

# The enthalpy and entropy interaction parameters of cesium chloride with saccharides (D-glucose, D-fructose and sucrose) in water at 298.15 K

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Received 23 May 2002; received in revised form 26 August 2002; accepted 3 September 2002

## Abstract

The transfer enthalpies have been measured for cesium chloride from pure water to aqueous saccharides (D-glucose, D-fructose and sucrose) solutions at 298.15 K. The McMillan–Mayer theory was employed to relate the excess thermodynamic function with a series of interaction parameters of solutes to obtain the enthalpy pair interaction parameters of cesium chloride with saccharides in water. Entropy interaction parameters can be evaluated through the enthalpy interaction parameters and the Gibbs free energy parameters. These parameters are discussed in detail to provide some information for the interaction of solute–solute and solute–solvent in CsCl–saccharide–water ternary system, and to investigate the influence of the size of metal ions and the number of hydroxyl in saccharides on these parameters.

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**Keywords:** Cesium chloride; Saccharides; Enthalpy and entropy interaction parameters

## 1. Introduction

Saccharides are essential in physiological process. They are not only the basic material for energy metabolism in organism, but also play a significant role in the configuration of biological molecules [1,2]. On the other hand, rare alkali metal cesium is important in some biological activities. Recently, the research on the relationship of cesium with some biological behavior are arousing interests, for example, it was found that the oxygen affinity in human red

blood cells [3,4], the formation of macromolecular protein clusters [5] and the charge translocation by the Na<sup>+</sup>/K<sup>+</sup>-ATPase [6,7], are connected with the existence of Cs<sup>+</sup>. Furthermore, it was reported that the decomposition, synthesis, metabolism, and transmembrane transport of saccharides have close relationship with the concentration of H<sup>+</sup>, Na<sup>+</sup> and other metal ions in body fluid. As the reaction medium of these activities is mostly multi-component aqueous solution, the studies about the interaction of saccharides with electrolytes in water are valuable to interpret the influence of electrolyte on some physiological behavior, and helpful to understand the essence of some biological phenomena, such as the transmembrane transport of saccharide, the non-enzymatic

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saccharification of saccharide with protein and lipid etc.

Because the properties of monosaccharide and oligosaccharide solutions are similar to those of an ideal solution, few research works have been focused on the basic physical chemistry properties of them. But with the development of studies related to the hydration of saccharide, it has been realized that the slight deviation of the properties of saccharide solution from ideal behavior has significant meaning for the research of their basic properties and the interactions of saccharide with other substances.

In our previous work, we have studied the activity coefficients, salting constants and Gibbs free energy parameters of cesium chloride with D-glucose, D-fructose and sucrose in water at 298.15 K using electrochemical method. In order to make further studies on the interaction of saccharides with CsCl in water, it is necessary to carry out systematic and extensive research works using more experimental methods. This work concentrates on the study of enthalpy and entropy interaction parameters through the measurements of thermal effects to provide more information for the interaction of cesium chloride with saccharides (D-glucose, D-fructose and sucrose) in water at 298.15 K.

## 2. Experimental

### 2.1. Reagents

Cesium chloride (mass fraction  $\geq 0.999$ , Jiangxi huali Co. Ltd.). Anhydrous D-glucose and sucrose (Shanghai Chem. Co., mass fraction  $\geq 0.99$ ). The D-fructose (mass fraction are approximately 0.96, Shanghai Chem. Co.), were recrystallized from water–EtOH mixtures. All the saccharides were dried under vacuum at 333 K and CsCl was heated at 773 K to constant weight and stored over P<sub>2</sub>O<sub>5</sub> in desiccators. Deionized and doubly distilled water with a conductivity of  $1.0 \times 10^{-4}$  to  $1.2 \times 10^{-4}$  S m<sup>-1</sup> at 298.15 K was used throughout this work.

### 2.2. The measurements of thermal effects

All the enthalpies of solutions were measured in RD496-III micro-calorimeter. The detailed description

about the structure and the technical parameters of this calorimeter has been given in [8]. An automatic electronic balance (Sartorius, made in German) with a sensitivity of 10 μg was employed to prepare solutions by accurate weighing.

