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Thermodynamics of the interaction of RbCl with some monosaccharides (D-glucose, D-galactose, D-xylose, and D-arabinose) in aqueous solutions at 298.15 K

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Abstract—The Gibbs energy interaction parameters of RbCl with some monosaccharides (D-glucose, D-galactose, D-xylose, and D-arabinose) in water, g_{ES}, were obtained from electromotive force (emf) measurements of the electrochemical cell without liquid junction and containing two ion-selective electrodes (ISE): K-ISE|RbCl(m_E)|ISE-Cl and K-ISE|RbCl(m_E),saccharide (m_S)|ISE-Cl, at 298.15 K. The enthalpy interaction parameters of RbCl with these monosaccharides in water, h_{ES}, are determined according to the McMillan–Mayer theory from the measurements of the enthalpies of mixing of aqueous RbCl solutions with aqueous monosaccharide solutions, as well as the enthalpies of dilution of RbCl and monosaccharide solutions in pure water at 298.15 K by a calorimetric method. Furthermore, the entropy interaction parameters, s_{ES}, can be evaluated through g_{ES} and h_{ES}. The results suggest that the electrostatic interactions of these monosaccharides with RbCl in water are predominant compared with structural interactions, and these parameters are controlled primarily by the stereochemical structure of the monosaccharides in water.

Keywords: Rubidium chloride; Monosaccharides; Thermodynamic interaction parameters

1. Introduction

Metal ions have an important influence on the hydration of saccharides. The thermal stability of saccharides in organisms is predominantly mediated through the changes of saccharides in solvent or the alteration of water structure caused by metal ions.[1,2] The interaction between saccharides and electrolyte in aqueous solutions is important and has been closely looked at since Angyal's pioneering studies.[3] However, it is well known that the conformational and configurational factors, which can affect the structures of saccharides in different solvents, are very complicated. This makes the direct study on the interaction mechanism of saccharides difficult. But investigations of the behavior of model compounds of saccharides, such as monosaccharides, in electrolyte + water mixtures will make the problem much simpler. These studies are usually effective and useful for examining the characteristics of carbohydrates in body fluids.

There have been some studies reported on the saccharide + electrolyte + water systems;[4–6] however, relatively few attempts have been made for Rb/Cs compounds. Rb^+ plays an important part in some physiological processes and is regarded as having a similar function to that of potassium ions in organisms, and of potassium ions can take place in some cases.[7] Rubidium has been considered to be one of the essential trace elements in the human body.[8]

In recent years, our laboratory has carried out a series of studies on the thermodynamics of the interaction of Rb^+/Cs^+ with biological model molecules of saccharides in water.[9–12] In one of our previous studies,[13] we determined the Gibbs free-energy interaction parameters of CsCl with glucose at different temperatures from

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electromotive force measurements. Then the enthalpy and entropy interaction parameters as well as isobaric heat capacity parameters were evaluated through these Gibbs free-energy parameters by means of the temperature coefficient method. However, these interaction parameters lack precision because of indirect access. In this work, the enthalpy interaction parameters are experimentally determined from the measurements of the enthalpies of mixing of aqueous RbCl solutions with aqueous monosaccharide solutions, as well as the enthalpies of dilution of RbCl and monosaccharide solutions in pure water at 298.15 K by a calorimetric method. This paper is not only expected to provide additional information on the interaction between Rb^+/Cs^+ and monosaccharides in water, but also to enable us to rationalize the hydration characteristics and examine the possible relationship between these thermodynamic parameters and the stereochemistry of saccharides.

2. Experimental

Rubidium chloride, mass fraction $\geqslant 0.999$, was synthesized from rubidium carbonate. The purification and determination of RbCl has been reported elsewhere.[14] Anhydrous D-glucose and D-arabinose (Shanghai Chem. Co., mass fraction $\geqslant 0.99$), the D-galactose and D-xylose (mass fraction approximately 0.96, Shanghai Chem. Co.), were recrystallized from water + EtOH mixtures. All the saccharides were dried under low pressure at $T = 338$ K for 6 h, and rubidium chloride was heated at $T = 773$ K to constant mass. All reagents were stored over silica gel in desiccators. Deionized and doubly distilled water was used throughout this work.

An electrochemical cell without a liquid junction was set up with a potassium ion-selective electrode (model PK-1, Shanghai Ruosull Technology Co. Ltd.) as the working electrode and a chloride ion-selective electrode (model PCL-1, Shanghai Ruosull Technology Co. Ltd.) as the reference electrode:

$$\text{K-ISE}|\text{RbCl}(m_E)|\text{ISE-Cl} \qquad \text{(I)}$$

$$\text{K-ISE}|\text{RbCl}(m_E),\text{monosaccharide}(m_S)|\text{ISE-Cl} \qquad \text{(II)}$$

where m_E and m_S are the molalities of RbCl and monosaccharide, respectively, expressed as the number of moles per kg of pure water. A pH/ISE meter (model PXSJ-216, Shanghai Rex Instrument Factory) was employed to measure the electromotive force (emf) of RbCl + monosaccharides + water solutions. The cell was thermostated with an accuracy of ±0.05 K, and the emf of the cell was measured at 298.15 K. The tested solutions were freshly prepared using an automatic electronic balance with a sensitivity of 10 μg. A magnetic stirrer was used to stir continuously these solutions in order to minimize concentration gradients in the cell.

