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A universal thermodynamic model of calculating mass action concentrations for structural units or ion couples in aqueous solutions and its applications in binary and ternary aqueous solutions

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Abstract: A universal thermodynamic model of calculating mass action concentrations for structural units or ion couples in ternary and binary strong electrolyte aqueous solution was developed based on the ion and molecule coexistence theory and verified in four kinds of binary aqueous solutions and two kinds of ternary aqueous solutions. The calculated mass action concentrations of structural units or ion couples in four binary aqueous solutions and two ternary solutions at 298.15 K have good agreement with the reported activity data from literatures after shifting the standard state and concentration unit. Therefore, the calculated mass action concentrations of structural units or ion couples from the developed universal thermodynamic model for ternary and binary aqueous solutions can be applied to predict reaction ability of components in ternary and binary strong electrolyte aqueous solutions. It is also proved that the assumptions applied in the developed thermodynamic model are correct and reasonable, i.e., strong electrolyte aqueous solution is composed of cations and anions as simple ions, H_2O as simple molecule and other hydrous salt compounds as complex molecules. The calculated mass action concentrations of structural units or ion couples in ternary and binary strong electrolyte aqueous solutions strictly follow the mass action law.

Key words: universal thermodynamic model; mass action concentration; activity; ternary aqueous solution; binary aqueous solution; ion and molecule coexistence theory; structural units; ion couples; components

1 Introduction

The thermodynamic properties of strong electrolyte aqueous solutions, such as activity of component, have been widely applied to biological and industrial processes[1], hydrometallurgy, environmental chemistry[2−5], geochemistry and so on[6]. However, with respect to abundant kinds of electrolyte aqueous solutions, the activity data are not enough to fulfill practical application, or the correlations between activity coefficient and concentration for various solutions have several formulas. In addition, not only ions, but also molecules, such as hydrous salt molecules, can exist in strong electrolyte aqueous solutions. Therefore, it is not very easy to determine activities of components in strong electrolyte aqueous solutions by using traditional activity calculation methods. To accurately predicate activities of components with limited data, it is of importance to develop a universal method to calculate activity of components in strong electrolyte aqueous solutions.

According to the fact that not only ions but also molecules can be found in metallurgical slags or melts at high temperature, the ion and molecule coexistence theory (IMCT) proposed by ZHANG[7−9] has been successfully applied to calculate mass action concentrations of structural units or ion couples to describe reaction ability, like classical concept of activity, for various metallurgical slags and metal melts. The essential cores of IMCT[7−9] are summarized as follows: 1) ions, simple and complex molecules exist in a solution simultaneously as structural units; 2) there are dynamic

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equilibriums of chemical reactions between ion couples and simple molecules to form complex molecules in a solution; 3) simple ions take part in chemical reactions of forming complex molecules with simple molecules as ion couples, which are composed of cations and anions based on electrovalence balance principle; 4) the calculated equilibrium mole fractions of structural units or ion couples are defined as mass action concentration, which are similar to activities of corresponding components.

The mass action concentrations of structural units or ion couples in binary aqueous solutions of KCl−H_2O, CsCl−H_2O, NaCl−H_2O and $BaCl_2$−H_2O[10]; NaBr−H_2O, $LiNO_3$−H_2O, HNO_3−H_2O and KF−H_2O[11]; KBr−H_2O, NH_4Br−H_2O and $ZnBr_2$−H_2O[11]; and ternary aqueous solutions of NaCl−KCl−H_2O[13]; RbCl−$RbNO_3$−H_2O[14]; $NaClO_4$−NaF−H_2O[15] at 298.15 K have been successfully calculated by using the developed thermodynamic model of calculating mass action concentrations for structural units or ion couples from IMCT[7−9]. The results[10−15] show that the calculated mass action concentrations of structural units or ion couples in above-mentioned binary and ternary aqueous solutions have good agreement with the reported activities of corresponding components in literatures. Therefore, it is verified that the application scope of IMCT[7−9] can be expanded from metallurgical slag and metal melts at high temperature to electrolyte aqueous solutions at low or ambient temperature. However, a universal thermodynamic model for binary and ternary aqueous solutions has not been reported and summarized in previous publications[10−15].

In this work, a universal thermodynamic model of calculating mass action concentrations for structural units or ion couples in ternary electrolyte aqueous solutions with hydrous salt compounds as complex molecules was developed based on IMCT[7−9]. Meanwhile, a universal thermodynamic model for binary aqueous solutions with hydrous salt compounds as complex molecules was also developed by simplifying the universal thermodynamic model for ternary solutions, and four kinds of binary aqueous solutions were chosen to verify the developed thermodynamic model as: 1) binary aqueous solutions without any hydrous salt compound formed; 2) binary solutions with $ECl{\cdot}2H_2O$ as formed hydrous salt compound with unknown standard molar Gibbs free energy $\Delta_r G^{\Theta}_{m,i}$; 3) binary aqueous solutions with $ECl{\cdot}2H_2O$ as formed hydrous salt compound with known $\Delta_r G^{\Theta}_{m,i}$; 4) binary aqueous solutions with $ECl{\cdot}H_2O$ and $ECl{\cdot}3H_2O$ as formed hydrous salt compounds with known $\Delta_r G^{\Theta}_{m,i}$. All universal thermodynamic models were verified from the previous published data of calculating mass action concentrations for structural units or ion couples in binary and ternary solutions[10−15] as examples. The ultimate aims of this work are to develop a universal thermodynamic model of calculating mass action concentrations for structural units or ion couples in binary and ternary electrolyte aqueous solutions and verify it in various special cases.

2 Establishment of universal thermodynamic model

2.1 Hypotheses

According to the facts that there are ions and molecules simultaneously in strong electrolyte aqueous solutions, the assumptions applied in the developed universal thermodynamic model of calculating mass action concentrations for structural units or ion couples in ternary strong electrolyte aqueous solutions can be proposed based on IMCT[7−9] by taking ECl−FCl−H_2O as an example aqueous solution as follows.

1) The structural units in ECl−FCl−H_2O ternary solutions are composed of E^+, F^+ and Cl^- as simple ions, H_2O as simple molecule, $ECl{\cdot}H_2O$, $ECl{\cdot}2H_2O$, ⋯, $ECl{\cdot}nH_2O$ or $FCl{\cdot}H_2O$, $FCl{\cdot}2H_2O$, ⋯, $FCl{\cdot}mH_2O$ as complex molecules. Each cation or anion of the simple ions in ECl−FCl−H_2O ternary solutions occupies only one position of structural units, but will take part in reaction of forming hydrous salt molecules in the form of ion couple as (E^++Cl^-), and (F^++Cl^-). For example, ECl in ECl−FCl−H_2O ternary solutions can be electrolyzed or separated into two simple ions as E^+ and Cl^- as two structural units, respectively; but ions of E^+ and Cl^- will take part in reaction of forming hydrous salt molecules as an ion couple (E^++Cl^-) in ECl−FCl−H_2O ternary solutions.

2) Formation of complex hydrous salt molecules by ion couples and simple molecule of H_2O is under dynamic equilibrium as

$$(E^+ + Cl^-) + H_2O = ECl{\cdot}H_2O \quad (1.1)$$

$$(E^+ + Cl^-) + 2H_2O = ECl{\cdot}2H_2O \quad (1.2)$$

$$\vdots$$

$$(E^+ + Cl^-) + nH_2O = ECl{\cdot}nH_2O \quad (1.n)$$

$$(F^+ + Cl^-) + H_2O = FCl{\cdot}H_2O \quad (2.1)$$

$$(F^+ + Cl^-) + 2H_2O = FCl{\cdot}2H_2O \quad (2.2)$$

$$\vdots$$

$$(F^+ + Cl^-) + mH_2O = FCl{\cdot}mH_2O \quad (2.m)$$

3) The structural units in ECl−FCl−H_2O strong solutions bear continuity in the investigated concentration range of solutes.

4) All chemical reactions of forming complex hydrous salt molecules in ECl−FCl−H_2O strong electrolyte ternary aqueous solutions as shown in Eq.(1) and Eq.(2) follow the mass action law.

2.2 Universal thermodynamic model for ternary systems

2.2.1. Model for ternary systems with all hydrous salt molecules formed

Based on the above-mentioned hypotheses, the structural units in a chloride ternary aqueous solution with all hydrous salt molecules formed as an example, i.e., ECl−FCl−H_2O ternary solution, are composed of E^+, F^+ and Cl^- as simple ions, H_2O as simple molecule, ECl H_2O, ECl $2H_2O$, ⋯, ECl nH_2O, and FCl H_2O, FCl $2H_2O$, ⋯, FCl mH_2O as complex molecules or hydrous salt molecules.

The morality m_i (mol/kg (H_2O)) is usually applied to represent concentration of components in strong electrolyte aqueous solution, i.e., mole number of solutes in 1 kg solvent of H_2O. Therefore, mole number of ECl, FCl and H_2O in ECl−FCl−H_2O ternary solution based on 1 kg H_2O before equilibrium is defined as $b_1 = n^0_{\mathrm{ECl}} = m_{\mathrm{ECl}}$, $b_2 = n^0_{\mathrm{FCl}} = m_{\mathrm{FCl}}$ and $b_3 = n^0_{\mathrm{H_2O}} = m_{\mathrm{H_2O}} = 1\,000\ \mathrm{g}/M_{\mathrm{H_2O}} = 55.6$ mol, respectively. The mole fractions of ECl, FCl and H_2O in ECl−FCl−H_2O ternary solution before equilibrium can be easily determined as $x_i = n^0_i / \sum n^0_i = n^0_i /(n^0_{\mathrm{ECl}} + n^0_{\mathrm{FCl}} + 55.6) = m_i /(m_{\mathrm{ECl}} + m_{\mathrm{FCl}} + 55.6)$.

