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CORRELATION OF PITZER ION INTERACTION PARAMETERS

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Abstract—A new correlation predicting the activity coefficients of aqueous electrolyte solutions between Pitzer ion interaction parameters and ionc properties (ionic charge, radius and entropy) is developed. The substances include uni-uni and uni-bi type of single salts for which data are available. The results of correlation show linear relations for uni-uni type, and quadratic equations for uni-bi type. Many of the trends in the calculated activity coefficients for electrolyte solutions can be correlated with respect to the effect of the ions on the structure of the water and explained by structure-making and -breaking concept. These kinds of correlation may be useful in predicting values for salts that have no measurement of the activity coefficients.

INTRODUCTION

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

These thermodynamic properties for aqueous solutions of single electrolytes, determined experimentally, have been reported extensively in the thermodynamic literature. However, experimental determination of these properties for mixed electrolyte solutions have received attention only relatively recently. One of the important thermodynamic properties of electrolyte solutions is the activity coefficient, $\gamma_{\pm}$. 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.

Among recently developed models of electrolyte solutions, ionic interaction models provide the simplest and the most coherent procedures for calculating the thermodynamic properties of electrolyte solutions. 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 electrolyte activity coefficients was developed by Pitzer and coworkers in the early 1970's [1-4]. The Pitzer model extended the Debye-Hückel equation, using a virial expansion for the excess Gibbs energy to account for the ionic strength dependence of the short range forces in binary and ternary ion interaction. Thus three or four ion interaction parameters are required for single salt solutions, depending on the valences of the ions involved. For multicomponent solutions, additional parameters are 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. The Pitzer model equations are described in some detail in previous papers [5, 6]. This virial expansion approach accurately represents the compositional dependence of the thermodynamic properties in most multicomponent electrolyte solutions. Also the Pitzer method has been applied to many different chemical systems [7-13], and has been shown to provide accurate estimate of activity coefficients at relatively high ionic strengths. However, the Pitzer model equations are semiempirical rather than the theoretically suggested form. Thus the exact physical meaning and interrelationship between the ion interaction parameters are not fully understood.

The purposes of this work are to correlate Pitzer

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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 the available data. In other words, the goals of the correlation efforts are to understand the relationship between Pitzer ion interaction parameters and 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 I A compounds using available ion interaction parameters and the values of ionic properties at 25°C.

THEORETICAL BASIS FOR CORRELATING ION INTERACTION PARAMETERS

1. Structure-making and -breaking Ions

In 1933, Bernal and Fowler [14] 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 [15] described these effects as occuring 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, samller ions of a given family are more structure making. Examples for cations and anions, in order of structure making influence are;

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

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

2. 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 [16], and oxides are increasingly acidic the higher the charge or the smaller the radius of the cation for constant charge [17]. According to Cartledge [17, 18], 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 [16]. Wood et al. [19] 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 instance, ions with the same charge and radius may have different entropies as a result of their differing electron configurations [16]. 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. 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 [20] used Harned and Owen's classification of ions as monovalent cations, halogenodes, 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 [21] 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 [22] reported a correlation between two of the binary interaction parameters, $\beta^{(0)}$ and $\beta^{(1)}$. Staples [23] found that $\beta^{(0)}$ correlates well with Z^2/r for group I A, II A and 8 cations. He also found that the apparent molar heat capacity of transition metal ions correlated with Z^2/r [24]. The salts to be used in this work include the group I A (Li^+, Na^+, K^+, Rb^+, Cs^-) halides, chlorates, perchlorates, nitrates, acetates, hydroxides, and sulfates. They were chosen for the following reasons: (1) these group compounds represent the typical electrolyte solutions for uni-uni, and uni-bi type. (2) the halides should associate minimally, especially with the group I A cations, (3) many of the compounds are of industrial importance and (4) 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. Pitzer ion interaction parameters for more than 300 single salts were obtained in previous work [5] from published activity and osmotic coefficient data at 25°C. Ion entropies are available at 25°C from Glushko [25] and Wagman et al. [26]. Ionic radii are available from several sources, i.e., Morris [27] and Marcus [28]. 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.

