Vol. 11 № 3 **Trans. Nonferrous Met. Soc. China** Jun. 2001

[Article ID] 1003- 6326(2001)03- 0425- 05

Modeling of thermodynamic properties of multi-component electrolyte solutions①

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[Abstract] An empiric equation, $G^{ex}_{H_2O}/(1-x(H_2O))^2=\alpha+\beta\cdot x(H_2O)/\ln(x(H_2O))$, representing the relation between the excess free energy $G^{ex}_{H_2O}$ and mole fraction of water $x(H_2O)$ in binary electrolyte solution, was developed and the parameters α and β in the equation were determined by fitting the experimental data for some binary aqueous systems of electrolytes such as $CuCl_2$, $NiCl_2$, HCl, NaCl, KCl, $CaCl_2$ and $BaCl_2$. The activities of water in such ternary and multi-component systems composed of 7 binaries as $HCl-H_2O-CuCl_2$, $HCl-H_2O-NiCl_2$, $HCl-H_2O-NaCl$, $NaCl-H_2O-KCl$, $NaCl-H_2O-CaCl_2$, $KCl-H_2O-CaCl_2$, $NaCl-H_2O-BaCl_2$, $KCl-H_2O-CaCl_2$ and $NaCl-H_2O-KCl-BaCl_2$ were predicted by a simplified sub-regular solution model developed by authors from the corresponding binary systems. The predicted results are in good agreement with the measured ones.

[Key words] activity; electrolyte; solution; model; interchange energy
[CLC number] O 645.16; O 642.4 **[Document code]** A

1 INTRODUCTION

The electrolyte solutions of $CuCl_2$, $NiCl_2$, $CoCl_2$, $ZnCl_2$, $CdCl_2$, $FeCl_2$, HCl, NaCl, KCl, $CaCl_2$, $MgCl_2$, $BaCl_2$, et al, were often involved in the hydrometallurgical processes. The thermodynamic properties of aqueous solutions of the electrolytes are very important to extractive metallurgy. Some models based on ion interaction for prediction of the thermodynamic properties of electrolyte solution have been proposed, such as Debye-Hückel theory and Pitzer theory[1]. Debye-Hückel theory can be applied well to extremely dilute solutions. Pitzer theory is the most successful one for electrolyte solutions so far, but some complicated parameters have to be determined experimentally. The regular solution model is a good one due to its simplicity[2]. It has successfully been applied in many non-electrolytic systems, such as alloy and organic solvent ones. There are few reports on its application in the electrolytic solutions. We have used a simplified regular solution model and sub-regular solution model to the molten salts[3,4] and aqueous solution systems of electrolytes[5], respectively, and obtained good results.

This paper is aimed at examining the availability of the regular solution model and sub-regular solution[6] model in ternary and multi-component aqueous solutions of electrolytes, determining the interchange energies of a series of salt-water pairs from the selective osmotic coefficients of electrolytes, and therefrom predicting the thermodynamic properties of ternary and multi-component systems from those of their sub-binary components.

As pointed out before[5] that the measurement of the thermodynamic properties for a ternary system is much more difficult and complex than those for binary system. Undoubtedly, the present investigation has guiding significance to practice.

2 INTERCHANGE ENERGIES FOR SALT-WATER BINARY SYSTEMS

To a binary system of aqueous solution of electrolyte, the relation between osmotic coefficient φ and activity of water $a(H_2O)$ can be written as

$$-vm_i\varphi=55.51\ln(a(H_2O)) \qquad (1)$$

where v is ion number of the electrolyte dissociation and m_i is molality of salt i.

According to the regular solution the excess free energy for the component j, G_j^{ex} can be related to

$$G_j^{ex}=\omega(1-x_j)^2 \qquad (2)$$

where ω represents the interchange energy of the component pairs i-j; x_j is the mole fraction of j-component.

Usually, as mentioned above, the regular solution model is used for non-electrolytic system. Here, if we treat the electrolyte as the independent particle instead of their ion form and water, also as independent one, ω can be evaluated by Eqn. (2) provided

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① **[Foundation item]** Project (59974033) supported by the National Natural Science Foundation of China
[Received date] 2000- 09- 07; **[Accepted date]** 2000- 11- 08

that $G^{ex}_{H_2O} = RT\ln(a(H_2O)/x(H_2O))$ is known.

