Thermodynamic Properties of L-Alanine in (RbCl or CsCl) + Water from 298.15 K to 313.15 K

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The enthalpy of mixing for aqueous heavy rare alkali metal chloride (RbCl, CsCl) solutions with aqueous L-alanine solutions, as well as the dilution enthalpies of RbCl, CsCl, and L-alanine solutions in pure water have been measured at 5 K intervals from 298.15 K to 313.15 K. The transfer enthalpies of RbCl and CsCl from pure water to aqueous L-alanine solutions can be obtained from these data. The enthalpic pair interaction parameters of RbCl and CsCl with L-alanine in water are evaluated according to the McMillan−Mayer theory and discussed in terms of the electrostatic interaction, structure interaction, and Savage-wood group additivity mode.

Introduction

Metal ions are essential to the structure and properties of proteins. The solubility, the stability, and the denaturation as well as the activity of proteins all have close relationship with metal ions.[1,2] It is well-known that the conformational and configurational factors that affect the structures of proteins in different solvents are very complicated. Therefore, the direct study of the interaction mechanism of proteins is not easy. However, the investigations of the behavior of model compounds of proteins, such as amino acids, peptides, and acylamide, can make the problem much simpler. These studies are usually employed to study the behavior of proteins in water, and they are evoking more and more interests.

The biological fluid of living organisms is a multicomponent aqueous solution in which there is an invariable pool of free amino acids and a specified quantity of ions. There have been many studies on the amino acid + electrolyte + water ternary system. Some enthalpic interaction parameters between some amino acids and alkali metal halides (LiCl, KCl, NaCl, NaBr, NaI) have been determined.[3,4] However, so far we have not found studies carried out on the interaction between amino acids and heavy rare alkali metal ions in water. The rare alkali metal ions rubidium and cesium play an important part in some physiological processes. It was reported that rubidium and cesium ions have similar functions to the potassium ion and can take the place of the potassium ion in some cases.[5] Moreover, rubidium has been regarded as one of the essential trace elements,[6] and cesium is also found to be able to induce the self-assembly of protein clusters and can effect charge translocation by the Na^+/K^+-ATPase.[7,8] Hence studies of the interaction between heavy rare alkali metal ions and α-amino acids in water are helpful in understanding the essence of some biological phenomena.

Our laboratory has concentrated on the interactions of heavy rare alkali metal ions with biological model molecules of saccharides and proteins in water recently.[9−13] As a part of the continuing studies on the thermodynamic and transfer properties of amino acids in aqueous electrolyte solutions, we report here the enthalpies of transfer of RbCl and CsCl from pure water to aqueous L-alanine solutions, and the enthalpic interaction parameters of RbCl and CsCl with L-alanine in water through measurements of thermal effects. This work is expected to provide more information on the interaction of Rb^+ and Cs^+ with α-amino acids in water from 298.15 K to 313.15 K.

Experimental Section

Rubidium chloride and cesium chloride (mass fraction ≥ 0.999) were prepared from rubidium carbonate and cesium carbonate, respectively. The purification and impurities in the samples has been reported elsewhere.[14,15] The L-alanine (Shanghai Chem. Co., mass fraction ≥ 0.99) was dried under low pressure at 338 K for 6 h. RbCl and CsCl were heated at 853 K and 773 K, respectively, to constant mass and stored over P_2O_5 in desiccators. Deionized and doubly distilled water was used throughout this work.

All the thermal effect of solutions was measured in an RD496-III calorimeter. The uncertainty of the temperatures is less than ± 0.05 K. An automatic electronic balance with a sensitivity of 10 μg was employed to prepare solutions.

The sensitivity of the calorimeter was determined using electrical calibration at 298.15 K. The Joule cell, which has a 1000 Ω electrical resistance, was supplied with 100 mW electric power for 100 s. The sensitivity obtained in this way was (63.994 ± 0.032) $\mu V \cdot mW^{-1}$. The uncertainty of thermal effect measurements was determined through chemical calibration at 298.15 K. The solution enthalpy $\Delta_{sol}H_m$ (∞) of potassium chloride in pure water was measured, and the results are shown in Table 1.