Table 1. Comparison with estimated $\gamma_\pm$ for uni-uni, and uni-bi type of electrolytes

m(mol/kg)	$\gamma_\pm$(exptl)	$\gamma_\pm{}^a$	$\gamma_\pm{}^b$	$\gamma_\pm{}^c$
		NaCl (1-1 type)		
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
2.00	0.668	0.667	0.778	0.714
3.00	0.714	0.713	0.897	0.764
4.00	0.783	0.781	1.062	0.838
5.00	0.874	0.872	1.280	0.935
6.00	0.986	0.985	1.562	1.057
		Na_2SO_4 (1-2 type)		
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
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

[a] using the original evaluated vaues of $\beta^{(0)}$ and $\beta^{(1)}$

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

[c] using 50% deviated value of $\beta^{(1)}$

As shown in previous paper, 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 the third virial coefficient, 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 uni-uni, and uni-bi types of electrolytes. The results of NaCl, and Na_2SO_4 are listed in Table 1. From these results, it is obvious that the predicted activity coefficients are more sensitive to $\beta^{(0)}$ than to $\beta^{(1)}$. Therefore a correlation method must predict the $\beta^{(0)}$ accurately if it is to provide accurate estimates of activity coefficients. Although Beutier and Renon [20] used Pitzer's correlation between $\beta^{(0)}$ and $\beta^{(1)}$; $\beta^{(0)}/[\beta^{(0)}+\beta^{(1)}]=0.3$ for uni-uni type 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 types of electrolytes which were covered in this work. The ratio, $\beta^{(0)}/\beta^{(1)}$ has close to the value 0.424 for uni-uni type, and 0.087 for uni-bi type of electrolytes. Using these results, it is possible to obtain directly an approximate values of the activity coefficients for any given electrolytes if only $\beta^{(0)}$ is known.

1. Uni-uni Type Electrolytes

It was observed that values of $\beta^{(0)}$ can be correlated with ionic properties for alkali compounds. Figure 1 shows that $\beta^{(0)}$ for alkali halides correlated well with

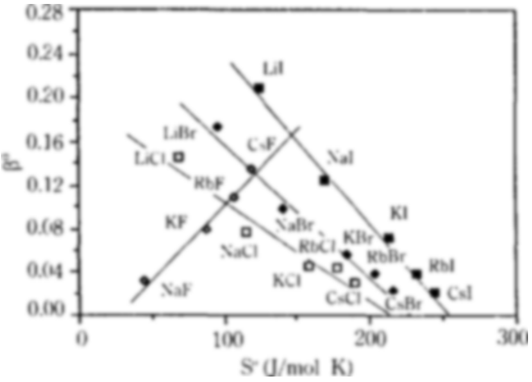


Fig. 1. Correlation between $\beta^{(0)}$ and the standard state molar entropy, S^o (J/mol K) for alkali halides.

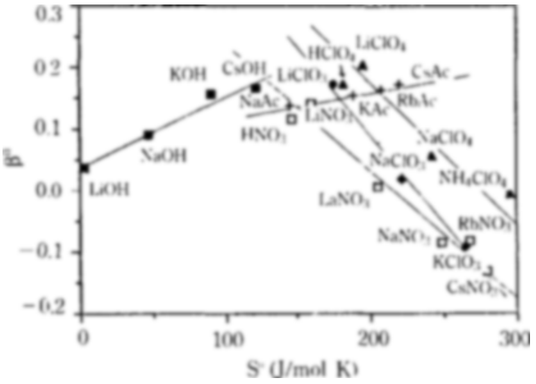


Fig. 2. Correlation between $\beta^{(0)}$ and the standard state molar entropy, S^o (J/mol K) for alkali chlorates, perchlorates (included $HClO_4$ and NH_4ClO_4), nitrates (included HNO_3), acetates and hydroxides.

the standard state molar entropy, S^o (J/mol K). The same kind of plots for alkali chlorates, perchlorates, nitrates, acetates and hydroxides were given in Figure 2. From these figures, it is obvious that the trends of $\beta^{(0)}$'s are the 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 Figures 1 and 2. The correlation results for each class are listed in Table 2. The standard deviation(SD) of fit for $\beta^{(0)}$ and the correlation coefficient, R which is a measure of the closeness of linear relationship, are also listed in Table 2. The correlation lines allow the evaluation of $\beta^{(0)}$ for a new compound in any class.

