

Relationships between Pitzer's ion interaction coefficients and ionic parameters of electrolyte solutions^①

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Abstract: Pattern recognition methods were used to treat the experimentally measured data of Pitzer's coefficients of 107 electrolytes, to find the relationships between the ionic structural parameters of these electrolytes and Pitzer's coefficients. It is found that these relationships can be approximately expressed as linear equations of four dimensionless numbers, (R_+/R_-) , $(R_+ + R_-)/Z_+ Z_-$, (Z_+/Z_-) and (R_i/R_1) , where R_+ and R_- are the cationic and anionic radii respectively; Z_+ and Z_- are the cationic and anionic charge numbers respectively, and (R_i/R_1) denotes the nonsphericity of some non-spherical ions. Besides, it is found that the difference of the nuclear magnetic resonance measured rotational relaxation time of water molecules around cations and anions, $|\Delta\tau|$, has good correlation with Pitzer's coefficients. The relationships can be interpreted by the theory of corresponding states of ionic solutions. Based on the relationships, an example of application to some hydrometallurgical process was discussed.

Key words: concentrated electrolyte solutions; Pitzer's coefficients; ionic parameters; corresponding state theory

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1 INTRODUCTION

Concentrated electrolyte solutions are common intermediate materials in hydrometallurgical and chemical industrial processes^[1]. And the activity coefficient is one of the basic properties of electrolyte solutions, which is useful for the estimation of the solubility of inorganic salts, the distribution and separation coefficients in liquid-liquid extraction processes, and the phase diagram of water-salt systems. A semi-empirical ion-ion interaction model, also the most popular method so far, proposed by Pitzer^[2], can be used to calculate the activity coefficients of concentrated electrolyte solutions. However, when this model is used to calculate the activity coefficients of electrolyte solutions, three coefficients, $\beta^{(0)}$, $\beta^{(1)}$ and C , have to be determined experimentally for each electrolyte. So it is desirable to find some mathematical model to correlate the values of these coefficients with some well-known ionic parameters such as ionic radius and ionic charges by the data processing of known data of some electrolyte solutions, in order to predict the unknown values of Pitzer's coefficients and activity coefficients of other electrolyte solutions. For this purpose, LI and CHEN^[3] have investigated the relationships between Pitzer's coefficients and the ionic radii of 1-1 type electrolytes. In this work, the re-

lationships of the values of $\beta^{(0)}$, $\beta^{(1)}$, C and their temperature coefficients of the electrolytes of different valence types with the ionic parameters of the cations and anions of electrolytes have been investigated, with their physical meaning discussed.

2 MODEL, DATA AND METHOD OF COMPUTATION

Reiss^[4] proposed the theory of corresponding state of ionic systems. In this theory the configurational integral and thermodynamic properties of ionic systems were considered as some functions of a series of dimensionless numbers consisting of ionic parameters:

$$I = f \{ [(R_+ + R_-)T / Z_+ Z_-], [R_+/R_-], [Z_+/Z_-], \dots \}$$

where R_+ , R_- are cationic and anionic radii respectively, Z_+ , Z_- are cationic and anionic charge numbers respectively, T is absolute temperature, $(R_+ + R_-)T / Z_+ Z_-$ represents the ratio of electrostatic potential energy to kinetic energy of ionic systems. Friedman^[5] proposed that the theory of corresponding state can be used to investigate the thermodynamic properties of aqueous electrolyte solutions.

On the other hand, in early fifty years of 20th century, Gurney^[6] proposed that the ions in elec-

