Calorimetric and Theoretical Study of the Interaction between Some Saccharides and Sodium Halide in Water

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Ⓢ *Supporting Information*

ABSTRACT: Dilution enthalpies and mixing enthalpies of sodium halide and some saccharides (glucose, galactose, xylose, arabinose, fructose, and sucrose) in aqueous solution were determined by calorimetric measurements at 298.15 K. The values were used to determine enthalpic pair interaction parameters. Combined with Gibbs energy pair parameters, entropic pair interaction parameters were also obtained. Theoretical calculations at the B3LYP/6-311++G(d,p) level were carried out to provide the information of structures and thermodynamic functions. The information reveals the thermodynamic essence of the interactions between sodium halide and saccharides in aqueous solutions. The experimental results and theoretical calculations show that the sign of enthalpic pair interaction parameter $2vh_{ES}$ is determined by the direct interaction between saccharides and ions, whereas the difference in value of $2vh_{ES}$ for different saccharides or electrolytes depends on the partial dehydration of saccharides or anions in aqueous solution. The difference in value of entropic pair interaction parameters depends partly on the different dominant interactions in the process of partial dehydration of saccharides or ions. An enthalpy−entropy compensation relationship was observed for the sodium bromide−aldopyranose−water systems. Remarkably, it can be conjectured that the hydration entropy of glucose is lower than for other monosaccharides. Perhaps it is one of the reasons why glucose plays an important role in living organisms rather than other monosaccharides.
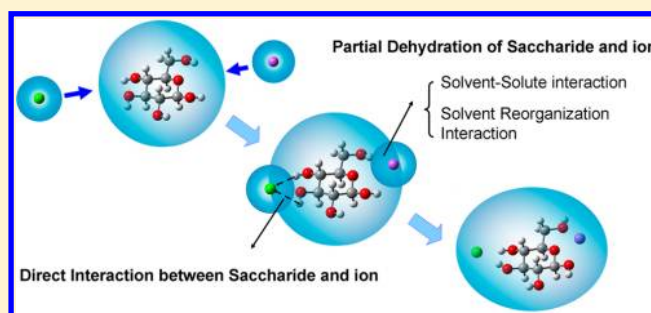
■ INTRODUCTION

As the most abundant bioorganic materials on the earth, carbohydrates play essential roles in biological processes, such as energy storage, matrices supporter, neurotransmission, and transfer of genetic information.[1,2] In those biological processes, owing to the low threshold for conformational modification of saccharides, the interactions between saccharides and receptors (proteins, lipids, metal cations, and so on) are usually specific and multivalent.[3,4] Additionally, for nearly all of the processes occurring in an aqueous environment, the interactions become much weaker and more complex between saccharides and receptors. So it is more difficult to deal with them both experimentally and theoretically. The traditional methods such as paper electrophoresis,[5] thermodynamics,[6,7] viscosity,[8] and volumetry[9,10] are accurate in investigating the interactions macroscopically but incapable of describing the microscopic states. Meanwhile, the spectroscopy[11,12] and theoretical calculations such as molecular dynamics[13] and quantum chemical calculation[14−16] are helpful to understand the interactions directly, but it is hard to establish a reliable model. Therefore, it is necessary to make further research on the interactions between saccharides and other molecules or ions in solution. Additionally the study of these interactions is

of significant interest for the pharmaceutical industry,[2] food industry,[17] fibers, surfactants,[18] and biological engineering.

Because monosaccharides are the basic units of carbohydrates, the majority of research has focused on the interaction of organic molecules,[19] amino acids,[20] and electrolytes[21] with monosaccharides by experimental methods. Also, theoretical computations were employed to investigate the interactions between monosaccharides and other molecules or ions in vacuo or solution.[22−24] In previous work, we investigated the interactions of some monosaccharides with cesium chloride and sodium chloride in water by the calorimetric method.[21,25] However, recent attention has been focused on the interaction between anions and saccharides.[26−28] Some experimental measurements for the sodium chloride−monosaccharide−water systems have been accomplished previously.[25] In order to explore the effect of different saccharides and anions on the saccharide−electrolyte interactions in water, we report here the thermodynamic interaction parameters of sodium bromide and sodium iodide with five monosaccharides and one disaccharide

in water. Since the preferred conformers of D-glucose and D-galactose have nearly the same contents and similar stereo-chemical structures with D-xylose and D-arabinose respectively in aqueous solution and each hexose has an extra $-CH_2OH$ group attached to C5,[29,30] we choose these four aldopyranoses as models to investigate the effects of different substituents. D-Fructose and sucrose are also investigated here as the representive of ketopyranoses and disaccharides, respectively. In addition, simple theoretical calculations at the B3LYP/6-311++G(d,p) level are carried out to provide information of structures and thermodynamic functions. On the basis of these relatively simple building models, we hope to gain some insights into the weak interactions of saccharides with electrolytes in water.