The mole numbers of structural units in ECl−FCl−H_2O ternary solution under dynamic reaction equilibrium condition based on 1 kg H_2O are defined according to IMCT[7−9] as follows:

$$\begin{aligned}
&n_1 = n_{\mathrm{E^+,\,ECl}} = n_{\mathrm{Cl^-,\,ECl}} = n_{\mathrm{ECl}},\\
&n_2 = n_{\mathrm{F^+,\,FCl}} = n_{\mathrm{Cl^-,\,FCl}} = n_{\mathrm{FCl}},\\
&n_3 = n_{\mathrm{H_2O}},\ n_{41} = n_{\mathrm{ECl\cdot H_2O}},\ n_{42} = n_{\mathrm{ECl\cdot 2H_2O}},\\
&\cdots,\\
&n_{4n} = n_{\mathrm{ECl}\cdot n\mathrm{H_2O}},\ n_{51} = n_{\mathrm{FCl\cdot H_2O}},\ n_{52} = n_{\mathrm{FCl\cdot 2H_2O}},\\
&\cdots,\\
&n_{5m} = n_{\mathrm{FCl}\cdot m\mathrm{H_2O}}
\end{aligned} \tag{3}$$

Hence, the total mole number of all structural units $\sum n_i$ in ECl−FCl−H_2O ternary solution under equilibrium condition based on 1 kg H_2O can be calculated according to the mass balance principle as

$$\begin{aligned}
\sum n_i = {} & 2n_1 + 2n_2 + n_3 + n_{41} + n_{42} + \cdots + n_{4n} + \\
& n_{51} + n_{52} + \cdots + n_{5m}
\end{aligned} \tag{4}$$

The mass action concentration of structural unit is defined as a ratio of equilibrium mole number of structural unit i to the total equilibrium mole number of all structural units in a system with a fixed amount according to IMCT[7−9], and can be calculated by

$$N_i = \frac{n_i}{\sum n_i} \quad (-) \tag{5}$$

It should be emphasized that mass action concentrations of all structural units in forms of ions, simple and complex molecules can be calculated from Eq.(5) directly[7−9]; however, mass action concentration of an ion couple from cation and anion, such as (E^++Cl^-), should be calculated as follows[7−9]:

$$N_{\mathrm{ECl}} = N_{\mathrm{E^+}} + N_{\mathrm{Cl^-}} = \frac{n_{\mathrm{E^+}} + n_{\mathrm{Cl^-}}}{\sum n_i} = \frac{2n_{\mathrm{ECl}}}{\sum n_i} \quad (-) \tag{6}$$

Therefore, the mass action concentrations of structural units or ion couples in ECl−FCl−H_2O ternary solution under equilibrium condition can be expressed as follows:

$$\begin{aligned}
&N_1 = \frac{2n_1}{\sum n_i} = N_{\mathrm{ECl}},\ N_2 = \frac{2n_2}{\sum n_i} = N_{\mathrm{FCl}},\\
&N_3 = \frac{n_3}{\sum n_i} = N_{\mathrm{H_2O}},\ N_{41} = \frac{n_{41}}{\sum n_i} = N_{\mathrm{ECl\cdot H_2O}},\\
&N_{42} = \frac{n_{42}}{\sum n_i} = N_{\mathrm{ECl\cdot 2H_2O}},\ \cdots,\\
&N_{4n} = \frac{n_{4n}}{\sum n_i} = N_{\mathrm{ECl}\cdot n\mathrm{H_2O}},\ N_{51} = \frac{n_{51}}{\sum n_i} = N_{\mathrm{FCl\cdot H_2O}},\\
&N_{52} = \frac{n_{52}}{\sum n_i} = N_{\mathrm{FCl\cdot 2H_2O}},\ \cdots,\\
&N_{5m} = \frac{n_{5m}}{\sum n_i} = N_{\mathrm{FCl}\cdot m\mathrm{H_2O}}
\end{aligned} \quad (-) \tag{7}$$

The possible dynamic reactions of forming various hydrous salt molecules and their corresponding equilibrium constants and mass action concentrations can be described as follows:

(E^++Cl^-)+H_2O=ECl·H_2O,

$$K^{\Theta}_{41} = \frac{N_{41}}{N_1 N_3},\ N_{41} = K^{\Theta}_{41} N_1 N_3 \tag{8.1}$$

(E^++Cl^-)+2H_2O=ECl·2H_2O,

$$K^{\Theta}_{42} = \frac{N_{42}}{N_1 N_3^2},\ N_{42} = K^{\Theta}_{42} N_1 N_3^2, \tag{8.2}$$

⋮

(E^++Cl^-)+$n$$H_2O$=ECl·$n$$H_2O$,

$$K^{\Theta}_{4n} = \frac{N_{4n}}{N_1 N_3^n},\ N_{4n} = K^{\Theta}_{4n} N_1 N_3^n \tag{8.n}$$

(F^++Cl^-)+H_2O=FCl·H_2O,

$$K^{\Theta}_{51} = \frac{N_{51}}{N_2 N_3},\ N_{51} = K^{\Theta}_{51} N_2 N_3 \tag{9.1}$$

(F^++Cl^-)+2H_2O=FCl·2H_2O,

$$K^{\Theta}_{52} = \frac{N_{52}}{N_2 N_3^2},\ N_{52} = K^{\Theta}_{52} N_2 N_3^2 \tag{9.2}$$

⋮

(F^++Cl^-)+$m$$H_2O$=FCl·$m$$H_2O$,

$$K^{\Theta}_{5m} = \frac{N_{5m}}{N_2 N_3^m},\ N_{5m} = K^{\Theta}_{5m} N_2 N_3^m \tag{9.m}$$

The mass balance of three components as ECl, FCl and H_2O in ECl−FCl−H_2O ternary solution based on 1 kg

H_2O according to IMCT[7−9] can be represented as follows:

$$b_1 = n^0_{\mathrm{ECl}} = m_{\mathrm{ECl}} = n_1 + n_{41} + n_{42} + \cdots + n_{4n} = \left(\frac{1}{2}N_1 + N_{41} + N_{42} + \cdots + N_{4n}\right)\sum n_i = \left(\frac{1}{2}N_1 + K^{\Theta}_{41}N_1N_3 + K^{\Theta}_{42}N_1N_3^2 + \cdots + K^{\Theta}_{4n}N_1N_3^n\right)\sum n_i \quad (10a)$$

$$b_2 = n^0_{\mathrm{FCl}} = m_{\mathrm{FCl}} = n_2 + n_{51} + n_{52} + \cdots + n_{5m} = \left(\frac{1}{2}N_2 + N_{51} + N_{52} + \cdots + N_{5m}\right)\sum n_i = \left(\frac{1}{2}N_2 + K^{\Theta}_{51}N_2N_3 + K^{\Theta}_{52}N_2N_3^2 + \cdots + K^{\Theta}_{5m}N_2N_3^m\right)\sum n_i \quad (10b)$$

$$b_3 = n^0_{\mathrm{H_2O}} = n_3 + n_{41} + 2n_{42} + \cdots + nn_{4n} + n_{51} + 2n_{52} + \cdots + mn_{5m} = (N_3 + N_{41} + 2N_{42} + \cdots + nN_{4n} + N_{51} + 2N_{52} + \cdots + mN_{5m})\sum n_i = (N_3 + K^{\Theta}_{41}N_1N_3 + 2K^{\Theta}_{42}N_1N_3^2 + \cdots + nK^{\Theta}_{4n}N_1N_3^n + K^{\Theta}_{51}N_2N_3 + 2K^{\Theta}_{52}N_2N_3^2 + \cdots + mK^{\Theta}_{5m}N_2N_3^m)\sum n_i = 55.6 \quad (10c)$$

Combining Eq.(10a)−Eq.(10b) to eliminate $\sum n_i$, the following formulations can be obtained as

$$\frac{1}{2}b_3N_1 - b_1N_3 + K^{\Theta}_{41}(b_3 - b_1)N_1N_3 + K^{\Theta}_{42}(b_3 - 2b_1)N_1N_3^2 + \cdots + K^{\Theta}_{4n}(b_3 - nb_1)N_1N_3^n - b_1K^{\Theta}_{51}N_2N_3 - 2b_1K^{\Theta}_{52}N_2N_3^2 - \cdots - mb_1K^{\Theta}_{5m}N_2N_3^m = 0 \quad (11a)$$

$$\frac{1}{2}b_3N_2 - b_2N_3 - b_2K^{\Theta}_{41}N_1N_3 - 2b_2K^{\Theta}_{42}N_1N_3^2 - \cdots - nb_2K^{\Theta}_{4n}N_1N_3^n + K^{\Theta}_{51}(b_3 - b_2)N_2N_3 + K^{\Theta}_{52}(b_3 - 2b_2)N_2N_3^2 + \cdots + K^{\Theta}_{5m}(b_3 - mb_2)N_1N_3^m = 0 \quad (11b)$$

According to the fact that the total equilibrium mole fraction of all structural units in a system with a fixed amount is 1.0, the following equation can be obtained as

$$\sum N_i = N_1 + N_2 + N_3 + N_{41} + N_{42} + \cdots + N_{4n} + N_{51} + N_{52} + \cdots + N_{5m} = N_1 + N_2 + N_3 + K^{\Theta}_{41}N_1N_3 + K^{\Theta}_{42}N_1N_3^2 + \cdots + K^{\Theta}_{4n}N_1N_3^n + K^{\Theta}_{51}N_2N_3 + K^{\Theta}_{52}N_2N_3^2 + \cdots + K^{\Theta}_{5m}N_2N_3^m = 1 \quad (-) \ (12)$$

The equilibrium constant K^{Θ}_i of all dynamic chemical reactions described in Eq.(1) and Eq.(2) can be calculated as follows:

$$K^{\Theta}_i = \exp[-\Delta_r G^{\Theta}_{\mathrm{m},\,i}/(RT)] \quad (-) \ (13)$$

Therefore, the equation groups of Eq.(10) and Eq.(12) or Eq.(11) and Eq.(12) are composed of the universal thermodynamic model of calculation mass action concentrations for structural units or ion couples N_i in ECl−FCl−H_2O ternary aqueous solution, respectively. There are four unknown parameters as N_1, N_2, N_3 and $\sum n_i$ with four independent equations in the universal thermodynamic model composing of Eq.(10) and Eq.(12), or three unknown parameters as N_1, N_2 and N_3 with three independent equations in the universal thermodynamic model composing of Eq.(11) and Eq.(12). It is clear that the real solutions of above-mentioned mass action concentrations of structural units or ion couples N_i and total mole fraction of all structural units $\sum n_i$ in ECl−FCl−H_2O ternary aqueous solution can be solely solved by combining Eq.(10) and Eq.(12) or Eq.(11) and Eq.(12) under condition of knowing equilibrium constant K^{Θ}_i. The equilibrium mole number of each structural unit n_i can be also determined by Eq.(5) or Eq.(6) after knowing N_i and $\sum n_i$.

The calculated mass action concentration N_i is based on pure mater as standard state and mole fraction x_i as concentration unit; however, the reported activity data of strong electrolyte aqueous solutions in literatures usually choose infinite dilute solution as standard state and molality m_i (mol/kg (H_2O)) as concentration unit. To compare the calculated mass action concentrations N_i and reported activity data a_i, a transformation coefficient L_i for solvent or L'_i for solutes should be introduced to shift standard state and concentration unit[10−15], and the transformed mass action concentration of components N'_i can be calculated as follows[10−15]:

$$L_{\mathrm{H_2O}} = \frac{a_{\mathrm{H_2O}}}{N_{\mathrm{H_2O}}},\ L'_i = \frac{a_i}{N_i} = \frac{m_i f'_i}{N_i},\ N'_i = \overline{L}'_i N_i \quad (-) \ (14)$$

It should be specially pointed out that mass action concentration of all ion couples, simple and complex (hydrous salts) molecules, such as ECl, FCl, H_2O, ECl·H_2O, ECl·2H_2O, ⋯, ECl·nH_2O, and FCl·H_2O, FCl·2H_2O, ⋯, FCl·mH_2O in ECl−FCl−H_2O ternary solution under equilibrium condition can be calculated from the developed universal thermodynamic model based on IMCT[7−9]. However, only activity data of three components in ECl−FCl−H_2O ternary solution as ECl, FCl and H_2O can be determined from viewpoints of classical experimental tests and traditional thermodynamics. Although concept of mass action concentration of components N_i, taking ECl as an example, has been applied in previous publications[7−15]

and this study, the real meaning of mass action concentration for ECl N_{ECl} is the sum of mass action concentration of two contained structural units in ECl as E^+ and Cl^-. From absolute viewpoint of IMCT[10−15], there is no mass action concentration of ECl as an independent component, because no independent ECl molecules can exist in ECl−FCl−H_2O ternary solution. Adopting concept of mass action concentration for ECl is just for convenient comparison of the reported ECl activity data with calculated mass action concentration of the same components.