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Table 1. Enthalpy of Solution ($\Delta_{sol}H_m$) of Potassium Chloride at Different Mass (m) in Water and the Ratio ($r = n(H_2O)/n(KCl)$) at T = 298.15 K

no.	m/mg	r	$\Delta_{sol}H_m$/kJ·mol^{-1}
1	8.01	3825	17.23
2	8.19	3762	17.15
3	12.02	2745	17.29
4	13.16	2561	17.25
5	15.00	2236	17.27
6	15.02	2228	17.24
7	15.04	2211	17.21

$\Delta_{sol}H_m{}^0 = 17.23 \pm 0.03$ kJ· mol^{-1} [a]

[a] The uncertainty is estimated as twice the standard deviation of the mean.

All the solutions are prepared by mass. The uncertainty of molalities of solutions is 0.0004 mol·kg^{-1} for electrolyte and 0.002 mol·kg^{-1} for amino acids.. The measurement of dilution enthalpy of electrolyte (RbCl, CsCl) and L-alanine as well as some mixing enthalpies, such as the points of the most diluted and the most concentrated of electrolyte, were performed five times, and the uncertainty of data reported is 0.4 J·mol^{-1}. Here the uncertainty is estimated as twice the standard deviation of the mean.

Results and Discussion

As $n(H_2O)/n(KCl)$ is large and the $\Delta_{sol}H_m$ is nearly unchanged with the mass of the sample, the mean value of $\Delta_{sol}H_m$ in Table 1 can be assumed to refer to infinite dilution. The experimental value (17.230 ± 0.03) kJ·mol^{-1} is in excellent agreement with that of (17.241 ± 0.018) kJ·mol^{-1} reported in the literature.[16]

According to the McMillan–Mayer theory,[17] excess thermodynamic properties of a multicomponent solution can be expressed by a virial expansion, which relates the non-ideal contributions of thermodynamic functions to a series of interaction parameters, such as pair, triplet, and higher order items. In this work, electrolyte + water and amino acid + water binary solutions were mixed into electrolyte + amino acid + water ternary solutions. When the McMillan–Mayer theory is applied to this system, the transfer enthalpies of electrolyte from pure water to aqueous L-alanine solutions can be expressed as follows:[18]

$$\begin{aligned}\Delta_{tr}H_m &= \Delta_{mix}H_m - \Delta_{dil}H_m(E) - \{m(A)^f/m(E)^f\}\Delta_{dil}H_m(A)\\ &= 2vh_{EA}m(A)^f + 3v^2h_{EEA}m(A)^fm(E)^f +\\ &\qquad 3vh_{EAA}\{m(A)^f\}^2 + \ldots \quad (1)\end{aligned}$$

where $m(E)$ and $m(A)$ are the molalities of electrolyte and amino acids, respectively; v is the stoichiometric number of the electrolyte; and h_{EA}, h_{EEA}, and h_{EAA} are the enthalpic pair and triplet interaction parameters. In the studied molality range, the contributions of quadruplet and higher order terms can be assumed to be negligible within experimental uncertainty.[19] $\Delta_{mix}H_m$ is the molar mixing enthalpy arising from electrolyte solutions mixed with L-alanine solutions. $\Delta_{dil}H_m(E)$ and $\Delta_{dil}H_m(A)$ are the molar dilution enthalpies of electrolyte solutions and L-alanine solutions in pure water, respectively. $\Delta_{tr}H_m$ is the molar transfer enthalpy of electrolyte from pure water to aqueous L-alanine solutions. The superscripts i and f denote to the molality before and after the mixing process. $\Delta_{mix}H_m$, $\Delta_{dil}H_m(E)$, and $\Delta_{dil}H_m(A)$ have the same $m(E)^i$, $m(A)^i$, $m(E)^f$, and $m(A)^f$ in the mixing and dilution process. The values of $\Delta_{dil}H_m(E)$, $\Delta_{dil}H_m(A)$, $\Delta_{mix}H_m$, and $\Delta_{tr}H_m$ from (298.15 to 313.15) K are given in Table 2 for CsCl and in Table 3 for RbCl.