2.1 NaCl-H_2O binary system

According to Eqn. (2), plotting G^{ex}_j vs $(1-x_j)^2$ will give a straight line for a strict regular solution (ω keeps constant). The slope of the line is the interchange energy, ω_{reg}. Robinson et al[7] collected the osmotic coefficient data in the range of concentration from 0.1~6 mol/L for NaCl-H_2O system. The relationship of $G^{ex}_{H_2O}$ against $(1-x(H_2O))^2$ for this system is shown in Fig. 1. With a linear fitting, the interchange energy is obtained as $-43\,250$ kJ·mol^{-1} when the system is treated as regular solution. However, it can be seen that the points of data do not fall completely on a straight line, being somewhat curved in the extremely low concentration range near pure water as shown in the lower left square of Fig. 1. This means that it is approximate to describe the binary system as a strict regular solution. If the system is treated as sub-regular solution, that is, ω_{sub} is considered as a function of composition, the relation between ω_{sub} and $x(H_2O)$ can be fitted to a curved equation as $\omega_{sub} = \alpha + \beta \cdot x(H_2O)/\ln(x(H_2O))$, where α and β are parameters being equal to -17.566 kJ·mol^{-1} and 2.096 kJ·mol^{-1}, respectively. The equation is represented by the solid line in Fig. 2.

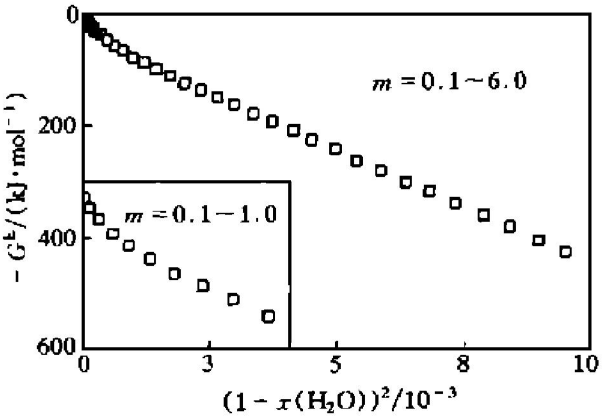

Fig. 1 $G^{ex}_{H_2O}$ as function of $(1-x(H_2O))^2$ for NaCl-H_2O system

2.2 MCl_n(M=Cu, Ni, Co, Zn, Cd, Fe, K, Ba, Ca, Mg, H)-H_2O binary systems

We systematically examine more than 80 electrolytes, and find that for a various of simple inorganic electrolyte solutions, the relations between $G^{ex}_{H_2O}/(1-x(H_2O))^2$ and mole fraction of water almost can be all fitted to the equation similar to those for NaCl-H_2O system, providing ω_{reg}= constant for regular solution or $\omega_{sub} = \alpha + \beta \cdot x(H_2O)/\ln(x(H_2O))$ for sub-regular solution. For the binary aqueous solutions of such chlorides as $CuCl_2$, $NiCl_2$, $ZnCl_2$, $CdCl_2$, $FeCl_2$, $CoCl_2$, KCl, $BaCl_2$, $CaCl_2$, $MgCl_2$ and HCl, the data of osmotic coefficients and corresponding concentrations are cited from literature [7]. With the same fitting process, ω can be obtained for the binary systems mentioned above, which, together with those for NaCl-H_2O system, are listed in Table 1.