Each set of measurements was performed at a fixed RbCl concentration, ranging from 0.005 to 0.1 mol kg^{-1}, and the molalities of the monosaccharides were increased from 0.005 to (1.5 or 2.0) mol kg^{-1} by adding solid monosaccharide. At each point, the emf was recorded only when the drift was less than 0.1 mV for 5 min. To ensure the stability of the electrode during each experimental process, the molality range of monosaccharides was defined according to its solubility and dissolution rate so as to ensure the electrodes staying in solution no longer than 1–2 h. After the emf of the last sample solution was measured, the electrodes were transferred to the original RbCl solution to measure the emf again. The two emf values of the RbCl solutions agree with each other within 0.5 mV. Some measurements, such as $0.005 \text{ mol kg}^{-1}$ (the most dilute) and 0.1 mol kg^{-1} (the most concentrated) of RbCl, were repeated three times, and the data adopted here are the mean value of the replicates.

The slope S of the electrode response was determined according to the empirical equation recommended by Hamer and Wu.[15] 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. 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 with the Nernst equation in the experimental concentration range.

All the thermal effects of the solutions were measured in an RD496-III calorimeter. 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 $63.994 \pm 0.042 \text{ mV W}^{-1}$. The accuracy and precision were determined through chemical calibration for measurement of enthalpy of solution ($\Delta_{\text{sol}}H_{\text{m}}$) of potassium chloride in pure water at 298.15 K. The experimental value $17.23 \pm 0.04 \text{ kJ mol}^{-1}$ is in excellent agreement with that of $17.24 \pm 0.05 \text{ kJ mol}^{-1}$ reported in the literature.[16]

The measurements of the enthalpies of mixing of aqueous RbCl solutions in the monosaccharide + water mixtures, as well as the enthalpies of dilution of RbCl and monosaccharide solutions in pure water at 298.15 K were performed in a device made of glass, which was especially designed to prevent high concentration RbCl solutions from eroding the measurement cell and the reference cell. The structure of this device is shown in Figure 1. This glass device includes an inner tube (containing electrolyte solutions) and an outer tube (containing saccharide + water mixtures or pure water).

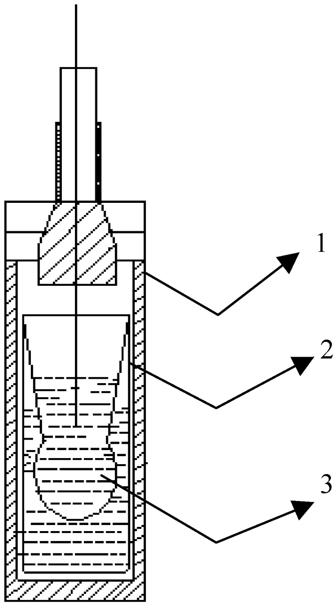


Figure 1. The structure of sample cell: (1) calorimetric cell, (2) outer tube, and (3) inner tube.

The inner tube has a very thin ball at the end, and the ball can be broken easily to effect the mixing of the solutions.

3. Results

According to the McMillan–Mayer theory,[17] the excess thermodynamic functions can be expressed in terms of pair and triplet interactions between the two solutes. For a solution of nonelectrolyte (N) and electrolyte (E), which dissociates into υ ions, it is given by

$$\begin{aligned} F(m_{\mathrm{N}}, m_{\mathrm{E}}) &= F^{0}(m_{\mathrm{N}}, m_{\mathrm{E}}) + F^{\mathrm{EX}}(m_{\mathrm{N}}) + F^{\mathrm{EX}}(m_{\mathrm{E}}) \\ &\quad + 2\upsilon f_{\mathrm{EN}} m_{\mathrm{E}} m_{\mathrm{N}} + 3\upsilon^{2} f_{\mathrm{EEN}} m_{\mathrm{E}}^{2} m_{\mathrm{N}} \\ &\quad + 3\upsilon f_{\mathrm{ENN}} m_{\mathrm{E}} m_{\mathrm{N}}^{2} + \cdots \end{aligned} \tag{1}$$

where $F^{0}(m_{\mathrm{N}}, m_{\mathrm{E}})$ 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. $F^{\mathrm{EX}}(m_{\mathrm{N}})$ and $F^{\mathrm{EX}}(m_{\mathrm{E}})$ 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.

For the transfer function of electrolyte from water to aqueous nonelectrolyte solution, we have from Eq. 1[18]

$$\begin{aligned} \Delta_{\mathrm{t}} F(\mathrm{W} \rightarrow \mathrm{W} + \mathrm{N}) &= F_{\mathrm{E}}(m_{\mathrm{N}}, m_{\mathrm{E}}) - F_{\mathrm{E}}^{0}(m_{\mathrm{E}}) \\ &= 2\upsilon f_{\mathrm{EN}} m_{\mathrm{N}} + 6\upsilon^{2} f_{\mathrm{EEN}} m_{\mathrm{E}} m_{\mathrm{N}} + 3\upsilon f_{\mathrm{ENN}} m_{\mathrm{N}}^{2} + \cdots \end{aligned} \tag{2}$$

where both $F_{\mathrm{E}}(m_{\mathrm{N}}, m_{\mathrm{E}})$ and $F_{\mathrm{E}}^{0}(m_{\mathrm{E}})$ are the partial molar quantities of electrolyte.

