/mol K)
Li_2SO_4
Na_2SO_4
K_2SO_4
Rb_2SO_4
Cs_2SO_4

Figure 3.12

Figure 3.13

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

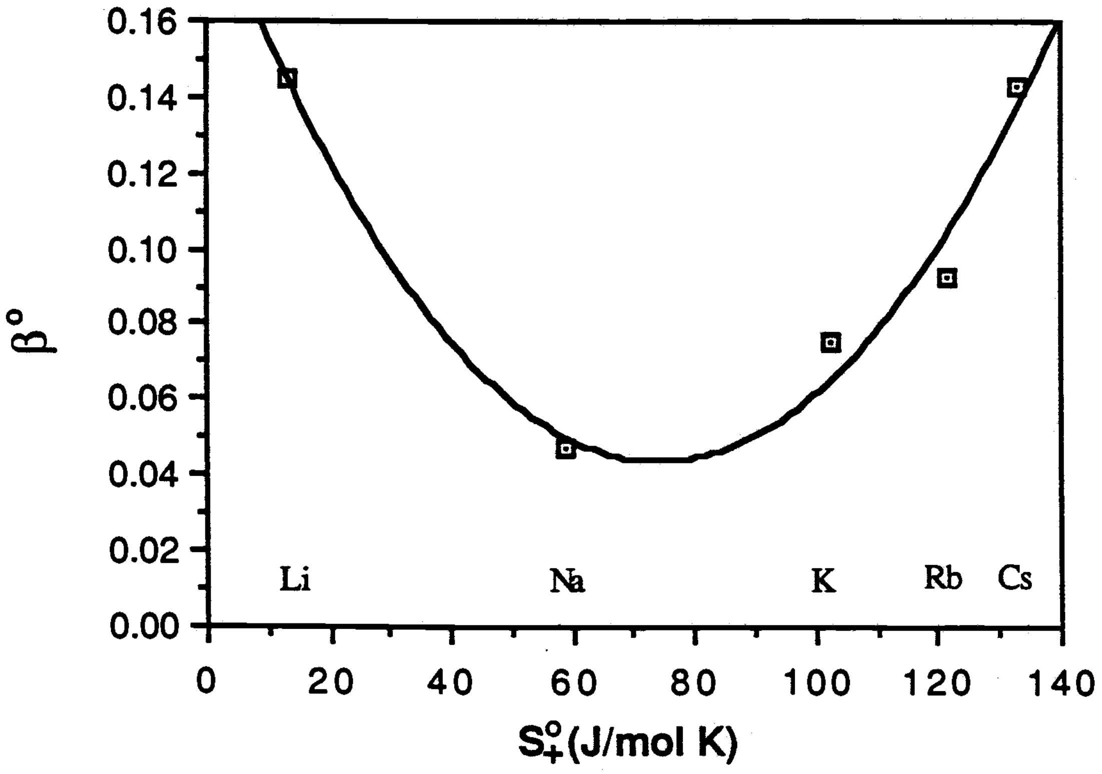
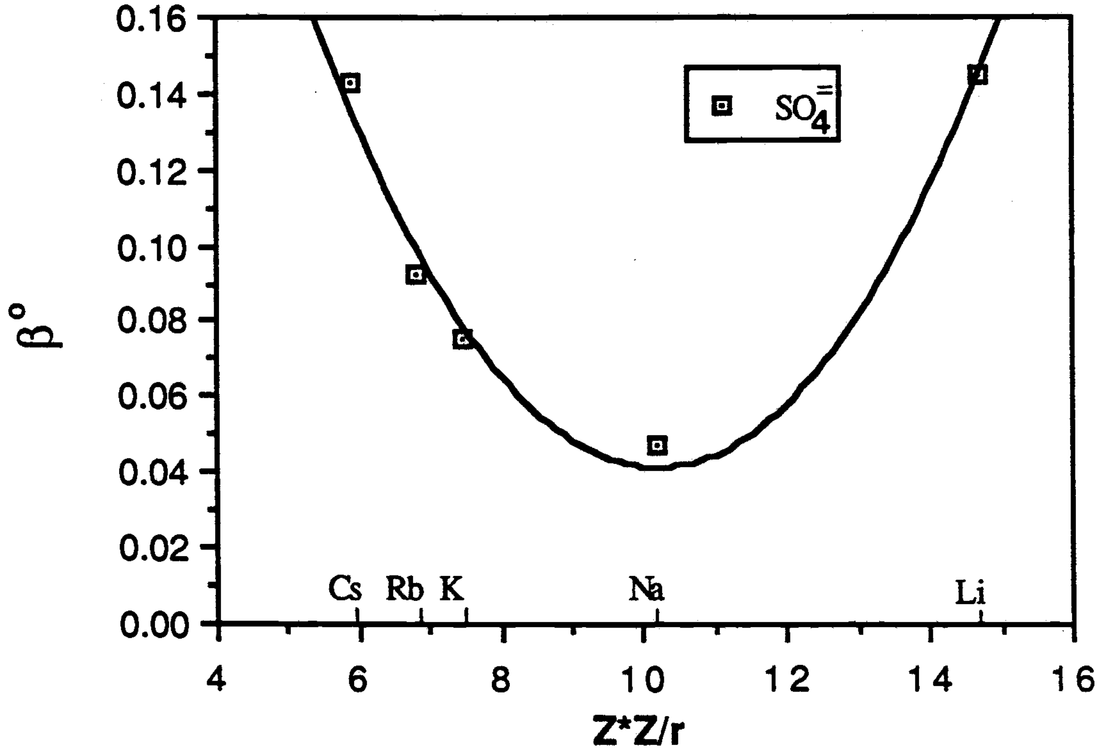

0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
β°
Li
Na
K
Rb
Cs
0
20
40
60
80
100
120
140
S°₊(J/mol K)

Figure 3.13

Figure 3.14

Correlation between $\beta^{(0)}$ and the Coulombic term, Z*Z/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.



0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
β°
SO$_4^=$
Cs
Rb
K
Na
Li
4
6
8
10
12
14
16
Z*Z/r

Figure 3.14

Figure 3.15

Plot of $\beta^{(0)}$ versus the ionic potential ratio, P_c/P_a for alkali sulfates.

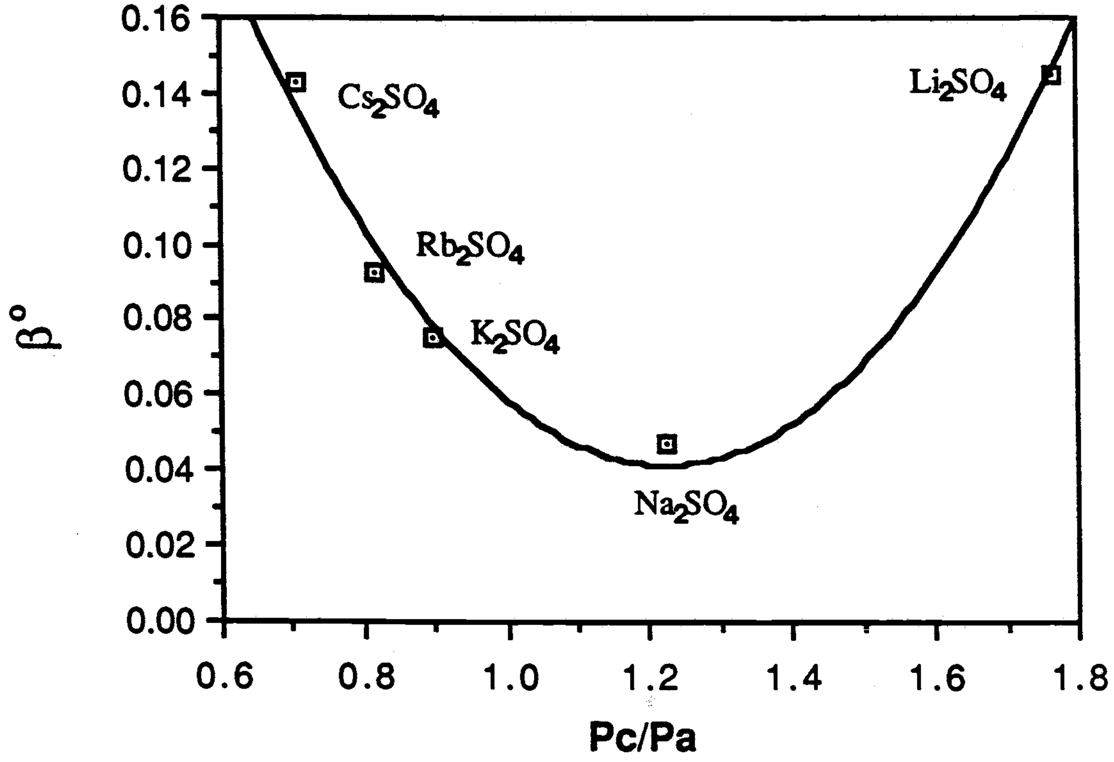

0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
β°
0.6
0.8
1.0
1.2
1.4
1.6
1.8
Pc/Pa
Cs2SO4
Rb2SO4
K2SO4
Na2SO4
Li2SO4

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 θ and ¥ for ions present at low concentration even if the total ionic strength is high. As shown in Table 3.1, θ is of the order of 0.1 and ¥ is of the order of 0.001. According to Lim et. al (21), the Pitzer ternary ion interaction parameter, $¥_{HNX}$ for the HX-NX_2-H_2O 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_2O systems (M=Li, Na, K, Cs, and X=Cl, Br, I, ClO_4) and HX-NX_2-H_2O systems (N=Ca, Mg, Sr, Ba, Ni, Co, Mn and X=Cl, Br) were chosen to examine the correlation between θ and ionic entropy. For HX-MX-H_2O systems, available values of θ_{HM} are plotted in Figure 3.16 as a function of ionic entropy of M^+. These values of θ_{HM} fall on a smooth curve with a maximum point. Table 3.11 represents the comparison of θ_{HM} for HX-MX-H_2O systems and curve fitting result. The same kind of procedure for HX-NX_2-H_2O 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^o, S^o_{++}, $Z*Z/r$, and P_c/P_a) for alkali sulfates

Class	Regression output	R
Alkali sulfates	$Y = 0.2378-0.0023*X_1+6.812*10^{-6}*X_1^2$	0.98
	$Y = 0.1935-0.0040*X_2+2.716*10^{-5}*X_2^2$	0.98
	$Y = 0.5739-0.1045*X_3+0.0051*X_3^2$	0.99
	$Y = 0.5735-0.8701*X_4+0.3558*X_4^2$	0.99

dependent variable: $Y = \beta^{(0)}$
independent " : $X_1 = S^o$ (J/mol K)
$X_2 = S^o_{++}$ (J/mol K)
$X_3 = Z*Z/r$ (nm)
$X_4 = P_c/P_a$

Figure 3.16

Plot of Θ_{HM} versus S^{o}_{+} (J/mol K) for HX-MX-H_2O systems, where M= Li, Na, K, Cs and X= Cl, Br, I, ClO_4.