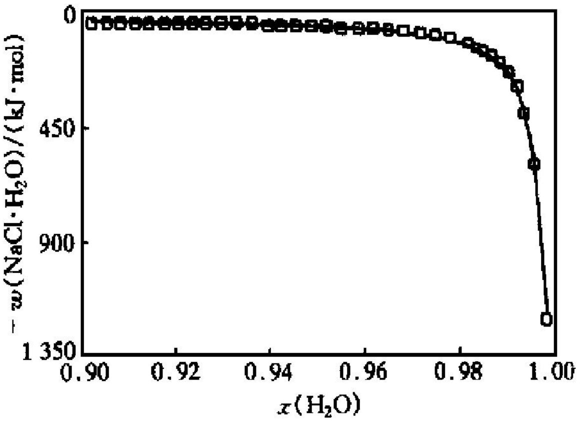

Fig. 2 Plot of ω(NaCl-H_2O) vs $x(H_2O)$ for NaCl-H_2O system

3 ACTIVITIES OF WATER IN TERNARY SOLUTIONS OF SOME ELECTROLYTES

We have derived a simplified solution model describing the thermodynamic properties of a ternary solution, component (1)-H_2O(2)-component (3), from its two binary components[5]. The model can been written as

$$G^{ex}_{H_2O}/(1-x(H_2O))^2 = \omega_{12}x^0_1 + \omega_{13}x^0_3 \qquad (3)$$

where x^0_1 and x^0_3 are the mole fractions of the components (1) and (3) in the sub-binary system of Eqns. (1)~(3).

For the $NiCl_2$(1)-H_2O(2)-HCl(3) system, substituting ω($NiCl_2$-H_2O) and ω(H_2O-HCl) into Eqn. (3), we can obtain $G^{ex}_{H_2O}/(1-x(H_2O))^2$ under a given $x^0(NiCl_2)$ or $x^0(HCl)$ (for $x^0(NiCl_2) + x^0(HCl) = 1$), and also activities and activity coefficients of water in the aqueous solution. The calculated and measured[8] results represented by solid line and square respectively are plotted in Fig. 3.

From Fig. 3 it can be seen that the results calculated and measured are in good agreement. However, we have noted that the difference between the calculated and measured values at high concentrations is larger than that at low concentrations. This fact can be explained as follows. The interaction between salts is supposed to be ignorable and only the interactions between each salt and water are considered in the simplified model[5]. In fact, the interaction between two electrolytes ($NiCl_2$ and HCl) has a significant effect on the activity of water at high concentrations, although the above supposal is reasonable at dilute and

Table 1 Parameters of some chloride-H_2O binary systems

Chloride	$\alpha/(kJ\cdot mol^{-1})$	$\beta/(kJ\cdot mol^{-1})$	r^2	$\omega_{reg}/(kJ\cdot mol^{-1})$	r^2_{reg}
NaCl	- 17.566	2.096	0.999 8	- 43.250	- 0.997 5
KCl	- 2.817	2.119	0.999 6	- 33.010	- 9.989 2
$BaCl_2$	- 51.455	3.688	0.999 2	- 160.370	- 0.992 9
$CaCl_2$	- 133.969	3.565	0.994 4	- 220 670	0.997 7
$MgCl_2$	- 155.191	3.590	0.995 0	- 261.170	- 0.999 7
$NiCl_2$	- 136.085	3.604	0.997 3	- 197.060	- 0.997 9
$ZnCl_2$	- 7.225	3.818	0.998 9	- 72.360	- 0.998 6
$CdCl_2$	+ 46.315	2.120	0.982 5	- 14.910	0.996 5
$CoCl_2$	- 124.026	3.645	0.998 5	- 187.450	0.995 9
$FeCl_2$	- 106.372	3.666	0.998 6	- 317.640	- 0.995 8
$CuCl_2$	- 55.369	3.705	0.999 6	- 88.550	- 0.986 3
HCl	- 44.319	2.106	0.998 8	- 43.610	0.997 1