2.2.2 Model for ternary systems without any hydrous salt molecule formed

As an extreme example, a universal thermodynamic model of calculating mass action concentrations for structural units or ion couples in ECl−FCl−H_2O ternary solution without any complex hydrous salt molecule formed can be also obtained by considering n, m and K_i^{Θ} as zero simultaneously in the equation groups of Eq.(10) and Eq.(12) or Eq.(11) and Eq.(12) choosing ECl−FCl−H_2O ternary solution as a representative.

The mole numbers of ECl, FCl and H_2O in ECl−FCl−H_2O ternary solution before reaction equilibrium based on 1 kg H_2O are represented as $b_1 = n^0_{ECl} = m_{ECl}$, $b_2 = n^0_{FCl} = m_{FCl}$, $b_3 = n^0_{H_2O} = m_{H_2O}$ =55.6 mol, respectively. The structural units in ECl−FCl−H_2O ternary solution without any hydrous salt molecule formed are composed of E^+, F^+ and Cl^- as simple ions, H_2O as simple molecules. The mole numbers of structural units in ECl−FCl−H_2O ternary solution without any hydrous salt molecule formed under dynamic reaction equilibrium condition based on 1 kg H_2O can be expressed as $n_1 = n_{E^+,\,ECl} = n_{Cl^-,\,ECl} = n_{ECl} = m_{ECl}$, $n_2 = n_{F^+,\,FCl} = n_{Cl^-,\,FCl} = n_{FCl} = m_{FCl}$, $n_3 = n_{H_2O} = 55.6$. Hence, the total mole number of all structural units $\sum n_i$ based on 1 kg H_2O in ECl−FCl−H_2O ternary solution without any hydrous salt molecule formed under equilibrium condition can be calculated according to the mass balance principle as

$$\sum n_i = 2n_1 + 2n_2 + n_3 = 2m_1 + 2m_2 + 55.6 \tag{15}$$

The mass balance of ECl, FCl and H_2O in ECl−FCl−H_2O ternary solution can be described by considering definition of mass action concentrations of structural units or ion couples in ECl−FCl−H_2O ternary solution shown in Eq.(10) as

$$b_1 = n^0_{ECl} = m_{ECl} = n_1 = \frac{1}{2} N_1 \sum n_i \tag{16a}$$

$$b_2 = n^0_{FCl} = m_{FCl} = n_2 = \frac{1}{2} N_2 \sum n_i \tag{16b}$$

$$b_3 = n^0_{H_2O} = m_{H_2O} = n_3 = N_3 \sum n_i = 55.6 \tag{16c}$$

The following equations can be obtained by combining Eq.(16a)−Eq.(16c) to eliminate $\sum n_i$ as

$$\frac{1}{2} b_3 N_1 - b_1 N_3 = 0 \tag{17a}$$

$$\frac{1}{2} b_3 N_2 - b_2 N_3 = 0 \tag{17b}$$

The following expression can be obtained according to the principle that the sum of all mole fraction of structural units in ECl−FCl−H_2O ternary solution with a fixed amount under equilibrium condition is equal to 1.0, as

$$N_1 + N_2 + N_3 = 1 \tag{18}$$

Therefore, the thermodynamic model of calculating mass action concentrations for structural units or ion couples in ECl−FCl−H_2O ternary solution without any hydrous salt molecule formed can be described by equation groups of Eq.(16) and Eq.(18) or Eq.(17) and Eq.(18). Substituting the known parameters as $b_1 = n^0_{ECl} = m_{ECl}$, $b_2 = n^0_{FCl} = m_{FCl}$ and b_3= $n^0_{H_2O}$=55.6 mol into Eq.(17)−Eq.(18), the thermodynamic model of calculating mass action concentrations for structural units or ion couples in ECl−FCl−H_2O ternary solution without any hydrous salt molecule formed can be simplified as

$$N_1 = \frac{2n_1}{\sum n_i} = \frac{2m_{ECl}}{2m_{ECl} + 2m_{FCl} + 55.6},$$

$$N_2 = \frac{2n_2}{\sum n_i} = \frac{2m_{FCl}}{2m_{ECl} + 2m_{FCl} + 55.6},$$

$$N_3 = \frac{n_3}{\sum n_i} = \frac{55.6}{2m_{ECl} + 2m_{FCl} + 55.6} \tag{19}$$

The transformation coefficient L_i or L_i' and transformed mass action concentration of components N_i can be obtained by Eq.(14) as described in Section 2.2.1.

2.3 Universal thermodynamic model for binary systems

2.3.1 Model for binary systems with all hydrous salt molecules formed

The structural units in ECl−H_2O binary strong electrolyte aqueous solution with all hydrous salt molecules formed are composed of E^+ and Cl^- as simple ions, H_2O as simple molecule and ECl·H_2O, ECl·2H_2O, ⋯, and ECl·nH_2O as complex hydrous salt molecules. Therefore, the mole numbers of ECl and H_2O in ECl−H_2O binary solution based on 1 kg H_2O before equilibrium is defined as $b_1 = n^0_{ECl} = m_{ECl}$ and b_3= $n^0_{H_2O} = m_{H_2O}$ = 1 000 g / M_{H_2O} = 55.6 mol, respectively. The mole fractions of ECl and H_2O in ECl−H_2O binary solution before equilibrium can be easily determined by $x_i = n_i^0 / \sum n_i^0 = n_i^0 / (n^0_{ECl} + 55.6) = m_i / (m_{ECl} + 55.6)$.

The mole number of structural units in ECl−H_2O

binary solution under dynamic reaction equilibrium condition based on 1 kg H_2O is defined according to IMCT[7−9] as follows:

$$n_1 = n_{E^+,\,ECl} = n_{Cl^-,\,ECl} = n_{ECl}, n_3 = n_{H_2O},$$
$$n_{41} = n_{ECl\cdot H_2O},\ n_{42} = n_{ECl\cdot 2H_2O},\ \cdots,\ n_{4n} = n_{ECl\cdot nH_2O} \tag{20}$$

Hence, the total mole number of all structural units $\sum n_i$ based on 1 kg H_2O in ECl−H_2O binary solution under equilibrium condition can be calculated according to the mass balance principle as

$$\sum n_i = 2n_1 + n_3 + n_{41} + n_{42} + \cdots + n_{4n} \tag{21}$$

Therefore, Eq.(10) can be rewritten to present the mass balance of ECl and H_2O in ECl−H_2O binary solution with all hydrous salt molecules formed under equilibrium condition based on 1 kg H_2O by ignoring parameters b_2, m and K_{5i}^{Θ} as

$$b_1 = n_{ECl}^0 = m_{ECl} = n_1 + n_{41} + n_{42} + \cdots + n_{4n} = \left(\frac{1}{2}N_1 + N_{41} + N_{42} + \cdots + N_{4n}\right)\cdot \sum n_i = \left(\frac{1}{2}N_1 + K_{41}^{\Theta}N_1N_3 + K_{42}^{\Theta}N_1N_3^2 + \cdots + K_{4n}^{\Theta}N_1N_3^n\right)\sum n_i \tag{22a}$$

$$b_3 = n_{H_2O}^0 = m_{H_2O} = n_3 + n_{41} + 2n_{42} = (N_3 + N_{41} + 2N_{42} + \cdots + nN_{4n})\sum n_i = (N_3 + K_{41}^{\Theta}N_1N_3 + 2K_{42}^{\Theta}N_1N_3^2 + \cdots + nK_{4n}^{\Theta}N_1N_3^n)\sum n_i = 55.6 \tag{22b}$$

The following equation can be obtained by combining Eq.(22a) and Eq.(22b) to eliminate $\sum n_i$ as

$$\frac{1}{2}b_3N_1 - b_1N_3 + K_{41}^{\Theta}(b_3 - b_1)N_1N_3 + K_{42}^{\Theta}(b_3 - 2b_1)N_1N_3^2 + \cdots + K_{4n}^{\Theta}(b_3 - nb_1)N_1N_3^n = 0 \tag{23}$$

According to the fact that the total equilibrium mole fraction of all structural units in a system with a fixed amount is 1.0, Eq.(12) can be simplified for ECl−H_2O binary solution as

$$N_1 + N_3 + K_{41}^{\Theta}N_1N_3 + K_{42}^{\Theta}N_1N_3^2 + \cdots + K_{4n}^{\Theta}N_1N_3^n = 1 \tag{−) (24}$$

Therefore, Eq.(22) and Eq.(24) or Eq.(23) and Eq.(24) are the developed universal thermodynamic model of calculating mass action concentrations for structural units or ion couples N_i in ECl−H_2O binary solution with all hydrous salt molecules formed, respectively. There are three unknown parameters as N_1, N_3 and $\sum n_i$ with three independent equations in the universal thermodynamic model composing of Eq.(22) and Eq.(24), or two unknown parameters as N_1 and N_3 with two independent equations in the universal thermodynamic model composing of Eq.(23) and Eq.(24). The real solutions of N_i and $\sum n_i$ for ECl−H_2O binary solution can be solely solved by combing Eq.(22) and Eq.(24) or Eq.(23) and Eq.(24) under condition of knowing K_{4i}^{Θ}. The equilibrium mole number of all structural units or ion couples n_i under equilibrium condition can be also calculated from definition formula of N_i in Eq.(5) or Eq.(6) after knowing N_i and $\sum n_i$. The expressions of K_i^{Θ}, L_i or L_i', and N_i' for ECl−H_2O binary solution are the same as equations described in Eq.(13) and Eq.(14).