Figures 3 and 4 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 [28] which are given in Table 3 were used in this correlation work in lieu of crystal ionic radii. Pauling's ionic radii [29], 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) was used as a tentative value of r_{aq}. The results of this correlation are also given in Table 4. The difference between the chlorides, bro-

Table 2. Results of regressions between $\beta^{(0)}$ and S^o for alkali compounds

Class	Regression output	SD	R
Alkali fluorides	$\beta^{(0)} = -0.0333 + 0.0014 \times S^o$	0.008	0.99
Alkali chlorides	$\beta^{(0)} = 0.1994 - 0.0009 \times S^o$	0.013	0.97
Alkali bromides	$\beta^{(0)} = 0.2826 - 0.0012 \times S^o$	0.008	0.99
Alkali iodides	$\beta^{(0)} = 0.3979 - 0.0015 \times S^o$	0.007	1.00
Alkali chlorates	$\beta^{(0)} = 0.6829 - 0.0029 \times S^o$	0.014	1.00
Alkali perchlorates[a]	$\beta^{(0)} = 0.5243 - 0.0018 \times S^o$	0.036	0.95
Alkali nitrates[b]	$\beta^{(0)} = 0.4241 - 0.0020 \times S^o$	0.024	0.98
Alkali acetates	$\beta^{(0)} = 0.0714 + 0.0005 \times S^o$	0.002	1.00
Alkali hydroxides	$\beta^{(0)} = 0.0474 + 0.0010 \times S^o$	0.012	0.98

[a] included $HClO_4$ and NH_4ClO_4

[b] included HNO_3

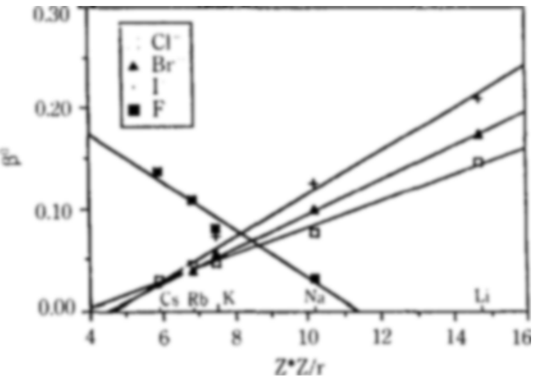


Fig. 3. Correlation between $\beta^{(0)}$ and the Coulombic term, Z^2/r which is logical correlating variable for alkali halides.

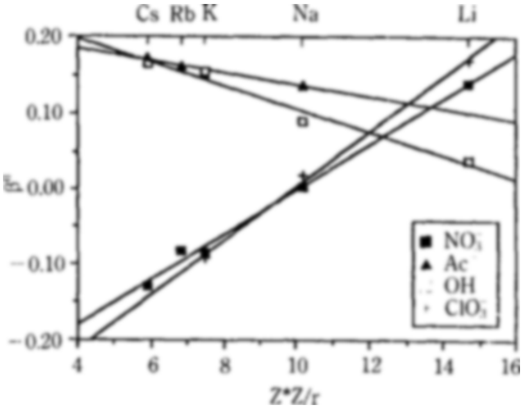


Fig. 4. Correlation between $\beta^{(0)}$ and the Coulombic term, Z^2/r which is logical correlating variable for alkali chlorates, nitrates, hydroxides, and acetates; Ac, Acetate ion.