■ EXPERIMENTAL SECTION AND COMPUTATIONAL METHODS

Reagents. D-Galactose, D-xylose, D-arabinose, and D-fructose (Biochem. R., the Second Shanghai Chem. Co.) were recrystallized from water−ethanol mixtures. D-Glucose (A.R., The Second Shanghai Chem. Co.) and sucrose (A.R. Beijing Chem. Co.) were used without further purification. These saccharides were dried under vacuum at 333 K to a constant weight. Sodium bromide (A.R. >99.0%, the Third Jiaozuo Chem. Co.) was recrystallized from doubly distilled water and dried under vacuum at 413 K to a constant weight. Sodium iodide (A.R. >99.0%, Beijing Chem. Co.) was twice recrystallized in ethanol, and dried under vacuum at 343 K. All of the reagents were stored over P_2O_5 in desiccators before use. Pure distilled deionized water was used with a specific conductivity of $1.0 \times 10^{-4} - 1.2 \times 10^{-4}$ S m^{-1} at 298 K.

Experimental Method. A precision semimicor-titration calorimeter established by Bai et al.[31] was used with an accuracy of ±0.2%. Energy equivalent calibration of the calorimeter and titration experimental method were the same as those described in the literature.[32,33] The sample cell was loaded with 12−15 g of aqueous saccharide solution, and then 0.5, 1, 1, 1, and 1.5 mL of the aqueous electrolyte solution were injected in turn into the sample cell with a Hamilton airproof injector with a 50 μL graduation. After each measurement, electric calibration of the calorimeter was carried out. In order to evaluate the reliability of the calorimeter, a test reaction of HCl with Tris was performed at the same condition.

Computational Methods. All calculations were performed using the Gaussian 03[34] software package in this study. Considering the varied complex conformations of saccharides in aqueous solution, only some preferred chair conforma-tions[29,30] of β-D-glucopyranose-$^4C_1$ (62%), β-D-galactopyrano-se-$^4C_1$ (64%), β-D-xylopyranose-$^4C_1$ (63%), and α-D-arabino-pyranose-$^1C_4$ (60%) were performed. We utilized the geo-metries of the lowest energy structures of D-glucose and D-galactose in aqueous solution obtained by Hoffmann et al.[35] and Rahal-Sekkal et al.,[36] respectively. The starting structures of D-xylose and D-arabinose were obtained from Guler et al.[37] Each structure of saccharides was optimized at the B3LYP/6-311++G(d,p) level. Because sodium halide is dissociated in aqueous solution, the sodium cation and halide anion were both optimized at the same level respectively. Many of the ion−saccharide complexes (Na$^+$−saccharide and X$^-$−saccharide) have numerous geometric conformers with energies close to the ground state. In that case, a number of initial structures were tested in calculations at the B3LYP/6-31+G level in order to find the global ground state geometry. Finally, nearly sixty

structures were further optimized at the B3LYP/6-311++(d,p) level of theory, and harmonic frequency calculations were computed for all structures, at the same level. The absence of imaginary frequencies proved that energy-minimized structures correspond well to the local minima of the energy landscape. Zero-point vibrational energies were computed in order to correct the energy. Basis set superposition errors (BSSE) were estimated using the full counterpoise method[38,39] and ranged between 2.3 and 5.6 kJ mol^{-1} for all structures examined here. All of the interaction values of thermal energies, enthalpies, free energies, and entropies for the ion−saccharide interactions in gas obtained using DFT calculations reported in Tables 3−5 include BSSE corrections.

■ RESULTS

Experimental Enthalpic and Entropic Pair Interaction Parameters. Molar dilution enthalpies of NaCl and some saccharides (D-glucose, D-galactose, D-xylose, D-arabinose, and D-fructose) in water have been reported in previous work,[25] and the experimental values of molar dilution enthalpies of NaBr, NaI, and sucrose are presented in the Supporting Information (Table S1).