2.3.2 Model for binary system without any hydrous salt molecule formed

The structural units in ECl−H_2O binary strong electrolyte aqueous solution without any hydrous salt complex molecule generated are composed of E^+ and Cl^- as simple ions, and H_2O as simple molecule. Hence, no equilibrium constant of forming hydrous salt complex molecules K_{4i}^{Θ} can exist in the universal thermodynamic model of calculating mass action concentrations for structural units or ion couples N_i in ECl−H_2O binary solution, as shown in Eq.(22) and Eq.(24) or Eq.(23) and Eq.(24), respectively. The mole numbers of ECl and H_2O in ECl−H_2O binary solution without any hydrous salt complex molecule generated before reaction equilibrium based on 1 kg H_2O are presented as $b_1 = n_{ECl}^0 = m_{ECl}$, $b_3 = n_{H_2O}^0 = m_{H_2O} =$ 55.6 mol. The mole numbers of structural units in ECl−H_2O ternary solution without any hydrous salt molecule formed under dynamic reaction equilibrium condition based on 1 kg H_2O can be expressed[7−9] as $n_1 = n_{E^+,\,ECl} = n_{Cl^-,\,ECl} = n_{ECl} = m_{ECl}$, $n_3 = n_{H_2O} =$ 55.6. Hence, the total mole number of all structural units $\sum n_i$ based on 1 kg H_2O in ECl−H_2O ternary solution without any hydrous salt molecule formed under equilibrium condition can be calculated according to the mass balance principle as

$$\sum n_i = 2n_1 + n_3 = 2m_1 + 55.6 \tag{25}$$

The mass balance of ECl and H_2O in ECl−H_2O binary solution without any hydrous salt molecule formed under equilibrium condition based on 1 kg H_2O can be presented by simplifying Eq.(22) as

$$b_1 = n_{ECl}^0 = m_{ECl} = n_1 = \frac{1}{2}N_1\sum n_i \tag{26a}$$

$$b_3 = n_{H_2O}^0 = m_{H_2O} = n_3 = N_3\sum n_i = 55.6 \tag{26b}$$

The following equation can be obtained by combining Eq.(26a) and Eq.(26b) to eliminate $\sum n_i$, as

$$\frac{1}{2}b_3N_1 - b_1N_3 = 0 \tag{27}$$

According to the fact that the total equilibrium mole fraction of all structural units in a system with a fixed amount is 1.0, Eq.(24) can be simplified for ECl−H_2O binary solution without any complex hydrous salt molecule formed as

$$N_1 + N_3 = 1 \quad (-) \tag{28}$$

The equation groups of Eq.(26) and Eq.(28) or Eq.(27) and Eq.(28) are the thermodynamic model of calculating mass action concentrations for structural units or ion couples N_i in ECl−H_2O binary solution without any complex hydrous salt molecule formed, respectively. N_i can be calculated by solving Eq.(26) and Eq.(28) or Eq.(27) and Eq.(28) as follows:

$$N_1 = \frac{2n_1}{\sum n_i} = \frac{2m_{\mathrm{ECl}}}{2m_{\mathrm{ECl}} + 55.6},$$
$$N_3 = \frac{n_3}{\sum n_i} = \frac{55.6}{2m_{\mathrm{ECl}} + 55.6} \tag{29}$$

The expressions of L_i or L_i' and N_i' for ECl−H_2O binary solution without any complex hydrous salt molecule formed are the same as equations described in Eq.(14).

2.3.3 Model for binary system with ECl·$2H_2O$ as formed hydrous salt molecule with unknown $\Delta_r G_{\mathrm{m},i}^{\Theta}$

In the case of no standard molar Gibbs free energy $\Delta_r G_{\mathrm{m},i}^{\Theta}$ of the existed complex hydrous salt molecules in ECl−H_2O binary solution can be found from related literatures, the common procedure of developing the thermodynamic model of calculating mass action concentrations for structural units or ion couples N_i from IMCT[7−9] is summarized as follows: 1) confirming the chemical formulas of possibly formed hydrous salt molecules from phase diagram of the studied ECl−H_2O binary solution; 2) establishing the thermodynamic model from the proposed universal thermodynamic model; 3) substituting the mass action concentrations N_i of ECl and H_2O in ECl−H_2O binary solution by the reported activities of ECl and H_2O in formulas of equilibrium constant K_{4i}^{Θ} for reactions of possibly formed hydrous salt molecules. When a relatively stable equilibrium constant K_{4i}^{Θ} is obtained for the reaction of formed hydrous salt molecule, the thermodynamic model can be solved by using the calculated K_{4i}^{Θ} to determine mass action concentrations of structural units or ion couples. Taking ECl·$2H_2O$ as formed hydrous salt molecule in ECl−H_2O binary solution with unknown $\Delta_r G_{\mathrm{m},i}^{\Theta}$ as an example, the procedure of developing thermodynamic model is explained in the following text.

Certainly, the structural units in ECl−H_2O binary solution with ECl·$2H_2O$ as hydrous salt molecule are E^+ and Cl^- as simple ions, H_2O as simple molecule and ECl·$2H_2O$ as complex hydrous salt molecule. The mole numbers of ECl and H_2O in ECl−H_2O binary solution with ECl·$2H_2O$ as formed hydrous salt molecule before reaction equilibrium based on 1 kg H_2O are presented as $b_1 = n_{\mathrm{ECl}}^0 = m_{\mathrm{ECl}}$, $b_3 = n_{\mathrm{H_2O}}^0 = m_{\mathrm{H_2O}}$ =55.6 mol. The mole numbers of structural units in ECl−H_2O ternary solution with ECl·$2H_2O$ as formed hydrous salt molecule formed under dynamic reaction equilibrium condition based on 1 kg H_2O can be expressed as $n_1 = n_{\mathrm{E^+,\,ECl}} = n_{\mathrm{Cl^-,\,ECl}} = n_{\mathrm{ECl}} = m_{\mathrm{ECl}}$, $n_3 = n_{\mathrm{H_2O}} = 55.6$, $n_{42} = n_{\mathrm{ECl\cdot 2H_2O}}$. Hence, the total mole number of all structural units $\sum n_i$ in ECl−H_2O binary solution with ECl·$2H_2O$ as formed hydrous salt molecules under equilibrium condition based on 1 kg H_2O can be calculated according to the mass balance principle as

$$\sum n_i = 2n_1 + n_3 + n_{42} \tag{30}$$

The mass balance of ECl and H_2O in ECl−H_2O binary solution based on 1 kg H_2O by Eq.(22) can be rewritten as

$$b_1 = n_{\mathrm{ECl}}^0 = m_{\mathrm{ECl}} = n_1 + n_{42} = (\frac{1}{2}N_1 + N_{42})\sum n_i = (\frac{1}{2}N_1 + K_{42}^{\Theta}N_1N_3^2)\sum n_i \tag{31a}$$

$$b_3 = n_{\mathrm{H_2O}}^0 = m_{\mathrm{H_2O}} = n_3 + 2n_{42} = \left(N_3 + 2N_{42}\right)\sum n_i = \left(N_3 + 2K_{42}^{\Theta}N_1N_3^2\right)\sum n_i = 55.6 \tag{31b}$$

The developed universal thermodynamic model of ECl−H_2O binary solution shown in Eq.(23) and Eq.(24) can be simplified as

$$\frac{1}{2}b_3N_1 - b_1N_3 + K_{42}^{\Theta}(b_3 - 2b_1)N_1N_3^2 = 0 \tag{32}$$

$$N_1 + N_3 + K_{42}^{\Theta}N_1N_3^2 = 1 \tag{33}$$

The chemical reaction equilibrium constant K_{42}^{Θ} of reaction for forming ECl·$2H_2O$ by Eq.(1.2) can be presented by considering Eq.(32) or Eq.(33), respectively, as

$$K_{42}^{\Theta} = \frac{N_{42}}{N_1N_3^2} = \frac{b_1N_3 - \frac{1}{2}b_3N_1}{(b_3 - 2b_1)N_1N_3^2},$$

$$K_{42}^{\Theta} = \frac{a_{42}}{a_1a_3^2} = \frac{a_{\mathrm{ECl\cdot 2H_2O}}}{a_{\mathrm{ECl}}a_{\mathrm{H_2O}}^2},$$

$$K_{42}^{\Theta} = \frac{b_1a_{\mathrm{H_2O}} - \frac{1}{2}b_3a'_{\mathrm{ECl}}}{(b_3 - 2b_1)a'_{\mathrm{ECl}}a_{\mathrm{H_2O}}^2}$$

$$K_{42}^{\Theta}=\frac{N_{42}}{N_1N_3^2}=\frac{1-N_1-N_3}{N_1N_3^2},$$

$$K_{42}^{\Theta}=\frac{a_{42}}{a_1a_3^2}=\frac{a_{\mathrm{ECl}\cdot 2\mathrm{H_2O}}}{a_{\mathrm{ECl}}a_{\mathrm{H_2O}}^2}, \tag{34a}$$

$$K_{42}^{\Theta}=\frac{1-a'_{\mathrm{ECl}}-a_{\mathrm{H_2O}}}{a'_{\mathrm{ECl}}a_{\mathrm{H_2O}}^2} \tag{34b}$$

It should be specially pointed out that N_i is calculated based on pure matter as standard state and mole fraction x_i as concentration unit, which is the same as the reported $a_{\mathrm{H_2O}}$ from literatures. Usually, activity of H_2O, $a_{\mathrm{H_2O}}$, but not activity coefficient of H_2O, is reported in related literatures. Unfortunately, only activity coefficient f'_i, not a_i, is reported from literatures for solute i, which is based on infinite dilute solution as standard state and molality m_i as concentration unit. Hence, only $a_{\mathrm{H_2O}}$ can be applied to replace $N_{\mathrm{H_2O}}$, while, a_{ECl}, i.e., product of the reported activity coefficient f'_{ECl} and m_{ECl}, cannot be used to substitute for N_{ECl} because N_{ECl} is less than 1.0 while a_{ECl} can be much larger than 1.0 when m_i is high enough. Under the circumstances, the calculated a'_{ECl} from multiplying the reported f'_{ECl} by x_{ECl}, which is less than 1.0, is recommended to substitute N_{ECl} in Eq.(34a) or Eq.(34b)[7−9]. However, the calculated K_{42}^{Θ} from Eq.(34a) is certainly not equal to that from Eq.(34b) because Eq.(34a) is formulated from mass balance of solute i and solvent H_2O, while Eq.(34b) is based on mole fraction of all structural units in a close system as 1.0 by using N_i as concentration unit. Therefore, the reported $a_{\mathrm{H_2O}}$ from literature and product of the reported f'_{ECl} and x_{ECl} as a'_{ECl} are applied in Eq.(34a) to determine K_{42}^{Θ} according to IMCT[7−9].

When the calculated K_{42}^{Θ} from Eq. (34a) by using reported $a_{\mathrm{H_2O}}$ and a'_{ECl} $(=x_{\mathrm{KCl}}f'_{\mathrm{KCl}})$ from literatures is constant with a very narrow fluctuation in various x_{ECl} or m_{ECl}, the calculated K_{42}^{Θ} can be applied in the developed thermodynamic model as shown in equation groups of Eq.(31) and Eq.(33) or Eq.(32) and Eq.(33) to solve N_i, $\sum n_i$ and n_i. The expressions of L_i or L'_i and N'_i for ECl−H_2O binary solution with ECl·$2H_2O$ as complex hydrous salt molecule are the same as equations described in Eq.(14).