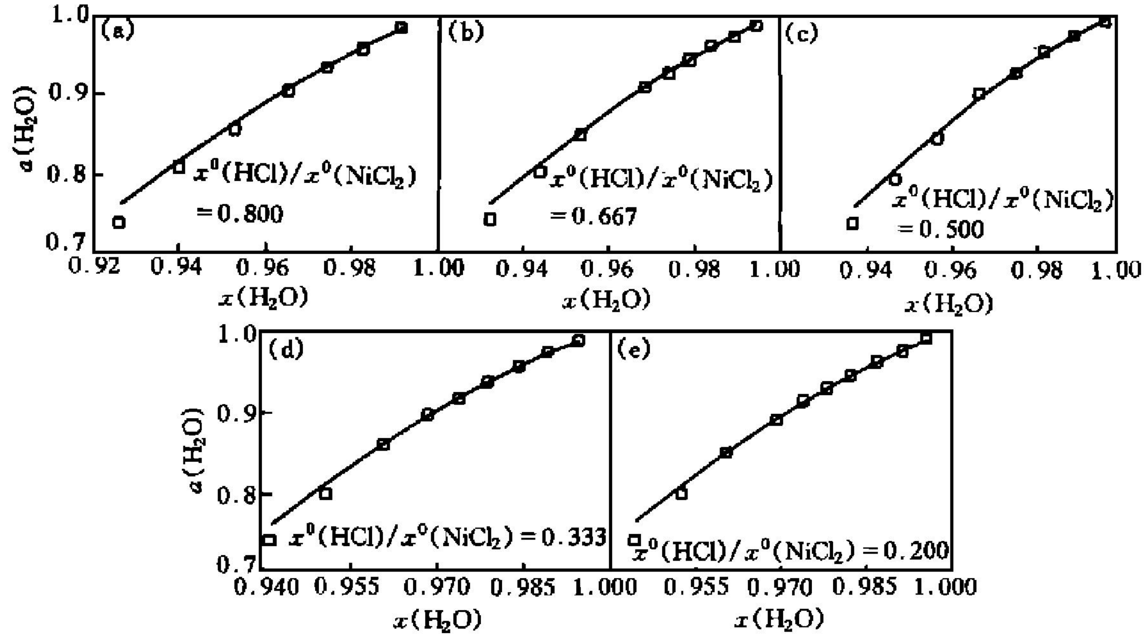

Fig. 3 Comparison between calculated and measured activities of water in $NiCl_2$-H_2O-HCl system

the lower concentrations.

By means of the same process as above description, the activities of water in $CuCl_2-H_2O-HCl$, $NaCl-H_2O-HCl$, $KCl-H_2O-NaCl$, $NaCl-H_2O-BaCl_2$, $KCl-H_2O-BaCl_2$, $NaCl-H_2O-CaCl_2$ and $KCl-H_2O-CaCl_2$ systems, are all calculated. The calculated and measured[8~10] results are plotted in Figs. 4~ 6, respectively.

4 ACTIVITIES OF WATER IN MULTI-COMPONENT SOLUTION SYSTEMS OF ELECTROLYTES

As an extension of Eqn. (3), the thermodynamic properties of water for an n-component system can be expressed as

$$G^{ex}_{H_2O}/(1-x(H_2O))^2 = \sum \omega(H_2O)\, x_i^0 \qquad (4)$$

in which x_i^0 is the mole fractions of components i in the n-1 sub-binary system except water. For the system of $NaCl-KCl-H_2O-BaCl_2$, substituting $\omega(H_2O-NaCl)$, $\omega(H_2O-KCl)$ and $\omega(H_2O-BaCl_2)$ into Eqn. (4), $a(H_2O)$ of the system can be obtained as shown in Fig. 6.

5 DISCUSSION

This is the first try to apply sub-regular solution model to the electrolyte solution. For the studied systems, the calculated results in good agreement with experimental ones show that the data from the binary electrolyte solutions and the simplified sub-regular solution model could be used to predict thermodynamic properties of multi-component solutions even containing 2∶1 electrolyte with enough precision, especially, in the dilute and lower concentration range.

