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Calculating models of mass action concentrations for structural units or ion couples in RbCl-H_2O binary system and RbCl-$RbNO_3$-H_2O ternary system

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Abstract: Thermodynamic models of calculating mass action concentrations for structural units or ion couples in RbCl-H_2O binary and RbCl-$RbNO_3$-H_2O ternary strong electrolyte aqueous solutions were developed based on the ion and molecule coexistence theory at 298.15 K. A transformation coefficient is needed to compare the calculated mass action concentration and the reported activity because they are obtained at different standard states and concentration units. The results show that the transformation coefficients between the calculated mass action concentrations and the reported activities of the same structural units or ion couples in RbCl-H_2O binary and RbCl-$RbNO_3$-H_2O ternary strong electrolyte aqueous solutions change in a very narrow range. The transformed mass action concentrations of structural units or ion couples in RbCl-H_2O binary system are in good agreement with the reported activities. The transformed mass action concentrations of RbCl and $RbNO_3$ in RbCl-$RbNO_3$-H_2O ternary solution are also in good agreement with the reported activities, a_{RbCl} and a_{RbNO_3}, with different total ionic strengths as 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0, 3.0 and 3.5 mol/kg, respectively. All those results mean the developed thermodynamic model of strong electrolyte aqueous solutions can reflect structural characteristics of RbCl-H_2O binary and RbCl-$RbNO_3$-H_2O ternary strong electrolyte aqueous solutions and the mass action concentration also strictly follows the mass action law.

Key words: mass action concentration; activity; ion and molecule coexistence theory; RbCl-H_2O; RbCl-$RbNO_3$-H_2O; structural unit; ion couple

1 Introduction

The ion and molecule coexistence theory developed by ZHANG[1−8] since 1980s has been successfully applied to calculate mass action concentrations of structural units or ion couples in binary metallic melts[1], binary metallurgical slags[2], ternary metallic melts[3−4], ternary metallurgical slags[5−6] and multi-component complex metallurgical slags[7−8]. Expanding application scopes of the ion and molecule coexistence theory to electrolyte aqueous solutions is an interesting and challenge task. It is well-known that electrolyte aqueous solutions can be applied in many fields, such as biochemical engineering[9−12], chemical engineering [13], hydrometallurgy, environmental chemistry, and geochemistry[14]. However, activity of components in electrolyte aqueous solutions, as one of main thermodynamic properties, is not enough, or scarce and contradictory among literatures, or imprecise to fulfill its practical applications.

It has been well-known that not only ions but also some simple or complex molecules can exist in electrolyte aqueous solutions. Therefore, the ion and molecule coexistence theory, which is developed to determine mass action concentration of structural units or ion couples to present reaction ability like activity, can be applied to describe reaction ability of electrolyte aqueous solutions.

Based on the successful applications of the ion and molecule coexistence theory for calculating mass action concentrations of structural units or ion couples in KCl-H_2O, CsCl-H_2O, NaCl-H_2O, $BaCl_2$-H_2O[15], NaBr-H_2O, $LiNO_3$-H_2O, HNO_3-H_2O, KF-H_2O binary strong electrolyte aqueous solutions[16], and NaCl-KCl-H_2O[17], it can be generally deduced that the calculated

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mass action concentrations of structural units or ion couples have close corresponding relation with the reported activities for strong electrolyte aqueous solutions. Therefore, the calculated mass action concentrations of structural units or ion couples from the ion and molecular coexistence theory can be effectively applied to present reaction ability of components in binary and ternary strong electrolyte aqueous solutions.

To further extend application scopes of the ion and molecule coexistence theory into multi-component strong electrolyte aqueous solutions, a thermodynamic model of calculating mass action concentrations for structural units or ion couples in $RbCl$-$RbNO_3$-H_2O ternary strong electrolyte aqueous solution has been proposed according to the developed universal thermodynamic model of calculating mass action concentrations for structural units or ion couples in ternary strong electrolyte aqueous solutions[15]. To clearly describe the proposed thermodynamic model of calculating mass action concentrations for structural units or ion couples in $RbCl$-$RbNO_3$-H_2O ternary aqueous solution, a thermodynamic model of calculating mass action concentrations for structural units or ion couples in $RbCl$-H_2O binary strong electrolyte aqueous solutions is also proposed by applying the developed thermodynamic model of calculating mass action concentrations for structural units or ion couples in binary strong electrolyte aqueous solutions reported elsewhere[15−17].

The calculated mass action concentrations of RbCl and $RbNO_3$ have been compared with the reported activities[18] with different total ionic strengths as 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0, 3.0 and 3.5 mol/kg in $RbCl$-$RbNO_3$-H_2O ternary solution at 298.15 K. Because the calculated mass action concentrations are usually based on pure species as standard state and mole fraction as concentration unit while the reported activity is based on infinite dilution as standard state and molality as concentration unit, a transformation coefficient should be needed for comparing the calculated mass action concentrations with the reported ones.