The whole process can be described as follows:

$$\text{electrolyte}\{m(E)^i\} + nH_2O(l) = \text{electrolyte}\{m(E)^f\},\ \Delta H_m = \Delta_{dil}H_m(E) \quad (2)$$

$$\text{amino acid}\{m(A)^i\} + nH_2O(l) = \text{amino acid}\{m(A)^f\},\ \Delta H_m = \Delta_{dil}H_m(A) \quad (3)$$

$$\text{electrolyte}\{m(E)^i\} + \text{amino acid}\{m(A)^i\} = \text{electrolyte}\{m(E)^f\}\text{amino acid}\{m(A)^f\},\ \Delta H_m = \Delta_{mix}H_m \quad (4)$$

$$\Delta_{tr}H_m = \Delta_{mix}H_m - \Delta_{dil}H_m(E) - \{m(A)^f/m(E)^f\}\Delta_{dil}H_m(A) \quad (5)$$

The enthalpy interaction parameters h_{EA}, h_{EEA}, and h_{EAA} can be obtained by fitting the experimental data to eq 1 by means of a least-squares procedure. The results show that h_{EEA} and h_{EAA} lack precision because of experimental errors. However, this is not very important because we are interested principally in the pair interaction parameter (h_{EA}), which are most important in dilute solution. The pair interaction parameters h_{EA} are given in Table 4. Furthermore, the h_{EA} values were analyzed as a function of temperature T using a least-squares routine. The best representation of the data was found to be

$$h_{EA} = a + bT + cT^2 \quad (6)$$

For RbCl + L-alanine + H_2O system: a = −927910.8 J·kg·mol^{-2}, b = 6032.7 J·kg·mol^{-2}·K^{-1}, c = −9.809 J·kg·mol^{-2}·K^{-2} with a correlation coefficient of 0.9999. For CsCl + L-alanine + H_2O system: $a = -1.101 \times 10^6$ J·kg·mol^{-2}, b = 7107.7 J·kg·mol^{-2}·K^{-1}, c = −11.478 J·kg·mol^{-2}·K^{-2} with a correlation coefficient of 0.9967.

The pair interaction parameters are related to each other in usual way.[20] From eq 6, it follows that

$$C_{p,EA} = -(b + 2cT) \quad (7)$$

where $C_{p,EA}$ is the isobaric capacity parameter. The obtained $C_{p,EA}$ values from (298.15 to 313.15) K are also included in Table 4. In Table 4, the h_{EA} values at all temperatures are negative, which indicates that the interaction of RbCl and CsCl with L-alanine in water is an exothermic process. The values of h_{EA} become more negative as the cation radius increases.

The values of the pair interaction parameters are the mean ionic pair interaction parameters of the ions dissociated by an electrolyte with a nonelectrolyte. It is generally considered that the interaction of an electrolyte and a nonelectrolyte is composed of electrostatic interaction and structural interactions. The concept of structural interaction, introduced by Frank and Robinson,[21] has been used to explain the concentration dependence of transfer functions of electrolytes.[22,23] For the enthalpy functions, the structural interaction consists principally of two factors: (a) partial desolvation of solutes during the process that they interact with other components in water; (b) the solvent reorganization in the neighborhood of the hydrophobic groups of the nonelectrolyte. These interactions were discussed in detail in ref 24, and the view has been widely accepted that in most cases the net effect of the co-sphere overlap on the hydration structure is breaking, which means that structural interaction should make positive contributions to the enthalpy interaction parameters.

Table 2. Molar Enthalpies of Dilution and Enthalpies of Mixing for Cesium Chloride (E) + Water and Cesium Chloride (E) + L-alanine (A) + Water System at Molality *m* (E) of Electrolyte and Molality *m* (A) of Amino Acids from *T* = 298.15 K to 313.15 K