However, it is also noted that the results calcu-

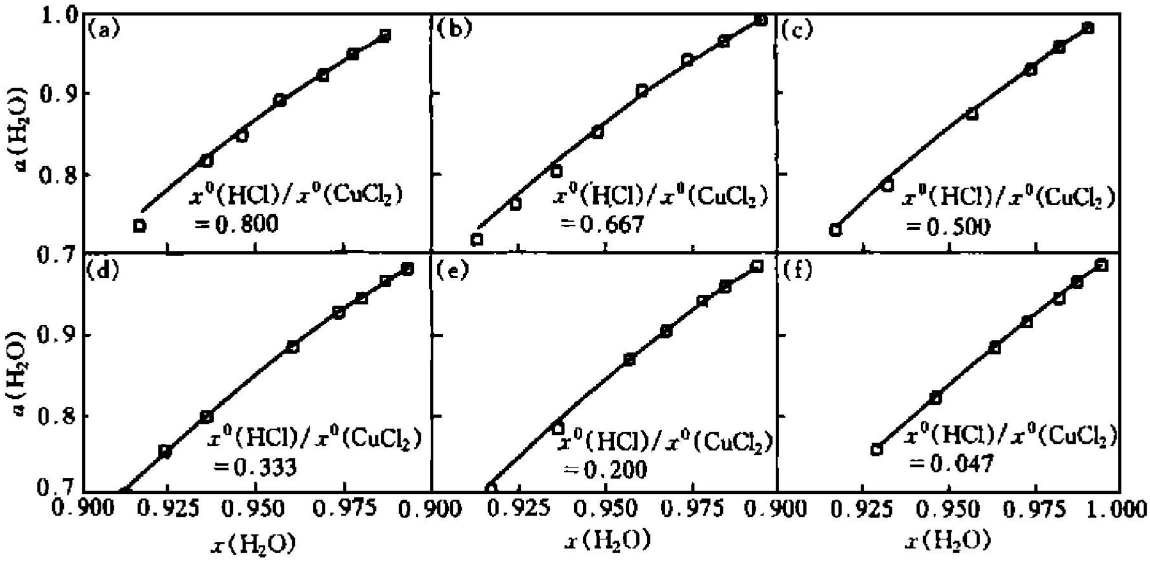

Fig. 4 Comparison between calculated and measured activities of water in $CuCl_2$-H_2O-HCl system

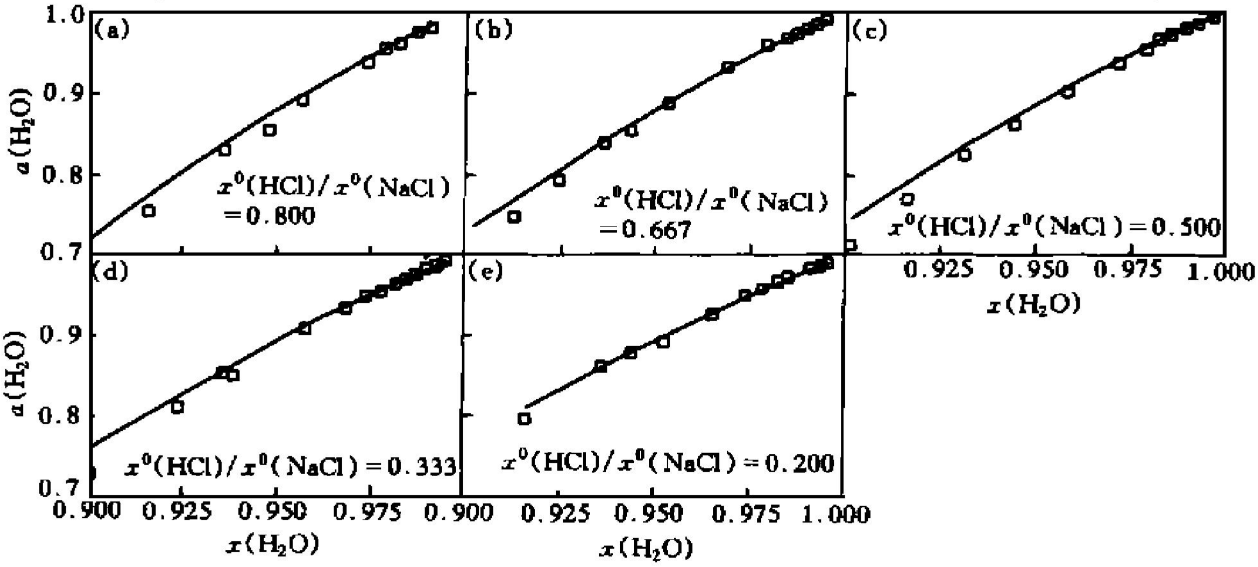

Fig. 5 Comparison between calculated and measured activities of water in NaCl-H_2O-HCl system