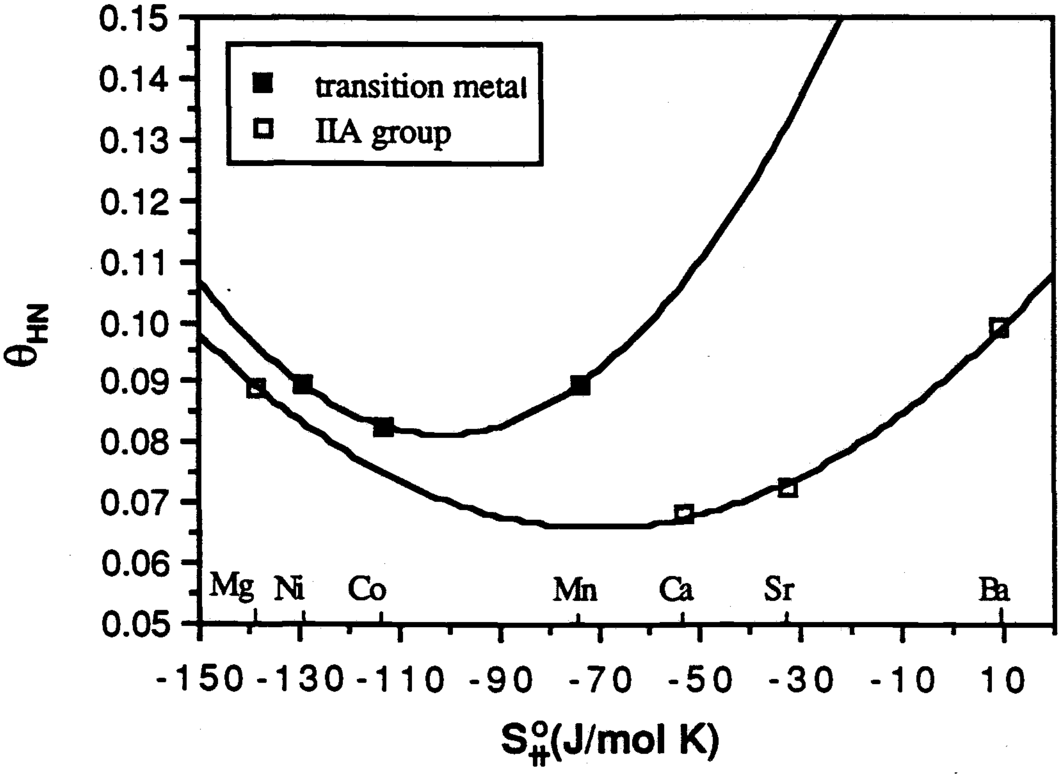

0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
θ_{HN}
■ transition metal
□ IIA group
Mg
Ni
Co
Mn
Ca
Sr
Ba
-150
-130
-110
-90
-70
-50
-30
-10
10
$S^o_{\#}$(J/mol K)

Figure 3.16

Table 3.11 Comparison of θ_{HM} and S^o_{M+}, and curve fitting result for $HX-MX-H_2O$ systems

M	X	θ_{HM}	S^o_+(J/mol K)
Li	Cl, Br, ClO_4	0.0151	13.40
Na	Cl, Br, ClO_4	0.0368	59.00
K	Cl, Br	0.0067	102.50
Cs	Cl	-0.0459	133.05

Regression output

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

R = 1.00

Figure 3.17

Plot of θ_{HN} versus S^o_{++} (J/mol K) for $HX-NX_2-H_2O$ systems, where N= Ca, Mg, Sr, Ba, Ni, Co, Mn and X= Cl, Br.

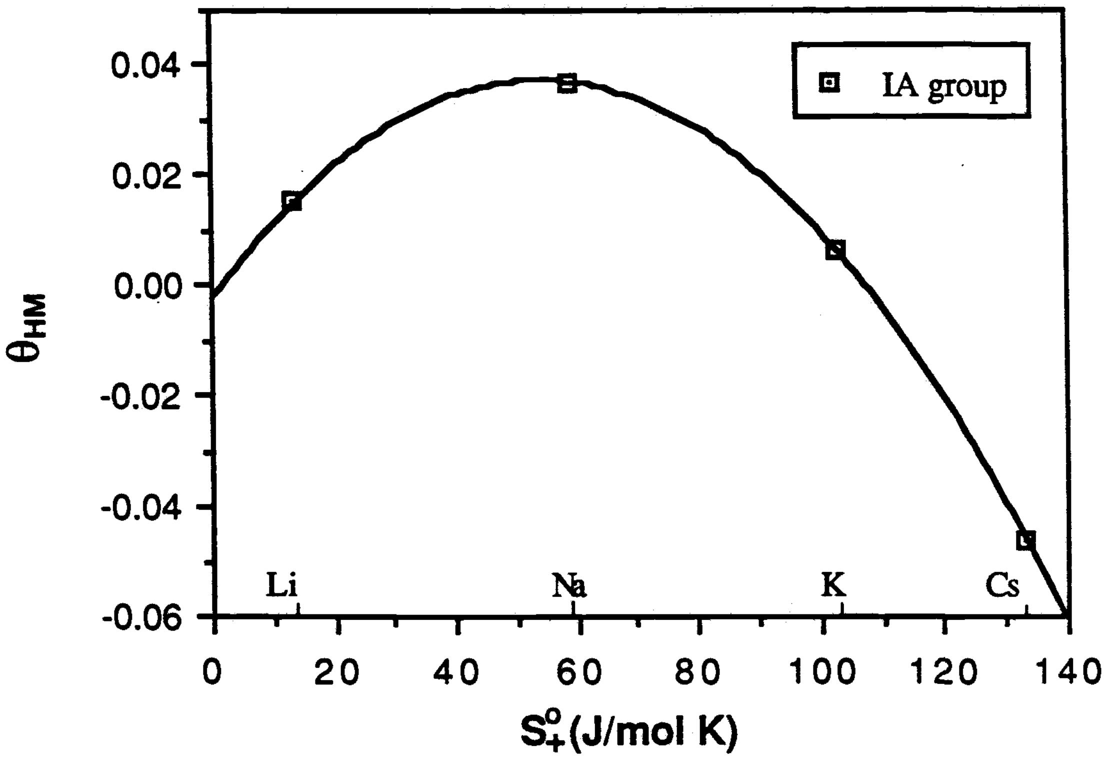

IA group
0.04
0.02
0.00
-0.02
-0.04
-0.06
θ_{HM}
Li
Na
K
Cs
0
20
40
60
80
100
120
140
S^o_+(J/mol K)

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 ($NaNO_3$, $NaClO_4$, $NaClO_3$, NaOH, and NaAc) respectively. The solid lines represent the calculation values as predicted by the correlation results of $\beta^{(0)}$ versus S^o. The experimental data are from Hamer and Wu (<u>22</u>, <u>23</u>).

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 $KClO_4$,

Table 3.12 Comparison of θ_{HN} and $S^o_{N^{+2}}$, and curve fitting result for $HX-NX_2-H_2O$ systems

N	X	θ_{HN}	S^o_{++}(J/mol K)
(alkali earth metal compounds)			
Mg	Cl	0.0891	-138.10
Ca	Cl, Br	0.0682	-53.10
Sr	Cl, Br	0.0728	-32.60
Ba	Cl, Br	0.0991	9.60
(transition metal compounds)			
Ni	Cl	0.0895	-128.90
Co	Cl	0.0829	-113.00
Mn	Cl	0.0899	-73.60

Regression output

1. N= Mg, Ca, Sr, Ba

$$\theta_{HN} = 0.0916+7.208*10^{-4}*(S^o_N)+5.093*10^{-6}*(S^o_N)^2$$

R = 1.00

2. N= Ni, Co, Mn

$$\theta_{HN} = 0.1921+0.0022*(S^o_N)+1.072*10^{-5}*(S^o_N)^2$$

R = 1.00

Figure 3.18

Comparison of experimental smoothed $\tau_{\pm}$ with calculated from correlation for NaCl, NaBr, NaI, and NaF at 25°C.

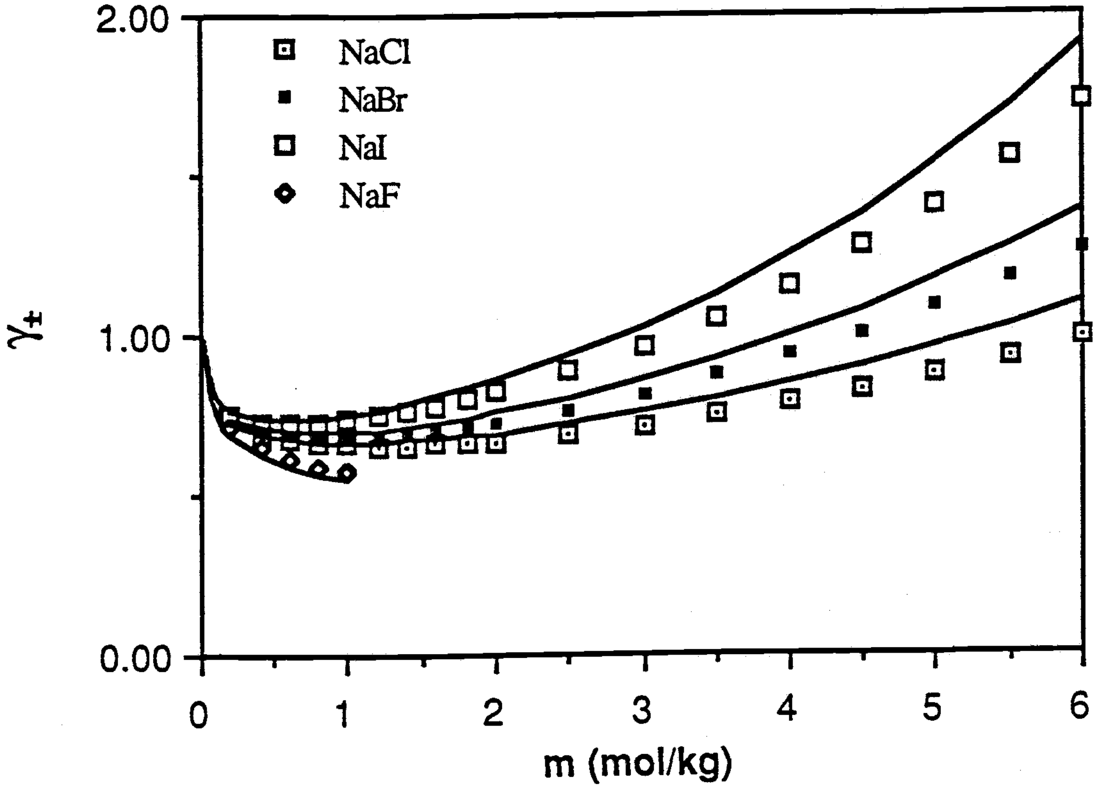


Figure 3.18

Figure 3.19

Comparison of experimental smoothed $\gamma_{\pm}$ with calculated from correlation for $NaNO_3$, $NaClO_4$, $NaClO_3$, NaOH, and NaAc at 25°C.

