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Activity coefficients and thermodynamic parameters for RbCl/CsCl + amide (acetamide, propanamide, and *n*-butanamide) + water system at 298.15 K

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Abstract

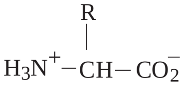
Electromotive force (emf) of the chemical cell without liquid-junction K-ISE | RbCl/CsCl (m_E) | ISE-Cl and K-ISE | RbCl/CsCl (m_E), amide (m_N) | ISE-Cl, have been measured at 298.15 K, where m_E = (0.005 to 0.5) mol kg^{-1} and m_N = (0.05 to 3.0) mol kg^{-1}. The activity coefficients of RbCl/CsCl in amide (acetamide, propanamide, and *n*-butanamide) + water mixture can be obtained from these electromotive force data and in the mean time the Gibbs free energy interaction parameters of RbCl/CsCl + amide pair in water, g_{EN}, as well as the salt constant, k_S, can be evaluated. The results show that both $g_{EN} > 0$, $k_S > 0$ at 298.15 K, and all the activity coefficients of electrolyte in amide + water mixture increase with increasing the m_N, but it is a little complicated for the dependence of activity coefficients on m_E. These thermodynamic parameters were discussed in terms of a model of the structural interaction and electrostatic interaction and the dependence of them on the number of carbon atoms in amide as well as the radius of metal ions were interpreted by the group additivity principle.

Keywords: RbCl/CsCl; Amide; Activity coefficients; Thermodynamic parameters

1. Introduction

Multi-components electrolyte solutions have great effects on the structure and properties of proteins including their solubility, denaturation, dissociation into subunits, and the activity of enzymes [1–3]. The complicated configurational and conformational factors, which can affect the structures of proteins in solutions, make the direct studies on proteins very difficult. Therefore, the investigations of the behavior of some model compounds of proteins like amino acids, peptides as well as amide are of importance. Now it is widely accepted that the model compounds of proteins include the following three types [4]:

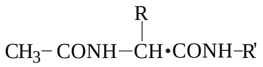
(1) amino acids and peptides



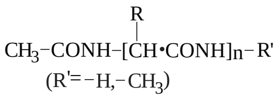
$H_3N^+{-}\underset{}{\overset{R}{CH}}{-}CO_2^-$

$H_3N^+{-}[\overset{R}{CH}\cdot CONH]_n{-}\overset{R}{CH}\cdot CO_2^-$

(2) amino acids and peptides being replaced in the end

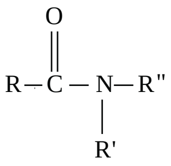


$CH_3{-}CONH{-}\overset{R}{CH}\cdot CONH{-}R'$



$CH_3{-}CONH{-}[\overset{R}{CH}\cdot CONH]_n{-}R'$ $(R' = -H, -CH_3)$

(3) amide



$R{-}\overset{O}{\overset{\|}{C}}{-}\underset{R'}{N}{-}R''$

(R, R', R" = –H,)

Amide is regarded as one of the model compounds of proteins. They have similar functional group as proteins and most of them can dissolve in water. They have both proton acceptor and donator, so it is easy for them to associate with each other or with water by hydrogen bond. Moreover, amides are often used as one of the effective denaturants for

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proteins. The denaturation increases with the increase of carbon atom number in amides. It is thought that this is caused by the hydrophobic interaction. On the other hand, the biological fluids are mostly a multi-component aqueous solution. These fluids contain a specified quantity of ions, such as sodium, potassium and chloride, etc., which are indispensable for the metabolic processes. So the thermodynamic studies on the interaction between amides and RbCl/CsCl in water can provide some useful information for the properties of proteins in electrolyte + water mixture and it is also very helpful for people to understand the behavior of proteins in a more complicated biological system.

The interaction of amides with non-electrolyte in water have been extensively studied thermochemically [5–10], volumetrically [11–14], etc. However, there are only few studies concerning with the amides + salt + water systems [15,16] and so far we have not found studies carried out on the investigations of interaction between amides and heavy rare alkali metal ions in water. The rare alkali metal rubidium and cesium have been found to play an important part in some physiological processes. It was reported that rubidium ion have similar function as potassium ion in organism and can take place of potassium ions in some cases. It has been now regarded as one of the essential trace elements in the body [17]. Cesium is also found to be able to induce the self-assembly of protein clusters [18] and can effect charge translocation by the Na^+/ K^+–ATPase [19]. Therefore the study of the interaction between Rb^+ and amides in water is helpful to know the physico-chemical essence of some biological phenomena.