$m(\mathrm{E})^{\mathrm{i}}$	$m(\mathrm{A})^{1}$	$m(\mathrm{E})^{\mathrm{f}}$	$m(\mathrm{A})^{\mathrm{f}}$	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}(\mathrm{E})$	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}(\mathrm{A})$	$\Delta_{\mathrm{tr}}H_{\mathrm{m}}$	$m(\mathrm{E})^{\mathrm{i}}$	$m(\mathrm{A})^{1}$	$m(\mathrm{E})^{\mathrm{f}}$	$m(\mathrm{A})^{\mathrm{f}}$	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}(\mathrm{E})$	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}(\mathrm{A})$	$\Delta_{\mathrm{tr}}H_{\mathrm{m}}$
$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$
(T = 298.15 K)															
1.4999	0.7506	0.0334	0.7332	38.9	1352.7	−1.3	−1312.6	1.4999	1.2506	0.1536	1.1219	88.0	1167.6	−12.4	−1067.3
1.4999	1.0006	0.0334	0.9777	32.1	1352.7	−1.8	−1320.9	1.4999	1.5006	0.1536	1.3463	47.7	1167.6	−23.5	−1096.5
1.4999	1.2506	0.0334	1.2219	20.6	1352.7	−1.9	−1330.1	1.4999	0.7501	0.2191	0.6404	285.3	1175.6	−6.7	−883.6
1.4999	1.5006	0.0334	1.4665	0.6	1352.7	−3.4	−1338.7	1.4999	1.0006	0.2191	0.8538	177.5	1175.6	−12.2	−985.9
1.4999	0.7506	0.0809	0.7094	115.8	1160.8	−8.2	−1036.7	1.4999	1.2506	0.2191	1.0674	114.5	1175.6	−16.8	−1044.3
1.4999	1.0006	0.0809	0.9459	75.5	1160.8	−9.0	−1080.3	1.4999	1.5006	0.2191	1.2807	71.3	1175.6	−18.1	−1098.3
1.4999	1.2506	0.0809	1.1825	43.5	1160.8	−6.8	−1110.5	1.4999	0.7501	0.2786	0.6106	372.4	1102.5	−4.7	−725.4
1.4999	1.5006	0.0809	1.4189	29.9	1160.8	−18.4	−1112.6	1.4999	1.0006	0.2786	0.8142	205.5	1102.5	−13.6	−883.4
1.4999	0.7506	0.1536	0.6732	202.2	1167.6	−8.6	−956.85	1.4999	1.2506	0.2786	1.0177	152.9	1102.5	−12.8	−936.8
1.4999	1.0006	0.1536	0.8975	119.4	1167.6	−13.6	−1014.6	1.4999	1.5006	0.2786	1.2212	95.0	1102.5	−11.5	−996.0
(T = 303.15 K)															
1.4999	0.7506	0.0417	0.7291	60.0	685.0	−8.6	−616.4	1.4999	1.2506	0.1875	1.0937	53.3	735.1	−16.7	−665.1
1.4999	1.0006	0.0417	0.9721	54.1	685.0	−15.4	−646.3	1.4999	1.5006	0.1875	1.3125	42.0	735.1	−15.7	−677.4
1.4999	1.2506	0.0417	1.2152	12.1	685.0	−7.5	−680.5	1.4999	0.7501	0.2647	0.6176	322.7	791.8	−10.6	−458.5
1.4999	1.5006	0.0417	1.4582	12.4	685.0	0.4	−673.0	1.4999	1.0006	0.2647	0.8235	92.7	791.8	−27.0	−678.1
1.4999	0.7506	0.1000	0.6999	105.3	756.1	−13.8	−637.0	1.4999	1.2506	0.2647	1.0294	96.1	791.8	−21.1	−674.6
1.4999	1.0006	0.1000	0.9333	70.7	756.1	−19.3	−666.2	1.4999	1.5006	0.2647	1.2352	64.0	791.8	−14.8	−713.0
1.4999	1.2506	0.1000	1.1666	35.9	756.1	−10.6	−709.6	1.4999	0.7501	0.3333	0.5837	391.3	656.4	−15.3	−249.9
1.4999	1.5006	0.1000	1.4000	26.4	756.1	−10.7	−719.1	1.4999	1.0006	0.3333	0.7778	204.9	656.4	−35.5	−416.0
1.4999	0.7506	0.1875	0.6562	218.1	735.1	−9.9	−507.2	1.4999	1.2506	0.3333	0.9723	113.0	656.4	−27.3	−516.1
1.4999	1.0006	0.1875	0.8749	130.2	735.1	−18.1	−586.9	1.4999	1.5006	0.3333	1.1667	69.6	656.4	−19.3	−547.4
(T = 308.15 K)															
1.4999	0.7506	0.0417	0.7292	35.2	449.3	−4.6	−409.5	1.4999	1.2506	0.1875	1.0936	64.5	627.9	−18.2	−535.2
1.4999	1.0006	0.0417	0.9721	25.9	449.3	−1.3	−432.1	1.4999	1.5006	0.1875	1.3124	39.2	627.9	−23.4	−565.3
1.4999	1.2506	0.0417	1.2152	16.8	449.3	−4.1	−428.4	1.4999	0.7501	0.2647	0.6176	221.5	637.9	−10.9	−405.5
1.4999	1.5006	0.0417	1.4583	7.4	449.3	−6.0	−435.9	1.4999	1.0006	0.2647	0.8236	128.5	637.9	−13.9	−496.2
1.4999	0.7506	0.1000	0.6998	91.8	611.1	−26.6	−492.5	1.4999	1.2506	0.2647	1.0294	97.0	637.9	−18.6	−521.9
1.4999	1.0006	0.1000	0.9332	75.5	611.1	−15.5	−560.0	1.4999	1.5006	0.2647	1.2352	61.2	637.9	−25.1	−551.7
1.4999	1.2506	0.1000	1.1667	55.6	611.1	−19.8	−535.7	1.4999	0.7501	0.3333	0.5833	323.9	662.1	−4.5	−333.7
1.4999	1.5006	0.1000	1.4000	24.6	611.1	−18.6	−567.8	1.4999	1.0006	0.3333	0.7778	196.4	662.1	−10.7	−455.0
1.4999	0.7506	0.1875	0.6562	187.1	627.9	−10.0	−430.8	1.4999	1.2506	0.3333	0.9723	112.8	662.1	−23.6	−525.7
1.4999	1.0006	0.1875	0.8749	108.5	627.9	−15.5	−503.6	1.4999	1.5006	0.3333	1.1668	67.9	662.1	−30.1	−564.0
(T = 313.15 K)															
1.4999	0.7506	0.0417	0.7292	15.8	522.3	−9.8	−496.7	1.4999	1.2506	0.1875	1.0936	63.4	483.2	−28.0	−391.8
1.4999	1.0006	0.0417	0.9721	17.0	522.3	−11.2	−494.1	1.4999	1.5006	0.1875	1.3124	22.8	483.2	−37.3	−423.2
1.4999	1.2506	0.0417	1.2152	11.3	522.3	−14.7	−505.8	1.4999	0.7501	0.2647	0.6176	158.4	476.8	−45.9	−272.5
1.4999	1.5006	0.0417	1.4583	10.2	522.3	−18.7	−493.4	1.4999	1.0006	0.2647	0.8236	121.5	476.8	−21.9	−333.4
1.4999	0.7506	0.1000	0.6998	79.1	518.3	−11.5	−427.7	1.4999	1.2506	0.2647	1.0294	83.8	476.8	−28.6	−364.5
1.4999	1.0006	0.1000	0.9332	67.9	518.3	−15.5	−435.2	1.4999	1.5006	0.2647	1.2352	50.7	476.8	−59.2	−366.7
1.4999	1.2506	0.1000	1.1667	34.7	518.3	−16.6	−467.0	1.4999	0.7501	0.3333	0.5833	180.4	469.5	−49.6	−219.4
1.4999	1.5006	0.1000	1.4000	11.7	518.3	−19.8	−486.8	1.4999	1.0006	0.3333	0.7778	163.9	469.5	−20.5	−285.2
1.4999	0.7506	0.1875	0.6562	153.1	483.2	−10.1	−320.0	1.4999	1.2506	0.3333	0.9723	94.5	469.5	−38.6	−336.4
1.4999	1.0006	0.1875	0.8749	95.0	483.2	−22.4	−365.8	1.4999	1.5006	0.3333	1.1668	61.9	469.5	−47.8	−359.8