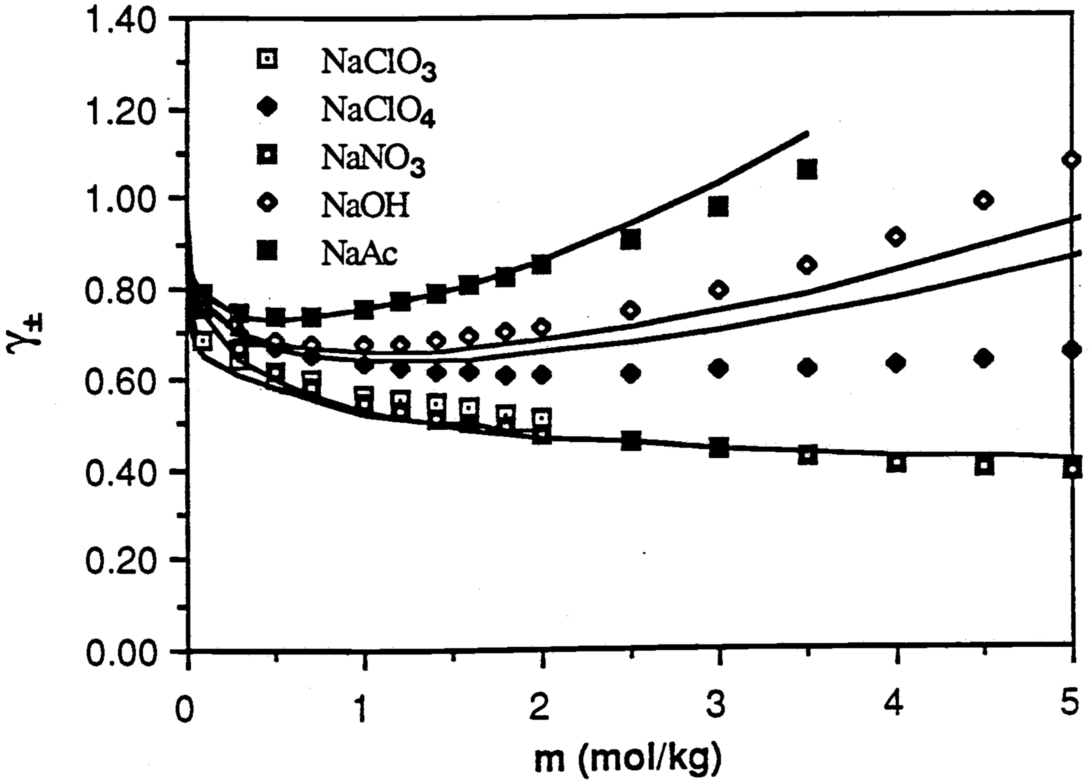

1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0
1
2
3
4
5
m (mol/kg)
$\gamma_\pm$
NaClO$_3$
NaClO$_4$
NaNO$_3$
NaOH
NaAc

Figure 3.19

$RbClO_4$, and $CsClO_4$. Thus the experimental data for $HClO_4$, and NH_4ClO_4 have been added to get the correlation relationship for perchlorates. It is clear that the correlation result for alkali perchlorates including $HClO_4$, and NH_4ClO_4 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 Cs_2SO_4. For the higher valence types, the plot of $\beta^{(0)}$ versus $\beta^{(1)}$ shows more scatter than that of 1-1 type but a clear trend of $\beta^{(0)}$ with $\beta^{(1)}$ is still apparent. Especially, in the case of Cs_2SO_4, the ratio of $\beta^{(0)}$ and $\beta^{(1)}$ 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 ($MgCl_2$, $MgBr_2$, and MgI_2), 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 resonable 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 $\tau_{\pm}$ with calculated from correlation results; (a) for Li_2SO_4, Na_2SO_4, and K_2SO_4, (b) for Rb_2SO_4 and (c) for Cs_2SO_4 at 25°C.

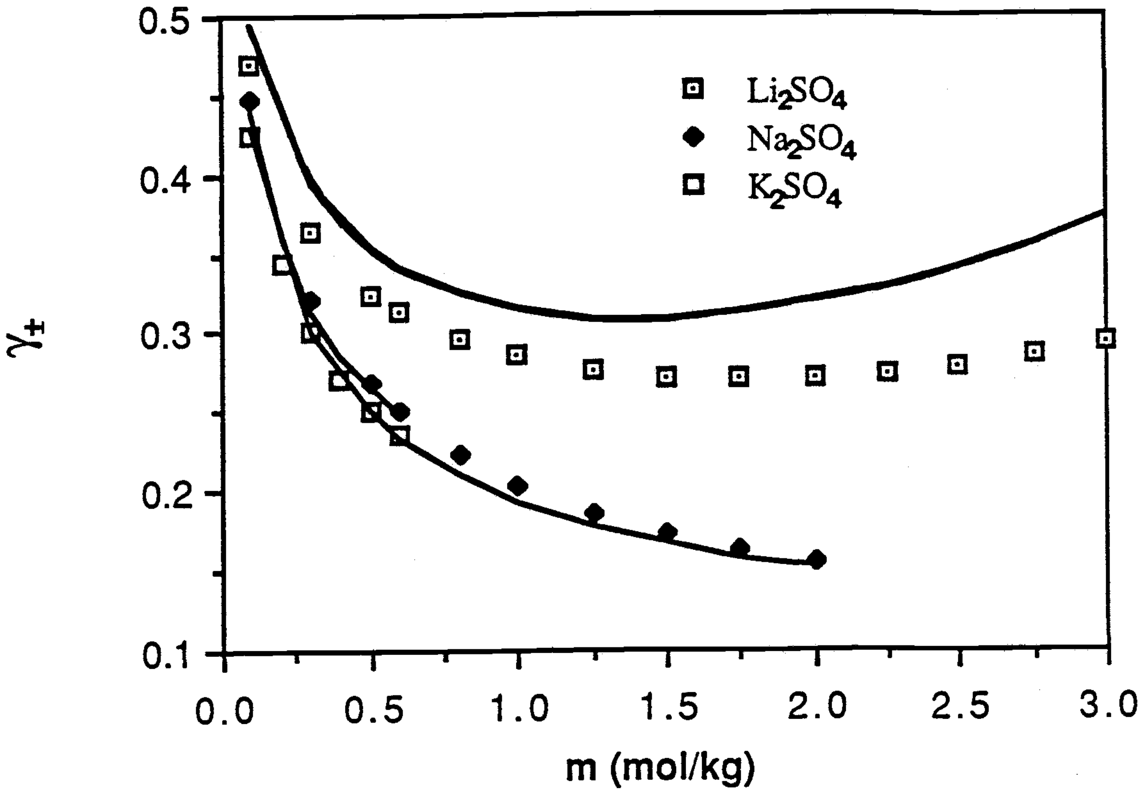

0.5
0.4
0.3
0.2
0.1
$\gamma_{\pm}$
0.0
0.5
1.0
1.5
2.0
2.5
3.0
m (mol/kg)
Li_2SO_4
Na_2SO_4
K_2SO_4

Figure 3.20a

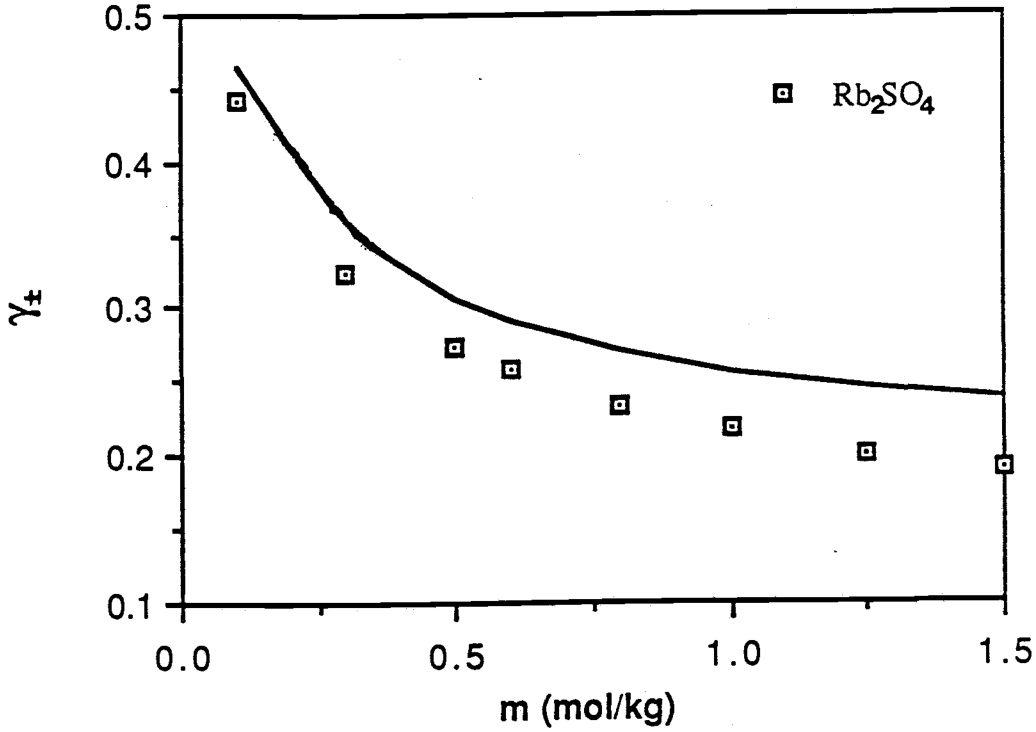


Figure 3.20b

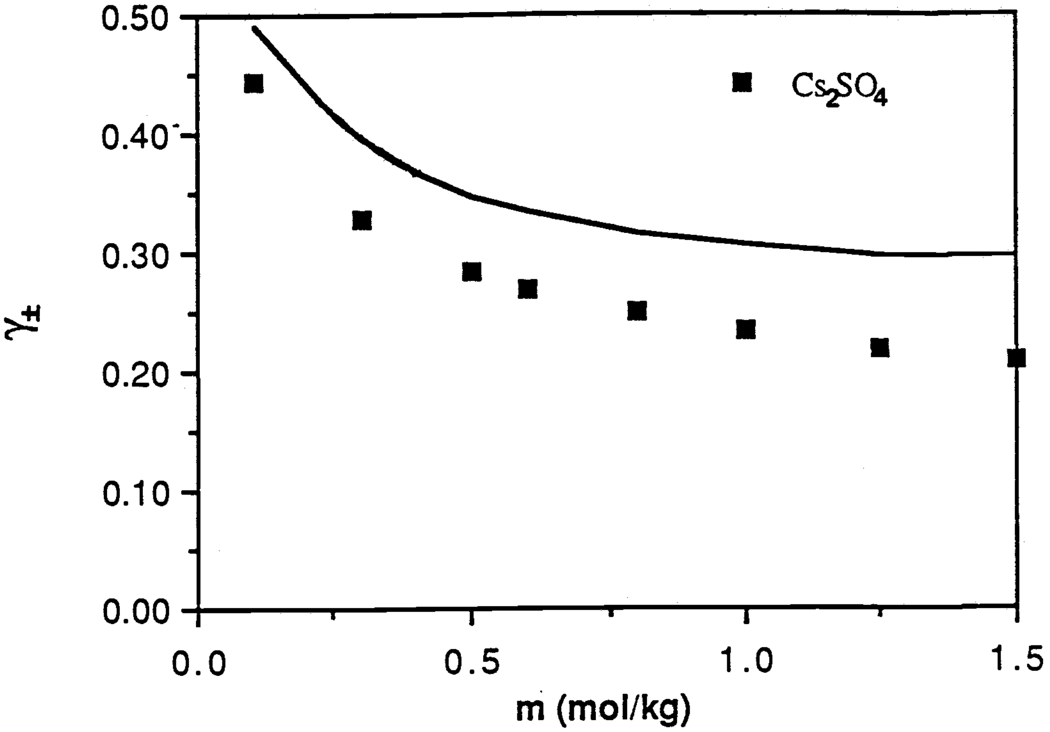


Figure 3.20c

Figure 3.21

Comparison of experimental smoothed $\tau_{\pm}$ 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.