2 Thermodynamic model of calculating mass action concentrations

2.1 Hypotheses

The main viewpoints of the ion and molecule coexistence theory for strong electrolyte aqueous solutions can be summarized as follows.

1) Strong electrolyte aqueous solutions are composed of Na^+, Ca^{2+}, Mg^{2+}, Rb^+, Cl^-, Br^-, F^-, NO_3^-, etc, as simple ions, H_2O as simple molecule, and hydrous salt compounds as complex molecules. It is assumed that each cation and anion of the simple ions occupies only one position of structural units, but will take part in the reaction of forming hydro salt molecules in the form of ion couple based on electrovalence balance. Choosing RbCl as an example, RbCl can be electrolyzed or separated into two simple ions as Rb^+ and Cl^-, respectively, as two structural units, but ions of Rb^+ and Cl^- will take part in the reaction of forming hydro salt molecules as an ion couple in form of (Rb^++Cl^-) in RbCl-contained aqueous solutions if there are hydro salt molecules formed.

2) There are dynamic reaction equilibria of forming complex hydro salt molecules between ion couples and simple molecules of H_2O.

3) The structural units in strong electrolyte aqueous solutions keep continuity in the investigated concentration range of compositions.

4) Chemical reactions of forming complex hydro slat molecules in strong electrolyte aqueous solution follow the mass action law.

2.2 Calculating model of mass action concentration for structural units or ion couples in $RbCl$-H_2O binary system

2.2.1 Structural units and calculating model

It has been confirmed[19] that RbCl and H_2O cannot form any hydrous salt molecule at 298.15 K. Hence, the structural units in $RbCl$-H_2O binary solution are Rb^+ and Cl^- as ions and H_2O as simple molecule. The molality m_i (mol/kg) is usually applied to present the concentration of components in strong electrolyte aqueous solution. Therefore, the amounts-of-substance of RbCl and H_2O in $RbCl$-H_2O binary solution based on 1 kg H_2O before dynamic reaction equilibrium is expressed as $b_1 = n^0_{RbCl} = m_{RbCl}$, $b_3 = n^0_{H_2O} = m_{H_2O} = 1\,kg/M_{H_2O} =$ 55.6 mol, respectively. The mole fraction of RbCl and H_2O before dynamic equilibrium can be determined by $x_i = n^0_i / \sum n^0_i = n^0_i /(n^0_{RbCl} + 55.6) = m_i /(m_{RbCl} + 55.6)$.

The equilibrium amount-of-substance of structural units in 1 kg H_2O in $RbCl$-H_2O binary solution is defined according to the ion and molecule coexistence theory as $n_1 = n_{Rb^+,\,RbCl} = n_{Cl^-,\,RbCl} = n_{RbCl}$ and $n_3 = n_{H_2O} = 55.6$ mol. The total amount of substance of all structural units in 1 kg H_2O in $RbCl$-H_2O binary solution under equilibrium condition, $\sum n_i$, can be calculated according to mass balance principle as

$$\sum n_i = 2n_1 + n_3 = 2n_{RbCl} + 55.6 \quad (1)$$

The mass action concentrations of each structural unit or ion couple, N_i, can be determined as

$$N_1 = \frac{2n_1}{\sum n_i} = \frac{2n_1}{2n_1 + n_3} = \frac{2n_{RbCl}}{2n_{RbCl} + 55.6} = N_{RbCl} \quad (2a)$$

$$N_3=\frac{n_3}{\sum n_i}=\frac{n_3}{2n_1+n_3}=\frac{55.6}{2n_{\rm RbCl}+55.6}=N_{\rm H_2O} \quad (2b)$$

The mass balance of RbCl and H_2O in 1 kg H_2O in RbCl-H_2O binary solution can be expressed as

$$b_1=n^0_{\rm RbCl}=n_1=n_{\rm RbCl}=\frac{1}{2}N_1\sum n_i \quad (3a)$$

$$b_3=n^0_{\rm H_2O}=n_3=n_{\rm H_2O}=N_3\sum n_i=55.6 \quad (3b)$$

The following equation can be obtained from the fact that the total equilibrium molar fraction of all structural units in a system is 1.0, that is

$$N_1+N_3=1 \quad (4)$$

The Eqs.(3) and (4) are the calculating thermodynamic models of mass action concentration for structural units or ion couples in RbCl-H_2O binary solution. There are three unknown parameters as N_1, N_3 and $\sum n_i$ with three independent equations in the thermodynamic model composed of Eq.(3) and Eq.(4). Therefore, the real solutions of above-mentioned mass action concentration of structural units or ion couples, N_i, and total amount of substance of all structural units, $\sum n_i$, in RbCl-H_2O binary solution can be solely solved by combining Eq.(3) and Eq.(4).