In the studied solutions, according to the Savage−Wood group additivity principle, it can be assumed that the interaction of electrolyte with the polar groups in a L-alanine (−NH_2, −COOH) is mainly an electrostatic interaction, accompanied by the desolvation of the solutes. This interaction results in a negative contribution to the enthalpy parameters; however, it will be partly counteracted by the positive contribution from the desolvation of the solutes. Because the ionic size of Cs^+ is larger than that of Rb^+, desolvation of Cs^+ is easier, and the counteractive effect on the negative contribution of electrostatic interaction is weaker than that of Rb^+. Therefore, the values of h_{EA} become more negative from Rb^+ to Cs^+. On the other hand, there is primarily an structural interaction between the electrolyte and the nonpolar groups in L-alanine. The larger ion has a larger dispersion force, so it has a greater effect on the hydrophobic hydration structure of the nonpolar groups in a L-alanine. Therefore, the positive contribution to h_{EA} arising from the structural interaction between the electrolyte and the nonpolar groups in L-alanine should be greater as the ionic radius increases. The two interactions of electrolyte with polar and nonpolar groups in a L-alanine have opposite effects on h_{EA} as the ionic size increases from RbCl to CsCl. The results in Table 4 suggest that the electrostatic interaction of RbCl and CsCl with polar groups in L-alanine is the dominant interaction in the examined solutions. Consequently, the value of h_{EA} becomes more negative with the ionic size of electrolyte increasing from RbCl to CsCl.