Table 3. Aqueous ionic radii (r_{aq})

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	F^-	0.135± 0.014
Zn^{2+}	0.069± 0.005	Cl	0.183± 0.003
Cu^{2+}	0.059± 0.005	Br^-	0.194± 0.003
Cd^{2+}	0.095± 0.004	I^-	0.222± 0.002
Al^{3+}	0.049± 0.002	NO_3	0.206± 0.006
Cr^{3+}	0.060± 0.002	SO_4^{2-}	0.240± 0.005
Fe^{3+}	0.065± 0.005		

mides, 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 5). Values of P_c/P_a and the correlation results for alkali halides are given in Table 5 and 6 respectively. Wood et al. [19] proposed the ratio, P_c/P_a should approach unity for salts whose cation and anion have similar effects on the structure of water.

2. Uni-bi Type Electrolytes

According to Figures 6-8, one finds interesting correlation between $\beta^{(0)}$ and ionic properties for alkali

Table 4. Results of regressions between $\beta^{(0)}$ and Z*Z/r for alkali compounds

Class	Regression output	SD	R
Alkali fluorides	$\beta^{(0)} = 0.2682 - 0.0236 \times (Z^*Z/r)$	0.009	0.99
Alkali chlorides	$\beta^{(0)} = -0.0485 + 0.0130 \times (Z^*Z/r)$	0.005	0.99
Alkali bromides	$\beta^{(0)} = -0.0745 + 0.0169 \times (Z^*Z/r)$	0.003	1.00
Alkali iodides	$\beta^{(0)} = -0.0980 + 0.0213 \times (Z^*Z/r)$	0.010	0.99
Alkali chlorates	$\beta^{(0)} = -0.3556 + 0.0360 \times (Z^*Z/r)$	0.009	1.00
Alkali perchlorates*	$\beta^{(0)} = 0.320 + 0.0242 \times (Z^*Z/r)$	0.032	0.98
Alkali nitrates	$\beta^{(0)} = -0.3001 + 0.0299 \times (Z^*Z/r)$	0.011	1.00
Alkali acetates	$\beta^{(0)} = 0.2152 - 0.0078 \times (Z^*Z/r)$	0.003	0.98
Alkali hydroxides	$\beta^{(0)} = 0.2461 - 0.0137 \times (Z^*Z/r)$	0.015	0.97

* included NH_4ClO_4

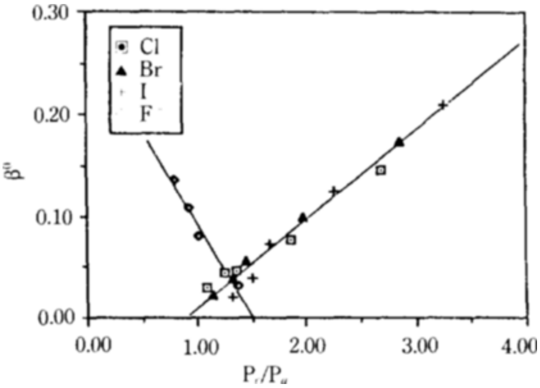


Fig. 5. Plot of $\beta^{(0)}$ versus the ionic potential ratio, P_c/P_a for alkali halides.

sulfates. A linear relations 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 trend of $\beta^{(0)}$ for these compounds coincide with the trends in the calculated activity coefficients. The correlation results are represented in Table 7.

COMPARISON OF CORRELATION RESULTS WITH EXPERIMENTAL DATA

Figures 9 and 10 show comparisons between the

Table 5. 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	Salt	P_c/P_a
LiF	1.985	KBr	1.488
LiCl	2.691	KI	1.657
LiBr	2.853	RbF*	0.912
LiI	3.265	RbCl*	1.237
NaF	1.378	RbBr*	1.311
NaCl	1.867	RbI*	1.500
NaBr	1.980	CsF	0.799
NaI	2.265	CsCl	1.083
KF	1.007	CsBr	1.148
KCl	1.366	CsI	1.314

*used Pauling's ionic radius (Rb^+ = 0.148 nm); (from Ref. 29)

Table 6. Results of regression between $\beta^{(0)}$ and P_c/P_a for alkali halides

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

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°. The experimental data are from Hamer and Wu [30, 31].