The calculated mass action concentrations of solute, i.e., N_1, is based on pure species as standard state and mole fraction, x_i, as concentration unit; however, the reported activities are usually based on infinite dilution as standard state and molality m_i as concentration unit. To compare the calculated mass action concentrations and the reported activities of solute, a transformation coefficient of RbCl, $L'_{\rm RbCl}$, in RbCl-H_2O binary solution is needed. The transformation coefficient, $L'_{\rm RbCl}$, and the transformed mass action concentration, $N'_{\rm RbCl}$, of RbCl in RbCl-H_2O binary solution can be described as follows:

$$L'_{\rm RbCl}=\frac{a_{\rm RbCl}}{N_{\rm RbCl}}=\frac{m_{\rm RbCl}f'_{\rm RbCl}}{N_{\rm RbCl}},$$

$$N'_{\rm RbCl}=\overline{L}'_{\rm RbCl}N_{\rm RbCl} \quad (5)$$

It should be specially pointed out that although no any hydro salt molecule can be formed in RbCl-H_2O binary solution at 298.15 K, there are not independent RbCl molecules, but Rb^+ and Cl^- ions in RbCl-H_2O binary solution. Using concept of mass action concentration for RbCl is just for convenience to compare the measured RbCl activity data with the calculated mass action concentrations of the same component because only activity data of two components in RbCl-H_2O binary solution as RbCl and H_2O can be determined and reported from viewpoints of classic experimental tests and traditional thermodynamics. The real meaning of mass action concentration for RbCl, $N_{\rm RbCl}$, is the sum of mass action concentration for two structural units in RbCl as Rb^+ and Cl^- in form of ion couple.

2.2.2 Results and discussion

The relationship between the transformed mass action concentration, $N'_{\rm RbCl}$, or the reported activity, $a_{\rm RbCl}$[20], and mole fraction of RbCl, $x_{\rm RbCl}$, in RbCl-H_2O binary solution at 298.15K is shown in Fig.1(a). Similarly, the calculated mass action concentration, $N_{\rm H_2O}$, against $x_{\rm H_2O}$ in RbCl-H_2O binary solution is illustrated in Fig.1(b). It can be observed from Fig.1(a) that the transformed mass action concentration, $N'_{\rm RbCl}$, is in good agreement with reported activity, $a_{\rm RbCl}$[21], in the investigated RbCl concentration range. The transformation coefficients $L'_{\rm RbCl}$ between the transformed mass action concentrations and the reported activities of RbCl in RbCl-H_2O binary solution are also listed in Table 1 in a molality range of RbCl from 0.1 to 6.0 mol/kg(H_2O). It can be observed from Table 1 that the transformation coefficients of RbCl, $L'_{\rm RbCl}$, are more

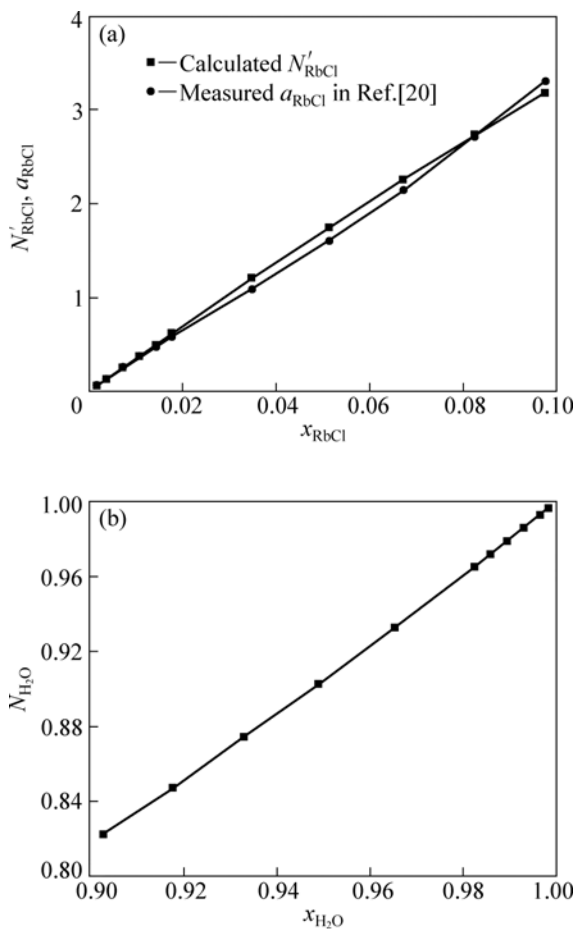


Fig.1 Comparison of transformed mass action concentrations ($N'_{\rm RbCl}$) with reported activities ($a_{\rm RbCl}$) of RbCl (a) and relationship between calculated mass action concentration ($N_{\rm H_2O}$) and mole fraction of H_2O ($x_{\rm H_2O}$) (b) in RbCl-H_2O binary solution at 298.15 K