The sensitivity of the calorimeter was measured through electrical calibration at 298.15 K. The Joule cell, which has 1000 Ω electrical resistance, was given 100 mW electric power for 100 s. The sensitivity obtained in this way was  $63.994 \pm 0.042 \mu\text{V mW}^{-1}$ . The accuracy and precision were determined through chemical calibration at 298.15 K. The dissolution enthalpy of potassium chloride at infinite dilution was measured and compared with the literature value. The experimental value  $17.235 \pm 0.024 \text{ kJ mol}^{-1}$  is in excellent agreement with that of  $17.241 \pm 0.018 \text{ kJ mol}^{-1}$  reported in [9]. The accuracy and precision calculated from the experimental results are 0.03% and 0.14%, respectively.

## 3. Results and discussion

According to the McMillan–Mayer theory [10], all the thermodynamic properties of multi-component solutions can be expressed as a virial expansion in *m* (molalities), which relates the non-ideal contributions of total thermodynamic function to a series of interaction parameters, such as pair, triplet and higher order items.

In this work, CsCl–water and saccharide–water binary solutions were mixed into CsCl–saccharide–water ternary solution. When the McMillan–Mayer theory is applied to this studied system, the transfer enthalpies of cesium chloride from pure water to aqueous saccharides (D-glucose, D-fructose and sucrose) solutions can be expressed as follows [11,12]:

$$\begin{aligned} \Delta H &= \Delta_m H^M - \Delta_m H_E^{\text{dil}} - \left( \frac{m_S^f}{m_E^f} \right) \Delta_m H_S^{\text{dil}} \\ &= 2\nu h_{ES} m_S^f + 3\nu^2 h_{EES} m_S^f m_E^f \\ &\quad + 3\nu h_{ESS} (m_S^f)^2 + \dots \end{aligned} \quad (1)$$

where *m<sub>E</sub>* and *m<sub>S</sub>* are the molalities of electrolyte and saccharides respectively, defined as mole/kg of pure water, *ν* is the number of ions in which the electrolyte dissociates. The *h<sub>ES</sub>*, *h<sub>EES</sub>* and *h<sub>ESS</sub>* are the enthalpic

pair and triplet interaction parameters. Within experimental uncertainty, the contributions of quadruplet and higher order terms to the enthalpy can be negligible [13]. The  $\Delta_m H^M$  is the molar mixing enthalpies arising from cesium chloride solutions mixed with saccharide solutions. The  $\Delta_m H_E^{dil}$  and  $\Delta_m H_S^{dil}$  are the molar dilution enthalpies of cesium chloride solutions and saccharide solutions in pure water, respectively. The  $\Delta H$  is the molar transfer enthalpies of CsCl from pure water to aqueous saccharides (D-glucose, D-fructose, and sucrose) solutions. The superscript “f” denotes the molalities after mixing.  $\Delta_m H^M$ ,  $\Delta_m H_E^{dil}$  and  $\Delta_m H_S^{dil}$  have the same initial and final molalities of CsCl and saccharides in the mixing and dilution process.

The  $\Delta_m H_E^{dil}$ ,  $\Delta_m H_S^{dil}$ ,  $\Delta_m H^M$  and  $\Delta H$  of CsCl–glucose–water, CsCl–fructose–water and CsCl–sucrose–water systems at 298.15 K are given in Tables 1–3. The enthalpy interaction parameters  $h_{ES}$ ,  $h_{EES}$  and  $h_{ESS}$  can be obtained by fitting the experimental data to the Eq. (1) using a least squares procedure. The pair interaction parameters  $h_{ES}$ , which will be discussed in this paper, are given in Table 4.

Then from the basic thermodynamic equation:

$$g_{ES} = h_{ES} - T s_{ES} \tag{2}$$

The entropic interaction parameters  $s_{ES}$  can be calculated by the obtained  $h_{ES}$  and the Gibbs free energy

parameters  $g_{ES}$  of the same systems, which will be reported and discussed in other paper. They are also listed in Table 4. In order to investigate the dependence of these parameters on the ionic size, the corresponding parameters of NaCl–saccharide–water system [11] are also included in Table 4.

From the data in Table 4, it can be seen that  $h_{ES}$  and  $s_{ES}$  are all negative, which indicated that the interactions of CsCl with these saccharides are exothermic and entropy decrease process. The values of  $h_{ES}$  and  $s_{ES}$  become more negative as the size of the metal ions increases from  $Na^+$  to  $Cs^+$ . The  $g_{ES}$  is positive suggested that the interaction of CsCl with D-glucose, D-fructose and sucrose is thermodynamic repulsive, that is, these saccharides have salting-out effect on CsCl.