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trolyte solutions could be classified into two classes: the structure-forming ion with small ionic radius and large charge numbers and the structure-breaking ion with large ionic radius and small charge numbers. The former has strong electric field to make the water molecules orientated into some local order, while the latter destroys the local order of water molecules in its hydration sphere. Gurney proposed that if the anion and cation belong to different classes, they will repel each other in concentrated electrolyte solutions since their hydrated spheres are incompatible with each other, and this incompatibility will make the activity coefficients increase. In recent years, the nuclear magnetic resonance (NMR) measurement indeed proved that the rotational correlation time (τ) of the water molecules in the hydrated sphere of ions with large radius and small charge number is shorter and that of ions with small radius and large charge number is longer. This is a direct evidence of the Gurney's concept. We have noted that the difference of τ of cation and anion, $|\Delta\tau|$, exhibits obvious correlation with (R_+/R_-) and (Z_+/Z_-) . So these two dimensionless numbers should be relevant to the "structure forming" and "structure breaking" phenomena. At the same time, the electrostatic potential between cation and anion and the kinetic energy of the ionic system should also be the important factors influencing the thermodynamic properties of electrolyte solutions. So that the dimensionless number $(R_+ + R_-)T/Z_+Z_-$ should also be an important factor in the corresponding state calculation. If there exists some nonspherical ions, it is reasonable to think that some dimensionless number denoting nonsphericity should be also considered. According to the concept of thermochemical radius of nonspherical ions, the ratio of thermochemical radius to the longest geometrical radius, denoted by (R_t/R_l) (the value for spherical ions is 1.0 calculated by Yashimirs'ki^[7]), should be an appropriate dimensionless number in corresponding state calculation.

Based on the above-mentioned argument, we try to choose a series of dimensionless numbers, including (R_+/R_-) , $[(R_+ + R_-)T/Z_+Z_-]$ (since the temperature data in this work are always constants, $(R_+ + R_-)/Z_+Z_-$ can be used instead of $(R_+ + R_-)T/Z_+Z_-$ in our computation), (Z_+/Z_-) and (R_t/R_l) as the independent variables to correlate with Pitzer's coefficients. Partial least squares (PLS) method^[8,9] and the method for feature selection by pattern recognition techniques have been used to reveal these relationships by data processing of known data of electrolyte solutions of following salts: LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsF, CsCl, CsBr, CsI, MgCl₂, MgBr₂, MgI₂, CaCl₂, CaBr₂, CaI₂, SrCl₂, SrBr₂, SrI₂, BaCl₂, BaBr₂, BaI₂, Mn-

Cl₂, FeCl₂, CoCl₂, NiCl₂, CoBr₂, CoI₂, AlCl₃, LaCl₃, CeCl₃, PrCl₃, NdCl₃, SmCl₃, EuCl₃, HoCl₃, GdCl₃, ErCl₃, TbCl₃, YbCl₃, LuCl₃, YCl₃, LiClO₄, LiClO₃, LiBrO₃, LiNO₃, NaClO₄, NaClO₃, NaBrO₃, NaNO₃, KClO₃, KBrO₃, RbNO₃, CsNO₃, Mg(ClO₄)₂, Mg(NO₃)₂, Ca(ClO₄)₂, Ca(NO₃)₃, Sr(ClO₄)₃, Sr(NO₃)₃, Ba(ClO₄)₃, Ba(NO₃)₂, Y(NO₃)₃, La(NO₃)₃, Pr(NO₃)₃, Nd(NO₃)₃, Sm(NO₃)₃, Eu(NO₃)₃, Gd(NO₃)₃, Tb(NO₃)₃, Dy(NO₃)₃, Ho(NO₃)₃, Er(NO₃)₃, Tm(NO₃)₃, Yb(NO₃)₃, Lu(NO₃)₃, La(ClO₄)₃, Pr(ClO₄)₃, Nd(ClO₄)₃, Sm(ClO₄)₃, Gd(ClO₄)₃, Tb(ClO₄)₃, Dy(ClO₄)₃, Ho(ClO₄)₃, Er(ClO₄)₃, Tm(ClO₄)₃, Yb(ClO₄)₃, Lu(ClO₄)₃, NiSO₄, CoSO₄, CuSO₄, ZnSO₄, MnSO₄, BeSO₄, Na₂SO₄, Na₂CO₃, K₂CO₃, NaBF₄.

The values of $\beta^{(0)}$, $\beta^{(1)}$ and C are quoted from Refs. [2] and [10]. PLS regression method and the feature selection methods by pattern recognition techniques are used in data processing work. The software used is "materials research advisor". Details of the computation methods and the used software are described in Refs. [11] and [12].