In general, the correlation results predicted accurately the activity coefficients of this group I A compounds as uni-uni 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 $KClO_4$, $RbClO_4$, 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

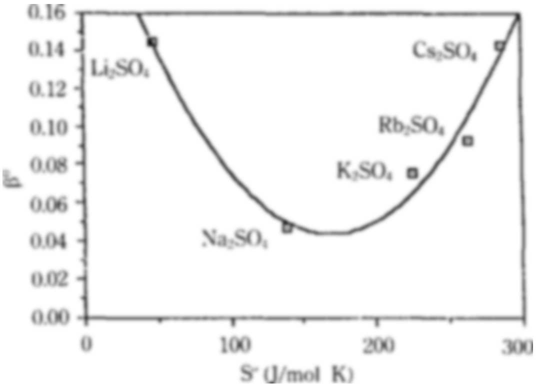


Fig. 6. Correlation between $\beta^{(0)}$ and the standard state molar entropy, S° (J/mol K) for alkali sulfates.

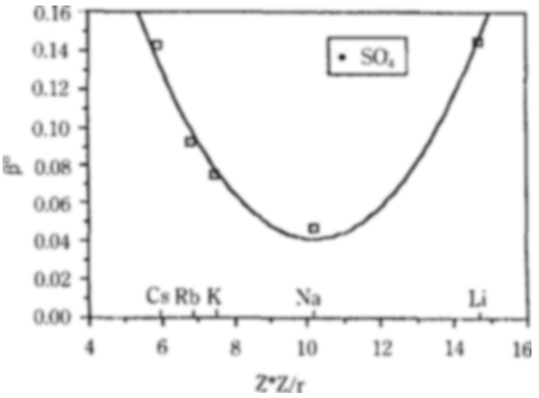


Fig. 7. Correlation between $\beta^{(0)}$ and the Coulombic term, Z^2/r for alkali sulfates, where Z is the charge on the cation and r(nm) is the aqueous ionic radius of cation.

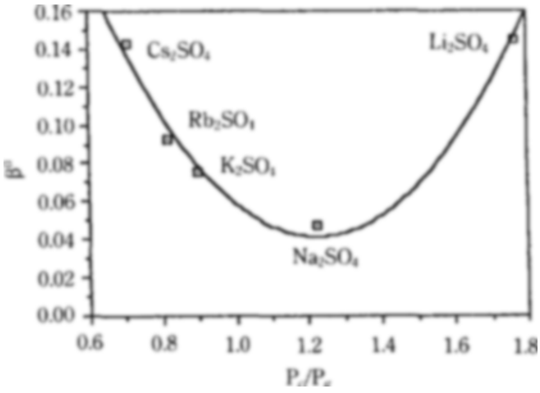


Fig. 8. Plot of $\beta^{(0)}$ versus the ionic potential ratio, P_c/P_a for alkali sulfates.

Table 7. Results of regression between $\beta^{(0)}$ and ionic properties for alkali sulfates

dependent variable: $Y=\beta^{(0)}$

independent variable: $X_1=S^o$ (J/mol K)

$X_2=Z^*Z/r$ (nm^{-1})

$X_3=P_c/P_a$

Class	Regression output	R
Alkali sulfates	$Y=0.2378-0.0023X_1+6.812\times10^{-6}X_1^2$	0.98
	$Y=0.5739-0.1045X_2+0.0051X_2^2$	0.98
	$Y=0.5735-0.8701X_3+0.3558X_3^2$	0.98

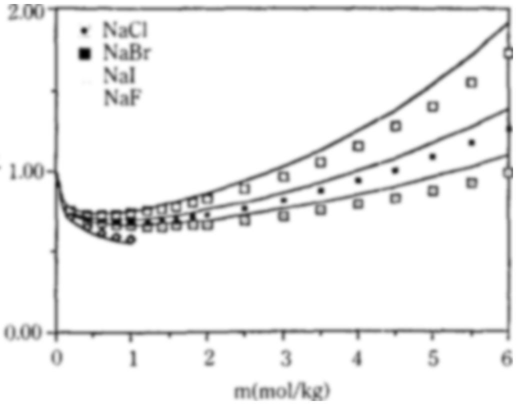


Fig. 9. Comparison of experimental smoothed $\gamma_\pm$ with calculated from correlation for NaCl, NaBr, NaI and NaF at 25°C (—: calculated, symbols: experimental).