The values of pair interaction parameters are the mean ionic pair interaction parameters of the ions dissociated by an electrolyte with a non-electrolyte. The interaction of ions with non-electrolyte consists of electrostatic and structural interactions. In this studied system, it can be assumed that the interaction of CsCl with the polar groups of saccharides (hydroxyl) is mainly electrostatic interaction, accompanied by the desolvation of the solutes, and the interaction of CsCl with the non-polar groups of saccharides is mainly structural interaction.

Table 1

The molar mixing enthalpies ( $\Delta_m H^M$ ) of aqueous cesium chloride solutions with aqueous D-glucose solutions, and the molar dilution enthalpies of cesium chloride and D-glucose solutions in pure water ( $\Delta_m H_E^{dil}$  and  $\Delta_m H_S^{dil}$ ), as well as the molar transfer enthalpies ( $\Delta H$ ) of cesium chloride from pure water to aqueous D-glucose solutions at 298.15 K

$m_E^i$ (mol kg <sup>-1</sup> )	$m_S^i$ (mol kg <sup>-1</sup> )	$m_E^f$ (mol kg <sup>-1</sup> )	$m_S^f$ (mol kg <sup>-1</sup> )	$\Delta_m H^M$ (J mol <sup>-1</sup> )	$\Delta_m H_E^{dil}$ (J mol <sup>-1</sup> )	$\Delta_m H_S^{dil}$ (J mol <sup>-1</sup> )	$\Delta H$ (J mol <sup>-1</sup> )
1.4999	0.2006	0.0817	0.1895	845.5	1026.9	-2.8	-178.6
1.4999	0.2006	0.1540	0.1798	788.9	965.5	-5.3	-171.3
1.4999	0.2006	0.2194	0.1710	733.2	900.4	-7.5	-159.7
1.4999	0.2006	0.2794	0.1630	690.6	846.7	-9.3	-146.8
1.4999	0.2006	0.3335	0.1558	639.7	788.9	-10.9	-138.3
1.4999	0.3993	0.0817	0.3776	591.0	1026.9	-8.2	-427.7
1.4999	0.3993	0.1540	0.3581	558.7	965.5	-15.2	-391.6
1.4999	0.3993	0.2194	0.3406	489.4	900.4	-21.5	-389.5
1.4999	0.3993	0.2794	0.3248	464.1	846.7	-27.2	-355.4
1.4999	0.3993	0.3335	0.3105	412.9	788.9	-34.2	-341.8
1.4999	0.6001	0.0817	0.5372	371.9	1026.9	-10.7	-644.3
1.4999	0.6001	0.1540	0.5097	335.5	965.5	-20.4	-609.6
1.4999	0.6001	0.2194	0.4849	303.2	900.4	-29.3	-567.9
1.4999	0.6001	0.2794	0.4624	263.1	846.7	-38.4	-545.2
1.4999	0.6001	0.3335	0.4419	232.5	788.9	-44.8	-511.6

Table 2

The molar mixing enthalpies ( $\Delta_m H^M$ ) of aqueous cesium chloride solutions with aqueous D-fructose solutions, and the molar dilution enthalpies of cesium chloride and D-fructose solutions in pure water ( $\Delta_m H_E^{\text{dil}}$  and  $\Delta_m H_S^{\text{dil}}$ ), as well as the molar transfer enthalpies ( $\Delta H$ ) of cesium chloride from pure water to aqueous D-fructose solutions at 298.15 K

$m_E^i$ (mol kg <sup>-1</sup> )	$m_S^i$ (mol kg <sup>-1</sup> )	$m_E^f$ (mol kg <sup>-1</sup> )	$m_S^f$ (mol kg <sup>-1</sup> )	$\Delta_m H^M$ (J mol <sup>-1</sup> )	$\Delta_m H_E^{\text{dil}}$ (J mol <sup>-1</sup> )	$\Delta_m H_S^{\text{dil}}$ (J mol <sup>-1</sup> )	$\Delta H$ (J mol <sup>-1</sup> )
1.4999	0.2001	0.0817	0.1899	868.4	1026.9	-2.7	-155.8
1.4999	0.2001	0.1540	0.1807	840.2	965.5	-5.2	-120.1
1.4999	0.2001	0.2194	0.1723	801.1	900.4	-7.5	-91.8
1.4999	0.2001	0.2794	0.1648	783.9	846.7	-9.6	-53.2
1.4999	0.2001	0.3335	0.1578	756.3	788.9	-11.6	-21.0
1.4999	0.3997	0.0817	0.3797	661.8	1026.9	-4.5	-360.6
1.4999	0.3997	0.1540	0.3614	623.8	965.5	-8.5	-333.2
1.4999	0.3997	0.2194	0.3447	583.4	900.4	-12.2	-304.8
1.4999	0.3997	0.2794	0.3296	552.8	846.7	-15.6	-278.3
1.4999	0.3997	0.3335	0.3157	522.6	788.9	-18.7	-247.6
1.4999	0.6003	0.0817	0.5696	541.0	1026.9	-7.4	-478.5
1.4999	0.6003	0.1540	0.5421	500.0	965.5	-14.1	-451.4
1.4999	0.6003	0.2194	0.5172	460.4	900.4	-19.9	-420.1
1.4999	0.6003	0.2794	0.4944	425.7	846.7	-25.3	-395.7
1.4999	0.6003	0.3335	0.4736	394.9	788.9	-30.2	-363.8