In the particular case of the Gibbs free-energies in the studied system, Eq. 2 is reduced to[19,20]

$$\begin{aligned} \Delta_{\mathrm{t}} G_{\mathrm{E}}(\mathrm{W} \rightarrow \mathrm{W} + \mathrm{S}) &= -nF\Delta E \\ &= \mu_{\mathrm{E}}(m_{\mathrm{S}}, m_{\mathrm{E}}) - \mu_{\mathrm{E}}^{0}(m_{\mathrm{E}}) \\ &= 2\upsilon g_{\mathrm{ES}} m_{\mathrm{S}} + 6\upsilon^{2} g_{\mathrm{EES}} m_{\mathrm{E}} m_{\mathrm{S}} + 3\upsilon g_{\mathrm{ESS}} m_{\mathrm{S}}^{2} \end{aligned} \tag{3}$$

where $\mu_{\mathrm{E}}(m_{\mathrm{S}}, m_{\mathrm{E}})$ and $\mu_{\mathrm{E}}^{0}(m_{E})$ are the chemical potentials of RbCl in an E + S + W ternary solution and an E + W binary solution, respectively. F is the Faraday constant, and ΔE is the difference of electromotive force. In the present case, $\Delta E = E\,(\text{cell II}) - E\,(\text{cell I})$. The emf values are reported in Table 1. The higher order terms have been neglected in Eq. 3. The pair and triplet interaction parameters can be obtained when Eq. 3 is fit to the experimental data using the least-squares routine.

Table 1. Emfs (in mV) of cell (I) and cell (II) for the RbCl + monosaccharide + water systems at 298.15 K

m_{S}/mol kg^{-1}	m(RbCl)/mol kg^{-1}				
	0.005	0.010	0.050	0.080	0.100
Emfs of RbCl + glucose + water					
0.000	−173.9	−140.9	−75.1	−43.3	−32.8
0.005	−173.9	−140.8	−75.0	−43.3	−32.7
0.010	−173.3	−140.7	−75.0	−43.2	−32.8
0.050	−172.9	−140.6	−74.9	−43.2	−32.7
0.100	−172.3	−140.4	−74.8	−43.1	−32.6
0.500	−171.4	−139.5	−74.3	−42.7	−32.4
1.000	−166.6	−137.1	−74.1	−42.5	−32.0
1.500	−162.3	−132.7	−72.0	−40.8	−30.9
2.000	−157.2	−131.3	−69.4	−40.2	−30.4
Emfs of RbCl + galactose + water					
0.000	−173.9	−140.9	−75.1	−43.3	−32.8
0.005	−173.9	−141.0	−75.2	−43.4	−33.1
0.010	−174.0	−141.0	−75.4	−43.6	−32.2
0.050	−174.1	−141.2	−75.8	−44.1	−33.8
0.100	−174.2	−141.7	−76.0	−44.3	−34.0
0.500	−174.7	−142.0	−76.3	−44.6	−34.3
1.000	−175.5	−142.7	−77.1	−45.4	−35.0
1.500	−176.6	−143.7	−78.0	−46.3	−36.5
Emfs of RbCl + xylose + water					
0.000	−173.9	−140.9	−75.1	−43.3	−32.8
0.005	−173.7	−140.8	−75.1	−43.3	−32.8
0.010	−173.6	−140.7	−75.0	−43.3	−32.8
0.050	−173.3	−140.6	−74.8	−43.2	−32.8
0.100	−173.0	−140.1	−74.7	−43.1	−32.7
0.500	−172.4	−139.7	−74.5	−42.9	−32.6
1.000	−171.6	−139.5	−74.2	−42.7	−32.3
1.500	−171.3	−139.0	−74.0	−42.4	−31.9
2.000	−170.5	−138.6	−73.3	−42.1	−31.7
Emfs of RbCl + arabinose + water					
0.000	−173.9	−140.9	−75.1	−43.3	−32.8
0.005	−173.9	−141.0	−75.2	−43.5	−33.1
0.010	−174.0	−141.1	−75.3	−43.6	−33.3
0.050	−174.2	−141.3	−75.6	−43.9	−33.5
0.100	−174.4	−141.4	−75.8	−44.1	−33.8
0.500	−175.0	−142.1	−76.5	−45.1	−34.8
1.000	−175.9	−143.3	−77.8	−46.1	−36.4
1.500	−177.1	−144.3	−78.7	−47.1	−38.2

Table 2. The Gibbs free-energy interaction parameters (g_{ES}), enthalpy interaction parameters (h_{ES}), and entropy interaction parameters (Ts_{ES}) as well as salting constants (k_S) for the RbCl + monosaccharide + water systems at 298.15 K

Monosaccharide	g_{ES}/J kg mol^{-2} [a]	h_{ES}/J kg mol^{-2} [a]	Ts_{ES}/J kg mol^{-2}	k_S/kg mol^{-1}
(RbCl, glucose)	367.8 ± 16.8	−187.4 ± 12.2	−555.2	0.5936
(HCl, glucose)[b]	116.7 ± 3.8	210	94	
(NaCl, glucose)[c]	56.08			
(CsCl, glucose)[d]	409.8	−205.9	−615.7	
(RbCl, galactose)	−36.0 ± 2.5	−366.0 ± 19.6	−330.0	−0.0580
(RbCl, xylose)	375.8 ± 25.4	−179.9 ± 10.6	−555.7	0.6065
(RbCl, arabinose)	13.0 ± 1.1	−343.5 ± 15.2	−356.5	0.0212

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

[b] Ref. 18.

[c] Ref. 38.

[d] Ref. 39.

The results are given in Table 2, together with the uncertainties of the values of the fit. Here, we are only interested in the pair parameters that are most important in dilute solution.

The salting constant, k_S, defined by Friedman[21] can be calculated by[22,23]

$$RT k_S = 2\upsilon g_{ES} \tag{4}$$

where R is the gas constant. The results are also included in Table 2.