Our group has focused on the interactions of Rb^+/Cs^+ with biological model molecules of saccharides and proteins, etc., in water for a few years [20–24]. As one part of the continuing studies on the interaction of Rb^+/Cs^+ with model compounds of proteins in water, we reported here the activity coefficients for RbCl/CsCl + amide (acetamide, propanamide, and *n*-butanamide) + water system and the interaction parameters of RbCl/CsCl with these amides in water, g_{EN} and k_S, at 298.15 K by means of electrochemical methods. It is expected to provide more fundamental information on the interaction of Rb^+/Cs^+ with proteins in water.

2. Experimental

RbCl/CsCl (mass fraction ≥ 0.999) was made from Rb_2CO_3/Cs_2CO_3. Their purification and determination have been reported elsewhere [25,26]). The mass fraction of the three amides (anhydrous acetamide (Tianjing Chem. Co.), propanamide (Tianjing Chem. Co), and *n*-butanamide (ACROS ORGANICS)) are all ≥ 0.99. The amides were dried under low pressure at $T = 338$ K for 6 h. RbCl was heated at $T = 853$ K and CsCl was heated at $T = 773$ K to have them at constant mass. All the reagents were stored over silica gel in desiccators. Deionized and doubly distilled water was used throughout this work.

A non-liquid-junction chemical cell was set up with the potassium ion-selective electrode as the working electrode and with the chloride ion-selective electrode as the reference electrode to measure the electromotive force (emf) of RbCl/CsCl + amide (acetamide, propanamide, and *n*-butanamide) + water solution:

$$\mathrm{K-ISE|RbCl/CsCl}(m_{\mathrm{E}})|\mathrm{ISE-Cl} \qquad \text{(I)}$$

$$\mathrm{K-ISE|RbCl/CsCl}(m_{\mathrm{E}}),\mathrm{amide}(m_{\mathrm{N}})|\mathrm{ISE-Cl} \qquad \text{(II)}$$

where m_E and m_N are the molalities of electrolyte and amide, respectively. The electromotive forces (emfs) of these cells were measured at $T = 298.15$ K. The cells were thermostated with accuracy of ±0.05 K. The test solutions were freshly prepared using an automatic electronic balance with a sensitivity of 10 μg. In order to minimize the concentration gradients in the cell, all the solutions were stirred continuously by a magnetic stirrer.

Each set of experiments was performed at a fixed electrolyte concentration, ranging from 0.005 to 0.5 mol kg^{-1} and the molalities of amides were increased from 0.05 to 3.0 mol kg^{-1} (acetamide and propanamide) or 2.5 mol kg^{-1} (*n*-butanamide) by adding solid amide. The choice of molality ranges of amide was based mainly on the solubility of amide and their dissolution rate. At each point, the emf was recorded only when the drift was less than 0.1 mV within 5 min. To ensure the stability of the electrode during each experimental process, the electrodes were allowed to stay in solution for only 1 to 2 h and, after the emf of the last sample solution was measured, the electrodes were transferred to the original RbCl/CsCl + water binary solution to examine the emf again. The two emf values can agree with each other with error less than 0.2 mV. Some experimental points such as 0.005 mol kg^{-1} (the most diluted) and 0.5 mol kg^{-1} (the most concentrated) of electrolyte solutions were replicated three times and the data reported are the average of the replicates that agree to each other within 0.3 mV.

3. Thermodynamic relations and results

The potential of an ion selective electrode (ISE) can be expressed as

$$E_i = E_i^0 \pm \frac{S_i}{Z_i}\ln a_i, \qquad (1)$$

where a_i is the activity of ion i and the constant E^0 is the emf of the measuring circuit of the cell and depends on activity of the ions in the inner solution and on the type of internal reference electrode of the cell. The constant S_i refers to the slope of the electrode response to ion i, and Z_i is the charge number of ion i.