The structural interaction is very sensitive to temperature. The positive contribution of structural interaction to h_{EA} will decrease with temperature increase and approach zero at high temperature.[25,26] In the studied system (shown as Figure 1), the negative contribution of the electrostatic interaction to h_{EA} is the more effective factor at lower temperature (298.15 K to 308.15 K); however, the structural interaction becomes dominant at a temperature > 308.15 K, and h_{EA} becomes more negative with the positive contribution to h_{EA} coming from the structural interaction decreased at higher temperature (308.15 K to 313.15 K). It is very interesting that the extreme value of h_{EA} occurred around the temperature that is similar to the body temperature of human beings. We do not know what the meaning of this phenomenon is to the physiological action

Table 3. Molar Enthalpies of Dilution and Enthalpies of Mixing for Rubidium Chloride (E) + Water and Rubidium Chloride (E) + L-Alanine (A) + Water System at Molality *m* (E) of Electrolyte and Molality *m* (A) of Amino Acids from *T* = 298.15 K to 313.15 K

$m(\mathrm{E})^{\mathrm{i}}$	$m(\mathrm{A})^{1}$	$m(\mathrm{E})^{\mathrm{f}}$	$m(\mathrm{A})^{\mathrm{f}}$	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}(\mathrm{E})$	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}(\mathrm{A})$	$\Delta_{\mathrm{tr}}H_{\mathrm{m}}$	$m(\mathrm{E})^{\mathrm{i}}$	$m(\mathrm{A})^{1}$	$m(\mathrm{E})^{\mathrm{f}}$	$m(\mathrm{A})^{\mathrm{f}}$	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}(\mathrm{E})$	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}(\mathrm{A})$	$\Delta_{\mathrm{tr}}H_{\mathrm{m}}$
$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{J\cdot mol^{-1}}$
(T = 298.15 K)															
1.4999	0.7506	0.0354	0.7328	20.8	705.6	−19.0	−667.9	1.4999	1.2506	0.1618	1.1151	45.8	858.9	−13.5	−779.6
1.4999	1.0006	0.0354	0.9762	15.7	705.6	−14.1	−675.8	1.4999	1.5006	0.1618	1.5611	11.1	858.9	−3.7	−844.2
1.4999	1.2506	0.0354	1.2203	2.3	705.6	−9.4	−698.5	1.4999	0.7501	0.2303	0.6348	211.3	847.0	−25.5	−630.1
1.4999	1.5006	0.0354	1.7084	4.3	705.6	−5.4	−695.8	1.4999	1.0006	0.2303	0.8464	97.5	847.0	−35.1	−714.5
1.4999	0.7506	0.0855	0.7072	58.9	789.9	−12.9	−718.1	1.4999	1.2506	0.2303	1.0580	47.5	847.0	−29.2	−770.3
1.4999	1.0006	0.0855	0.9428	49.7	789.9	−17.1	−723.1	1.4999	1.5006	0.2303	1.4813	17.6	847.0	−17.4	−812.1
1.4999	1.2506	0.0855	1.1788	6.3	789.9	−15.9	−747.7	1.4999	0.7501	0.2921	0.6040	163.2	804.9	−23.3	−618.4
1.4999	1.5006	0.0855	1.6500	8.7	789.9	1.3	−782.7	1.4999	1.0006	0.2921	0.8052	182.4	804.9	−21.4	−601.1
1.4999	0.7506	0.1618	0.6691	142.3	858.9	−22.6	−694.0	1.4999	1.2506	0.2921	1.0064	80.8	804.9	−14.5	−709.7
1.4999	1.0006	0.1618	0.8920	85.2	858.9	−16.4	−757.3	1.4999	1.5006	0.2921	1.4090	22.1	804.9	−11.7	−751.2
(T = 303.15 K)															
1.4999	0.7506	0.0417	0.7291	47.9	331.5	−8.6	−274.9	1.4999	1.2506	0.1875	1.0939	44.7	503.1	−16.7	−441.7
1.4999	1.0006	0.0417	0.9721	20.3	331.5	−15.4	−295.7	1.4999	1.5006	0.1875	1.3126	23.9	503.1	−15.7	−463.5