When the McMillan–Mayer theory is applied to the enthalpy effect, the transfer enthalpies of RbCl from pure water to monosaccharide + water mixture can be expressed as follows:[24]

$$\begin{aligned}\Delta_{tr}H_m &= \Delta_{mix}H_m - \Delta_{dil}H_m(E) - (m_S^f/m_E^f) \\ &\quad \cdot \Delta_{dil}H_m(S) \\ &= 2 \cdot \upsilon \cdot h_{ES} \cdot m_S^f + 3 \cdot \upsilon^2 \cdot h_{EES} \cdot m_S^f \cdot m_E^f \\ &\quad + 3 \cdot \upsilon \cdot h_{ESS} \cdot (m_S^f)^2 + \cdots ,\end{aligned} \tag{5}$$

where the $\Delta_{mix}H_m$ is the molar enthalpy of mixing arising from RbCl solutions mixed with monosaccharide + water mixture. The $\Delta_{dil}H_m(E)$ and $\Delta_{dil}H_m(S)$ are the molar enthalpies of dilution of RbCl solutions and monosaccharide solutions in pure water, respectively. The $\Delta_{tr}H_m$ is the molar transfer enthalpy of RbCl from pure water to monosaccharide + water mixture; ‘i’ and ‘f’ denote to the molality before and after the mixing process. $\Delta_{mix}H_m$, $\Delta_{dil}H_m(E)$, and $\Delta_{dil}H_m(S)$ have the same $m(E)^i$, $m(S)^i$, $m(E)^f$, and $m(S)^f$ in the mixing and dilution processes. The values for $\Delta_{mix}H_m$, $\Delta_{dil}H_m(E)$, $\Delta_{dil}H_m(S)$, and $\Delta_{tr}H_m$ are tabulated in Table 3.

The whole process can be described as follows:

$$\text{RbCl}(m_E^i) + n \cdot H_2O(l) = \text{RbCl}(m_E^f), \quad \Delta H_m = \Delta_{dil}H_m(E) \tag{6}$$

$$\text{saccharide}(m_S^i) + n \cdot H_2O(l) = \text{saccharide}(m_S^f), \quad \Delta H_m = \Delta_{dil}H_m(S) \tag{7}$$

$$\text{RbCl}(m_E^i) + \text{saccharide}(m_S^i) = \text{RbCl}(m_E^f) \cdot \text{saccharide}(m_S^f), \quad \Delta H_m = \Delta_{mix}H_m \tag{8}$$

The enthalpy interaction parameters h_{ES}, h_{EES}, and h_{ESS} can be obtained by fitting the experimental data to Eq. 5 using a least-squares procedure. The results show that h_{EES} and h_{ESS} lack precision because of experimental errors. However, this is not very important because we are principally interested in the pair interaction parameter, h_{ES}, just like g_{ES}. The enthalpy pair interaction parameters h_{ES} are also given in Table 2.

Then the entropy interaction parameters can be evaluated from the following equation:

$$g_{ES} = h_{ES} - Ts_{ES} \tag{9}$$

The results are also included in Table 2.

4. Discussion

It can be seen from Table 2 that both $g_{ES} > 0$, $k_S > 0$. This means that the relationship between RbCl and these monosaccharides in water is repulsive, and these monosaccharides can be salted out by RbCl. Moreover, Table 2 indicates that both h_{ES} and s_{ES} are negative, which means that the interaction of RbCl with these monosaccharides results in a decrease of entropy in the concerned systems.

The above phenomena can be interpreted in terms of the structural interaction and electrostatic interaction models. The interactions between RbCl and monosaccharides should include four types:

Rb^+–R (R represents hydrophobic alkyl groups),
Cl^-–R ,
Rb^+–O (O is hydrophilic groups, such as –OH, –C=O, and –O–) ,
Cl^-–O .

The Rb^+–O pair interaction, which is primarily electrostatically attractive, contributes a negative value to h_{ES} and g_{ES}. However, this negative contribution would be partly counteracted by the positive contribution from the Rb^+–R interaction that is mainly a structural

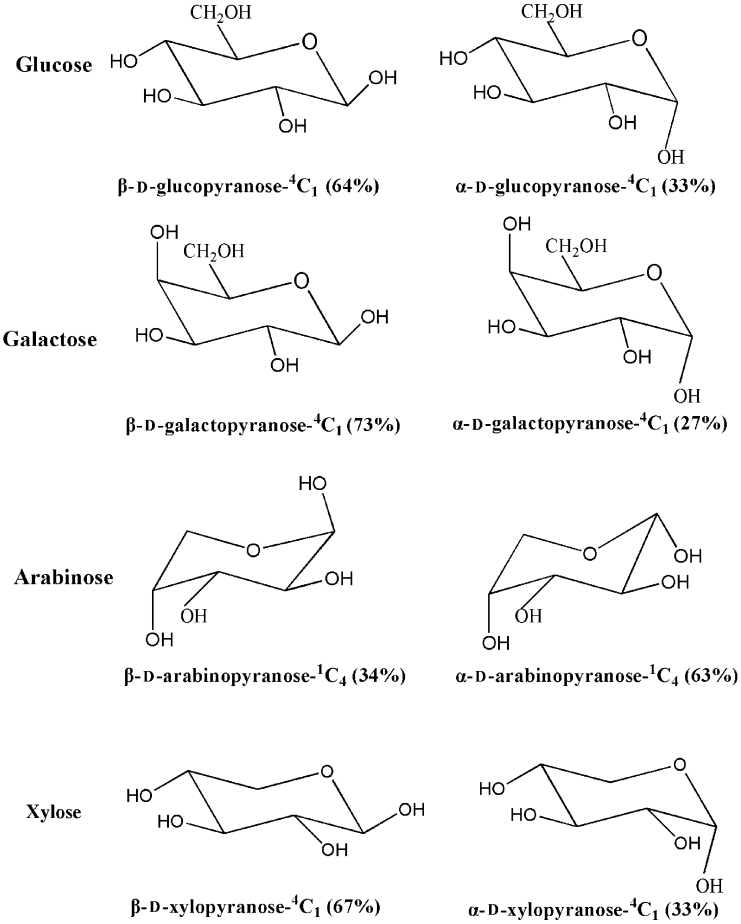
Table 3. The molar mixing enthalpies $\Delta_{\text{mix}}H_\text{m}$ of aqueous rubidium chloride solutions with aqueous saccharide solutions, and the molar transfer enthalpies $\Delta_{\text{tr}}H_\text{m}$ of rubidium chloride from pure water to aqueous saccharide solutions, as well as the molar dilution enthalpies of rubidium chloride and saccharides solution in pure water $\Delta_{\text{dil}}H_\text{m}(\text{E})$ and $\Delta_{\text{dil}}H_\text{m}(\text{S})$ at $T = 298.15$ K