Table 1 Transformation coefficients between calculated mass action concentrations and reported activities of RbCl in RbCl-H_2O solutions

m_{RbCl}/(mol·kg^{-1})	0.1	0.2	0.4	0.6	0.8	1.0
L'_{RbCl}	21.32	19.85	18.39	17.61	17.13	16.79
m_{RbCl}/(mol·kg^{-1})	2.0	3.0	4.0	5.0	6.0	
L'_{RbCl}	16.27	16.51	17.11	17.81	18.62	

or less discrete, but an average datum of L'_{RbCl} can be calculated to be 17.95. Therefore, it can be deduced that the calculated mass action concentrations can be applied to express reaction ability of RbCl and have a close relationship with the reported activities of RbCl in RbCl-H_2O binary solution. All hypotheses used during the development of the thermodynamic model are reasonable and have got the facts of intrinsic structure of RbCl-H_2O binary solution.

2.3 Calculating model of mass action concentration for structural units or ion couples in RbCl-RbNO$_3$-H$_2$O ternary system

2.3.1 Structural units and calculating model

It has been known[19] that RbCl and $RbNO_3$ will be completely ionized and no hydrous salt molecules can be formed in RbCl-RbNO$_3$-H$_2$O ternary system at 298.15 K. Based on the ion and molecule coexistence theory, the structural units in RbCl-RbNO$_3$-H$_2$O ternary solution are composed of Rb^+, Cl^- and NO_3^- as simple ions, and H_2O as simple molecule. According to above-mentioned hypotheses for strong electrolyte aqueous solution, the amount-of-substance of solutes and solvent in RbCl-RbNO$_3$-H$_2$O ternary solution based on 1 kg H_2O before dynamic reaction equilibrium can be expressed as $b_1 = n^0_{RbCl} = m_{RbCl}$, $b_2 = n^0_{RbNO_3} = m_{RbNO_3}$ and $b_3 = n^0_{H_2O} = m_{H_2O} = 55.6$ mol, respectively. The mole fraction of component i before equilibrium is presented as $x_i = n_i^0/\sum n_i^0 = n_i^0/(n^0_{RbCl} + n^0_{RbNO_3} + 55.6) = m_i/(m_{RbCl} + m_{RbNO_3} + 55.6)$.

The equilibrium amount-of-substance of above-mentioned structural units in RbCl-RbNO$_3$-H$_2$O ternary solution can be presented as $n_1 = n_{Rb^+,\,RbCl} = n_{Cl^-,\,RbCl} = n_{RbCl}$, $n_2 = n_{Rb^+,\,RbNO_3} = n_{NO_3^-,\,RbNO_3} = n_{RbNO_3}$ and $n_3 = n_{H_2O}$ =55.6 mol. Hence, the total amount- of- substance of all structural units in 1 kg H_2O in RbCl-RbNO$_3$-H$_2$O ternary solution under equilibrium, $\sum n_i$, can be expressed according to mass balance principle as

$$\sum n_i = 2n_1 + 2n_2 + n_3 = 2n_{RbCl} + 2n_{RbNO_3} + 55.6 \tag{6}$$

The mass action concentrations of structural units or ion couples in RbCl-RbNO$_3$-H$_2$O ternary solution, i.e., RbCl, $RbNO_3$ and H_2O, are presented as

$$N_1 = \frac{2n_1}{\sum n_i} = \frac{2n_1}{2n_1 + 2n_2 + n_3} = \frac{2n_{RbCl}}{2n_{RbCl} + 2n_{RbNO_3} + 55.6} = N_{RbCl} \tag{7a}$$

$$N_2 = \frac{2n_2}{\sum n_i} = \frac{2n_2}{2n_1 + 2n_2 + n_3} = \frac{2n_{RbNO_3}}{2n_{RbCl} + 2n_{RbNO_3} + 55.6} = N_{RbNO_3} \tag{7b}$$

$$N_3 = \frac{n_3}{\sum n_i} = \frac{n_3}{2n_1 + 2n_2 + n_3} = \frac{55.6}{2n_{RbCl} + 2n_{RbNO_3} + 55.6} = N_{H_2O} \tag{7c}$$