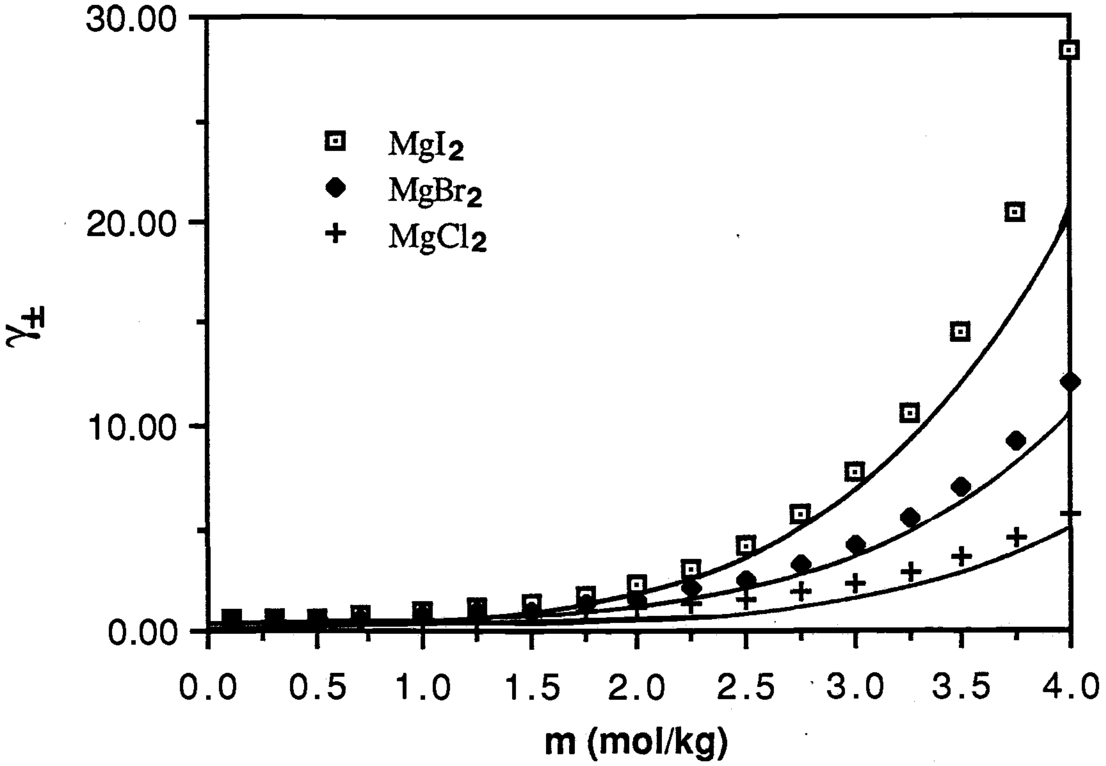


Figure 3.21a

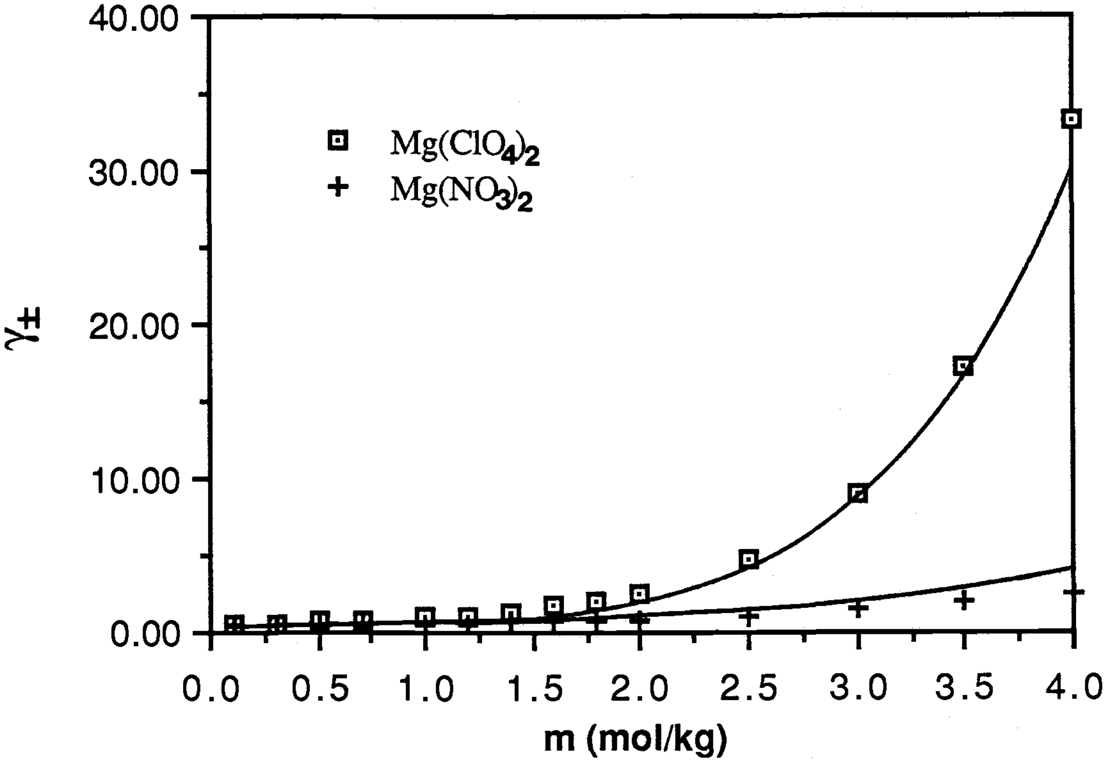


Figure 3.21b

Figure 3.22

Comparison of experimental values of γ_{HCl} for HCl-$MgCl_2$-H_2O system with values calculated from correlation at various ionic strengths.

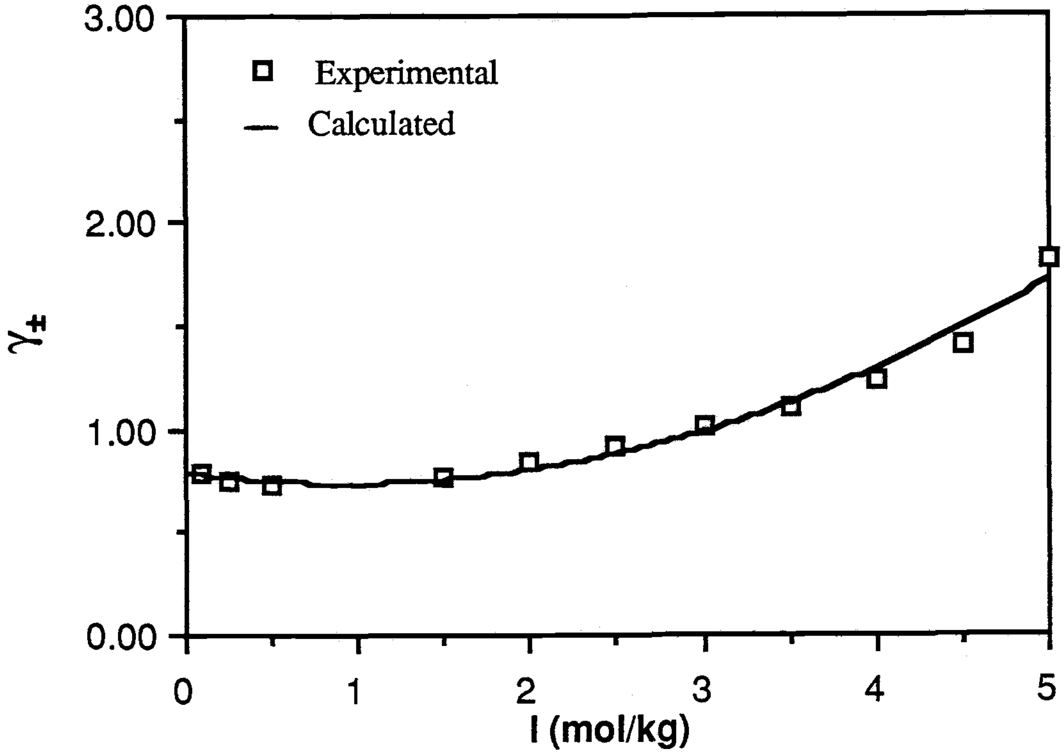


Figure 3.22

and various ionic strengths. The ternary ion interaction parameter, θ_{HMg} for system of $HCl-MgCl_2-H_2O$ 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 $\ln\gamma_\pm$ 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 elctrolytes 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 cleary needed in this area in the future.

REFERENCES

1. Silvester, L.F., and Pitzer, K.S., Thermodynamics of Electrolytes. 8. High-Temperature Properties, Including Enthalpy and Heat Capacity, with Application to Sodium Chloride., J. Phys. Chem., 81, 1822-1828 (1977).

2. Rogers, P.S.Z., and Pitzer, K.S., Volumetric Properties of Aqueous Sodium Chloride Solutions., J. Phys. Chem. Ref. Data, 11, 15-81 (1982).

3. Pitzer, K.S., Theory: Ion Interaction Approach, in Activity Coefficients in Electrolyte Solutions, Vol. 1, Pytkowicz, R.M., Editor CRC Press, Inc., Boca Raton, FL (1979).

4. Bernal, J.D., and Fowler, R.H., A Theory of Water and Ionic Solution with Particular Reference to Hydrogen and Hydroxyl Ions., J. Chem. Phys., 1, 515-548 (1933).

5. Blandamer, M.J., Structure and Properties of Aqueous Salt Solutions, Chem. Soc. London Quart. Rev., 24, 169-184 (1970).

6. Gurney, R.W., Ionic Processes in Solution, McGraw-Hill Book Company, New York (1962).

7. Huheey, J.E., Inorganic Chemistry: Priciples of Structure and Reactivity, 2nd ed., New York, Harper and Row p.889 (1978).