$m(\text{E})^\text{i}$/mol kg^{-1}	$m(\text{S})^\text{i}$/mol kg^{-1}	$m(\text{E})^\text{f}$/mol kg^{-1}	$m(\text{S})^\text{f}$/mol kg^{-1}	$\Delta_{\text{mix}}H_\text{m}$/J mol^{-1}	$\Delta_{\text{dil}}H_\text{m}(\text{E})$/J mol^{-1}	$\Delta_{\text{dil}}H_\text{m}(\text{S})$/J mol^{-1}	$\Delta_{\text{tr}}H_\text{m}$/ J mol^{-1}
Rubidium chloride + glucose + water							
1.4999	0.2006	0.0817	0.1895	559.9	867.3	−2.8	−154.6
1.4999	0.2006	0.1540	0.1798	604.6	930.2	−5.3	−170.3
1.4999	0.2006	0.2194	0.1710	582.4	894.1	−7.5	−154.2
1.4999	0.2006	0.2794	0.1630	540.5	835.7	−9.3	−135.9
1.4999	0.2006	0.3335	0.1558	509.9	793.6	−10.9	−122.8
1.4999	0.3993	0.0817	0.3776	354.3	867.3	−8.2	−354.8
1.4999	0.3993	0.1540	0.3581	405.8	930.2	−15.2	−359.2
1.4999	0.3993	0.2194	0.3406	385.8	894.1	−21.5	−337.3
1.4999	0.3993	0.2794	0.3248	346.6	835.7	−27.2	−311.9
1.4999	0.3993	0.3335	0.3105	305.6	793.6	−34.2	−303.8
1.4999	0.6001	0.0817	0.5372	201.5	867.3	−10.7	−505.1
1.4999	0.6001	0.1540	0.5097	241.4	930.2	−20.4	−518.4
1.4999	0.6001	0.2194	0.4849	218.8	894.1	−29.3	−496.0
1.4999	0.6001	0.2794	0.4624	168.0	835.7	−38.4	−479.3
1.4999	0.6001	0.3335	0.4419	132.3	793.6	−44.8	−466.5
Rubidium chloride + galactose + water							
1.4999	0.1999	0.0817	0.1892	506.1	867.3	−1.4	−209.8
1.4999	0.1999	0.1540	0.1795	534.7	930.2	−2.5	−243.0
1.4999	0.1999	0.2194	0.1708	509.7	894.1	−3.5	−230.9
1.4999	0.1999	0.2794	0.1628	481.2	835.7	−4.3	−200.2
1.4999	0.1999	0.3335	0.1556	452.9	793.6	−4.9	−185.8
1.4999	0.3998	0.0817	0.3770	163.3	867.3	−3.6	−550.4
1.4999	0.3998	0.1540	0.3577	195.2	930.2	−6.7	−578.3
1.4999	0.3998	0.2194	0.3402	172.2	894.1	−9.5	−562.4
1.4999	0.3998	0.2794	0.3244	140.7	835.7	−12.3	−532.7
1.4999	0.3998	0.3335	0.3101	111.6	793.6	−14.5	−517.5
1.4999	0.6002	0.0817	0.5678	−5.57	867.3	−4.2	−718.6
1.4999	0.6002	0.1540	0.5387	58.6	930.2	−7.9	−713.7
1.4999	0.6002	0.2194	0.5125	34.7	894.1	−11.3	−698.1
1.4999	0.6002	0.2794	0.4887	23.8	835.7	−14.4	−647.5
1.4999	0.6002	0.3335	0.4669	12.4	793.6	−17.4	−613.8
Rubidium chloride + xylose + water							
1.4999	0.2001	0.0817	0.1893	471.1	867.3	−3.4	−192.8
1.4999	0.2001	0.1540	0.1797	593.9	930.2	−6.3	−130.0
1.4999	0.2001	0.2194	0.1709	569.6	894.1	−8.9	−115.6
1.4999	0.2001	0.2794	0.1630	534.9	835.7	−11.2	−89.6
1.4999	0.2001	0.3335	0.1557	512.8	793.6	−13.3	−67.5
1.4999	0.3993	0.0817	0.3780	281.6	867.3	−7.2	−368.5
1.4999	0.3993	0.1540	0.3587	335.3	930.2	−13.6	−371.3
1.4999	0.3993	0.2194	0.3412	299.5	894.1	−19.5	−365.1
1.4999	0.3993	0.2794	0.3254	280.6	835.7	−24.9	−320.2
1.4999	0.3993	0.3335	0.3109	244.5	793.6	−29.9	−309.2
1.4999	0.5999	0.0817	0.5676	174.5	867.3	−10.5	−532.3
1.4999	0.5999	0.1540	0.5385	241.9	930.2	−19.6	−518.7
1.4999	0.5999	0.2194	0.5123	209.8	894.1	−27.6	−506.7
1.4999	0.5999	0.2794	0.4885	175.5	835.7	−34.8	−475.4
1.4999	0.5999	0.3335	0.4668	151.3	793.6	−41.5	−450.8
Rubidium chloride + arabinose + water							
1.4999	0.2001	0.0817	0.189	534.4	867.3	−1.9	−231.0
1.4999	0.2001	0.1540	0.1796	587.6	930.2	−3.6	−239.0
1.4999	0.2001	0.2194	0.1709	553.2	894.1	−4.9	−236.0
1.4999	0.2001	0.2794	0.1630	514.8	835.7	−6.2	−214.7
1.4999	0.2001	0.3335	0.1557	487.7	793.6	−7.3	−198.6
1.4999	0.4003	0.0817	0.3787	283.4	867.3	−4.7	−459.2
1.4999	0.4003	0.1540	0.3593	331.6	930.2	−8.9	−469.7
1.4999	0.4003	0.2194	0.3418	318.3	894.1	−12.8	−443.0
1.4999	0.4003	0.2794	0.3259	294.4	835.7	−16.4	−404.9