Table 3

The molar mixing enthalpies ( $\Delta_m H^M$ ) of aqueous cesium chloride solutions with aqueous sucrose solutions, and the molar dilution enthalpies of cesium chloride and sucrose solutions in pure water ( $\Delta_m H_E^{\text{dil}}$  and  $\Delta_m H_S^{\text{dil}}$ ), as well as the molar transfer enthalpies ( $\Delta H$ ) of cesium chloride from pure water to aqueous sucrose solutions at 298.15 K

$m_E^i$ (mol kg <sup>-1</sup> )	$m_S^i$ (mol kg <sup>-1</sup> )	$m_E^f$ (mol kg <sup>-1</sup> )	$m_S^f$ (mol kg <sup>-1</sup> )	$\Delta_m H^M$ (J mol <sup>-1</sup> )	$\Delta_m H_E^{\text{dil}}$ (J mol <sup>-1</sup> )	$\Delta_m H_S^{\text{dil}}$ (J mol <sup>-1</sup> )	$\Delta H$ (J mol <sup>-1</sup> )
1.4999	0.1004	0.0817	0.0949	867.9	1026.9	-3.8	-155.2
1.4999	0.1004	0.1540	0.0904	838.5	965.5	-7.2	-119.8
1.4999	0.1004	0.2194	0.0862	807.6	900.4	-10.4	-82.4
1.4999	0.1004	0.2794	0.0824	778.1	846.7	-13.3	-55.3
1.4999	0.1004	0.3335	0.0789	750.5	788.9	-15.9	-22.5
1.4999	0.2008	0.0817	0.1899	692.4	1026.9	-6.6	-327.9
1.4999	0.2008	0.1540	0.1807	670.6	965.5	-12.6	-282.3
1.4999	0.2008	0.2194	0.1723	631.3	900.4	-18.2	-250.9
1.4999	0.2008	0.2794	0.1648	600.0	846.7	-23.2	-223.5
1.4999	0.2008	0.3335	0.1578	579.2	788.9	-27.9	-181.8
1.4999	0.3001	0.0817	0.2848	535.0	1026.9	-9.4	-482.5
1.4999	0.3001	0.1540	0.2711	487.4	965.5	-17.9	-460.2
1.4999	0.3001	0.2194	0.2586	442.4	900.4	-25.7	-432.3
1.4999	0.3001	0.2794	0.2472	404.0	846.7	-32.9	-409.8
1.4999	0.3001	0.3335	0.2368	367.8	788.9	-39.5	-381.6

Table 4

Pair interaction parameters for saccharide–CsCl and saccharide–NaCl in water at 298.15 K

Electrolyte–saccharide	$2\nu g_{ES}$ (J kg mol <sup>-2</sup> )	$2\nu h_{ES}$ (J kg mol <sup>-2</sup> )	$2\nu T s_{ES}$ (J kg mol <sup>-2</sup> )
CsCl–glucose	1639	-823.9	-2462.9
CsCl–fructose	2019	-772.8	-2791.8
CsCl–sucrose	2158	-1065.3	-3223.3
NaCl–glucose	224	-676	-900
NaCl–fructose	207	-1284	-1491
NaCl–sucrose	302	-985	-1287

The concept of structural interaction, introduced by Frank and Robinson [14], has been used in many literatures [15–17] to explain the dependence of transfer functions of electrolytes on concentration. For the enthalpy functions, the structural interaction consists principally of partial desolvation of solutes that interact with each other, and the solvent reorganization in the neighborhood of hydrophobic groups of the non-electrolyte. It was generally believed that in most cases the net effect of the co-sphere overlap on the hydration structure is destructive, which means that structural interaction would make positive contributions to the enthalpic interaction parameters [18].