Table 1
The ratios of the ionic activity coefficient of RbCl in the presence ($\gamma_{\pm}^{\mathrm{II}}$) and absence ($\gamma_{\pm}^{\mathrm{I}}$) of amide at different m_{E} and m_{N} at T=298.15 K

m_{N}/mol kg^{-1}	m_{E}/mol kg^{-1}						
	0.005	0.01	0.03	0.08	0.1	0.2	0.5
$\gamma\pm^{II}/\gamma\pm^{I}$ (RbCl–acetamide–water)							
0.05	1.0158	1.0199	1.0039	1.0099	1.0259	1.0020	1.0059
0.1	1.0198	1.0219	1.0079	1.0119	1.0360	1.0079	1.0079
0.3	1.0259	1.0259	1.0119	1.0259	1.0649	1.0119	1.0138
0.7	1.0421	1.0401	1.0279	1.0381	1.0818	1.0279	1.0320
1.0	1.0463	1.0463	1.0320	1.0483	1.0990	1.0401	1.0401
1.5	1.0545	1.0566	1.0670	1.0628	1.1077	1.0524	1.0608
2.0	1.0670	1.0670	1.0733	1.0670	1.1120	1.0691	1.0691
2.5	1.0776	1.0755	1.0861	1.0797	1.1186	1.0776	1.0818
3.0	1.0882	1.0882	1.0947	1.0840	1.1363	1.0904	1.0882
$\gamma\pm^{II}/\gamma\pm^{I}$ (RbCl–propanamide–water)							
0.05	1.0138	1.0178	1.0059	1.0039	1.0020	1.0119	1.0159
0.1	1.0401	1.0239	1.0099	1.0059	1.0099	1.0158	1.0199
0.3	1.0524	1.0299	1.0198	1.0178	1.0381	1.0259	1.0299
0.7	1.0712	1.0608	1.0239	1.0380	1.0608	1.0463	1.0463
1.0	1.0947	1.0733	1.0360	1.0524	1.0776	1.0587	1.0650
1.5	1.1011	1.0990	1.0628	1.0818	1.0882	1.0840	1.1098
2.0	1.1098	1.1208	1.0733	1.1076	1.0925	1.1011	1.1274
2.5	1.1274	1.1408	1.1011	1.1120	1.1011	1.1208	1.1521
3.0	1.1566	1.1476	1.1076	1.1142	1.1208	1.1430	1.1589
$\gamma\pm^{II}/\gamma\pm^{I}$ (RbCl–n-butanamide–water)							
0.05	1.0178	1.0079	1.0320	1.0463	1.0299	1.0504	1.0691
0.1	1.0279	1.0158	1.0381	1.0504	1.0340	1.0545	1.0776
0.3	1.0608	1.0691	1.0712	1.0608	1.0545	1.0712	1.0947
0.7	1.1098	1.1386	1.1098	1.1076	1.0947	1.0968	1.1252
1.0	1.1521	1.1709	1.1566	1.1363	1.1120	1.1186	1.1363
1.5	1.2245	1.2390	1.2030	1.1589	1.1230	1.1408	1.1543
2.0	1.3351	1.2912	1.2537	1.1819	1.1274	1.1657	1.1750
2.5	1.4246	1.3430	1.2836	1.2054	1.1566	1.1773	1.1983

For cells (I) and (II), assuming $S \approx S_{+} \approx S_{-} \approx \frac{S_{+}+S_{-}}{2}$ leads to

$$E(\mathrm{I}) = E^{0}(\mathrm{I}) + S\left[\frac{Z_{+}+Z_{-}}{vZ_{+}Z_{-}}\right]\ln a_{\mathrm{E}}(\mathrm{I}), \tag{2}$$

$$E(\mathrm{II}) = E^{0}(\mathrm{II}) + S\left[\frac{Z_{+}+Z_{-}}{vZ_{+}Z_{-}}\right]\ln a_{\mathrm{E}}(\mathrm{II}), \tag{3}$$

where E (I) and E (II) are emfs of cells (I) and (II), respectively, and E^{0} (I)=E^{0} (II)=$E_{+}^{0}-E_{-}^{0}$. Here, a_{E} is the activity of electrolyte defined as

$$a_{\mathrm{E}} = (m_{\pm}\gamma_{\pm})^{\upsilon}, \tag{4}$$

$m_{\pm}$ and $\gamma_{\pm}$ are, respectively, mean ionic molality and activity coefficients of the electrolyte and $\upsilon=\upsilon_{+}+\upsilon_{-}$, where υ_{+} and υ_{-} are the stoichiometric numbers of cation and anion. Subtracting Eq. (2) from Eq. (3) and rearranging gives

$$\ln\{\gamma_{\pm}(\mathrm{II})/\gamma_{\pm}(\mathrm{I})\}=\{(E(\mathrm{II})-E(\mathrm{I})/S)\cdot\{(Z_{+}Z_{-})/(Z_{+}+Z_{-})\}. \tag{5}$$