1.4999	1.2506	0.0417	1.2151	12.5	331.5	−7.5	−314.5	1.4999	0.7501	0.2647	0.6175	253.0	494.6	−10.6	−230.9
1.4999	1.5006	0.0417	1.4581	2.6	331.5	0.4	−329.3	1.4999	1.0006	0.2647	0.8236	152.4	494.6	−27.1	−315.2
1.4999	0.7506	0.1000	0.7000	76.9	512.9	−13.8	−422.2	1.4999	1.2506	0.2647	1.0293	51.8	494.6	−21.2	−421.7
1.4999	1.0006	0.1000	0.9332	63.7	512.9	−19.3	−429.9	1.4999	1.5006	0.2647	1.2351	38.0	494.6	−14.8	−441.8
1.4999	1.2506	0.1000	1.1667	19.5	512.9	−10.6	−482.8	1.4999	0.7501	0.3333	0.5833	283.5	480.6	−15.3	−181.8
1.4999	1.5006	0.1000	1.4000	6.0	512.9	−10.7	−496.2	1.4999	1.0006	0.3333	0.7778	188.1	480.6	−35.5	−256.9
1.4999	0.7506	0.1875	0.6563	157.0	503.1	−9.9	−336.2	1.4999	1.2506	0.3333	0.9722	77.1	480.6	−27.3	−376.1
1.4999	1.0006	0.1875	0.8750	96.3	503.1	−18.1	−388.7	1.4999	1.5006	0.3333	1.1666	47.0	480.6	−19.3	−404.3
(T = 308.15 K)															
1.4999	0.7506	0.0417	0.7292	29.6	223.6	−4.6	−189.4	1.4999	1.2506	0.1875	1.0936	68.0	479.9	−18.2	−393.7
1.4999	1.0006	0.0417	0.9721	5.6	223.6	−1.3	−216.7	1.4999	1.5006	0.1875	1.3124	39.5	479.9	−23.4	−416.9
1.4999	1.2506	0.0417	1.2152	4.4	223.6	−4.1	−215.0	1.4999	0.7501	0.2647	0.6176	196.7	584.0	−10.9	−376.4
1.4999	1.5006	0.0417	1.4583	4.3	223.6	−6.0	−213.2	1.4999	1.0006	0.2647	0.8236	129.4	584.0	−13.9	−441.3
1.4999	0.7506	0.1000	0.6998	49.7	379.1	−26.6	−302.9	1.4999	1.2506	0.2647	1.0294	76.7	584.0	−18.6	−488.3
1.4999	1.0006	0.1000	0.9332	38.5	379.1	−15.5	−325.1	1.4999	1.5006	0.2647	1.2352	47.8	584.0	−25.1	−511.1
1.4999	1.2506	0.1000	1.1667	31.9	379.1	−19.8	−327.4	1.4999	0.7501	0.3333	0.5833	249.0	677.6	−4.5	−424.1
1.4999	1.5006	0.1000	1.4000	26.3	379.1	−18.6	−334.2	1.4999	1.0006	0.3333	0.7778	150.8	677.6	−10.7	−516.1
1.4999	0.7506	0.1875	0.6562	134.3	479.9	−10.0	−335.6	1.4999	1.2506	0.3333	0.9723	100.1	677.6	−23.6	−553.9
1.4999	1.0006	0.1875	0.8749	94.4	479.9	−15.5	−369.9	1.4999	1.5006	0.3333	1.1668	65.4	677.6	−30.1	−582.1
(T = 313.15 K)															
1.4999	0.7506	0.0417	0.7292	24.7	338.2	−9.8	−303.7	1.4999	1.2506	0.1875	1.0936	15.0	495.5	−28.0	−452.4
1.4999	1.0006	0.0417	0.9721	9.6	338.2	−11.2	−317.3	1.4999	1.5006	0.1875	1.3124	12.5	495.5	−37.3	−445.7
1.4999	1.2506	0.0417	1.2152	8.8	338.2	−14.7	−327.1	1.4999	0.7501	0.2647	0.6176	130.6	357.1	−45.9	−180.6
1.4999	1.5006	0.0417	1.4583	7.4	338.2	−18.7	−332.1	1.4999	1.0006	0.2647	0.8236	78.8	357.1	−21.9	−256.4
1.4999	0.7506	0.1000	0.6998	58.9	388.5	−11.5	−318.2	1.4999	1.2506	0.2647	1.0294	25.9	357.1	−28.6	−302.6
1.4999	1.0006	0.1000	0.9332	31.0	388.5	−15.5	−342.4	1.4999	1.5006	0.2647	1.2352	25.4	357.1	−59.2	−272.2
1.4999	1.2506	0.1000	1.1667	15.4	388.5	−16.6	−356.6	1.4999	0.7501	0.3333	0.5833	137.3	307.8	−49.6	−120.9
1.4999	1.5006	0.1000	1.4000	10.0	388.5	−19.8	−358.8	1.4999	1.0006	0.3333	0.7778	82.7	307.8	−20.5	−204.7
1.4999	0.7506	0.1875	0.6562	80.7	495.5	−10.1	−404.6	1.4999	1.2506	0.3333	0.9723	52.0	307.8	−38.6	−212.3
1.4999	1.0006	0.1875	0.8749	46.2	495.5	−22.4	−426.8	1.4999	1.5006	0.3333	1.1668	35.0	307.8	−47.8	−225.1