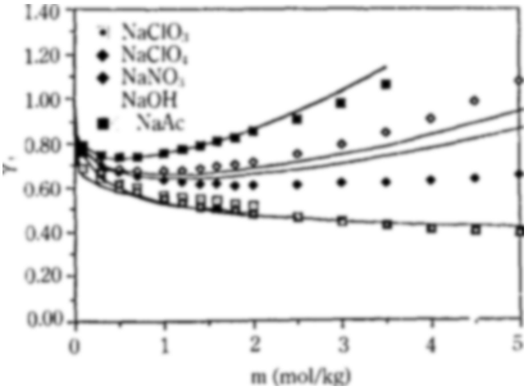
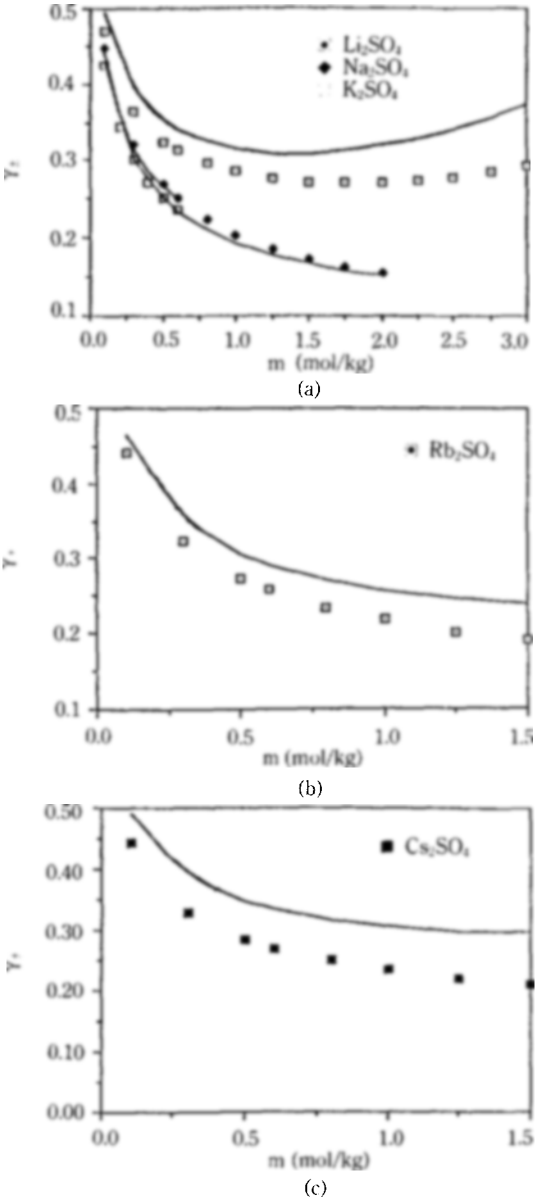


Fig. 10. Comparison of experimental smoothed $\gamma_\pm$ with calculated from correlation for $NaNO_3$, $NaClO_4$, $NaClO_3$, NaOH and NaAc at 25°C (—: calculated, symbols: experimental).

is clear that the correlation result for alkali perchlorates including $HClO_4$, and NH_4ClO_4 is not as good as other class.



(a)

(b)

(c)

Fig. 11. Comparison of experimental smoothed $\gamma_\pm$ with calculated from correlation; (a) for Li_2SO_4, Na_2SO_4, and K_2SO_4 (b) for Rb_2SO_4 and (c) Cs_2SO_4 at 25°C (—: calculated, symbols: experimental).