The ratio of the mean activity coefficients of RbCl/CsCl $\{\gamma_{\pm}(\mathrm{II})/\gamma_{\pm}(\mathrm{I})\}$ in the presence of amide to those in the absence of amide at the same electrolyte molality can be calculated from the emf values of cells (II) and (I) according to Eq. (5) (the values of S can be obtained from experimental data).

The potassium ion selective electrode has excellent response both to Rb^{+} and Cs^{+}. Because the electrolyte (RbCl/CsCl) is a high purity reagent, in which the content of impurities, such as Na^{+} and K^{+}, is very low, there is no interference to the emf measurements of $\mathrm{Rb}^{+}/\mathrm{Cs}^{+}$. So, the potassium ion selective electrode can be used to obtain the emf values instead of a rubidium/cesium ion selective electrode in this work.

The slope S of the electrode response was determined by using activity coefficients of RbCl/CsCl that were calculated by the empirical equation recommended by Hamer and Wu [27]. The typical value of S obtained from linear regression analysis of the experimental points was 25.43 ± 0.02 mV with a correlation coefficient of 0.9996 for Rb^{+} and 25.09 ± 0.05 mV with a correlation coefficient of 0.9990 for Cs^{+}. Reasonable agreement between the experimental and theoretical values (25.61 mV at T=298.15 K of the Nernst equation) was found, which suggested that the potassium ion selective electrode behaves in accordance to the Nernst equation in the experimental range.

Table 2
The ratios of the ionic activity coefficient of CsCl in the presence ($\gamma\pm^{\mathrm{II}}$) and absence ($\gamma\pm^{\mathrm{I}}$) of amide at different m_{E} and m_{N} at T=298.15 K

m_{N}/mol kg^{-1}	m_{E}/mol kg^{-1}						
	0.005	0.01	0.03	0.08	0.1	0.2	0.5
$\gamma\pm^{II}/\gamma\pm^{I}$ (CsCl–acetamide–water)							
0.05	1.0100	1.0100	1.0365	1.0242	1.0469	1.0490	1.0040
0.1	1.0161	1.0181	1.0469	1.0365	1.0616	1.0637	1.0262
0.3	1.0303	1.0303	1.0744	1.0595	1.0765	1.0765	1.0511
0.7	1.0574	1.0532	1.1004	1.0787	1.1026	1.0938	1.0851
1.0	1.0680	1.0722	1.1270	1.0916	1.1203	1.1248	1.1203
1.5	1.0808	1.0830	1.1520	1.1026	1.1338	1.1497	1.1519
2.0	1.0982	1.1026	1.1752	1.1225	1.1589	1.1869	1.1728
2.5	1.1048	1.1270	1.1917	1.1406	1.1612	1.2230	1.2084
3.0	1.1181	1.1566	1.2012	1.1728	1.1705	1.2476	1.2476
$\gamma\pm^{II}/\gamma\pm^{I}$ (CsCl–propanamide–water)							
0.05	1.0365	1.0242	1.0120	1.0080	1.0140	1.0616	1.0283
0.1	1.0427	1.0407	1.0201	1.0201	1.0181	1.0637	1.0490
0.3	1.0744	1.0595	1.0448	1.0448	1.0469	1.0722	1.0658
0.7	1.0960	1.0744	1.0616	1.0637	1.0637	1.0873	1.0873
1.0	1.1181	1.1004	1.0787	1.0744	1.0808	1.1004	1.0938
1.5	1.1315	1.1136	1.1026	1.0960	1.0960	1.1248	1.1136
2.0	1.1543	1.1474	1.1136	1.1114	1.1114	1.1315	1.1158
2.5	1.1822	1.1682	1.1292	1.1248	1.1158	1.1360	1.1248
3.0	1.2108	1.1799	1.1728	1.1566	1.1474	1.1635	1.1682
$\gamma\pm^{II}/\gamma\pm^{I}$ (CsCl–n-butanamide–water)							
0.05	1.0040	1.0201	1.0060	1.0000	0.9940	1.0181	1.0161
0.1	1.0161	1.0365	1.0140	1.0040	0.9980	1.0242	1.0201
0.3	1.0658	1.0616	1.0490	1.0201	1.0161	1.0324	1.0283
0.7	1.1497	1.1270	1.1338	1.0616	1.0490	1.0595	1.0344
1.0	1.2451	1.1964	1.1635	1.0873	1.0701	1.0765	1.0511
1.5	1.3646	1.2829	1.2132	1.1136	1.0960	1.1114	1.0680
2.0	1.4956	1.3810	1.2576	1.1360	1.1136	1.1158	1.0722
2.5	1.6656	1.4545	1.3113	1.1406	1.1203	1.1203	1.0765