2.3.4 Model for binary system with ECl·$2H_2O$ as formed hydrous salt molecule with known $\Delta_rG_{\mathrm{m},i}^{\Theta}$

The structural units in ECl−H_2O binary solution with ECl·$2H_2O$ as formed hydrous salt molecule with known $\Delta_rG_{\mathrm{m},i}^{\Theta}$ consist of E^+ and Cl^- as simple ions, H_2O as simple molecule and ECl·$2H_2O$ as complex molecule. The mole numbers of ECl and H_2O in ECl−H_2O binary solution with ECl·$2H_2O$ as formed hydrous salt molecule before reaction equilibrium based on 1 kg H_2O are presented as $b_1=n_{\mathrm{ECl}}^0=m_{\mathrm{ECl}}$, $b_3=n_{\mathrm{H_2O}}^0=m_{\mathrm{H_2O}}$ =55.6 mol. The mole number of structural units in ECl−H_2O binary solution with ECl·$2H_2O$ as formed hydrous salt molecule under dynamic reaction equilibrium condition based on 1 kg H_2O can be expressed as $n_1=n_{\mathrm{E^+,\,ECl}}=n_{\mathrm{Cl^-,\,ECl}}=n_{\mathrm{ECl}}=m_{\mathrm{ECl}}$, $n_3=n_{\mathrm{H_2O}}$ =55.6, $n_{42}=n_{\mathrm{ECl}\cdot 2\mathrm{H_2O}}$. Hence, the total mole number of all structural units $\sum n_i$ in ECl−H_2O binary solution with ECl·$2H_2O$ as formed hydrous salt molecule under equilibrium condition based on 1 kg H_2O can be calculated according to the mass balance principle as

$$\sum n_i=2n_1+n_3+n_{42} \tag{35}$$

The mass balance of ECl and H_2O in ECl−H_2O binary solution based on 1 kg H_2O can be presented by Eq.(31) or Eq.(32), and equilibrium constant K_{42}^{Θ} can be calculated from $\Delta_rG_{\mathrm{m,\,ECl_2\cdot 2H_2O}}^{\Theta}$ by Eq.(13).

Therefore, the thermodynamic model of ECl−H_2O binary solution with ECl·$2H_2O$ as formed hydrous salt with known $\Delta_rG_{\mathrm{m},i}^{\Theta}$ is presented by combining of Eq.(31) and Eq.(33) or Eq.(32) and Eq.(33). Therefore, parameters as N_i, $\sum n_i$ and n_i in ECl−H_2O binary solution with ECl·$2H_2O$ as formed hydrous salt with known $\Delta_rG_{\mathrm{m},i}^{\Theta}$ can be solved. The expressions of L_i or L'_i and N'_i for ECl−H_2O binary solution with ECl·$2H_2O$ as complex hydrous salt molecule with known $\Delta_rG_{\mathrm{m},i}^{\Theta}$ are the same as equations described in Eq.(14).

2.3.5 Model for binary system with ECl·H_2O and ECl·$3H_2O$ as formed hydrous salt molecule with known $\Delta_rG_{\mathrm{m},i}^{\Theta}$

In the case of forming ECl·H_2O and ECl·$3H_2O$ as hydrous salt molecules with known $\Delta_rG_{\mathrm{m},i}^{\Theta}$, the structural units in ECl−H_2O binary solution are composed of E^+ and Cl^- as simple ions, H_2O as simple molecule, ECl·H_2O and ECl·$3H_2O$ as complex molecules. The mole numbers of ECl and H_2O in ECl−H_2O binary with ECl·H_2O and ECl·$3H_2O$ as formed hydrous salt molecules before reaction equilibrium based on 1 kg H_2O is presented as $b_1=n_{\mathrm{ECl}}^0=m_{\mathrm{ECl}}$, $b_3=n_{\mathrm{H_2O}}^0=m_{\mathrm{H_2O}}$ =55.6 mol. The mole number of structural units in ECl−H_2O binary solution with ECl·H_2O and ECl·$3H_2O$ as formed hydrous salt molecules under dynamic reaction equilibrium condition based on 1 kg H_2O can be expressed as $n_1=n_{\mathrm{E^+,\,ECl}}=n_{\mathrm{Cl^-,\,ECl}}=n_{\mathrm{ECl}}=m_{\mathrm{ECl}}$, $n_3=n_{\mathrm{H_2O}}$ =55.6, $n_{41}=n_{\mathrm{ECl}\cdot\mathrm{H_2O}}$, $n_{43}=n_{\mathrm{ECl}\cdot 3\mathrm{H_2O}}$. Hence, the total mole number of all structural units $\sum n_i$ based on 1 kg H_2O in ECl−H_2O binary solution with ECl·H_2O and ECl·$3H_2O$ as formed hydrous salt molecules under equilibrium condition can be calculated according to the mass balance principle as

$$\sum n_i=2n_1+n_3+n_{41}+n_{43} \tag{36}$$

The mass balance of ECl and H_2O in ECl−H_2O

binary solution with $ECl{\cdot}H_2O$ and $ECl{\cdot}3H_2O$ as formed hydrous salt molecules with known $\Delta_r G^{\Theta}_{m,i}$ can be presented by simplifying Eq.(22) as

$$b_1 = n^0_{ECl} = m_{ECl} = n_1 + n_{41} + n_{43}$$
$$= (\frac{1}{2}N_1 + N_{41} + N_{43})\sum n_i$$
$$= (\frac{1}{2}N_1 + K^{\Theta}_{41}N_1N_3 + K^{\Theta}_{43}N_1N_3^3)\sum n_i \quad (37a)$$

$$b_3 = n^0_{H_2O} = m_{H_2O} = n_3 + n_{41} + 3n_{43}$$
$$= \left(N_3 + N_{41} + 3N_{43}\right)\sum n_i$$
$$= \left(N_3 + K^{\Theta}_{41}N_1N_3 + 3K^{\Theta}_{43}N_1N_3^3\right)\sum n_i = 55.6 \quad (37b)$$

Eq.(23) and Eq.(24) can be rewritten for $ECl{-}H_2O$ binary solution with $ECl{\cdot}H_2O$ and $ECl{\cdot}3H_2O$ as formed hydrous salt molecules with known $\Delta_r G^{\Theta}_{m,i}$ as follows:

$$\frac{1}{2}b_3N_1 - b_1N_3 + K^{\Theta}_{41}(b_3 - b_1)N_1N_3 +$$
$$K^{\Theta}_{43}(b_3 - 3b_1)N_1N_3^3 = 0 \quad (38)$$

$$N_1 + N_3 + K^{\Theta}_{41}N_1N_3 + K^{\Theta}_{43}N_1N_3^3 = 1 \quad (39)$$

The thermodynamic model of $ECl{-}H_2O$ binary solution with $ECl{\cdot}H_2O$ and $ECl{\cdot}3H_2O$ as formed hydrous salt molecules with known $\Delta_r G^{\Theta}_{m,i}$ is represented by combining Eq.(37) and Eq.(39) or Eq.(38) and Eq.(39). The parameters as N_i, $\sum n_i$ and n_i can be solved by combining Eq.(37) and Eq.(39) or Eq.(38) and Eq.(39). The equilibrium constants of K^{Θ}_{41} and K^{Θ}_{43}, L_i or L'_i and N'_i for $ECl{-}H_2O$ binary solution with $ECl{\cdot}H_2O$ and $ECl{\cdot}3H_2O$ as formed hydrous salt molecules with known $\Delta_r G^{\Theta}_{m,i}$ are also the same as equations described in Eq.(13) and Eq.(14), respectively.

3 Application of universal thermodynamic model

3.1 Application of developed models in binary aqueous solutions

3.1.1 Model application in binary aqueous solutions without any hydrous salt molecule formed

The representatives of $ECl{-}H_2O$ binary solutions without any hydrous salt complex molecule generated are $KCl{-}H_2O$, $CsCl{-}H_2O$, $KBr{-}H_2O$ and $NH_4Br{-}H_2O$ according to their phase diagrams[16]. Hence, the mass action concentrations of structural units or ion couples in $KCl{-}H_2O$[10], $CsCl{-}H_2O$[10], $KBr{-}H_2O$[12] and $NH_4Br{-}H_2O$[12] binary aqueous solutions at 298.15 K have been calculated by the developed thermodynamic model of calculating mass action concentrations for structural units or ion couples in $ECl{-}H_2O$ binary solution without any hydrous salt complex molecule generated. Taking $KCl{-}H_2O$[10] binary solution as an example, the application of the developed universal thermodynamic model is briefly demonstrated hereinbelow.

The mass action concentrations of KCl and H_2O in $KCl{-}H_2O$ binary solution without any hydrous salt molecule formed at 298.15 K can be calculated by Eq.(29) directly. The transformation coefficients L'_{KCl} and L_{H_2O} in various molalities of KCl are listed in Table 1, the relationships between N_{KCl} and reported activity[17] a_{KCl} $(=m_{KCl}f'_{KCl})$ against x_{KCl}, N'_{H_2O} and reported a_{H_2O}[17] against x_{H_2O}, are illustrated in Fig.1, respectively.

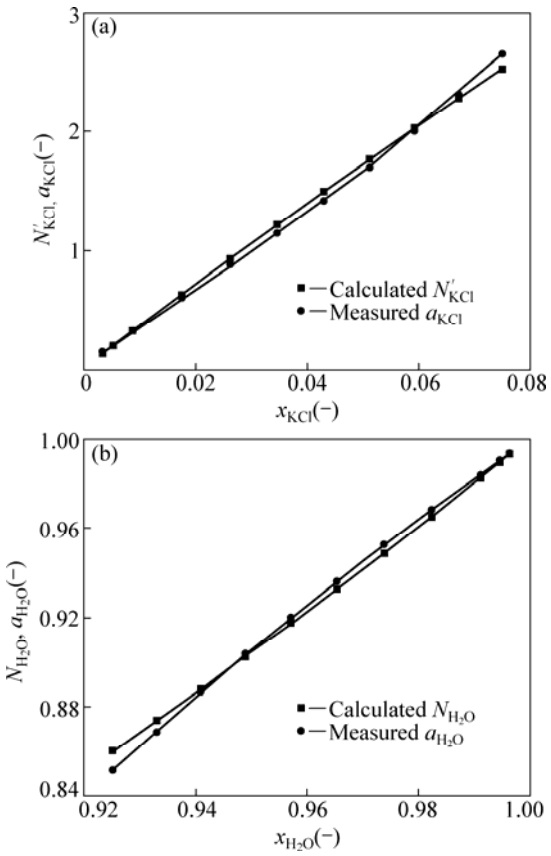

Fig.1 Comparison of calculated mass action concentrations N'_{KCl} and N_{H_2O} with measured activities of KCl and H_2O as a_{KCl} $(=m_{KCl}f'_{KCl})$ and a_{H_2O} in Ref.[17] for $KCl{-}H_2O$ binary solution without forming any complex hydrous salt molecule at 298.15 K

It can be seen from Table 1 that the transformation coefficients of KCl (L'_{KCl}) keep constant with a small fluctuation range with an average datum of 18.099; meanwhile, L_{H_2O} is also stable with 1.000 as average datum. It can be also observed from Fig.1 that N'_{KCl} and N_{H_2O} are in good agreement with the report in Ref.[17] a_{KCl} $(=m_{KCl}f'_{KCl})$ and a_{H_2O}. Therefore, it can be suggested that the calculated mass action concentrations can be applied to present reaction ability of KCl and H_2O, and have a close corresponding relation with reported activity data; all hypotheses used

Table 1 Transformation coefficients between calculated mass action concentrations and reported activities of structural units or ion couples for investigated six strong electrolyte aqueous solutions with various molalities of solutes at 298.15 K and equilibrium constant of forming $NaCl·2H_2O$ in $NaCl-H_2O$ binary solution at 298.15 K