In Figure 11(a), (b) and (c) activity coefficients of alkali sulfates from experimental source and correlation results are plotted as a function of molality. The solid lines also show the predicted values from the correlation between $\beta^{(0)}$ and S^o. 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

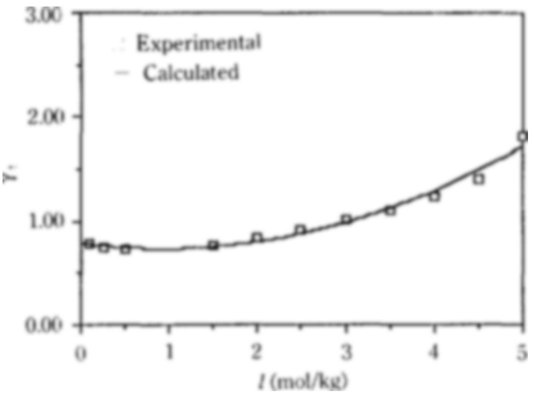


Fig. 12. Comparison of experimental smoothed γ_{HCl} for HCl-$MgCl_2$-H_2O system with values calculated from correlation at various ionic strengths.

of $\beta^{(0)}$ versus $\beta^{(1)}$ shows more scatter than that of uni-uni 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 uni-bi type of electrolytes.

Figure 12 is a another plot of comparisons of activity coefficients of HCl in the ternary mixture at 25℃ and various ionic strengths. The results from using the correlations fit the experimental data well. The experimental points are data from Roy et al. [32].

RESULTS AND 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 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℃.

The alkali metal halides (chlorides, bromides, and iodides) each class have $\beta^{(0)}$ values in decreasing order for Li^+, K^+, Rb^+, and Cs^+, but for alkali metal fluorides, there is a increasing trend of $\beta^{(0)}$ from NaF to CsF, as shown in Figures 1 and 3. The decrease in ln γ 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 I A 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 (Figures 1 and 2).

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 Figures 6-8. The $\beta^{(0)}$ values for nitrates are relatively low in all cases regardless of the structure making or breaking character of the cation (Figure 4). This suggests some tendency toward ion pair formation as is also indicates by spectroscopic data in several cases [33, 34].

According to Prtzer and Mayorga [2], the second virial coefficient for a single electrolytes is a weighted mean of the interactions between pair of ions with signs, + +, − −, and + −. Two ion interaction parameters, $\beta^{(0)}$ and $\beta^{(1)}$ for the short range binary interaction of a single electrolyte represent + − interactions term and, + + and − − interactions term respectively. The relative weighting of + − interaction is greatest at low ionic strength. At high ionic strength, the + − and − − terms become more important but never equal to the weight of the + − interaction. As discussed earlier, the result of sensitivity test for $\beta^{(0)}$ and $\beta^{(1)}$ support this concept.

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

If $\beta^{(0)}$ is predicted accurately by correlation with ionic properties and the effect of the third virial coefficient is small, the prediction of activity coefficients for a single electrolyte becomes possible using the convenient approximation for evaluating $\beta^{(1)}$. As a result, the correlation of ion interaction parameters with ionic properties seems to work well for uni-uni, and uni-bi types of electrolytes. Thus the regression outputs from our results are stored on the file in a computer and the activity coefficients can be calculated simply be identifying the salt and defining the class. However, for ternary mixture, since there are limited experimental data, the available set of Pitzer mixing parameters is not sufficient to obtain a generalized correlation. More experimental work is clearly needed in this area in the future.

NOMENCLATURE

C^Φ : Pitzer ion interaction parameter [kg^2/mol^2]
I : ionic strength [mol/kg]

m : molality [mol/kg]
P : ionic potential [Z/r]
r : ionic radius [nm]
R : correlation coefficient
S^o : standard state molar entropy [J/mol K]
SD : standard deviation
Z : ionic charge

Greek Letters

$\beta^{(0)}$, $\beta^{(1)}$: Pitzer ion interaction parameters [kg/mol]
$\gamma_\pm$: mean activity coefficient

Subscripts

a : anion
aq : aqueous state
c : cation
i : ionic species i

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