3 RESULTS AND COMPUTATION

3.1 Pitzer's coefficients expressed as approximate equations of dimensionless numbers

Based on the results of PLS regression, it has been found that there are good correlations between the Pitzer's coefficients of electrolytes of 1-1, 2-1, 3-1, 1-2, 2-2 valence types and four dimensionless numbers, (R_+/R_-) , $(R_+ + R_-)/Z_+Z_-$, (Z_+/Z_-) and (R_t/R_l) , as shown in Figs. 1-3. These relationships can be also approximately expressed as the following linear equations:

$$\begin{aligned}\beta^{(0)} = & 0.0561(R_+/R_-) - 0.0422[(R_+ + R_-)/Z_+Z_-] + \\ & 0.2180(Z_+/Z_-) + 0.1771(R_t/R_l) - 0.2843\end{aligned}$$

(Correlation coefficient between calculated and experimental values is 0.968. The averaged PRESS is 0.031).

$$\begin{aligned}\beta^{(1)} = & 1.1513(R_+/R_-) - 0.9786[(R_+ + R_-)/Z_+Z_-] + \\ & 1.3623(Z_+/Z_-) + 0.3328(R_t/R_l) + 0.5631\end{aligned}$$

(Correlation coefficient between calculated and experimental values is 0.902. The averaged PRESS is 0.196).

$$\begin{aligned}10^3 C^\phi = & 1.8874(R_+/R_-) - 10.8250[(R_+ + R_-)/Z_+Z_-] - 27.4160(Z_+/Z_-) + \\ & 22.1980(R_t/R_l) + 35.4577\end{aligned}$$

(Correlation coefficient between calculated and experimental values is 0.927. The averaged

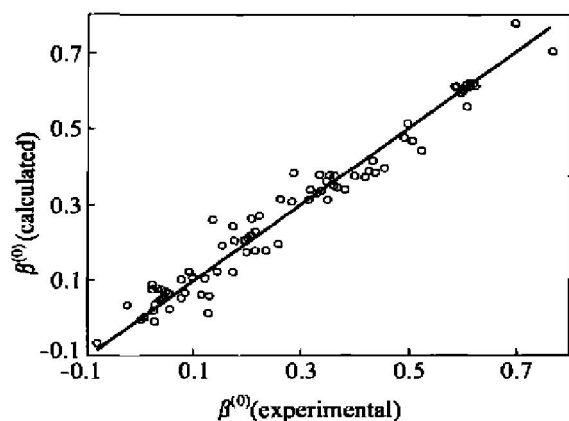


Fig. 1 Comparison of experimental values and calculated values of $\beta^{(0)}$

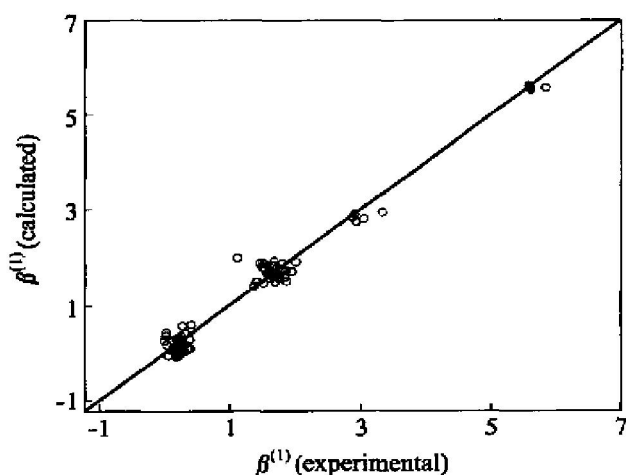


Fig. 2 Comparison of experimental values and calculated values of $\beta^{(1)}$

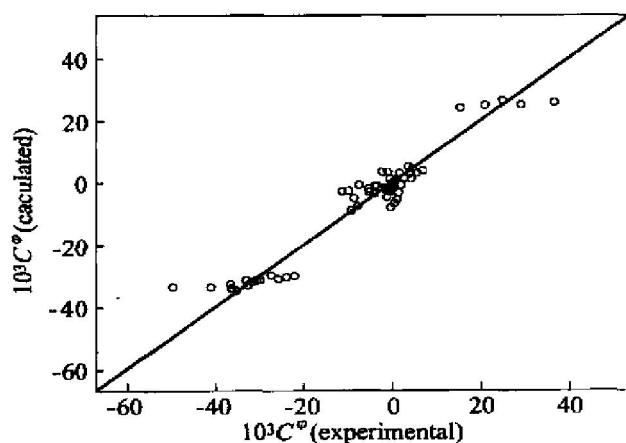


Fig. 3 Comparison of experimental values and calculated values of C

PRESS is 0.163).