The mass balance of solutes and solvent in 1 kg H_2O in RbCl-RbNO$_3$-H$_2$O ternary solution can be expressed, based on the ion and molecules coexistence theory, as

$$b_1 = n^0_{RbCl} = n_1 = n_{RbCl} = \frac{1}{2}N_1\sum n_i \tag{8a}$$

$$b_2 = n^0_{RbNO_3} = n_2 = n_{RbNO_3} = \frac{1}{2}N_2\sum n_i \tag{8b}$$

$$b_3 = n^0_{H_2O} = n_3 = n_{H_2O} = N_3\sum n_i = 55.6 \tag{8c}$$

The following equation can also be obtained from the fact that the total equilibrium molar fraction of all structural units in a system is 1.0, as

$$N_1+N_2+N_3=1 \tag{9}$$

The Eqs.(8) and (9) consist of the calculating thermodynamic model of mass action concentration for RbCl-RbNO$_3$-H$_2$O ternary solution. There are four unknown parameters as N_1, N_2, N_3 and $\sum n_i$ with four independent equations in the thermodynamic model composed of Eq.(8) and Eq.(9). The real solutions of above-mentioned mass action concentration of structural units or ion couples, N_i, and total amount of substance of all structural units, $\sum n_i$, in RbCl-RbNO$_3$-H$_2$O ternary solution can be solely solved by combining Eq.(8) and Eq.(9).

To compare the calculated mass action concentrations and the reported activities of solutes, the transformation coefficients of RbCl, L'_{RbCl}, and $RbNO_3$, L'_{RbNO_3}, and the transformed mass action concentration, N'_{RbCl} and N'_{RbNO_3}, can be described as follows:

$$L'_{RbCl} = \frac{a_{RbCl}}{N_{RbCl}} = \frac{m_{RbCl}\,f'_{RbCl}}{N_{RbCl}},$$

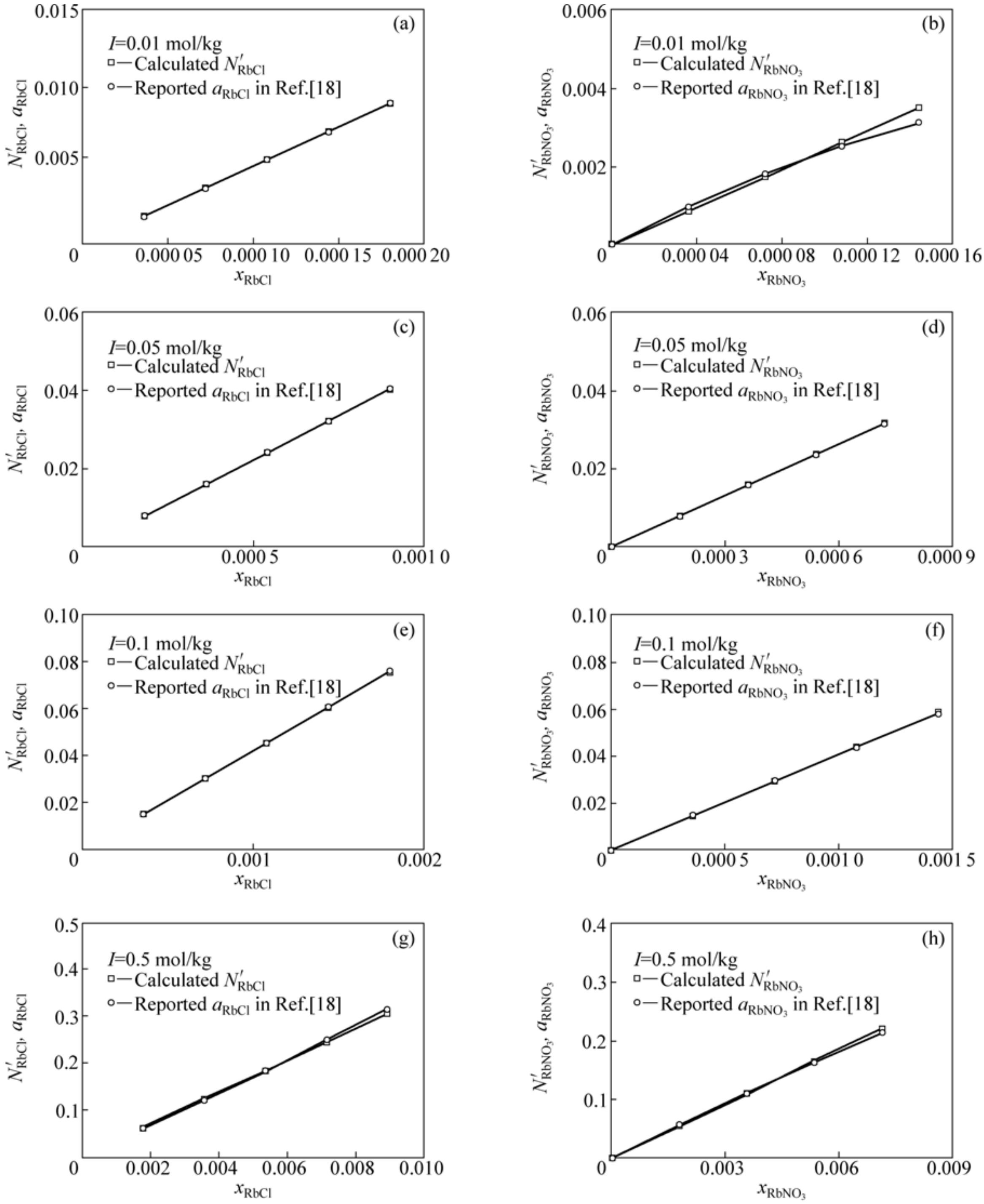
$$L'_{RbNO_3}=\frac{a_{RbNO_3}}{N_{RbNO_3}}=\frac{m_{RbNO_3}f'_{RbNO_3}}{N_{RbNO_3}} \quad (10)$$