Table 4. Enthalpic Pair Interaction Parameters and Isobaric Capacity Parameters for L-Alanine + Rubidium Chloride and L-Alanine + Cesium Chloride) in Water from 298.15 K to 313.15 K

T/K	$2\upsilon h_{\mathrm{EA}}/(\mathrm{J\cdot kg\cdot mol^{-2}})$	$C_{\mathrm{p,EA}}/(\mathrm{J\cdot kg\cdot mol^{-2}\cdot K^{-1}})$
(RbCl-L-Alanine)		
298.15	−1221.6 ± 14.7	−3108.1 ± 34.2
303.15	−544.4 ± 8.2	−3059.1 ± 36.7
308.15	−368.9 ± 6.3	−3010.1 ± 33.1
313.15	−672.7 ± 10.8	−3065.4 ± 36.7
(CsCl-L-Alanine)		
298.15	−2193.3 ± 24.1	−3685.5 ± 40.5
303.15	−1112.4 ± 15.6	−3628.1 ± 39.9
308.15	−733.0 ± 9.5	−3570.8 ± 42.8
313.15	−799.9 ± 8.8	−3513.4 ± 38.6

in body exactly, but it is sure important and warrants further careful consideration. Heat capacity is a very sensitive probe for studying structural interactions. The negative values of $C_{\mathrm{p,EA}}$ mean that the interaction of RbCl and CsCl with L-alanine in water results in a reduction in the structure of the solution.

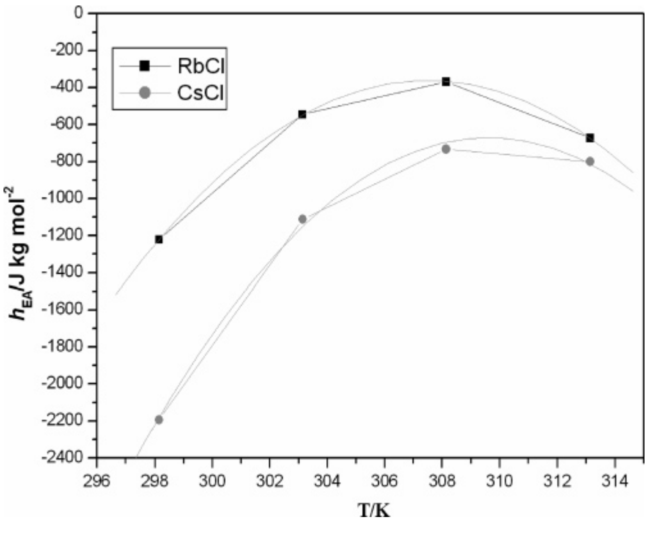

Figure 1. Temperature dependence of the enthal pair interaction parameters for RbCl + alanine and CsCl + alanine in water.

Conclusions

The transfer enthalpies of cesium chloride and rubidium chloride from pure water to aqueous L-alanine solutions from (298.15 to 313.15) K were measured, and the thermodynamic parameters (including enthalpy and heat capacity interaction parameters for eletrolyte + L-alanine pair in water) were evaluated in terms of the McMillan−Mayer theory. The results show that the interaction between RbCl or CsCl and L-alanine is exothermic, and the enthalpic interaction parameter decreases with increasing temperature from 298.15 K to 308.15 K and then increases slightly at temperatures > 308.15K. Moreover, the maximum value of h_{EA} occurrs at 308.15 K, which is close to the body temperature of human beings.

The values of h_{EA} and $C_{p,EA}$ become more negative as the size of the electrolyte ions increases from Rb^+ to Cs^+. This results from the electrostatic interaction and structure interaction.

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