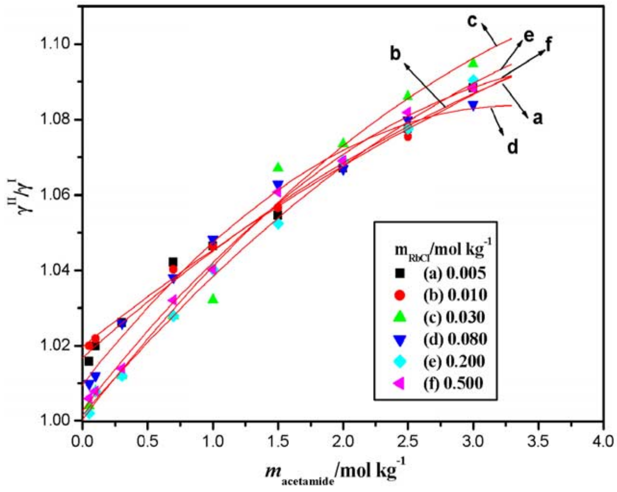

Fig. 1. Dependence of γ^{II}/γ^{I} of given RbCl molalities on $m_{\text{Acetamide}}$.

The ratio of the mean activity coefficients of RbCl/CsCl in the presence of amide to those in the absence of amide at the same electrolyte molality is given in Tables 1 and 2. In addition, Figs. 1–3 are given to describe these results for RbCl+amide+water systems as examples.

From the tables, it can be seen that at T=298.15 K, $\gamma_{\pm}$ (II)/$\gamma_{\pm}$ (I) ratio of electrolyte increased with increasing of m_N but decreased with increasing of m_E in most cases.

According to the McMillan–Mayer theory [28], the excess thermodynamic functions can be expressed in terms of pair and triplet interactions between the two solutes. For a solution of electrolyte (E) and non-electrolyte (N) in water, it is given by

$$\begin{aligned} F(m_N, m_E) = {} & F^o(m_N, m_E) + F^{EX}(m_N) + F^{EX}(m_E) \\ & + 2\upsilon f_{EN} m_E m_N + 3\upsilon^2 f_{ENN} m_E^2 m_N \\ & + 3\upsilon f_{ENN} m_E m_N^2 + \ldots \end{aligned} \quad (6)$$

where $F^o(m_N, m_E)$ is the total thermodynamic function of the ternary solution when it is assumed that the ions are neutral particles and there are no interactions between the solutes. $F^{EX}(m_N)$ and $F^{EX}(m_E)$ are the excess functions of the binary N+W and E+W solutions, respectively. f_{EN}, f_{EEN} and f_{ENN} are the pair and triplet interaction parameters that take into account all new sources of nonideality in the ternary solution.

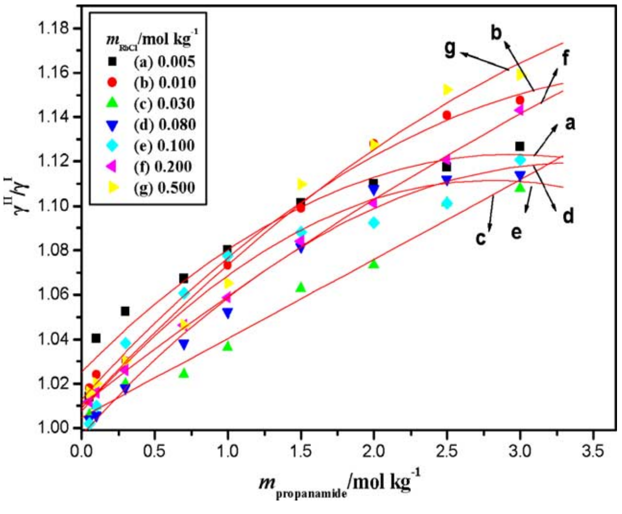

Fig. 2. Dependence of γ^{II}/γ^{t} of given RbCl molalities on $m_{\text{Propanamide}}$.