$$N'_{RbCl}=\bar{L}'_{RbCl}N_{RbCl},$$

$$N'_{RbNO_3}=\bar{L}'_{RbNO_3}N_{RbNO_3} \quad (11)$$

2.3.2 Results and discussion

The activity coefficients of RbCl and $RbNO_3$ in RbCl-$RbNO_3$-H_2O ternary solution have been reported elsewhere[18] in a range of total ionic strength, i.e., $I=m_{RbCl}+m_{RbNO_3}$, from 0.01 to 3.5 mol/kg with different ionic strength fraction of $RbNO_3$, $v_{RbNO_3}=m_{RbNO_3}/I=m_{RbNO_3}/(m_{RbCl}+m_{RbNO_3})$ as 0, 0.2, 0.4, 0.6, and 0.8 at each total ionic strength, respectively. The transformed mass action concentrations, N'_{RbCl} and N'_{RbNO_3}, have been compared with the reported activities[18], a_{RbCl} and a_{RbNO_3}, with different I, i.e., various mole fraction of RbCl, x_{RbCl}, and $RbNO_3$, x_{RbNO_3}, as illustrated in Figs.2(a)−(r), respectively. It can be observed from Figs.2(a)−(r) that the transformed mass action concentrations, N'_{RbCl} and N'_{RbNO_3}, are in



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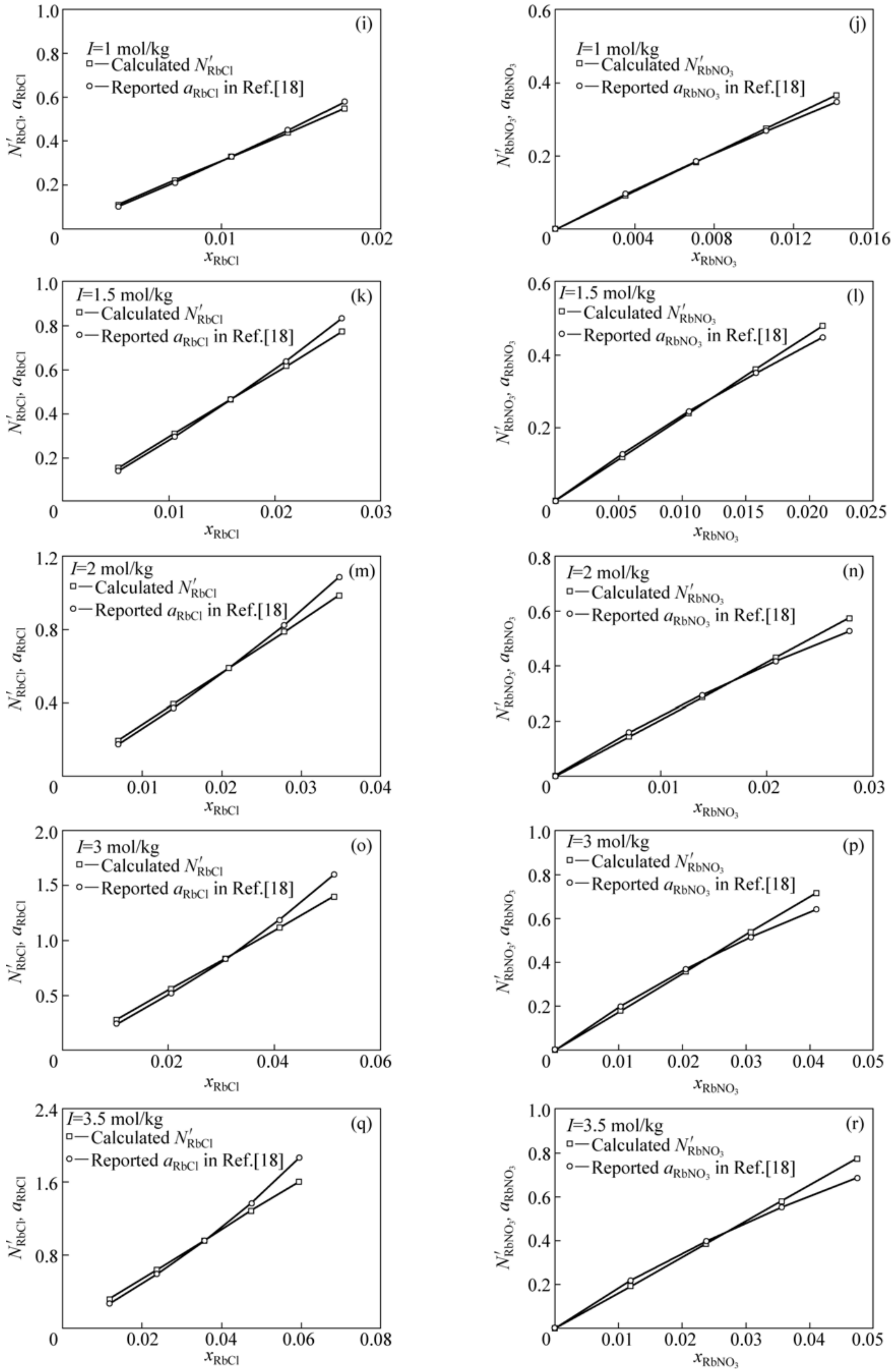