8. Cartledge, G.H., Studies on the Periodic System. I. The Ionic Potential as a Periodic Function., J. Am. Chem. Soc., 50, 2855-2863 (1928).

9. Cartledge, G.H., Studies on the Periodic System. II. The ionic Potential and Related Properties., J. Am. Chem. Soc., 50, 2863-2872 (1928).

10. Wood, S.A., Crerar, D.A., Brantley, S.L., and Borcsik, M., Mean Molal Stoichiometric Activity Coefficients of Alkali Halides and Related Electrolytes in Hydrothermal Solutions., Am. J. Sci., 284, 668-705 (1984).

11. Buetier, D., and Renon, H., Representation of NH_3-H_2S-H_2O, NH_3-CO_2-H_2O and NH_3-SO_2-H_2O Vapor-Liquid Equilibria., Ind. Eng. Chem. Process Des. Dev., 17(3), 220-230 (1978).

12. Criss, C.M., and Cobble, J.W., The Thermodynamic Properties of High Temperature Aqueous Solutions. IV. Entropies of the Ions up to 200° C and the Correspondence Principle., J. Am. Chem. Soc., 86, 5385-5393 (1964).

13. Staple, B.R., Personal Communication (1986).

14. Staple, B.R., Evaluated Thermal Properties of Aqueous Transition Metal Chlorides: Mn, Fe, Co, Ni, and Zn, Proc. Ninth Intl. Assn. for Properties of Steam Conf., Moscow (Sept. 2-7, 1984).

15 Chen, C-C, Britt, H.I., Boston, J.F., and Evans, L.B., Extension and Application of the Pitzer Equation for Vapor-Liquid Equilibrium of Aqueous Electrolyte Systems with Molecular Solutes., AIChE J., 25, 820-831 (1979).

16. Glushko, V.P., Thermodynamic Constants of Matter, Vol. 1-10, Academy of Science of the U.S.S.R., Moscow (1965)

17. Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.M., Halow, I., Bailey, S.M., Churney, K.L., and Nutall, R.L., NBS Tables of Chemical Thermodynamic Properties-Selected values for Inorganic and C1-C12 Organic Substance in SI Units. J. Phys. Chem. Ref. Data, Vol. 11, Supplement No. 2 (1982).

18. Morris, D.F.C., Ionic Radii and Enthalpies of Hydration of Ions., Structure Bonding, 4, 63-82 (1968).

19. Marcus, Y., Ionic Radii in Aqueous Solutions., J. Solution Chem., 12, No.2 271-275 (1983).

20. Pauling, L., Nature of the Chemical Bond., Cornell Univ. Press., Ithaca (1960).

21. Lim, T-K, Khoo, K.H., and Chan, C-Y, Activity Coefficients for the System $HBr+SrBr_2+H_2O$ at 25°C., J. Solution Chem., 9, No.10, 785-789 (1980).

22. Hamer, W.J., and Wu, Y.C., Osmotic Coefficients and Mean Activity Coefficients of Uni-Univalent Electrolytes in Water at 25°C., J. Phys. Chem. Ref. Data, 1, 1047-1099 (1972).

23. Wu, Y.C., and Hamer, W.J., Revised Values of the Osmotic Coefficients and Mean Activity Coefficients of Sodium Nitrate in Water at 25°C., J. Phys. Chem. Ref. Data, 9, 513-518 (1980).

24. Roy, R.N., Gibbons, J.J., Bliss, D.P.,Jr., Casebolt, R.G., and Baker, B.K., Activity Coefficients for Ternary Systems: VI. The System $HCl+MgCl_2+H_2O$ at Different Temperatures; Application of Pitzer's Equations., J. Solution Chem., 9, 911-930 (1980).

25. Peleg, M., A Raman Spectroscopic Investigation of the Magnesium Nitrate-Water System., J. Phys. Chem., 76, 1019-1025 (1972).

26. Lemley, A.T.G., and Plane, R.A., Raman Spectrophotometric Study of Ion Pairing in Aqueous Zinc Nitrate Systems., J. Chem. Phys., 57, 1648-1653 (1972).

27. Pitzer, K.S., and Mayorga, G., Thermodynamics of Electrolytes. II. Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent., J. Phys. Chem., 77, 2300-2308 (1973).

BIBLIOGRAPHY

Bernal, J.D., and Fowler, R.H., A Theory of Water and Ionic Solution with Particular Reference to Hydrogen and Hydroxyl Ions., J. Chem. Phys., 1, 515-548 (1933).
Blandamer, M.J., Structure and Properties of Aqueous Salt Solutions, Chem. Soc. London Quart. Rev., 24, 169-184 (1970).

Bonner, O.D., The Osmotic and Activity Coefficients of Some Salts Having Relatively Large Molar Volumes., J. Chem. Eng. Data, 21, 498-499 (1976).

Bonner, O.D., The Osmotic and Activity Coefficients of Tetrasodium and tetrapotassium Adenosine-5'-Triphosphate., J. Chem. Thermodynamics, 11, 563-565 (1979).

Bonner, O.D., The Osmotic and Activity Coefficients of Some Pyrophosphates., J. Chem. Thermodynamics, 11, 559-562 (1979).

Bonner, O.D., Osmotic and Activity Coefficients of Lithium Chlorate and Lithium Bromate., J. Chem. Eng. Data, 24, 210-211 (1979).

Bonner, O.D., Osmotic and Activity Coefficients of Methyl-Substituted Ammonium Perchlorates at 298,15 K., J. Chem. Eng. Data, 27, 62-64 (1982).

Boyd, G.E., Solute Activity Coefficients in Dilute Aqueous Electrolyte Mixtures II. The Ternary System: $NaClO_4+La(ClO_4)_3+H_2O$ at 298.15 K., J. Chem. Thermodynamics, 10, 415-424 (1978).

Buetier, D., and Renon, H., Representation of NH_3-H_2S-H_2O, NH_3-CO_2-H_2O and NH_3-SO_2-H_2O Vapor-Liquid Equilibria., Ind. Eng. Chem. Process Des. Dev., 17(3), 220-230 (1978).

Butler, J.N., and Huston, R., Activity Coefficients and Ion Pairs in the Systems Sodium Chloride-Sodium Bicarbonate-Water and Sodium Chloride-Sodium Carbonate-Water., J. Phys. Chem., 74, 2976-2983 (1970).

Butler, J.N., and Huston, R., Potentiometric Studies of Multicomponent Activity Coefficients Using the Lanthanum Fluoride Membrane Electrode., Anal. Chem., 42, 1308-1311 (1970).

Cartledge, G.H., Studies on the Periodic System. II. The ionic Potential and Related Properties., J. Am. Chem. Soc., 50, 2863-2872 (1928).
Cartledge, G.H., Studies on the Periodic System. I. The Ionic Potential as a Periodic Function., J. Am. Chem. Soc., 50, 2855-2863 (1928).

Chen, C-C, Britt, H.I., Boston, J.F., and Evans, L.B., Extension and Application of the Pitzer Equation for Vapor-Liquid Equilibrium of Aqueous Electrolyte Systems with Molecular Solutes., AIChE J., 25, 820-831 (1979).

Childs, C.W., Downes, C.J., and Platford, R.F., Thermodynamics of Multicomponent Electrolyte Solutions: Aqueous Mixtures of Two Salts from Among NaCl, KCl, NaH_2PO_4, and KH_2PO_4 at 25°C., J. Solution Chem., 3, 139-147 (1974).

Criss, C.M., and Cobble, J.W., The Thermodynamic Properties of High Temperature Aqueous Solutions. IV. Entropies of the Ions up to 200° C and the Correspondence Principle., J. Am. Chem. Soc., 86, 5385-5393 (1964).

Davies, C.W., The Extent of Dissociation of Salts in Water. Part VIII An Equation for the Mean Ionic Activity Coefficient of an Electrolyte in Water, and a Revision of the Dissociation Constants of Some Sulphates, J. Chem. Soc., 2093 (1938).

Davies, C.W., Ion Association, Butterworths Scientific Publications, London (1962).

Debye, D., and Hückel, E., Theory of Electrolytes. II The Limiting Law of Electrical Conductivity., Physik. Z., 24, 305-325 (1923).

Debye, D., and Hückel, E., Theory of Electrolytes. I Lowering of Freezing Point and Related Phenomena., Physik. Z., 24, 185-206 (1923).

Downes, C.J., Osmotic and Activity Coefficients for Mixtures of Potassium Chloride and Strontium Chloride in Water at 298.15 K., J. Chem. Thermodynamics, 6, 317-323 (1974).

Downes, C.J., and Pitzer, K.S., Thermodynamics of Electrolytes. Binary Mixtures Formed from Aqueous NaCl, Na_2SO_4, $CuCl_2$, and $CuSO_4$ at 25°C., J. Solution Chem, 5, 389-398 (1976).

Downes, C.J., Osmotic and Activity Coefficients for System $NaCl-MnCl_2-H_2O$ at 25°C., J. Chem. Eng. Data, 18, 412-416 (1975).

Downes, C.J., Thermodynamics of Mixed Electrolyte Solutions: The Systems $H_2O-NaCl-CoCl_2$ and $H_2O-CaCl_2-CoCl_2$ at 25°C., J. Solution Chem., 4, 191-204 (1975).

Edward, T.J., Maurer, G., Newman, J., and Prausnitz, J. M., Vapor-Liquid Equilibria in multicomponent Aqueous Solutions of Volatile Weak Electrolytes., AIChE J., 24, 966-976 (1978).

Felmey, A.R., and Weare, J.H., The Prediction of Borate Mineral Equilibria in Natural Waters: Application to Searles Lake, California., Geochimica et Cosmochimica Acta, 50, 2771-2783 (1986).

Frederick, W.J., Jr., Kelly, B., Kim, H.C., and McIntyre, M.J., Modeling Electrolyte Behavior in Pulp and Paper Processes., AIChE National Summer Meeting, Minneapolis (August 16-19, 1987).

Friedman, H.L., Ionic Solution Theory., Interscience: New York, 1962.
Glushko, V.P., Thermodynamic Constants of Matter, Vol. 1-10, Academy of Science of the U.S.S.R., Moscow (1965)

Goldberg, R.N., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-Univalent Compounds of Lead, Copper, Manganese, and Uranium., J. Phys. Chem. Ref. Data , 8, 1005-1050 (1979).

Goldberg, R.N., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-Univalent Compounds of Zinc, Cadmium, and Ethylene Bis (Trimethylammonium) Chloride and Iodie., J. Phys. Chem. Ref. Data , 10, 1-55 (1981).

Goldberg, R.N., Nuttall, R.L., and Staples, B.R., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Iron Chloride and the Bi-Univalent Compounds of Nickel and Cobalt., J. Phys. Chem. Ref. Data, 8, 923 -1003 (1979).

Goldberg, R.N., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Thirty-Six Uni-Bivalent Electrolytes., J. Phys. Chem. Ref. Data, 10, 671-764 (1981).