The interactions of metal ions with the polar groups of non-electrolyte are electrostatic, which make negative contribution to the enthalpic parameters, but they would be partly counteracted by the desolvation of the solutes. Because the ionic size of  $\text{Cs}^+$  is larger than that of  $\text{Na}^+$ , it was easy for the desolvation of  $\text{Cs}^+$ , its counteractive effect on the electrostatic interaction is weaker. So the values of  $h_{\text{ES}}$  tend to be more negative from  $\text{Na}^+$  to  $\text{Cs}^+$ . On the other hand, there is an interaction between electrolyte and the non-polar groups of non-electrolyte, in which the larger ion has the larger dispersion force, and would make greater effect on the hydrophobic hydration structure of non-polar groups of non-electrolyte. Therefore, the positive contribution to  $h_{\text{ES}}$  arising from the structural interaction between the electrolyte and the non-polar groups of non-electrolyte will also be greater as the ionic size increases. The two interactions of electrolyte with polar and non-polar groups of non-electrolyte have opposite effects on  $h_{\text{ES}}$  with the ionic size increasing. The results in Table 4 suggest that the interactions of cesium chloride with polar groups of saccharides are the dominant interaction in the studied systems. So the values of  $h_{\text{ES}}$  became more negative with increasing ionic size of metals from  $\text{Na}^+$  to  $\text{Cs}^+$  for the same saccharide (except fructose).

The number of hydroxyl in these saccharides also has influence on  $h_{\text{ES}}$ . Because hydroxyl is polar group, the hydration of it is exothermic and its partial dehydration is endothermic on the contrary, which has positive contribution to  $h_{\text{ES}}$ . This would counteract the negative contribution arising from the electrostatic interaction of CsCl with these hydroxyls. The thermal effects of electrostatic interaction is greater than that from dehydration, therefore, the more is the number

of hydroxyl, the more negative is the  $h_{\text{ES}}$ . There are more hydroxyls in sucrose than that in glucose and fructose, so the  $h_{\text{ES}}$  of CsCl with sucrose is more negative compared with that of CsCl with glucose and fructose.

The fact that  $s_{\text{ES}}$  is negative indicates that the interaction of CsCl with saccharide will improve the order of the CsCl–saccharide–water system. This may be explained by the fact that the hydration of ions of electrolyte would destroy the structure of water, mainly the ice-mountain structure (Gurney layer) [19], so the dehydration of ions would improve the water structure and give negative contribution to  $s_{\text{ES}}$ . This has been demonstrated by some literature [11]. For the contributions coming from saccharides, there has been no definite conclusion about whether saccharides are hydrophilic or hydrophobic. But no matter what kind of hydration it is, the contribution of dehydration of saccharides to  $s_{\text{ES}}$  is more less and can be negligible compared with that of electrolyte.

Furthermore, The driving power of salting-out effect can be analyzed and concluded from the value of  $g_{\text{ES}}$ ,  $h_{\text{ES}}$  and  $s_{\text{ES}}$  interaction parameters. It can be seen that whether the  $g_{\text{ES}}$  is negative or positive depend on entropy, which means that the salting-out effect of glucose, fructose and sucrose on CsCl is entropy driving process.

#### 4. Conclusion

The transfer enthalpies of CsCl from pure water to aqueous saccharides (D-glucose, D-fructose and sucrose) solutions were measured in a micro-calorimeter and the thermodynamic parameters (including enthalpy and entropy interaction parameters) were determined according to the McMillan–Mayer theory.

The interactions of CsCl with the saccharides are exothermic and can improve the order in the CsCl–saccharide–water systems. The values of  $h_{\text{ES}}$  and  $s_{\text{ES}}$  become more negative as the size of the metal ions increases from  $\text{Na}^+$  to  $\text{Cs}^+$ .

D-Glucose, D-fructose and sucrose have salting-out effect on CsCl and it is an entropy driving process.

Obviously, the studies on the interaction parameters of CsCl with saccharides in water are very helpful to disclose the thermodynamic essence in these systems.

## Acknowledgements

Acknowledgements should be expressed to the financial support from the National Natural Science Foundation of China (20171032).

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