According to the McMillan−Mayer theory,[40−42] the mixing enthalpy of sodium halide and saccharide aqueous solutions can be expressed as follows:

$$\Delta H^M(m_E, m_S) = H(m_E, m_S) - H_W^0 - m_E H_E^0 - m_S H_S^0$$
$$= v^2 h_{EE} m_E^2 + 2 v h_{ES} m_E m_S + h_{SS} m_S^2$$
$$+ v^3 h_{EEE} m_E^3 + 3 v^2 h_{EES} m_E^2 m_S$$
$$+ 3 v h_{ESS} m_E m_S^2 + h_{SSS} m_S^3 + ... \quad (1)$$

where $H(m_E, m_S)$ represents the enthalpy of the solution containing 1 kg of solvent (water), m_E and m_S are the molalities of sodium halide and saccharide, respectively, H_w^0 is the standard enthalpy of 1 kg of pure water, and H_E^0 and H_S^0 are the standard partial molar enthalpies of sodium halide and saccharide, respectively. v is the number of ions in the chemical formula, and h_{EE}, h_{ES}, h_{SS}, h_{EEE}, h_{EES}, h_{ESS}, and h_{SSS} are the enthalpic virial coefficients (interaction parameter) representing the pair and triplet interactions between the subscripted species.

In order to calculate the enthalpic interaction parameters, the dilution enthalpies of saccharide and sodium halide can be expressed by eqs 1 and 2 according to the method proposed by Desnoyers et al.[41,42]

$$\Delta_m H_S^{dil}(m_S^i \rightarrow m_S^f)$$
$$= h_{ss}(m_S^f - m_S^i) + h_{sss}[(m_S^f)^2 - (m_S^i)^2] + ... \quad (2)$$

$$\Delta_m H_E^{dil}(m_E^i \rightarrow m_E^f)$$
$$= v^2 h_{EE}(m_E^f - m_E^i) + v^3 h_{EEE}[(m_E^f)^2 - (m_E^i)^2]$$
$$+ ... \quad (3)$$

where superscripts "i" and "f" refer to initial and final states. Values of the interaction parameters (h_{SS}, h_{SSS}...) were obtained by fitting eq 2 with experimental dilution enthalpy and presented in the Supporting Information (Table S2), and the values of the enthalpic pair parameter h_{SS} which can be used to describe saccharide−saccharide interactions between solvated molecules are presented in Table 1. Then the molar dilution

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Table 1. Enthalpic Pair Parameters of Interactions between Saccharide Molecules in Water at 298.15 K

saccharide	glucose	galactose	xylose	arabinose	fructose	sucrose
h_{SS}/J kg mol^{-2}	−154.44	−270.17	−195.74	−145.60	542.86	937.31

Table 2. Pair Interaction Parameters for Saccharide−NaX in Water at 298.15 K

	$2\nu g_{ES}$/J kg mol^{-2}			$2\nu h_{ES}$/J kg mol^{-2}			$2\nu T s_{ES}$/J kg mol^{-2}		
saccharide	NaCl	NaBr^c	NaI^c	NaCl	NaBr^d	NaI^d	NaCl	NaBr^e	NaI^e
xylose	302^a	102	49	−618^a	−760	−1060	−920^a	−862	−1109
glucose	224^a	114	95	−676^a	−775	−1017	−900^a	−889	−1112
arabinose	69^a	−91	−262	−1160^a	−1399	−1560	−1229^a	−1308	−1298
galactose	−45^a	−89	−252	−1213^a	−1469	−1871	−1168^a	−1380	−1619
fructose	207^b	−44	−108	−1274^b	−977	−1209	−1481^b	−933	−1101
sucrose	302^b	164	52	−983^b	−1328	−2052	−1285^b	−1492	−2104

^{a}Data from ref 43. ^{b}Data from ref 44. ^{c}Data from ref 45. ^{d}Data calculated from experimental data presented in the Supporting Information, Tables S3 and S4. ^{e}Calculated according to $2\nu T s_{ES} = 2\nu h_{ES} − 2\nu g_{ES}$.
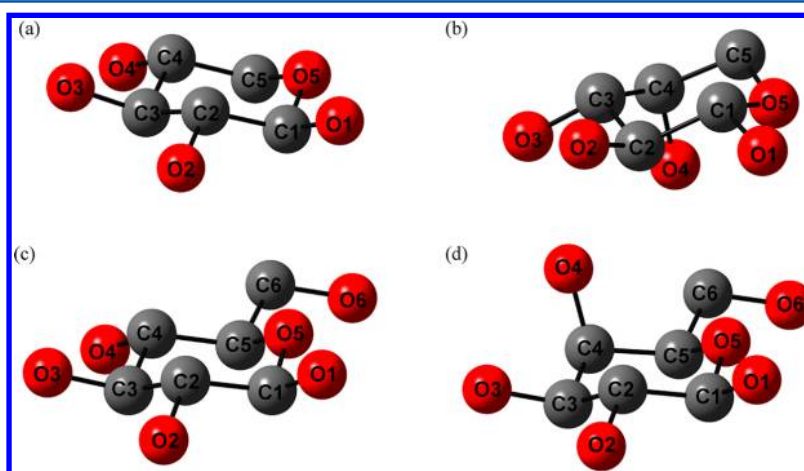