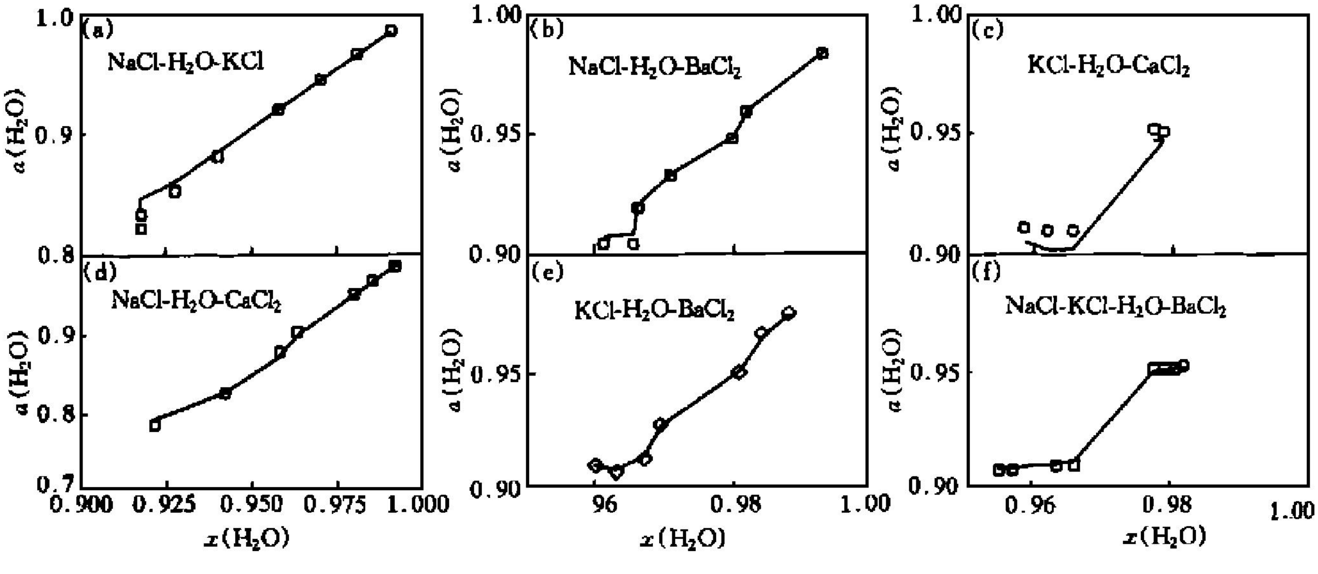

Fig. 6 Comparison between calculated and measured activities of water in some ternary and multi-component systems

lated at high concentration (over 4 mol/L) somewhat differ from those measured, which implies the effects of ignoring of the interaction between salt(1) and salt (3) in a ternary aqueous solution on water activities in high concentrations, although the interaction of electrolyte(1)- electrolyte (3) is indirect in regard to direct interaction of electrolyte (1) and electrolyte (3) to H_2O.

6 CONCLUSIONS

1) From the osmotic coefficients of corresponding binary systems, the interchange energies of such electrolytes as $CuCl_2$, $NiCl_2$, $CoCl_2$, $ZnCl_2$, $CdCl_2$, $FeCl_2$, HCl, NaCl, KCl, $CaCl_2$, $MgCl_2$ and $BaCl_2$ with water have been determined respectively as a function of water composition as: $\omega_{ij} = \alpha + \beta \cdot x(H_2O)/\ln(x(H_2O))$.

2) The activities of water in ternary and multi-component systems composed of some binary systems such as HCl-H_2O-$CuCl_2$, HCl-H_2O-$NiCl_2$, HCl-H_2O-$NaCl$, $NaCl$-H_2O-KCl, $NaCl$-H_2O-$CaCl_2$, KCl-H_2O-$CaCl_2$, $NaCl$-H_2O-$BaCl_2$, KCl-H_2O-$CaCl_2$ and $NaCl$-H_2O-KCl-$BaCl_2$ are calculated by a simplified sub-regular solution model developed. The model is simple and the results are in good agreement well with the measured ones.

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(Edited by LONG Huai-zhong)