3.2 Temperature coefficients of $\beta^{(0)}$, $\beta^{(1)}$ and C expressed as approximate equations of dimensionless numbers

For 1-1, 2-1, 3-1 and 1-2 type electrolytes, it has been found by computation that the temperature

coefficients of $\beta^{(0)}$ (denoted by α_0) $\beta^{(1)}$ (denoted by α_1) and C (denoted by α_2) can be approximately expressed by the following linear equations of dimensionless numbers:

$$10\alpha_0 = 11.05(R_+ + R_-)/Z_+ Z_- - 2.47(R_+/R_-) + 11.18(Z_+/Z_-) - 23.3017(R_t/R_l) - 14.29$$

(Correlation coefficient between calculated and experimental values is 0.902. The averaged PRESS is 0.267).

$$10\alpha_1 = 14.24(R_+ + R_-)/Z_+ Z_- + 1.17(R_+/R_-) + 43.22(Z_+/Z_-) - 5.02(R_t/R_l) - 69.55$$

(Correlation coefficient between calculated and experimental values is 0.953. The averaged PRESS is 0.142).

$$10\alpha_2 = 4.10(R_+/R_-) - 3.80(R_+ + R_-)/Z_+ Z_- - 6.80(Z_+/Z_-) + 27.19(R_t/R_l) - 14.82$$

(Correlation coefficient between calculated and experimental values is 0.907. The averaged PRESS is 0.268).

3.3 Relationships between $\beta^{(0)}$, $\beta^{(1)}$ and $|\Delta T|$ of cation and anion measured by NMR

Fig. 4 and Fig. 5 illustrate the quantitative relationships of $|\Delta T|^{[13]}$ (measured by NMR) with $\beta^{(0)}$ and $\beta^{(1)}$ respectively. It can be seen that large $|\Delta T|$ corresponds to larger $\beta^{(0)}$ and $\beta^{(1)}$, and the solution with larger activity coefficients.

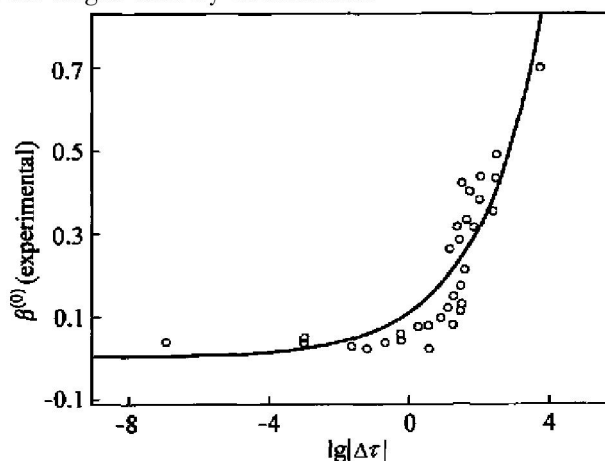


Fig. 4 Relationship between $|\Delta T|$ and $\beta^{(0)}$

4 DISCUSSION

The electrolyte solutions used in hydrometallurgy are usually mixed electrolyte solutions, while in this work the relationships between Pitzer's coefficients and ionic structural parameters are obtained from the data of solutions of single electrolytes. But in Pitzer's work it has been concluded that the error is usually very small if the activity coefficients of mixed elec-