Goldberg, R.N., and Nuttall, R.L., Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: The Alkaline Earth Metal Halides., J. Phys. Chem. Ref. Data, 7, 263-310 (1978).

Groves, K.O., Dye, J.L., and Brubaker, C.H. Jr., Activity Coefficients and Conductances of High-Charge (4-1, 1-4, 1-2) Electrolytes, II., J. Am. Chem. Soc., 82, 4445-4448 (1960).

Guggenheim, E.A., and Turgeon, J.C., Specific Interaction of Ions, Trans. Faraday Soc., 51, 747-761 (1955).

Guggenheim, E.A., The Specific Thermodynamic Properties of Aqueous Solutions of Strong Electrolytes, Phil. Mag. 19, 588-643 (1935).

Güntelberg, E., Interaction of Ions, Z. Physik. Chem., 123, 199-247 (1926).

Gurney, R.W., Ionic Processes in Solution, McGraw-Hill Book Company, New York (1962).
Huheey, J.E., Inorganic Chemistry: Priciples of Structure and Reactivity, 2nd ed., New York, Harper and Row p.889 (1978).

Hamer, W.J., and Wu, Y.C., Osmotic Coefficients and Mean Activity Coefficients of Uni-Univalent Electrolytes in Water at 25°C., J. Phys. Chem. Ref. Data, 1, 1047 -1099 (1972).

Harned, H.S., and Owen, B.B., The Physical Chemistry of Electrolyte Solutions., 3rd ed., Reinhold: New York, N.Y., 1958.

Harned, H.S., and Paxton, T.R., The Thermodynamics of Ionized Water in Strontium Chloride Solutions from Electromotive Force Measurements., J. Phys. Chem., 57, 531-535 (1953).

Harvie, C.E., Eugster, H.P., and Weare, J.H., Mineral Equilibria in the Six-Component Seawater System, Na-K-Mg Ca-SO_4-Cl-H_2O at 25°C, II: Compositions of the Saturated Solutions., Geochim. Cosmochim. Acta., 46, 1603-1618 (1982).

Harvie, C.E., and Weare, J.H., The Prediction of Mineral Solubilities in Natural Waters: the Na-K-Mg-Ca-SO_4-H_2O System from Zero to High Concentration at 25°C., Geochim. Cosmochim. ACta.,44, 981-997 (1980).

Harvie, C.E., Møller, N., and Weare, J.H., The Prediction of Mineral Solubilities in Natural Water: the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O System to High Ionic Strengths at 25°C., Geochimica et Cosmochimica Acta, 48, 723-751 (1984).

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

Hückel, E., The Theory of Concentrated Aqueous Solutions of Strong Electrolytes., Physik. Z., 26, 93-147 (1924).

Huston, R., and Butler, J.N., Activity Measurements in Concentrated Sodium Chloride-Potassium Chloride Electrolytes Using cation-Sensitive Glass Electrodes., Anal. Chem., 41, 1695-1698 (1969).

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

Kalman, E., and Schwabe, K., Osmotic and Activity Coefficients of Ammonium Thiocyanate in Aqueous Solutions at 25°C., J. Solution Chem., 8, 1-4 (1979).

Kangro, W., and Groeneveld, A., Concentrated Aqueous Solutions I., Z. Phys. Chem. (Frankfurt am Main), 32, 110-126 (1962).

Kelly, B., and Frederick, W.J., Jr., Application of Chemical Engineering Principle in the Forest Products and Related Industries., Kayihan, F., and Krieger-Brackett, B., Editors. AIChE Forest Products Division, Seattle, 1986.

Khoo, K.H., Lim, T.K., and Chan, C.Y., Ionic Interactions in the System HBr+$BaBr_2$+H_2O at 25°C., J. Solution Chem., 8, 277-282 (1979).

Khoo, K.H., Chan C.Y., and Lim, T.K., Thermodynamics of Electrolyte Solutions. The System HCl+$CaCl_2$+H_2O at 298.15°K., J. Solution Chem., 6, 651-662 (1977).

Khoo, H.K., Activity Coefficients in Mixed-Electrolyte Solutions., J. Chem. Soc., Faraday Trans. 1, 82, 1-12 (1986).

Khoo, K.H., Lim, T.K., and Chan, C.Y., Activity Coefficients for the System HBr+$CaBr_2$+H_2O at 298.15 K., J. Chem. Soc. Faraday Trans. 1, 75, 1067-1072 (1979).

Khoo, K.H., Chan, C.Y., and Lim, T.K., Activity Coefficients for the System $HCl+BaCl_2+H_2O$ at 298.15 K., J. Chem. Soc. Faraday Trans. 1, 74, 837-845 (1978).

Khoo, K.H., Lim, T.K., and Chan, C.Y., Activity Coefficients for $HCl+NiCl_2+H_2O$ at 298.15°K and Effects of Higher-Order Electrostatic Terms., J. Solution Chem., 7, 291-301 (1978).

Khoo, K.H., Lim, T.K., and Chan, C.Y., Activity Coefficients for the System $HCl+CoCl_2+H_2O$ at 298.15 K., J. Chem. Soc. Faraday Trans. 1, 74, 2037-2044 (1978).

Kim, H.T., and Frederick, W.J.,Jr., Evaluation of Pitzer Ion Interaction Parameters of Aqueous Electrolytes at 25 C. 1. Single Salt Parameters., J. Chem. Eng. Data,(in press).

Lemley, A.T.G., and Plane, R.A., Raman Spectrophotometric Study of Ion Pairing in Aqueous Zinc Nitrate Systems., J. Chem. Phys., 57, 1648-1653 (1972).

Libus, Z., Zak, E., and Sadowaska, T., Osmotic Coefficients of Aqueous Rare-Earth Ethylsulphates., J. Chem. Thermodynamics, 16, 257-266 (1984).

Libus, Z., Sadowaska, T., and Trzaskowski, J., Osmotic Coefficients of Aqueous Rare-Earth Perchlorates and Nitrates., J. Chem. Thermodynamics, 11, 1151-1161 (1979).

Lim T.K., Khoo, K.H., and Chan, C.Y., Activity Coefficients for the System Hydrogen Bromide+Strontium Bromide+Water at 25°C., J. Solution Chem., 9, 785-789 (1980).

Lindenbaum, S., Rush, R.M., and Robinson, R.A., Osmotic and Activity Coefficients for Mixtures of Lithium Chloride with Barium Chloride and Cesium Chloride with barium Chloride in Water at 298.15 K., J. Chem. Thermodynamics, 4, 381-389 (1972).

Macaskill, J.B., Robinson, R.A., and Bates, R.G., Osmotic and Activity Coefficients of Guanidinium Chloride in Concentrated Aqueous Solutions at 25°C., J. Chem. Eng. Data, 22, 411-412 (1977).

Marcus, Y., Ionic Radii in Aqueous Solutions., J. Solution Chem., 12, No.2 271-275 (1983).

Morris, D.F.C., Ionic Radii and Enthalpies of Hydration of Ions., Structure Bonding, 4, 63-82 (1968).

Pauling, L., Nature of the Chemical Bond., Cornell Univ. Press., Ithaca (1960).

Peiper, J.C., and Pitzer, K.S., Thermodynamics of Aqueous Carbonate Solutions Including Mixtures of Sodium Carbonate, Bicarbonate, and Chloride., J. Chem. Thermodynamics, 14, 613-638 (1982).

Peleg, M., A Raman Spectroscopic Investigation of the Magnesium Nitrate-Water System., J. Phys. Chem., 76, 1019-1025 (1972).

Pitzer, K.S., and Kim, J., Thermodynamics of Electrolytes. IV: Actiivty and Osmotic Coefficients for Mixed Electrolytes. J. Am. Chem. Soc., 96, 5701-5707 (1974).

Pitzer, K.S., Thermodynamic Properties of Aqueous Solutions of Bivalent Sulfates., J. Chem. Soc., Faraday Trans., 68, 101-113 (1972).

Pitzer, K.S., Theory: Ion Interaction Approach, in Activity Coefficients in Electrolyte Solutions, Vol. 1, Pytkowicz, R.M., Editor CRC Press, Inc., Boca Raton, FL (1979).

Pitzer, K.S., Thermodynamics of Electrolytes I: Theoretical basis and general equations., J. Phys. Chem., 77, 268-277 (1973).

Pitzer, K.S., and Mayorga, G., Thermodynamics of Electrolytes II: Activity and osmotic coefficients for strong electrolytes with one or both ions univalent., J. Phys. Chem., 77, 2300-2308 (1973).

Pitzer, K.S., Peterson, J.R., and Silvester, L.F., Thermodynamics of Electrolytes. IX. Rare Earth Chlorides, Nitrates, and Perchlorates., J. Solution Chem., 7, 45-56 (1978).

Pitzer, K.S., and Mayorga, G., Thermodynamics of Electrolytes. III: Activity and Osmotic Coefficients for 2-2 electrolytes., J. Solution Chem., 3, 539-546 (1974).

Pitzer, K.S., Thermodynamics of Electrolytes: V. Effects of Higher-Order Electrostatic Terms., J. Solution Chem., 4, 249-265 (1975).

Platford, R.F., Thermodynamics of Mixed Salt Solutions: Excess Gibbs Energies of Mixing for the Six Ternary Systems Formed from Aqueous $MgCl_2$, $Mg(NO_3)_2$, $CaCl_2$, and $Ca(NO_3)_2$ at 25°C., J. Chem. Thermodynamics, 3, 319-324 (1971).

Platford, R.A., Osmotic and Activity Coefficients of Some Simple Borates in Aqueous Solution at 25°C., Can. J. Chem., 47, 2771-2773 (1969).

Rard, J.A., and Miller, D.G., Isopiestic Ditermination of the Osmotic Coefficients of Aqueous Na_2So_4, $MgSO_4$, and Na_2SO_4-$MgSO_4$ at 25°C. J. Chem. Eng. Data, 26, 33-38 (1981).

Rard, J.A., and Miller, D.C., Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25°C. 4. $La(NO_3)_3$, $Pr(NO_3)_3$, and $Nd(NO_3)_3$., J. Chem. Eng. Data, 24, 348-354 (1979).

Rard, J.A., Shiers, L.E., Heiser, D.J., and Spedding, F.H., Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25°C. 3. The Rare Earth Nitrates., J. Chem. Eng. Data, 22, 337-347 (1977).

Rard, J.A., Weber, H.O., and Spedding, F.H., Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25°C. 2. The Rare Earth Perchlorates., J. Chem. Eng. Data, 22, 187-201 (1977).

Robinson, R.A., Roy, R.N., and Bates, R.G., System Water-Hydrochloric Acid Ammonium Chloride at 25°. Harned's Rule, J. Solution Chem., 3, 837-846 (1974).

Robinson, R.A., Wood, R.H., and Reilly, P.J., Calculation of Excess Gibbs Energies and Activity Coefficients from Isopiestic Measurements on Mixtures of Lithium and Sodium Salts., J. Chem. Thermodynamics, 3, 461-471 (1971).

Robinson, R.A., and Stokes, R.H., Electrolyte Solutions, 2nd ed., Butterworths: London, 1959.