$KCl-H_2O$			$NaCl-H_2O$				$KF-H_2O$		HNO_3-H_2O		$NaCl-KCl-H_2O$ $r=m_{NaCl}/m_{KCl}=4.0$				$RbCl-RbNO_3-H_2O$ $I=m_{RbCl}+m_{RbNO_3}=$ 0.50 mol/kg (H_2O)				
m_{KCl}	L'_{KCl}	L_{H_2O}	m_{NaCl}	K^{Θ}_{42}	L'_{NaCl}	L_{H_2O}	m_{KF}	L'_{KF}	m_{HNO_3}	L'_{HNO_3}	m_{NaCl}	m_{NaCl}	L'_{NaCl}	L'_{KCl}	v_{RbNO_3}	m_{RbCl}	m_{NbNO_3}	L'_{RbCl}	L'_{RbNO_3}
0.2	20.048	1.001	0.2	0.881	62.351	0.998	0.1	1 987	0.1	95 250	0.4	0.1	57.524	17.813	0.0	0.5	0.0	17.81	−
0.3	19.249	1.001	0.3	0.938	60.034	0.997	0.2	1 864	0.2	89 277	0.8	0.2	54.305	16.550	0.2	0.4	0.1	17.55	16.05
0.5	18.338	1.002	0.5	1.016	57.196	0.995	0.4	1 716	0.4	83 561	1.2	0.3	53.061	15.954	0.4	0.3	0.2	17.29	15.75
1.0	17.338	1.003	1.0	1.119	54.200	0.991	0.6	1 646	0.6	80 621	1.6	0.4	52.833	15.693	0.6	0.2	0.3	17.03	15.46
1.5	17.023	1.004	1.5	1.168	53.251	0.986	0.8	1 605	0.8	78 514	2.0	0.5	53.254	15.592	0.8	0.1	0.4	16.78	15.18
2.0	17.016	1.004	2.0	1.188	53.294	0.979	1.0	1 573	1.0	77 104	2.4	0.6	54.139	15.603					
2.5	17.210	1.003	2.5	1.189	53.885	0.972	2.0	1 516	2.0	74 592	3.2	0.8	57.400	15.826					
3.0	17.525	1.002	3.0	1.172	55.000	0.964	3.0	1 531	3.0	74 495	4.0	1.0	62.333	16.223					
3.5	17.935	0.999	3.5	1.142	56.539	0.953	4.0	1 591	4.0	76 386									
4.0	18.412	0.994	4.0	1.096	58.487	0.944	5.0	1 672	5.0	78 311									
4.5	18.992	0.990	4.5	1.040	60.752	0.933	6.0	1 781	6.0	80 170									
			5.0	0.972	63.396	0.921													
			5.5	0.891	66.406	0.907													
			6.0	0.798	69.772	0.894													
Ave.	18.099	1.000		1.043	58.897	0.960		1 611		80 753			55.606	16.157				17.29	15.61

in the developed thermodynamic model are reasonable and can depict the intrinsic structure of $KCl-H_2O$ binary aqueous solution.

3.1.2 Model application in binary system with $ECl·2H_2O$ as formed hydrous salt molecule with unknown $\Delta_r G^{\Theta}_{m,i}$

$NaCl-H_2O$ is a representative of $ECl-H_2O$ binary aqueous solution with $ECl·2H_2O$ as hydrous salt molecule with unknown $\Delta_r G^{\Theta}_{m,i}$ based on its phase diagram[18]. The developed thermodynamic model of calculating mass action concentrations for structural units or ion couples in $ECl-H_2O$ binary solution with $ECl·2H_2O$ as formed hydrous salt molecule without $\Delta_r G^{\Theta}_{m,i}$ has been successfully applied in $NaCl-H_2O$ binary solution[10] at 298.15 K by using the determined stable equilibrium constant K^{Θ}_{42} through substituting N_{NaCl} in formula of K^{Θ}_{42} by product of reported f'_{NaCl} [17] and x_{NaCl} as a_{NaCl} and replacing N_{H_2O} in formula of K^{Θ}_{42} by the reported a_{H_2O}, respectively. The determined K^{Θ}_{42} has an average datum as 1.043 with a small fluctuation in various molalities of NaCl in $NaCl-H_2O$ binary solution as shown in Table 1 at 298.15 K. The transformation coefficient L'_{NaCl} and L_{H_2O} are stable with 58.897 and 0.960 as average datum, respectively, as shown in Table 1.

The transformed mass action concentrations N'_{NaCl} and N_{H_2O} have been compared with the reported activities[17], a_{NaCl} $(=m_{NaCl}f'_{NaCl})$ and a_{H_2O}, in Fig.2 in various mole fractions of NaCl and H_2O before equilibrium, respectively. There is a good corresponding relation between N'_{NaCl} and a_{NaCl}, N'_{H_2O} and a_{H_2O}, with small deviation, respectively. Therefore, $NaCl·2H_2O$ surely exists in $NaCl-H_2O$ binary solution as described in phase diagram of $NaCl-H_2O$ binary solution[18], the developed thermodynamic model of $NaCl-H_2O$ binary solution can represent the intrinsic structure of $NaCl-H_2O$ binary solution.

3.1.3 Model application in binary system with $ECl·2H_2O$ as formed hydrous salt molecule with known $\Delta_r G^{\Theta}_{m,i}$

$NaBr-H_2O$, $KF-H_2O$ and $ZnBr_2-H_2O$ are representatives of $ECl-H_2O$ binary aqueous solution with $ECl·2H_2O$ as hydrous salt molecule with known $\Delta_r G^{\Theta}_{m,i}$ from their phase diagrams[16]. The established thermodynamic model of calculating mass action concentrations for structural units or ion couples in $ECl-H_2O$ binary solution with $ECl·2H_2O$ as formed hydrous salt molecule with known $\Delta_r G^{\Theta}_{m,i}$ has been

successfully applied in NaBr−H_2O and KF−H_2O[11], and $ZnBr_2$−H_2O[12] binary aqueous solutions at 298.15 K. Taking KF−H_2O[11] binary solution as an example to demonstrate the thermodynamic model of binary solution with KF·$2H_2O$ as formed hydrous salt molecule with known $\Delta_r G^{\Theta}_{m,i}$ at 298.15 K, the calculated L'_{KF} in various molalities of KF has an average datum of 1611.0 as summarized in Table 1.

The transformed mass action concentration N'_{KF} and reported activity[19] $a_{KF}(=m_{KF}f'_{KF})$ are compared in Fig.3. There is a good corresponding relation between N'_{KF} and a_{KF} $(=m_{KF}f'_{KF})$ with a small deviation. It can be seen from Table 1 that the transformation coefficient of KF (L'_{KF}) are relatively constant with 1611.0 as an average value. Hence, the hypotheses in the developed thermodynamic model of KF−H_2O binary system are reasonable; the calculated mass action concentration of KF can represent reaction ability of KF in KF−H_2O binary system; KCl·$2H_2O$ surely exists in KF−H_2O binary solution as described in phase diagram of KF−H_2O binary solution[16]; the established thermodynamic model of KCl−H_2O binary solution can represent the intrinsic structural properties of KCl−H_2O binary solution.

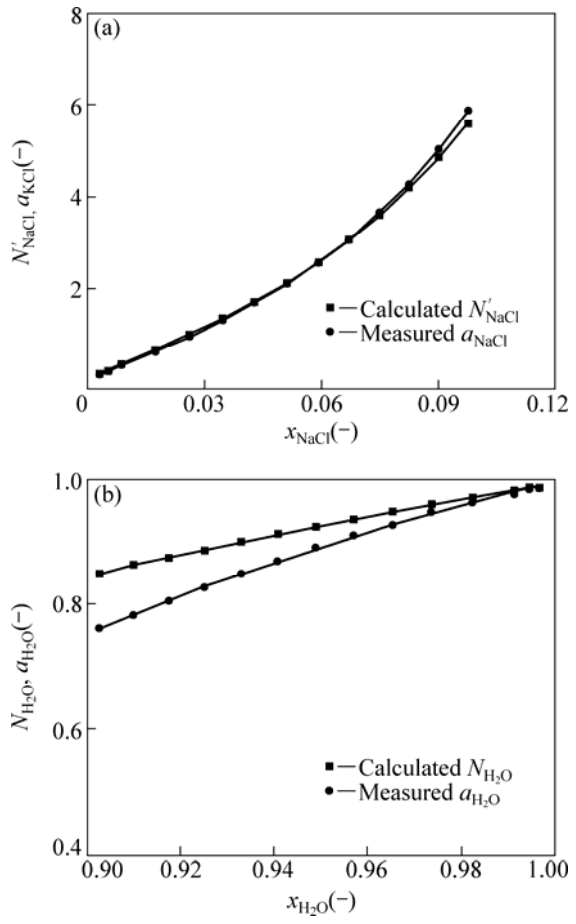

Fig.2 Comparison of calculated mass action concentrations N'_{NaCl} and N_{H_2O} with measured activities of NaCl and H_2O as a_{NaCl} $(=m_{NaCl}f'_{NaCl})$ and a_{H_2O}, in Ref.[17] for NaCl−H_2O binary solution with NaF·$2H_2O$ as formed hydrous salt molecule at 298.15 K

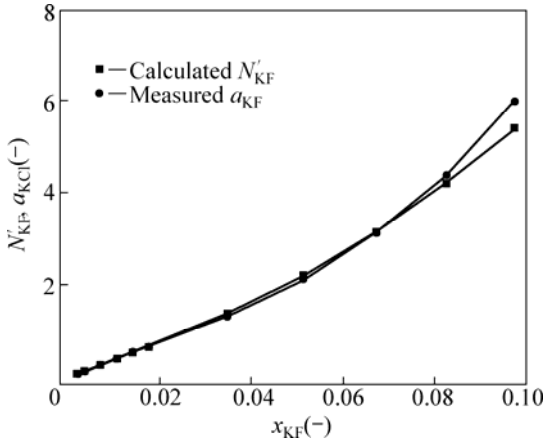

Fig.3 Comparison of calculated mass action concentration N'_{KF} with measured activity of KF as a_{KF} $(=m_{KF}f'_{KF})$ in Ref.[19] for KF−H_2O binary solution with KF·$2H_2O$ as formed hydrous salt molecule at 298.15 K

3.1.4 Model application in binary system with ECl·H_2O and ECl·$3H_2O$ as formed hydrous salt molecules with known $\Delta_r G^{\Theta}_{m,i}$

HNO_3−H_2O is a representative of ECl−H_2O binary aqueous solution with ECl·H_2O and ECl·$3H_2O$ as formed hydrous salt molecules with known $\Delta_r G^{\Theta}_{m,i}$ from its phase diagram[16]. The developed thermodynamic model of calculating mass action concentrations for structural units or ion couples in ECl−H_2O binary with ECl·H_2O and ECl·$3H_2O$ as formed hydrous salt molecules with known $\Delta_r G^{\Theta}_{m,i}$ has been successfully applied in HNO_3−H_2O binary solution at 298.15 K as reported in previous publication[11]. The calculated L'_{HNO_3} has a narrow deviation with an average of 80 753.0 in large molality range as listed in Table 1. The transformed mass action concentrations of HNO_3 N'_{HNO_3} and reported activity[19] a_{HNO_3} $(=m_{HNO_3}f'_{HNO_3})$ with mole fraction x_{HNO_3} before equilibrium as horizontal axis are compared in Fig.4. There is a good corresponding relationship between N'_{HNO_3} and a_{HNO_3} $(=m_{HNO_3}f'_{HNO_3})$ with a small deviation. It can be deduced from Fig.4 that the structural properties of considering HNO_3·H_2O and HNO_3·$3H_2O$ as formed hydrous salt molecules in HNO_3−H_2O binary solution from phase diagram[16] are reasonable.