Fig.2 Comparison of transformed mass action concentrations, N'_{RbCl} and N'_{RbNO_3}, with reported activities, a_{RbCl} and a_{RbNO_3}, of RbCl and $NbNO_3$ in RbCl-$RbNO_3$-H_2O ternary solution with total ionic strength I as 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0, 3.0, and 3.5 mol/kg, respectively, at 298.15 K

Table 2 Transformation coefficients, L'_{RbCl}, and L'_{RbNO_3}, in total ionic strength range from 0.01 to 3.5 mol/kg (H_2O) with different ionic strengths of $RbNO_3$, v_{RbNO_3}, as 0, 0.2, 0.4, 0.5, 0.6 and 0.8, respectively, and calculated mass action concentration of H_2O in $RbCl$-$RbNO_3$-H_2O ternary solution

I/(mol·kg^{-1})	v_{RbNO_3}	m_{RbCl}/ (mol·kg^{-1})	m_{RbNO_3}/ (mol·kg^{-1})	L'_{RbCl}	L'_{RbNO_3}	N_{H_2O}
0.01	0.0	0.010	0.000	25.00	−	0.999 640
	0.2	0.008	0.002	24.89	13.56	0.999 640
	0.4	0.006	0.004	24.95	12.60	0.999 640
	0.6	0.004	0.006	25.08	11.75	0.999 640
	0.8	0.002	0.008	24.70	10.84	0.999 640
		Average of L'_i		24.92	12.19	
0.05	0.0	0.050	0.000	22.55	−	0.998 205
	0.2	0.040	0.010	22.50	22.30	0.998 205
	0.4	0.030	0.020	22.46	22.15	0.998 205
	0.6	0.020	0.030	22.38	22.15	0.998 205
	0.8	0.010	0.040	22.30	22.07	0.998 205
		Average of L'_i		22.44	22.17	
0.10	0.0	0.100	0.000	21.18	−	0.996 416
	0.2	0.080	0.020	21.10	20.65	0.996 416
	0.4	0.060	0.040	21.01	20.53	0.996 416
	0.6	0.040	0.060	20.92	20.44	0.996 416
	0.8	0.020	0.080	20.88	20.34	0.996 416
		Average of L'_i		21.02	20.49	
0.50	0.0	0.500	0.000	17.81	−	0.982 332
	0.2	0.400	0.100	17.55	16.05	0.982 332
	0.4	0.300	0.200	17.29	15.75	0.982 332
	0.6	0.200	0.300	17.03	15.46	0.982 332
	0.8	0.100	0.400	16.78	15.18	0.982 332
		Average of L'_i		17.29	15.61	
1.00	0.0	1.000	0.000	16.68	−	0.965 278
	0.2	0.800	0.200	16.23	13.85	0.965 278
	0.4	0.600	0.400	15.80	13.40	0.965 278
	0.6	0.400	0.600	15.39	12.97	0.965 278
	0.8	0.200	0.800	15.00	12.56	0.965 278
		Average of L'_i		15.82	13.20	
1.50	0.0	1.500	0.000	16.27	−	0.948 805
	0.2	1.200	0.300	15.64	12.54	0.948 805
	0.4	0.900	0.600	15.07	11.98	0.948 805
	0.6	0.600	0.900	14.53	11.45	0.948 805
	0.8	0.300	1.200	14.00	10.96	0.948 805
		Average of L'_i		15.10	11.73	
2.00	0.0	2.000	0.000	16.17	−	0.932886
	0.2	1.600	0.400	15.36	11.61	0.932886
	0.4	1.200	0.800	14.64	10.95	0.932886
	0.6	0.800	1.200	13.98	10.36	0.932886
	0.8	0.400	1.600	13.34	9.83	0.932886
		Average of L'_i		14.70	10.69	
3.00	0.0	3.000	0.000	16.42	−	0.902 597
	0.2	2.400	0.600	15.22	10.27	0.902 597
	0.4	1.800	1.200	14.25	9.48	0.902 597
	0.6	1.200	1.800	13.37	8.82	0.902 597
	0.8	0.600	2.400	12.48	8.25	0.902 597
		Average of L'_i		14.35	9.21	
3.50	0.0	3.5	0.0	16.67	−	0.888 179
	0.2	2.8	0.7	15.26	9.75	0.888 179
	0.4	2.1	1.4	14.19	8.93	0.888 179
	0.6	1.4	2.1	13.23	8.24	0.888 179
	0.8	0.7	2.8	12.21	7.67	0.888 179
		Average of L'_i		14.31	8.65	