Rogers, P.S.Z., and Pitzer, K.S., Volumetric Properties of Aqueous Sodium Chloride Solutions., J. Phys. Chem. Ref. Data, 11, 15-81 (1982).

Roy, R.N., Gibbons, J.J., Trower, J.K., and Lee, G.A., Application of Pitzer's Equations on the System $HCl+MnCl_2+H_2O$ at Various Temperatures. V., J. Solution Chem., 9, 535-551 (1980).

Roy, R.N., Gibbons, J.J., Ovens, L.K., Bliss, G.A., and Hartley, J.J., Activity Coefficients for the System $HCl+CaCl_2+H_2O$ at Various Temperatures., J. Chem. Soc. Faraday Trans. 1, 78, 1405-1422 (1981).
Roy, R.N., Gibbons, J.J., Bliss, D.P.,Jr., Casebolt, R.G., and Baker, B.K., Activity Coefficients for Ternary Systems: VI. The System $HCl+MgCl_2+H_2O$ at Different Temperatures; Application of Pitzer's Equations., J. Solution Chem., 9, 911-930 (1980).

Rush, R.M., and Johnson, J.S., Isopiestic Measurements of the Osmotic and Activity Coefficients for the Systems $HClO_4+UO_2(ClO_4)_2+H_2O$ and $NaClO_4+UO_2(ClO_4)_2+H_2O$ at 25°C., J. Chem. Thermodynamics, 3, 779-793 (1971).

Rush, R.M., and Johnson, J.S., Isopiestic Measurements of the Osmotic and Activity Coefficients for the Systems $HClO_4-LiClO_4-H_2O$, $HClO_4-NaClO_4-H_2O$, and $LiClO_4-NaClO_4-H_2O$., J. Phys. Chem., 72, 767-774 (1968).

Sanker, M., Macaskill, J.B., and Bates, R.G., Activity Coefficients of Hydrochloric Acid and Ionic Interactions in the System $HCl-CsCl-H_2O$ from 5 to 50° C., J. Solution Chem, 10, 169-179 (1981).

Silvester, L.F., and Pitzer, K.S., Thermodynamics of Electrolytes. 8. High-Temperature Properties, Including Enthalpy and Heat Capacity, with Application to Sodium Chloride., J. Phys. Chem., 81, 1822-1828 (1977).

Spedding, F.H., Weber, H.O., Saeger, V.W., Petheram, H.H., Rard, J.A., and Habenschuss, A.J., Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25°C. 1. The Rare Earth Chlorides., Chem. Eng. Data, 21, 341 -360 (1976).

Staple, B.R., Evaluated Thermal Properties of Aqueous Transition Metal Chlorides: Mn, Fe, Co, Ni, and Zn, Proc. Ninth Intl. Assn. for Properties of Steam Conf., Moscow (Sept. 2-7, 1984).

Staple, B.R., Personal Communication (1986).

Staples, B.R., Activity and Osmotic Coefficients of Aqueous Sulfuric Acid at 298.15 K., J. Phys. Chem. Ref. Data, 10, 779-798 (1981).

Staples, B.R., Activity and Osmotic Coefficients of Aqueous Alkali Metal Nitrites., J. Phys. Chem. Ref., 10, 765-777 (1981).

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.M., Halow, I., Bailey, S.M., Churney, K.L., and Nutall, R.L., NBS Tables of Chemical Thermodynamic Properties-Selected values for Inorganic and C1-C12 Organic Substance in SI Units. J. Phys. Chem. Ref. Data, Vol. 11, Supplement No. 2 (1982).

White, D.R., Jr., and Bates R.G., Osmotic Coefficients and Activity Coefficients of Aqueous Mixtures of Sodium Chloride and Sodium Carbonate at 25°C., Aust. J. Chem, 33, 1903-1908 (1980).

Whitfield, M., The Extension of Chemical Models for Sea Water to Include Trace Components at 25°C and 1 atm Pressure., Geochim. Cosmochim. Acta., 39, 1545-1557 (1975).

Whitfield, M., An Improved Specific Interaction Model for Seawater at 25°C and 1 Atmosphere Total Pressure., Mar. Chem., 3, 197-213 (1975).

Wood, S.A., Crerar, D.A., Brantley, S.L., and Borcsik, M., Mean Molal Stoichiometric Activity Coefficients of Alkali Halides and Related Electrolytes in Hydrothermal Solutions., Am. J. Sci., 284, 668-705 (1984).

Wu, Y.C., Rush, R.M., and Scatchard, G., Osmotic and Activity Coefficients for Binary Mixtures of Sodium Chloride, Sodium Sulfate, Magnesium Sulfate, and Magnesium Chloride in Water at 25°C. I. Isopiestic Measurements on the Four Systems with Common Ions., J. Phys. Chem., 72, 4048-4053 (1968).

Wu, Y.C., and Harmer, W.J., Revised Values of the Osmotic Coefficients and Mean Activity Coefficients of Sodium Nitrate in Water at 25°C., J. Phys. Chem. Ref. Data, 9, 513-518 (1980).

Wynveen, R.A., Dye, J.L., and Brubaker, C.H. Jr., Activity Coefficient and Conductivity Measurements of High-Charge (3-1, 1-3, 3-2) Electrolytes, I., J. Am. Chem. Soc., 82, 4441-4445 (1960).

Zemaitis, J.F., Jr., Clark, D.M., Rafal, M., and Scrivner, N.C., Handbook of Aqueous Electrolyte Thermodynamics, AIChE, New York (1986).

APPENDICES

APPENDIX 1

Program Pitzer

A complete listing of the program Pitzer is given. This program is used to determine the J0(X) and J1(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.

```
C
C     *MAIN PROGRAM PITZER*
C
      PROGRAM PITZER(INPUT,OUTPUT)
      EXTERNAL F1,F2
      COMMON RX,A
      REAL J0,J1,VAL1,VAL2,A,B,AERR,RERR
      INTEGER MAXFCN,N,IER
C
      OPEN(5,FILE='OUT1')
      WRITE(*,110)
  110 FORMAT(//,8X,'X',11X,'J0',11X,'J1',/)
C
   10 PRINT*,'ENTER X VALUE'
      READ(*,*,END=30) RX
C
C     *COMPUTE J0*
C
      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
C
C     *COMPUTE J1*
C
      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
```

```
C
C     *FUNCTION F1*
C
      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
C
C     *FUNCTION F2*
C
      REAL FUNCTION F2(N,X)
      COMMON RX
      REAL X(N)
      F2=(1.0-(1.0+RX/X(1)*EXP(-1.0*X(1)))*
     1   EXP(-1.0*RX/X(1)*EXP(-1.0*X(1))))*X(1)**2
      RETURN
      END
C
C     *SUBROUTINE TARGET*
C
      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
   10 CONTINUE
    1 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.) GOTO 2
   20 CONTINUE
    2 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
   30 CONTINUE
    3 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
   40 CONTINUE
    4 Y=Y-0.0001
      DO 50 I=1,50
      Y=Y+0.00001
      C=-1.0*RX/Y*EXP(-1.0*Y)
```

```
   IF(C.GT.-80) GO TO 5
50 CONTINUE
 5 A=Y-0.00001
   RETURN
   END
```

APPENDIX 2

Comparison of $\gamma_{\pm}$ of single salts between experimental data and calculated values from correlation results at 25°C

I	NaCl		NaBr		NaI	
(mol/kg)	Exp	Cal*	Exp	Cal*	Exp	Cal*
0.02	0.872	0.870	0.873	0.872	0.874	0.874
0.05	0.822	0.819	0.824	0.823	0.827	0.828
0.10	0.779	0.775	0.783	0.781	0.789	0.791
0.20	0.734	0.730	0.742	0.741	0.753	0.757
0.30	0.709	0.706	0.720	0.721	0.735	0.742
0.40	0.693	0.690	0.706	0.709	0.726	0.735
0.50	0.681	0.680	0.697	0.701	0.722	0.732
0.60	0.673	0.673	0.692	0.697	0.721	0.733
0.70	0.667	0.668	0.688	0.696	0.722	0.735
0.80	0.662	0.665	0.687	0.695	0.725	0.740
0.90	0.659	0.664	0.686	0.696	0.729	0.745
1.00	0.657	0.663	0.687	0.699	0.734	0.752
1.20	0.655	0.665	0.691	0.706	0.747	0.768
1.40	0.656	0.669	0.697	0.715	0.763	0.787
1.60	0.658	0.675	0.706	0.727	0.781	0.808
1.80	0.662	0.683	0.717	0.741	0.801	0.832
2.00	0.668	0.692	0.730	0.757	0.823	0.859
2.50	0.688	0.721	0.768	0.803	0.887	0.934
3.00	0.714	0.757	0.816	0.858	0.963	1.023
3.50	0.746	0.799	0.871	0.922	1.051	1.126
4.00	0.783	0.848	0.934	0.995	1.153	1.245
4.50	0.826	0.902	1.005	1.077	1.269	1.381
5.00	0.874	0.963	1.083	1.169	1.402	1.536
5.50	0.928	1.030	1.169	1.272	1.552	1.712
6.00	0.986	1.104	1.261	1.387	1.723	1.913

* Calculated from correlation results

I	NaF		$NaClO_3$		$NaClO_4$	
(mol/kg)	Exp	Cal*	Exp	Cal*	Exp	Cal*
0.02	0.868	0.864	0.771	0.752	0.872	0.869
0.05	0.813	0.805	0.719	0.692	0.821	0.817
0.10	0.764	0.751	0.687	0.655	0.777	0.771
0.20	0.710	0.690	0.664	0.629	0.729	0.724
0.30	0.676	0.653	0.646	0.608	0.702	0.698
0.40	0.652	0.626	0.631	0.592	0.683	0.681
0.50	0.633	0.606	0.619	0.578	0.668	0.669
0.60	0.617	0.589	0.608	0.567	0.657	0.660
0.70	0.604	0.575	0.598	0.557	0.648	0.654
0.80	0.592	0.563	0.590	0.548	0.641	0.649
0.90	0.582	0.553	0.575	0.534	0.635	0.646
1.00	0.573	0.544	0.563	0.522	0.630	0.644
1.20			0.553	0.513	0.622	0.643
1.40			0.545	0.505	0.616	0.644
1.60			0.537	0.499	0.612	0.647
1.80			0.523	0.487	0.610	0.652
2.00			0.514	0.480	0.608	0.658
2.50					0.608	0.679
3.00					0.612	0.706
3.50					0.618	0.738
4.00					0.626	0.775
4.50					0.636	0.817
5.00					0.648	0.863
5.50					0.662	0.914
6.00					0.678	0.971