Table 3 (*continued*)

$m(E)^i$/mol kg^{-1}	$m(S)^i$/mol kg^{-1}	$m(E)^f$/mol kg^{-1}	$m(S)^f$/mol kg^{-1}	$\Delta_{mix}H_m$/J mol^{-1}	$\Delta_{dil}H_m(E)$/J mol^{-1}	$\Delta_{dil}H_m(S)$/J mol^{-1}	$\Delta_{tr}H_m$/ J mol^{-1}
1.4999	0.4003	0.3335	0.3115	270.4	793.6	−19.5	−383.7
1.4999	0.5998	0.0817	0.5657	23.2	867.3	−7.6	−636.5
1.4999	0.5998	0.1540	0.5368	98.4	930.2	−13.9	−617.9
1.4999	0.5998	0.2194	0.5106	79.3	894.1	−19.6	−595.2
1.4999	0.5998	0.2794	0.4869	56.2	835.7	−24.7	−554.8
1.4999	0.5998	0.3335	0.4653	28.1	793.6	−29.4	−536.1

interaction. The concept of structural interaction, introduced by Frank and Robinson,[25] has been used to explain the concentration dependence of transfer functions of electrolytes.[26,27] 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. 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 h_{ES} and g_{ES}. The interaction of the Cl$^-$–R pair, in which structural interaction is the leading part, also contributes a positive value to h_{ES} and g_{ES}. The interaction of the Cl$^-$–O pair is electrostatically repulsive, and contributes a positive value to g_{ES}, h_{ES}, and Ts_{ES}. The contribution of the structural interaction is less than that of the electrostatic interaction; however, in some cases, it even becomes predominant when the hydrophobic alkyl group is large enough. So in the systems studied, electrostatic interactions of Rb$^+$ and Cl$^-$ with polar groups in the saccharides are the predominant interactions. The electrostatic interaction of Rb$^+$–O pair and Cl$^-$–O has opposite effects on h_{ES} and g_{ES}, and the results suggest that the value of g_{ES} are controlled by the interaction of the Cl$^-$–O pair,[28] while the h_{ES} are controlled by Rb$^+$–O pair interaction. These are in agreement with



β-D-glucopyranose-$^4C_1$ (64%)

α-D-glucopyranose-$^4C_1$ (33%)

β-D-galactopyranose-$^4C_1$ (73%)

α-D-galactopyranose-$^4C_1$ (27%)

β-D-arabinopyranose-$^1C_4$ (34%)

α-D-arabinopyranose-$^1C_4$ (63%)

β-D-xylopyranose-$^4C_1$ (67%)

α-D-xylopyranose-$^4C_1$ (33%)

Figure 2. Percentage ratio of the predominant anomers in water at 298.15 K.

the suggestion of Kelley and Lilley that the experimental free-energy pair interaction parameters are fairly well represented by the electrostatic interactions only.

In order to compare the interaction parameters of other electrolyte–saccharide–water systems with the results in this work, we also included in Table 2 the g_{ES} and h_{ES} of HCl–glucose, NaCl–glucose, as well as a CsCl–glucose pair in water. It can be seen that g_{ES}(HCl–glucose) is higher than g_{ES}(NaCl–glucose), however, they are much lower than g_{ES}(RbCl–glucose) and g_{ES}(CsCl–glucose). Zhuo et al. have suggested so-called 'H^+-induced structural changes',[18] which are mainly as follows: an H^+ and a chain glucose molecule can form a stable glucose–H^+(aq) ion, which breaks the equilibria: α-D-glucose (36.4%) = chain D-glucose (0.01%) = β-D-glucose (63.6%). So the cyclic structures will be transferred into chain structures. The decyclization will make a positive contribution to g_{ES}, h_{ES}, and Ts_{ES}. A similar process would not occur in the interaction of M^+(metal ions) with D-glucose because of the large volume of hydrated M^+ ions. They show that g_{ES}(H^+–glucose) is more positive than g_{ES}(Na^+–glucose) through group additivity analysis. This is why g_{ES}(HCl–glucose) > g_{ES}(NaCl–glucose). As for the larger g_{ES}(RbCl–glucose) and g_{ES}(CsCl–glucose), it may lie in the fact that the larger ions have a larger hydrated layer and are connected with more water molecules through hydrogen bonds. For example, it has been reported that in cesium 5-sulfosalicylate, the cesium atoms can be 11-coordinated with Cs–O contacts in the range from 3.093 to 3.781 Å.[29] So the hydrated Rb^+ and Cs^+ would need more energy to break the hydrogen bonds and react with the saccharide molecules. This would make a more positive contribution to the g_{ES}.