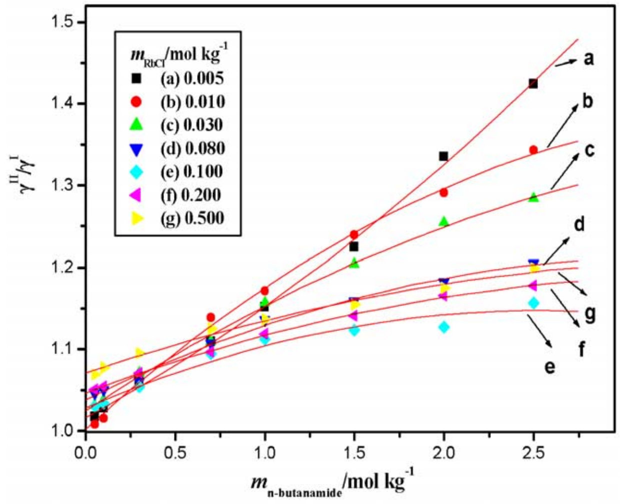

Fig. 3. Dependence of γ^{II}/γ^{I} of given RbCl molalities on $m_{n\text{-butanamide}}$.

For the transfer function of electrolyte from water to aqueous non-electrolyte solution, the equation can be changed as:

$$\begin{aligned} \Delta_t F(\mathrm{W} \rightarrow \mathrm{W}+\mathrm{N}) &= F_E(m_N, m_E) - F_E^o(m_E) \\ &= 2\upsilon f_{EN} m_N + 6\upsilon^2 f_{EEN} m_E m_N + 3\upsilon f_{ENN} m_N^2 \\ &\quad + \ldots \end{aligned} \quad (7)$$

where both $F_E(m_N, m_E)$ and $F_E^o(m_E)$ are the partial mole quantities of electrolyte.

In particular case of Gibbs free energies, Eq. (7) is reduced to [29–31]:

$$\begin{aligned} \Delta_t G_E(\mathrm{W} \rightarrow \mathrm{W}+\mathrm{N}) &= -nF\Delta E \\ &= \mu_E(m_N, m_E) - \mu_E^o(m_E) \\ &= 2\upsilon g_{EN} m_N + 6\upsilon^2 g_{EEN} m_E m_N \\ &\quad + 3\upsilon g_{ENN} m_N^2 \end{aligned} \quad (8)$$

where $\mu_E(m_N, m_E)$ and $\mu_E^o(m_E)$ are the chemical potentials of electrolyte in E+N+W ternary solution and E+W binary solution, respectively, F is the Faraday constant, and ΔE is the difference of electromotive forces. In the present case, $\Delta E = E$ (cell II) $- E$ (cell I). The higher-order terms have been neglected in Eq. (8). The pair and triplet Gibbs free energies interaction parameters can be obtained from least-squares analysis of the experimental data. It is observed that g_{ENN} values are very small; however their deviations are large. Therefore, the interaction parameters were obtained from Eq. (8) in which the term containing g_{ENN} was neglected. These parameters are given in Table 3, together with the uncertainties of the fit. It appears that the g_{EEN} lack

Table 3
Gibbs free energy interaction parameters for the RbCl/CsCl+amides+water system at 298.15 K

Amides	g_{EN}[a]	g_{EEN}[a]	k_S[a]
	(J kg mol^{-3})	(J kg^2 mol^{-2})	(mV)
RbCl+ amide+ water			
Acetamide	68.16±5.15	38.31±55.17	0.110±0.042
Propanamide	94.88±6.82	−127.02±73.17	0.153±0.023
N-butanamide	152.01±11.14	108.25±302.18	0.245±0.033
CsCl+ amide+ water			
Acetamide	121.29±8.12	437.98±129.9	0.196±0.066
Propanamide	130.76±10.93	−155.62±117.17	0.211±0.054
N-butanamide	165.17±12.77	−1280.89±47.00	0.267±0.046

[a] The uncertainties are estimated as twice the standard deviation of the fit.

precision because of experimental errors. However, this is not important because we are only interested in the pair parameters that are most important in dilute solution.