* Calculated from correlation results

I (mol/kg)	$NaNO_3$ Exp	$NaNO_3$ Cal*	NaOH Exp	NaOH Cal*	NaAc Exp	NaAc Cal*
0.02	0.867	0.863	0.870	0.870	0.875	0.874
0.05	0.811	0.803	0.819	0.819	0.830	0.828
0.10	0.760	0.748	0.775	0.774	0.793	0.791
0.20	0.702	0.685	0.731	0.729	0.760	0.758
0.30	0.666	0.646	0.708	0.704	0.745	0.743
0.40	0.639	0.618	0.694	0.689	0.739	0.736
0.50	0.618	0.596	0.685	0.678	0.737	0.734
0.60	0.600	0.578	0.679	0.671	0.738	0.735
0.70	0.585	0.563	0.676	0.666	0.740	0.737
0.80	0.571	0.551	0.674	0.662	0.745	0.742
0.90	0.559	0.539	0.673	0.660	0.750	0.748
1.00	0.549	0.530	0.674	0.659	0.757	0.755
1.20	0.530	0.513	0.678	0.660	0.772	0.771
1.40	0.515	0.499	0.684	0.664	0.789	0.790
1.60	0.501	0.488	0.692	0.669	0.808	0.813
1.80	0.489	0.478	0.702	0.677	0.828	0.837
2.00	0.478	0.470	0.714	0.685	0.850	0.864
2.50	0.456	0.454	0.749	0.713	0.911	0.941
3.00	0.437	0.442	0.794	0.747	0.981	1.032
3.50	0.422	0.433	0.847	0.787	1.060	1.137
4.00	0.408	0.426	0.911	0.833		
4.50	0.396	0.421	0.987	0.885		
5.00	0.386	0.417	1.076	0.943		
5.50	0.378	0.414	1.181	1.007		
6.00	0.372	0.412	1.302	1.077		

* Calculated from correlation results

I (mol/kg)	Li_2SO_4 Exp	Li_2SO_4 Cal*	Na_2SO_4 Exp	Na_2SO_4 Cal*	K_2SO_4 Exp	K_2SO_4 Cal*
0.06	0.645	0.657	0.637	0.630	0.625	0.634
0.15	0.544	0.564	0.529	0.517	0.511	0.524
0.30	0.469	0.495	0.446	0.430	0.424	0.440
0.60	0.400	0.431	0.366	0.347	0.343	0.359
0.90	0.364	0.395	0.321	0.302	0.300	0.315
1.20	0.341	0.372	0.291	0.272	0.272	0.286
1.50	0.325	0.355	0.268	0.250	0.251	0.265
1.80	0.313	0.342	0.251	0.234	0.236	0.249
2.10	0.303	0.333	0.236	0.220		
2.40	0.296	0.326	0.224	0.210		
2.70	0.289	0.320	0.213	0.200		
3.00	0.285	0.316	0.204	0.193		
3.75	0.276	0.310	0.186	0.177		
4.50	0.271	0.310	0.173	0.167		
5.25	0.270	0.314	0.162	0.158		
6.00	0.270	0.321	0.155	0.152		
6.75	0.273	0.330				
7.50	0.278	0.342				
8.25	0.285	0.357				
9.00	0.294	0.373				

* Calculated from correlation results

I	Rb_2SO_4		Cs_2SO_4	
(mol/kg)	Exp	Cal*	Exp	Cal*
0.06	0.635	0.645	0.634	0.655
0.15	0.526	0.544	0.526	0.561
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
3.75	0.201	0.245	0.219	0.298
4.50	0.190	0.238	0.208	0.297

* Calculated from correlation results

I (mol/kg)	MgI_2		$MgBr_2$		$MgCl_2$	
	Exp	Cal*	Exp	Cal*	Exp	Cal*
0.06	0.677	0.689	0.672	0.679	0.672	0.668
0.15	0.602	0.626	0.593	0.608	0.590	0.587
0.30	0.557	0.595	0.543	0.566	0.535	0.534
0.60	0.535	0.589	0.512	0.544	0.494	0.495
0.90	0.543	0.606	0.511	0.546	0.481	0.483
1.20	0.564	0.634	0.522	0.558	0.480	0.482
1.50	0.594	0.669	0.541	0.578	0.486	0.488
1.80	0.632	0.711	0.565	0.603	0.496	0.498
2.10	0.677	0.760	0.595	0.634	0.511	0.513
2.40	0.729	0.817	0.630	0.669	0.530	0.531
2.70	0.789	0.881	0.670	0.710	0.552	0.552
3.00	0.858	0.954	0.715	0.756	0.577	0.577
3.75	1.074	1.179	0.854	0.897	0.656	0.652
4.50	1.369	1.480	1.037	1.081	0.760	0.750
5.25	1.772	1.880	1.277	1.318	0.894	0.873
6.00	2.326	2.410	1.590	1.624	1.066	1.027
6.75	3.090	3.115	2.001	2.016	1.283	1.216
7.50	4.148	4.052	2.539	2.519	1.558	1.451
8.25	5.618	5.299	3.247	3.165	1.908	1.739
9.00	7.673	6.962	4.180	3.993	2.350	2.094
9.75	10.552	9.183	5.413	5.059	2.910	2.532
10.50	14.598	12.153	7.042	6.431	3.621	3.071
11.25	20.296	16.131	9.199	8.198	4.523	3.736
12.00	28.330	21.467	12.054	10.478	5.669	4.556
12.75	39.665	28.634	15.831	13.423	7.127	5.569
13.50	55.649	38.271	20.823	17.230	8.985	6.820
14.25	78.163	51.244	27.408	22.156	11.358	8.368
15.00	109.808	68.727	36.074	28.537	14.396	10.284
15.75			47.441	36.810	18.298	12.656
16.50			62.288	47.545	23.329	15.597
17.25					29.847	19.243
18.00						

* Calculated from correlation results

I (mol/kg)	$Mg(ClO_4)_2$ Exp	 Cal*	$Mg(NO_3)_2$ Exp	 Cal*
0.30	0.577	0.609	0.522	0.531
0.60	0.565	0.612	0.480	0.491
0.90	0.576	0.637	0.467	0.478
1.20	0.599	0.673	0.465	0.475
1.50	0.633	0.716	0.469	0.480
1.80	0.673	0.768	0.478	0.489
2.10	0.723	0.828	0.488	0.503
2.40	0.780	0.897	0.501	0.519
2.70	0.849	0.976	0.518	0.539
3.00	0.925	1.065	0.536	0.562
3.60	1.112	1.279	0.580	0.617
4.20	1.355	1.553	0.631	0.685
4.80	1.667	1.901	0.691	0.768
5.40	2.080	2.342	0.758	0.866
6.00	2.590	2.904	0.835	0.983
7.50	4.780	5.070	1.088	1.377
9.00	8.990	9.048	1.449	1.970
10.50	17.260	16.406	1.936	2.863
12.00	33.300	30.104	2.590	4.210
13.50			3.500	6.247
15.00			4.740	9.336

* 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:

$$A(c) = bB + cC \tag{1}$$

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

$$K_{sp} = a_B{}^b a_C{}^c / a_A \tag{2}$$

Assuming the salt is pure and of activity one,

$$K_{sp} = a_B{}^b a_C{}^c \tag{3}$$

or

$$K_{sp} = (m_B \tau_B)^b (m_C \tau_C)^c \tag{4}$$

Since charge balance shows, $m_B = bm_A$ and $m_C = cm_A$, and the mean activity coefficient is the thermodynamically defined:

$$\tau_A{}^{(b+c)} = (\tau_B{}^b \tau_C{}^c) \tag{5}$$

Finally, the solubility product is

$$K_{sp} = (Qm_A\gamma_A)^{b+c} \tag{6}$$

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 $KCl-H_2O$ 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,

$$K_{sp} = (m_{KCl}\gamma_{KCl})^2 = 8.003$$

If assuming ideal activity coefficients ($\gamma_{KCl} = 1$), 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: $Na_2SO_4(c) = 2Na^+(aq) + SO_4^{2-}(aq)$

$m = 1.957$ mol/kg (saturated solution)

$\tau_{\pm} = 0.1558$ (Goldberg, 1981)

Thus,

$$K_{sp} = 4(m\tau_{\pm})^3 = 0.1134$$

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

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

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

2-1 TYPE ELECTROLYTE

For: $MgCl_2(c) = Mg^{2+}(aq) + 2Cl^-(aq)$

$m = 5.840$ mol/kg (saturated solution)

$\tau_{\pm} = 32.6458$ (Goldberg and Nuttall, 1978)

Thus,

$$K_{sp} = 4(m\tau_{\pm})^3 = 2.772*10^7$$

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

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

The value of deviation as the absolute value for solubility is $3.16*10^3$% when using the $\tau_{\pm}=1$.

If using 50% deviation of $\tau_{\pm}$, one get

$m = 3.89$ mol/kg (33.4% deviation for solubility)

APPENDIX 4

Comparison of $\tau_{\pm}$ for KCl between experimental smoothed data and calculated values from various correlation results.

M(mol/kg)	$\ln\gamma_{\pm}$(KCl)				
	Exptl	Cal^1	Cal^2	Cal^3	Cal^4
0.001	-0.036	-0.036	-0.036	-0.036	-0.036
0.002	-0.050	-0.050	-0.050	-0.050	-0.050
0.005	-0.076	-0.077	-0.077	-0.077	-0.077
0.010	-0.104	-0.106	-0.106	-0.106	-0.106
0.020	-0.140	-0.143	-0.143	-0.144	-0.145
0.050	-0.203	-0.210	-0.210	-0.212	-0.213
0.100	-0.264	-0.273	-0.273	-0.277	-0.279
0.200	-0.333	-0.346	-0.347	-0.353	-0.358
0.300	-0.375	-0.393	-0.394	-0.402	-0.408
0.400	-0.408	-0.426	-0.427	-0.438	-0.446
0.500	-0.432	-0.451	-0.453	-0.465	-0.475
0.600	-0.453	-0.472	-0.474	-0.488	-0.499
0.700	-0.468	-0.488	-0.491	-0.506	-0.519
0.800	-0.483	-0.502	-0.505	-0.522	-0.536
0.900	-0.494	-0.514	-0.516	-0.535	-0.550
1.000	-0.504	-0.523	-0.526	-0.547	-0.563
1.200	-0.521	-0.538	-0.541	-0.565	-0.584
1.400	-0.534	-0.549	-0.552	-0.579	-0.600
1.600	-0.545	-0.555	-0.560	-0.589	-0.613
1.800	-0.552	-0.560	-0.564	-0.597	-0.622
2.000	-0.557	-0.561	-0.566	-0.602	-0.630
2.500	-0.566	-0.559	-0.565	-0.607	-0.641
3.000	-0.566	-0.548	-0.555	-0.604	-0.643
3.500	-0.560	-0.531	-0.539	-0.595	-0.640
4.000	-0.552	-0.510	-0.518	-0.582	-0.631
4.500	-0.538	-0.485	-0.495	-0.564	-0.620
4.803*	-0.529	-0.468	-0.479	-0.553	-0.611

Cal^1; using correlation between $\beta^{(0)}$ and S^o
Cal^2; " " " $\beta^{(0)}$ and $S^o{}_+$
Cal^3; " " " $\beta^{(0)}$ and Z*Z/r
Cal^4; " " " $\beta^{(0)}$ and Pc/Pa
* ; saturated solution.