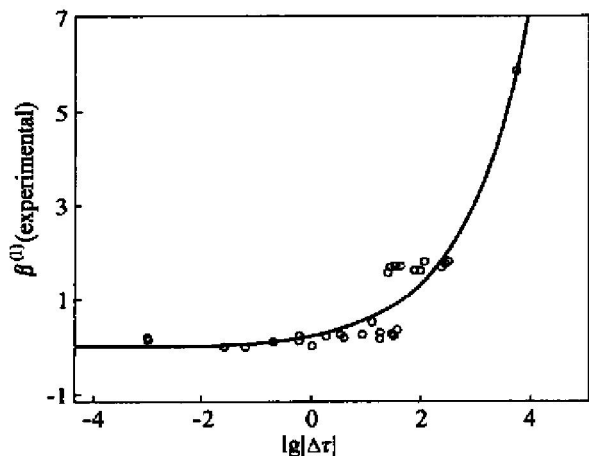


Fig. 5 Relationship between $|\Delta T|$ and $\beta^{(1)}$

trolyte solutions are calculated by using Pitzer's coefficients obtained from solution of single electrolytes^[14]. So that the relationships obtained in this work should be also useful for the rough estimation of the thermodynamic properties of mixed electrolyte solutions. In these cases, $\beta^{(0)}$ and $\beta^{(1)}$ can be used to estimate the interaction between a cation-anion pair in mixed electrolyte solutions. This is useful in salting out effect investigation for liquid-liquid extraction work. For example, the separation of ReO_4^- and MoO_4^{2-} ions in rhenium production can be performed by liquid-liquid extraction by trioctylamine salt extractants. In order to increase the separation coefficients of these two anions, salting out effect can be used. Since the ionic radii and nonsphericity of these two anions are quite similar, only the ionic charge number is different. The calculation indicates that the ion-ion repelling effect between Mg^{2+} and ReO_4^- is stronger than that between Mg^{2+} and MoO_4^{2-} . So the addition of magnesium salt can make the separation coefficient increase. Our experimental works have confirmed this prediction: the addition of magnesium sulphates can increase the separation coefficient significantly.

5 CONCLUSIONS

It has been found that the coefficients $\beta^{(0)}$, $\beta^{(1)}$ and C of Pitzer's model of electrolyte solutions can be expressed as some linear functions of four dimensionless numbers: (R_+/R_-) , $(R_+ + R_-)/Z_+ Z_-$, (Z_+/Z_-) and (R_t/R_l) . This empirical relationship can be explained by the theory of corresponding states of ionic systems. There is some obvious correlation between the values of Pitzer's

coefficients of electrolytes and the values of $|\Delta T|$. This empirical relationship can be explained by Gurney's model about the structure-forming and structure-breaking effect in electrolyte solutions.

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REFERENCES

- [1] FANG Zheng, FANG Yuan, ZHANG Quanru, et al. Modeling of thermodynamic properties of multicomponent electrolyte solutions[J]. Trans Nonferrous Met Soc China, 2001, 11(3): 425-429.
- [2] Pitzer K S. Activity Coefficients in Electrolyte Solutions [M]. 2nd Ed. Boca Raton: CRC Press, 1991.
- [3] SUN Weiran, LI Yirgui, CHEN Xirmin. Pitzer's parameter and ionic radius[J]. Trans Nonferrous Met Soc China, 1992, 2(3): 37-40.
- [4] Reiss H, Mayer S W, Katz J L. Theory of corresponding state of ionic systems[J]. Journal of Chemical Physics, 1961, 35: 820-826.
- [5] Friedman H L, Larsen B. Corresponding states for ionic fluids[J]. Journal of Chemical Physics, 1979, 70: 92-100.
- [6] Gurney R W. Ionic Processes in Solution [M]. New York: McGraw-Hill Book Company Inc, 1953.
- [7] Yashimirskii K B. Thermochemistry of Complex Compounds [M]. Moscow: Press of Academy of Sciences of USSR, 1951. (in Russian)
- [8] Wold S, Ruhe H, Wold H, et al. The collinearity problem in linear regression. the partial least squares (PLS) approach to generalized inverse[J]. SIAM Journal of Scientific and Statistical Computations, 1984, 5: 735-743.
- [9] Rosipal R, Trejo L J. Kernel partial least squares regression in reproducing kernel hilbert space[J]. Journal of Machine Learning Research, 2001(2): 97-123.
- [10] Pitzer K S, Mayorga G. Thermodynamics of electrolytes II [J]. Journal of Physical Chemistry, 1973, 77: 2300-2308.
- [11] CHEN Niariyi, QIN Pei, CHEN Ruiliang, et al. Application of Pattern Recognition in Chemistry and Chemical Engineering [M]. Beijing: Science Press, 2000.
- [12] CHEN Niariyi, LU Weirong, CHEN Ruiliang, et al. Chemometric methods applied to industrial optimization and materials optimal design [J]. Chemometrics and Intelligent Laboratory Systems, 1999, 45: 329-333.
- [13] Ohtaki H, Radnai T. Structure and dynamics of hydrated ions[J]. Chemical Review, 1993, 93: 1157-1204.
- [14] Pitzer K S, Kim J J. Thermodynamics of electrolytes IV [J]. Journal of American Chemical Society, 1974, 96: 5701-5707.

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