The hydration of saccharides depends on their stereochemistries. Several attempts have been made to rationalize the hydration characteristics of saccharides. Franks et al.[30] and Suggett[31,32] introduced the important distinction between equatorial (e-OH) and axial hydroxy (α-OH) groups, and predicted that any properties that depend on the saccharide hydration will correlate well with the number of e-OH groups in saccharide molecules. It is suggested that an e-OH group is more favorable than a α-OH group on the formation of hydrogen bonding with water molecules in aqueous solution, and it is concluded that these e-OH groups can promote the formation of labile cages of water molecules.[33] Galema and co-workers also came to a similar conclusion from a study of kinetic medium effects and volumetric properties of saccharides.[34–36] From Table 3, it can be concluded that there is a close relationship between h_{ES} and g_{ES} with the stereostructure of these monosaccharides in water. The g_{ES} of the RbCl + glucose and RbCl + xylose pair is more positive than that of RbCl + galactose and RbCl + arabinose pair, while the h_{ES} of the former is less negative than that of the latter. This is consistent with the different conformations of these monosaccharides in water. The dominant conformation of D-glucose and D-xylose in water is 1e2e3e4e (e stands for an equatorial hydroxyl group), whereas that of D-galactose and D-arabinose is 1e2e3e4α (α stands for axial hydroxyl group), as it is shown in Figure 2. D-Glucose and D-xylose are more compatible with the structure of water,[34–36] which means that they fit better into the water structure than D-galactose and D-arabinose do. So, the dehydration of D-glucose and D-xylose requires more energy, and consequently makes a more positive contribution both to g_{ES} and h_{ES} than that of

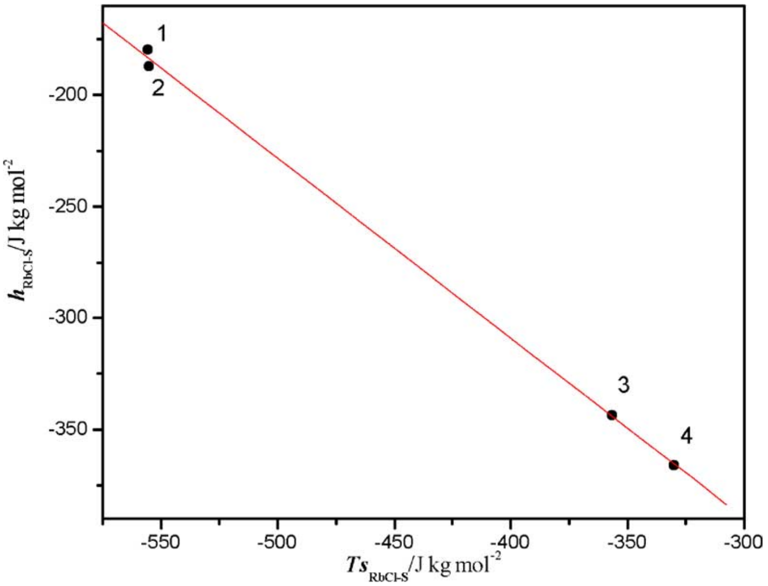


Figure 3. Correlation between $Ts_{RbCl\text{-}S}$ and $h_{RbCl\text{-}S}$: (1) D-xylose, (2) D-glucose, (3) D-arabinose, and (4) D-galactose.

D-galactose and D-arabinose does. In addition, the data in Table 3 show that both the difference of g_{ES} and h_{ES} between the RbCl + glucose and RbCl + xylose pair, as well as that between the RbCl + galactose and RbCl + arabinose pair, is very small, which suggests that the interaction of RbCl with the CHOH (exo) gives very small contribution to g_{ES} and h_{ES}.

Just like g_{ES} and h_{ES}, the entropy interaction parameter s_{ES} can also identify the stereostructure of these monosaccharides in water. A similar characteristic was also found about s_{ES}: the s_{ES} (RbCl + glucose), and s_{ES}(RbCl + xylose) is more negative than s_{ES}(RbCl + galactose) and s_{ES}(RbCl + arabinose). The small difference of s_{ES} between the RbCl + glucose and the RbCl + xylose pair, as well as that between the RbCl + galactose and the RbCl + arabinose pair, indicates that the interaction of RbCl with the CHOH (exo) results in a small increase of entropy of the system. Furthermore, we note that there is an enthalpy–entropy compensation correlation between Ts_{ES} and h_{ES} as shown in Figure 3. The straight line is obtained through a least-squares analysis. The correlation coefficient is 0.999. This seems to indicate that the interactions of RbCl with the saccharides in water are essentially controlled by the modification of the hydration of the species (Rb^+, Cl^-, and the monosaccharide molecule). A similar correlation was also found by Morel and co-workers between h_{ES}($CaCl_2$–saccharide) and Ts_{ES}($CaCl_2$–saccharide), as well as h_{ES}(KCl–saccharide) and Ts_{ES}(KCl–saccharide) parameters for some monosaccharides.[37]