3.2 Application of developed models in ternary aqueous solutions

3.2.1 Model application in ternary systems with formed hydrous salt molecules

The developed thermodynamic model of calculating mass action concentrations for structural units or ion

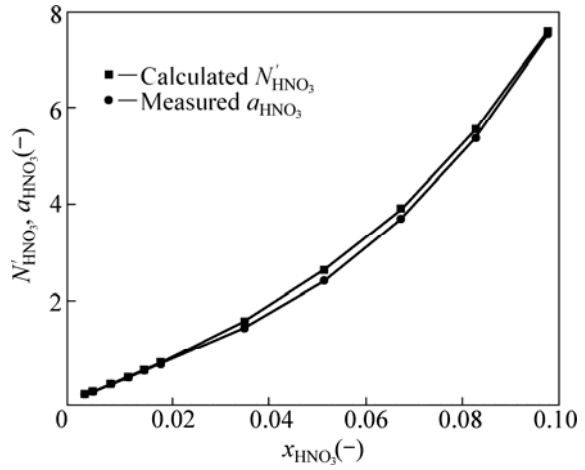

Fig.4 Comparison of calculated mass action concentration N'_{HNO_3} with measured activity of HNO_3 a_{HNO_3} $(=m_{HNO_3}f'_{HNO_3})$ in Ref.[19] for HNO_3−H_2O binary solution with $HNO_3{\cdot}H_2O$ and $HNO_3{\cdot}3H_2O$ as formed hydrous salt molecules at 298.15 K

couples in ternary aqueous solution has been successfully applied in NaCl−KCl−H_2O[13] and $NaClO_4$−NaF−H_2O [15] ternary solutions with formed hydrous salt molecules at 298.15 K. Choosing NaCl−KCl−H_2O ternary solution with $NaCl{\cdot}2H_2O$ as hydrous salt molecule at 298.15 K as an example, the structural units in NaCl−KCl−H_2O ternary solution are composed of Na^+, K^+, and Cl^- as simple ions, H_2O as simple and $NaCl{\cdot}2H_2O$ as complex molecules from the phase diagram[18]. The mass balance of NaCl, KCl and H_2O in NaCl−KCl−H_2O ternary solution based on 1 kg H_2O shown in Eq.(10) can be simplified as

$$b_1 = n^0_{NaCl} = m_{NaCl} = n_1 + n_{42} = (\frac{1}{2}N_1 + N_{42})\sum n_i = (\frac{1}{2}N_1 + K^{\Theta}_{42}N_1N_3^2)\sum n_i \quad (40a)$$

$$b_2 = n^0_{FCl} = m_{KCl} = n_2 = \frac{1}{2}N_2\sum n_i \quad (40b)$$

$$b_3 = n^0_{H_2O} = m_{H_2O} = n_3 + 2n_{42} = (N_3 + 2N_{42})\sum n_i = (N_3 + 2K^{\Theta}_{42}N_1N_3^2)\sum n_i = 55.6 \quad (40c)$$

Eq.(11) and Eq.(12) can be rewritten for NaCl−KCl−H_2O ternary solution as follows:

$$\frac{1}{2}b_3N_1 - b_1N_3 + K^{\Theta}_{42}(b_3 - 2b_1)N_1N_3^2 = 0 \quad (41a)$$

$$\frac{1}{2}b_3N_2 - b_2N_3 - 2b_2K^{\Theta}_{42}N_1N_3^2 = 0 \quad (41b)$$

$$\sum N_i = N_1 + N_2 + N_3 + N_{42} = N_1 + N_2 + N_3 + K^{\Theta}_{42}N_1N_3^2 = 1 \quad (42)$$

Therefore, the equation groups of Eq.(40) and Eq.(42) or Eq.(41) and Eq.(42) are composed of the universal thermodynamic model of calculation mass action concentrations for structural units or ion couples N_i in NaCl−KCl−H_2O ternary solution, respectively. The mass action concentrations of NaCl, KCl and H_2O in NaCl−KCl−H_2O ternary solution have been calculated and reported in detail in previous publication[13] in different mole number ratios of NaCl to KCl, i.e., r=m_{NaCl}/m_{KCl}, as 0.2, 0.5, 1.0, 2.0, 3.0, and 4.0, respectively, under condition of knowing K^{Θ}_{42} as described in Section 3.1.2 as 1.042[13]. The transformed mass action concentration N'_{NaCl}, N'_{KCl} and N_{H_2O} have been compared with the reported activities[20], a_{NaCl} $(=m_{NaCl}f'_{NaCl})$, a_{KCl} $(=m_{KCl}f'_{KCl})$ and a_{H_2O}, with different r.

As a representative of results, the transformation coefficients L'_{NaCl} and L'_{KCl} with r of 4.0 are listed in Table 1 as 55.606 and 16.157, respectively; meanwhile, comparison of N'_{NaCl}, N'_{KCl} and N_{H_2O} with the reported activities[20], a_{NaCl} $(=m_{NaCl}f'_{NaCl})$, a_{KCl} $(=m_{KCl}f'_{KCl})$ and a_{H_2O}, is also given in Fig.5 with r of 4.0, respectively.

It can be observed from Fig.5 that the transformed mass action concentrations N'_{NaCl}, N'_{KCl} and N_{H_2O}, are in good agreement with the reported activities[20], a_{NaCl} $(=m_{NaCl}f'_{NaCl})$, a_{KCl} $(=m_{KCl}f'_{KCl})$ and a_{H_2O} with r of 4.0. It is shown from Table 1 that L'_{NaCl} and L'_{KCl} remain constant with small deviations with r of 4.0. Hence, the developed thermodynamic model of calculating mass action concentrations for structural units or ion couples in NaCl−KCl−H_2O ternary solution can be successfully applied to predict reaction ability and reflect structural characteristics.

3.2.2 Model application in ternary systems without any hydrous salt molecule formed

The developed thermodynamic model for ternary solution without any hydrous salt molecule formed has been successfully applied in RbCl−$RbNO_3$−H_2O ternary solution[14] at 298.15 K. Certainly, the structural units in RbCl−$RbNO_3$−H_2O ternary solution at 298.15 K are composed of Rb^+, Cl^- and NO_3^- as simple ions, H_2O as simple molecule from the phase diagram[18]. The mass balance of RbCl, $RbNO_3$ and H_2O in RbCl−$RbNO_3$−H_2O ternary solution based on 1 kg H_2O shown in Eq.(10) can be simplified as

$$b_1 = n^0_{RbCl} = m_{RbCl} = n_1 = \frac{1}{2}N_1\sum n_i \quad (43a)$$

$$b_2 = n^0_{RbNO_3} = m_{RbNO_3} = n_2 = \frac{1}{2}N_2\sum n_i \quad (43b)$$

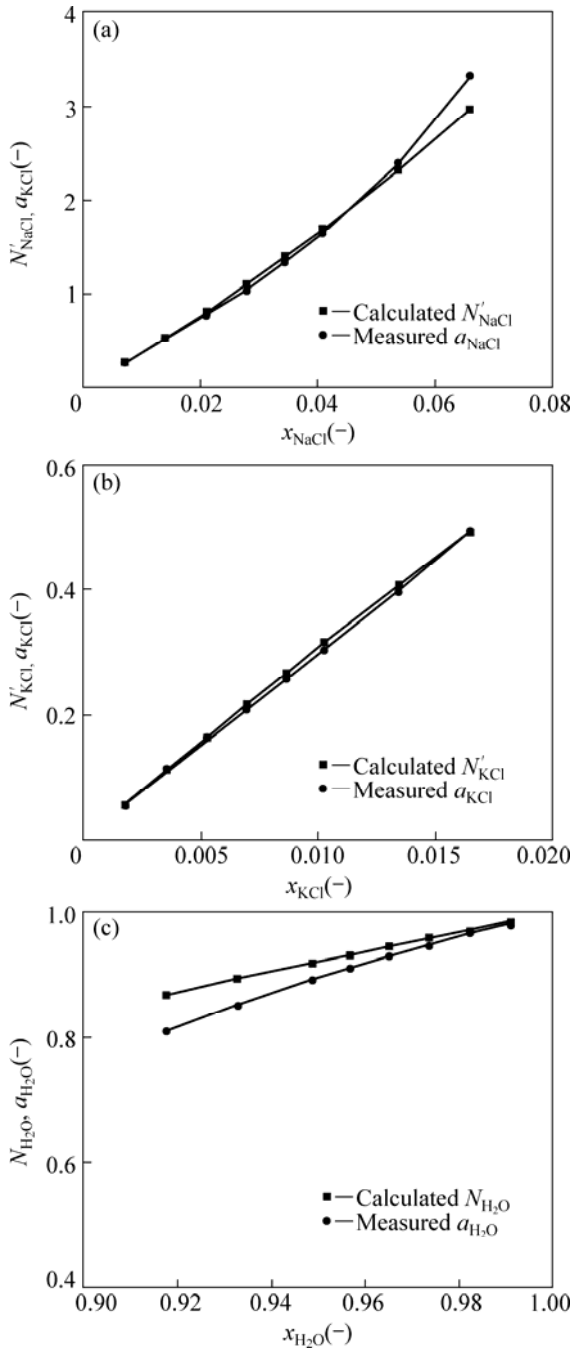

Fig.5 Comparison of calculated mass action concentrations N'_{NaCl}, N'_{KCl} and N_{H_2O} with reported activities of NaCl, KCl and H_2O as a_{NaCl} $(=m_{NaCl}f'_{NaCl})$, a_{KCl} $(=m_{KCl}f'_{KCl})$ and a_{H_2O} in Ref.[20] for NaCl−KCl−H_2O ternary system with r of 4.0 at 298.15 K

$$b_3 = n^0_{H_2O} = m_{H_2O} = n_3 = N_3\sum n_i = 55.6 \quad (43c)$$

Eq.(11) and Eq.(12) can be expressed for RbCl−$RbNO_3$−H_2O ternary solution, respectively, as

$$\frac{1}{2}b_3N_1 - b_1N_3 = 0 \quad (44a)$$

$$\frac{1}{2}b_3N_2 - b_2N_3 = 0 \quad (44b)$$

$$\sum N_i = N_1 + N_2 + N_3 = 1 \quad (45)$$

Therefore, the equation groups of Eq.(43) and Eq.(45) or Eq.(44) and Eq.(45) are composed of the universal thermodynamic model of calculation mass action concentrations for structural units or ion couples N_i in RbCl−$RbNO_3$−H_2O ternary solution, respectively. The mass action concentrations of RbCl, $RbNO_3$ and H_2O in RbCl−$RbNO_3$−H_2O ternary solution have been calculated and reported in detail in previous publication[14] in a range of the total ionic strength, i.e., $I = m_{NaClO_4} + m_{NaF}$, from 0.1 to 0.9 mol/kg (H_2O) in 0.1 mol/kg (H_2O) step with different ionic strength fractions of $NaClO_4$, $v_{RbNO_3} = m_{RbNO_3}/I = m_{RbNO_3}/(m_{RbCl} + m_{RbNO_3})$, as 0, 0.2, 0.4, 0.5, 0.6 and 0.8, respectively[14]. The transformed mass action concentrations N'_{RbCl} and N'_{RbNO_3} have been compared with the reported activities[21], a_{RbCl} $(=m_{RbCl}f'_{RbCl_3})$ and a_{RbNO_3} $(=m_{RbNO_3}f'_{RbNO_3})$ with different I values reported elsewhere[14].