The salting constant, k_S, defined by Friedman [32], can be calculated by [33,34]

$$RTk_S = 2\upsilon g_{EN}$$

where R is the gas constant. The results are also included in Table 3.

4. Discussion

Tables 1 and 2 and Figs. 1 2 3 show that the rations of activity coefficients of electrolyte, $\gamma\pm(\mathrm{II})/\gamma\pm(\mathrm{I})$, can increase with the adding of amide. The principle reason for this phenomenon lies in that the hydration of polar group of amide results in the decrease of effective solvent for electrolyte. However, at the same electrolyte concentration, the increase of $\gamma\pm$ (II)/$\gamma\pm$ (I) will be more tender with the increasing of amide. This can be attributed to the increase of association between ions and the polar group in amide. This association can result in the more strong dissolution, so the activity coefficients decrease at more concentrated solution.

In addition, it can be seen from Table 3 that both $g_{EN}>0$ and $k_S>0$. This means that the relationship between RbCl/CsCl and amide is thermodynamically repulsive and amide is being salted-out by RbCl/CsCl in water. The g_{EN} increases both with the increasing number of carbon atom from acetamide *n*-butyramide as well as ion radius from Rb^+ to Cs^+.

This can be interpreted in terms of the structural interaction and electrostatic interaction models. It is generally believed that the interaction of ions with a non-electrolyte consists of electrostatic and structural interactions. The concept of structural interactions was first introduced by Frank and Robinson [35]. It was often used to explain the concentration dependence of transfer functions of electrolytes. In Ref. [36], it was discussed in detail and now has been widely accepted that, in most cases, the net effect of co-sphere overlap on the hydration structure is destructive. This destruction of hydrogen bond (endothermic reaction) results in the increase of g_{EN}, while the rising of order in the system (entropy increase) will cause the decrease of g_{EN}. These two opposite effects on g_{EN} will counter each other and, in all, structural interaction should make positive contributions to g_{EN}. For the studied system here, the structural interaction between RbCl/CsCl and amide is composed principally of partial desolvation of solutes that interact with each other, as well as the solvent reorganization in the neighborhood of the hydrophobic groups of the amides.

Here we think the interaction between RbCl/CsCl and amide should include the following four types:

i) Rb^+/Cs^+–R (R represents non-polar group in amide, that is, hydrophobic alkyl groups)
ii) Cl^-–R
iii) Rb^+/Cs^+–O (O are the polar groups in amide, they are hydrophilic groups –C=O, $-NH_2$)
iv) Cl^-–O

In the system investigated, g_{EN} is the sum of the Gibbs free energy interaction parameters of the pair of Rb^+/Cs^+ and Cl^- with the amide. There are two opposite polar groups in amide. One is carbonyl group (–C=O), which is a proton acceptor, and can easily interact electrostatic attractively with Rb^+/Cs^+ and electrostatic repulsively with Cl^-; the other is amino group ($-NH_2$). It is a proton donor and will interact electrostatic attractively with Cl^- and electrostatic repulsively with Rb^+/Cs^+. Moreover, there is positive contribution from Rb^+/Cs^+–R pair and Cl^-–R pair interaction as well as the desolvation of solutes. Both of them are all structural interactions. Obviously, the experimental results suggest that the signs of the contributions of RbCl/CsCl+amide pair to g_{EN} are mainly controlled by the electrostatic repulsive interaction of Cl^- with –C=O and Rb^+/Cs^+ with $-NH_2$. These are in agreement with the suggestion of Kelley and Lilley [37] that the experimental free-energy pair interaction parameters are fairly well represented by the electrostatic interaction only. However, the positive contribution from structural interaction will be more and more important with the increase of hydrophobic alkyl groups and even becomes predominant. This is why the g_{EN} increases with increasing number of carbon atoms from acetamide to *n*-butanamide.

Furthermore, the larger ion has the larger dispersion force, so that it has a greater effect on the hydrophobic hydration structure of non-polar alkyl group in amide. Therefore the positive contribution to g_{EN} arising from the structural interaction between RbCl/CsCl and non-polar alkyl group in amide will be greater as the ionic size increase from Rb^+ to Cs^+.

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