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References

1. Banipal, P. K.; Banipal, T. S.; Ahluwalia, J. C. *J. Chem. Thermodyn.* **2002**, *34*, 1825–1846.
2. Hernandez-Luis, F.; Amado-Gonzalez, E.; Esteso, M. A. *Carbohydr. Res.* **2003**, *338*, 1415–1424.
3. Angyal, S. J. *Aust. J. Chem.* **1972**, *25*, 1957–1966.
4. Zhuo, K.; Wang, J.; Zhou, J.; Lu, J. *J. Phys. Chem. B* **1998**, *102*, 3574–3577.
5. Gaio, P.; Cavalieri, F.; Pizzoferrato, L., et al. *Int. J. Biol. Macromol.* **1999**, *25*, 309–315.
6. Hernandez-Luis, F.; Grandoso, D.; Lemus, M. *J. Chem. Eng. Data* **2004**, *49*, 668–674.
7. Love, W. D.; Burch, G. E. *J. Lab. Clin. Med.* **1953**, *41*, 351–362.
8. Nielsen, F. H. *Clin. Nutr. Essent. Trace Elem. Miner.* **2000**, 11–36.
9. Jiang, Y.; Hu, M.; Wang, J.; Zhuo, K.; Xia, S. *J. Chem. Thermodyn.* **2004**, *36*, 671–676.
10. Jiang, Y.; Wang, J.; Zhuo, K.; Gao, S.; Xia, S.; Hu, M. *Chem. J. Chin. Univ.* **2003**, *24*, 1842–1846.
11. Jiang, Y.; Wang, J.; Lu, Y.; Zhuo, K.; Gao, S.; Xia, S.; Hu, M. *Thermochim. Acta* **2003**, *400*, 37–42.
12. Jiang, Y.; Wang, J.; Zhuo, K.; Gao, S.; Xia, S.; Hu, M. *J. Chin. Chem. Soc.* **2003**, *50*, 947–952.
13. Jiang, Y.; Hu, M.; Mu, P.; Wang, J.; Zhuo, K. *J. Chem. Eng. Data* **2004**, *49*, 1418–1421.
14. Jiang, Y.; Gao, S.; Hu, M.; Fang, Q.; Xia, S.; Chai, M. *Chem. Anal. (Warsaw)* **2002**, *48*, 1–8.
15. Hamer, W. J.; Wu, Y. C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047–1099.
16. Ji, M.; Liu, M.; Gao, S.; Shi, Q. *Instrum. Sci. Technol.* **2001**, *29*, 53–57.
17. McMillan, W. G.; Mayer, J. E. *J. Chem. Phys.* **1945**, *13*, 276–305.
18. Zhuo, K.; Wang, J.; Zhou, J.; Lu, J. *J. Phys. Chem. B* **1997**, *101*, 3447–3451.
19. Maestre Alvarez, A.; Morel-Desrosiers, N.; Morel, J. P. *Can. J. Chem.* **1987**, *65*, 2656–2660.
20. Zhuo, K.; Wang, J.; Liu, W.; Lu, J. *Chin. J. Chem.* **1996**, *22*, 193–199.
21. Friedman, H. L. *The Physics and Chemistry of Aqueous Ionic Solutions*; D. Reidel Publishing: Dordrecht, 1987; p 61.
22. Perron, G.; Joly, D.; Desnoyers, J. E.; Avedikian, L.; Morel, J. P. *Can. J. Chem.* **1978**, *56*, 552–559.
23. Zhuo, K.; Wang, J.; Gao, Y.; Lu, J. *Can. J. Chem. B* **1999**, *77*, 232–236.
24. Lu, Y.; Bai, T.; Xie, W.; Lu, J. *Thermochim. Acta* **1998**, *319*, 11.
25. Frank, H. S.; Robinson, A. L. *J. Chem. Phys.* **1940**, *8*, 933–938.
26. Avedikian, L.; Perron, G.; Desnoyers, J. E. *J. Solution Chem.* **1975**, *4*, 331–346.
27. Schrier, M. Y.; Turner, P. J.; Schrier, E. E. *J. Phys. Chem.* **1975**, *79*, 1391–1396.
28. Kelley, B. P.; Lilley, T. H. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2771–2778.
29. Hu, M.; Geng, C.; Li, S.; Du, Y.; Jiang, Y.; Liu, Z. *J. Organomet. Chem.* **2005**, *690*, 3118–3124.
30. Franks, F.; Ravenhill, J. R.; Reid, D. S. *J. Solution Chem.* **1972**, *1*, 3–16.
31. Suggett, A.; Clark, A. H. *J. Solution Chem.* **1976**, *5*, 1–15.
32. Suggett, A. *J. Solution Chem.* **1976**, *5*, 33–46.
33. Barone, G.; Castronuovo, G.; Doucas, D.; Ella, V.; Mattia, C. V. *J. Phys. Chem.* **1983**, *87*, 1931–1937.
34. Galema, S. A.; Engberts, J. B. F. N.; Blandamer, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 9665–9666.
35. Galema, S. A.; Høiland, H. *J. Phys. Chem.* **1991**, *95*, 5321–5326.
36. Galema, S. A.; Blandamer, M. J.; Engberts, J. B. F. N. *J. Org. Chem.* **1992**, *57*, 1995–2001.
37. Morel, J. P.; Lhermet, C.; Desnoyers, J. E. *Can. J. Chem.* **1986**, *64*, 996–1001.
38. Zhuo, K.; Wang, J.; Gao, Y.; Lu, J. *Carbohydr. Res.* **2000**, *325*, 46–55.
39. Jiang, Y.; Gao, S.; Xia, S.; Hu, M.; Wang, J.; Zhuo, K. *J. Chem. Thermodyn.* **2003**, *35*, 493–501.