As a representative of results, the transformation coefficients L'_{RbCl} and L'_{RbNO_3} with I of 0.5 mol/kg (H_2O) are listed in Table 1, meanwhile, comparison of N'_{RbCl} and N'_{RbNO_3} with the reported activities[21], a_{RbCl} $(=m_{RbCl}f'_{RbCl_3})$ and a_{RbNO_3} $(=m_{RbNO_3}f'_{RbNO_3})$, are also given in Fig.6 under condition of I of 0.5 mol/kg (H_2O), respectively.

It can be obtained from Table 1, Fig.6 and other results described in previous publication elsewhere[14] that N'_{RbCl} and N'_{RbNO_3} are in good agreement of reported activities[21], a_{RbCl} $(=m_{RbCl}f'_{RbCl_3})$ and a_{RbNO_3} $(=m_{RbNO_3}f'_{RbNO_3})$ in a large change range of I; the transformation coefficients, L'_{RbCl} and L'_{RbNO_3}, listed in Table 1, keep constant with 17.29 and 15.61 as average datum with small deviations under condition of I as 0.50 mol/kg (H_2O) for various v_{RbNO_3}, respectively. Therefore, the developed thermodynamic model of calculation mass action concentrations for structural units or ion couples in RbCl−$RbNO_3$−H_2O ternary solution can be successfully applied to predict reaction ability and reflect structural characteristics.

4 Discussion and error analysis

Although the transformed mass action concentrations of structural units or ion couples N'_i in various binary and ternary aqueous solutions have good consistency with the reported activity a_i $(=m_if'_i)$, small difference between N'_i and a_i can be observed for some solutions in high concentration range of solute. The

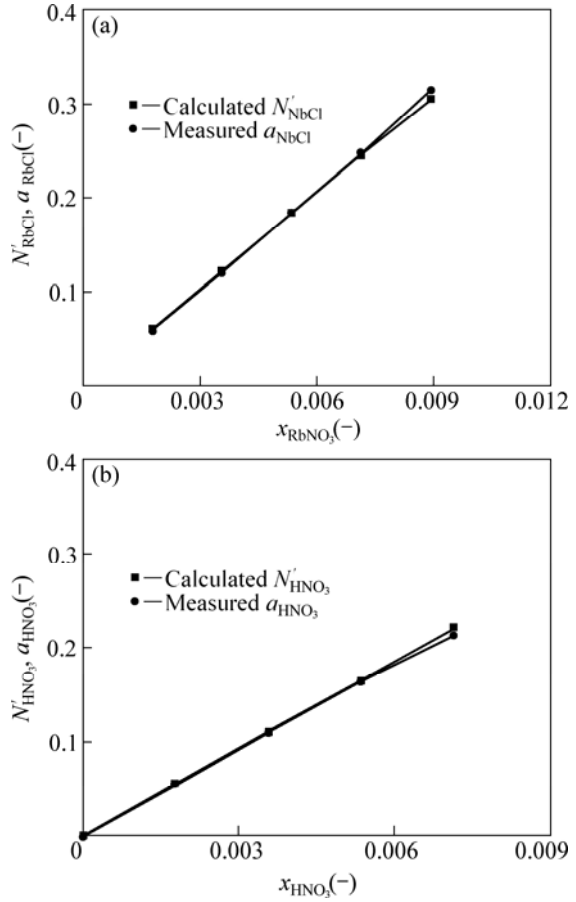

Fig.6 Comparison of mass action concentrations N'_{RbCl} and N'_{RbNO_3} with reported activities of RbCl and $NbNO_3$ as a_{RbCl} and a_{RbNO_3} in Ref.[21] for RbCl−$RbNO_3$−H_2O ternary solution with total ionic strength I of 0.5 mol/kg (H_2O) at 298.15 K

reasons of small errors of the transformed mass action concentrations of structural units or ion couples with the reported activities can be summarized as follows:

1) Solute in high concentration range almost reaches saturation.

2) A transformation coefficient L'_i must be used when comparing the calculated mass action concentration N_i and the reported activity a_i $(=m_i f'_i)$ of solute i. However, the calculated N_i is based on pure matter as standard state and mole fraction x_i as concentration unit, while the reported a_i $(=m_i f'_i)$ is relative to infinite dilution as standard state and molality m_i as concentration unit. The average transformation coefficient $\overline{L'_i}$ is the average of ratios for a_i to N_i with various solute concentrations in the investigated concentration range, some errors can be certainly generated from the average calculated transformation coefficient $\overline{L'_i}$. The idea method is to compare the calculated mass action concentrations of structural units or ion couples and reported activities relative to pure matter as standard state and mole fraction x_i as concentration unit for solutes.

3) To some strong electrolyte aqueous solutions, equilibrium constant K_i^{Θ} of reactions for forming hydrous salt molecules cannot be accurately calculated because its free formation energy $\Delta_r G_{m,i}^{\Theta}$ cannot be found from related literatures. The suggested method to get K_i^{Θ} by ZHANG[7−9] is calculating K_i^{Θ} by substituting N_i in formula of K_i^{Θ} by product of reported activity coefficient f'_i multiplying by x_i as a'_i $(=x_i f'_i)$ for solute, but not traditional activity a_i $(=m_i f'_i)$ for solute, with a relatively stable in an acceptable fluctuation range. It is not an absolutely correct, but an acceptable method. The average datum K_i^{Θ} can certainly induce some deviations.

5 Conclusions

1) A universal thermodynamic model of calculating mass action concentrations for structural units or ion couples in ternary and binary strong electrolyte aqueous solutions based on the ion and molecular coexistence theory has been developed and verified in four kinds of binary and two kinds of ternary aqueous solutions. The calculated mass action concentrations of structural units or ion couples in four binary and two ternary solutions have good agreement with the reported activity data from literatures after shifting the standard state and concentration unit.

2) The mass action concentrations of structural units or ion couples calculated from the developed universal thermodynamic model for calculating mass action concentrations of structural units or ion couples in ternary and binary aqueous solutions can be applied to predict reaction ability of components in ternary and binary strong electrolyte aqueous solutions.

3) The developed universal thermodynamic model for ternary and binary aqueous solutions provides a useful method to judge structural characteristics of ternary and binary strong electrolyte aqueous solutions.

4) It is confirmed from the developed universal thermodynamic model for ternary and binary aqueous solutions that ternary and binary strong electrolyte aqueous solutions are composed of cations and anions as simple ions, H_2O as simple molecule, and other hydrous salt compounds as complex molecules.

5) The calculated mass action concentrations of structural units or ion couples in the investigated ternary and binary strong electrolyte aqueous solutions strictly follow the mass action law.

Symbol list

a_i—Reported activity of component i in aqueous solutions as $m_i f'_i$, (−);

a'_i—Activity of component i in aqueous solutions

defined as $x_i f_i'$, (−);

b_i—Total mole number of components i before chemical reaction equilibrium in aqueous solutions, mol;

f_i'—Activity coefficient of component i relative to infinite dilute solution as standard state and molality m_i as concentration unit, (−);

I—Total ionic strength of solutes i and j in aqueous solutions as m_i+m_j, mol/kg (H_2O);

K^{Θ}—Chemical equilibrium constant, (−);

L_i'—Transformation coefficient of component i between the calculated mass action concentration chosen pure matter as standard state and mole fraction x_i as concentration unit and the reported activity relative to infinite dilute solution as standard state and molality m_i as concentration unit, (−);

$\overline{L_i'}$—Average of L_i', (−);

m_i—Molality of component i in aqueous solutions, mol/kg (H_2O);

M_{H_2O}—Mole mass of H_2O, 18 g/mol;

n_i^0—Total mole number of components i before chemical reaction in aqueous solutions, same as b_i, mol;

n_i—Equilibrium mole number of structural unite i or ion couple i in aqueous solutions, mol;

N_i—Mass action concentrations of structural unite i or ion couple i in aqueous solutions, (−);

N_i'—Transformed mass action concentration of structural unit i or ion couple i in aqueous solutions, (−);

R—Gas constant, 8.314×10^{-3} kJ/(mol·K);

r—Ratio of molality for solute i to solute j, (−);

T—Absoulte temperature, K;

v_i—Ionic strength fraction of component i as m_i/I, (−);

x_i—Mole fraction of components i before equilibrium, (−);

$\Delta_r G_{m,i}^{\Theta}$—Standard molar Gibbs free energy of forming hydrous salt compound i as complex molecule, kJ/mol;

$\sum n_i$—Total mole number of all structural units in aqueous solutions under equilibrium condition, mol;

$\sum n_i^0$—Total mole number of structural units before dynamic equilibrium, mol.

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计算水溶液结构单元或离子对的质量作用浓度通用热力学模型及其在二元和三元水溶液中的应用

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摘 要：基于离子与分子共存理论，建立了计算二元和三元强电解质水溶液中结构单元或离子对的质量作用浓度的通用热力学模型；同时，采用 4 种二元水溶液和 2 种三元水溶液验证该通用热力学模型。通过转换标准态和浓度单位，用所建立的通用热力学模型计算出的 298.15 K 时 4 种二元水溶液和 2 种三元水溶液中结构单元或离子对的质量作用浓度和文献中报道的活度值吻合得很好。因此，可采用本研究提出的通用热力学模型计算出的二元和三元水溶液结构单元或离子对的质量作用浓度预报二元和三元强电解质水溶液中组元的反应能力；同样，也可证实本研究提出的通用热力学模型的假设条件是正确和合理的，即强电解质水溶液是由阳离子和阴离子、H_2O 分子和其他水合盐复杂分子组成的。基于该通用热力学模型计算出的二元和三元强电解质水溶液结构单元或离子对的质量作用浓度严格服从质量作用定律。

关键词：通用热力学模型；质量作用浓度；活度；二元水溶液；三元水溶液；离子−分子共存理论；结构单元；离子对；组元

(Edited by YANG Hua)