good agreement of the reported activities[18], a_{RbCl} and a_{RbNO_3}, in a large change range of I, i.e., with various x_{RbCl} and x_{RbNO_3}, respectively. The transformation coefficients, L'_{RbCl} and L'_{RbNO_3}, listed in Table 2, show that L'_{RbCl} and L'_{RbNO_3} keep constant with small deviations for different I, respectively. The calculated mass action concentrations of H_2O, N_{H_2O}, are also summarized in Table 2 with different I. Hence, the ion and molecule coexistence theory can be successfully applied to calculate the reaction ability of components in $RbCl$-$RbNO_3$-H_2O ternary strong electrolyte aqueous solutions.

The common ion in $RbCl$-$RbNO_3$-H_2O ternary system is Rb^+, which can be generated from RbCl as well as $RbNO_3$. However, the calculated mass action concentration of RbCl only considers the contribution of Rb^+ and Cl^- which exist in RbCl, but not the contribution of Rb^+ in $RbNO_3$. The same method is also used to calculate the mass action concentration of $RbNO_3$. The treatment of the effect of common ion, i.e., Rb^+ in $RbCl$-$RbNO_3$-H_2O ternary system, on calculation of mass action concentration for RbCl and $RbNO_3$ needs further investigation in viewpoint of electrochemistry for strong electrolyte aqueous solutions.

The wonderful agreement between the transformed mass action concentrations and the reported activities suggests that the developed thermodynamic model can exactly reflect the structural characteristics of $RbCl$-$RbNO_3$-H_2O ternary solution and the mass action law is applicable to $RbCl$-$RbNO_3$-H_2O ternary strong electrolyte aqueous solution.

The calculated mass action concentrations of structural units or ion couples in $RbCl$-$RbNO_3$-H_2O ternary solution are valid by transformation coefficient, which need the reported activity data based on infinite dilution as standard state and molality as concentration unit. This maybe is the main reason for more or less deviation shown in Figs.2(a)−(r). The reasonable method is to compare the calculated mass action concentration of components and the measured activity with pure matter as standard state and mole fraction as concentration unit.

3 Conclusions

1) The calculated mass action concentrations of structural units or ion couples in $RbCl$-H_2O binary and $RbCl$-$RbNO_3$-H_2O ternary strong electrolyte aqueous solutions are in good agreement with the reported activities from literatures. Therefore, the developed thermodynamic model of calculating mass action concentrations for structural units or ion couples in $RbCl$-H_2O binary and $RbCl$-$RbNO_3$-H_2O ternary strong electrolyte aqueous solutions can be successfully applied to predict the reaction ability of components.

2) The ion and molecule coexistence theory in combination with the mass action law (if necessary when hydrous salt molecules as complex molecules exist) can be successfully applied to describe the structural characteristics of $RbCl$-H_2O binary and $RbCl$-$RbNO_3$-H_2O ternary strong electrolyte aqueous solutions.

3) As there are visible deviations between the calculated mass action concentrations and the reported activities in high concentration range for two investigated aqueous solutions, it is absolutely necessary to carry out further investigation on reaction ability of structural units or ion couples in strong electrolyte aqueous solutions based on pure species as standard state and mole fraction as concentration unit.

Symbol list

a_i	Reported activity of component i;
b_i	Total amount-of-substance of component i before chemical reaction in aqueous solutions, mol;
I	Total ionic strength, mol/kg;
K	Chemical equilibrium constant;
L'_i	Transformation coefficient of component i between calculated mass action concentration chosen pure matter as standard state and mole fraction x_i as concentration unit and reported activity chosen 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 amount of substance of components i before chemical reaction in aqueous solutions, same as b_i, mol;
n_i	Equilibrium amount of substance of structural unite i or ion couple i in aqueous solutions, mol;
N_i	Mass action concentration 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;
x_i	Mole fraction of component i before equilibrium;
$\sum n_i$	Total amount of substance of all structural units, mol;
$\sum n_i^0$	Total amount of substance of all components before dynamic equilibrium, mol;
v_i	Ionic strength of component i.

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