Figure 1. Numbering scheme and ring conformations for the optimized preferred chair conformations of aldopyranoses in gas phase calculated at the B3LYP/6-311++G(d,p) level of theory. (a) β-D-Xylopyranose-$^4C_1$ (b) α-D-arabinopyranose-$^1C_4$ (c) β-D-glucopyranose-$^4C_1$, and (d) β-D-galactopyranose-$^4C_1$.

enthalpy of saccharides $\Delta_m H_S^{dil}$ was calculated by eq 2 and presented in the Supporting Information (Tables S3 and S4).

Now an auxiliary function ΔH^* was introduced to facilitate the calculation.

$$\Delta H^* = \Delta_m H_E^M(m_E, m_S) − \Delta_m H_E^{dil}(m_E^i \to m_E^f)$$
$$− (m_S^f/m_E^f)\Delta_m H_S^{dil}(m_S^i \to m_S^f) = 2\nu h_{ES}$$
$$m_S^f + 3\nu^2 h_{EES} m_E^f m_S^f + 3\nu h_{ESS}(m_S^f)^2 + ... \quad (4)$$

$\Delta_m H_E^M$ is the molar mixing enthalpy of sodium halide in aqueous saccharide solution, and its values are presented in the Supporting Information (Tables S3 and S4). Because the initial and final molalities of sodium halide in aqueous solution are in conformance with that in aqueous saccharide solutions, the experimental dilution enthalpic values of sodium halide in water can be used directly. The obtained ΔH^* together with the initial and final molalities of sodium halide and saccharides in aqueous solutions are listed in the Supporting Information (Tables S3 and S4), which were fitted to eq 4 by an analysis of nonlinear least-squares regressions to obtain the pair and triplet interaction parameters h_{ES}, h_{EES}, and h_{ESS}. Table 2 lists the values of h_{ES}, together with the values of Gibbs energy interaction parameters $g_{ES}^{43,45}$ and entropic interaction parameters s_{ES}.

Theoretical Results for Sodium Cation−Aldopyranose and Halide Anion (Cl$^-$, Br$^-$)−Aldopyranose Complexes. The optimized preferred chair conformations of β-D-glucopyranose-$^4C_1$, β-D-galactopyranose-$^4C_1$, β-D-xylopyranose-$^4C_1$, and α-D-arabinopyranose-$^1C_4$ with numbering scheme and ring-conformer nomenclature are provided in Figure 1. The interaction parameters of aldopyranoses with Na$^+$, Cl$^-$, and Br$^-$ were calculated at the B3LYP/6-311++G(d,p) level. A number of low energy conformations for each complex were determined, and several low energy conformers are provided in Figures S1 and S2. Structures are named by their ring conformation and their binding sites to the sodium cation and halide anion. Computed data (Cartesian coordinates optimized at B3LYP/6-311++G(d,p) and dipole moments) of all complexes are presented in the Supporting Information. The electronic energies, enthalpies, free energies, and entropies of interaction between aldopyranoses and ions in gas phase can be expressed as follows:

$$\Delta E_{ES} = (E + E_{ZPE} + E_{BSSE})_{ES} − (E + E_{ZPE})_E$$
$$− (E + E_{ZPE})_S \quad (5)$$

$$\Delta H_{ES} = (H + E_{BSSE})_{ES} − H_E − H_S \quad (6)$$

$$\Delta G_{ES} = (G + E_{BSSE})_{ES} − G_E − G_S \quad (7)$$

$$\Delta S_{ES} = (\Delta H_{ES} - \Delta G_{ES})/T \qquad (8)$$

The values of them are reported in Tables 3−5. All of the values of electronic energies, enthalpies, free energies, and entropies obtained using DFT calculations include BSSE corrections.

■ DISCUSSION

Since it is difficult to elucidate the complicated contributions from triplet interaction parameters, only the pair interaction parameters are discussed in this work. The thermodynamic pair interaction parameters are essentially a measure of the change in the corresponding thermodynamic functions as two solute molecules move from infinite separation to some finite small distance in solution.[46] They can be used to describe the total effects of interactions between solute molecules taking place with the competitive participation of solvent molecules. As known, the total effects of interactions in the mutually approaching process include overlap of the solvation cospheres of solute molecules and direct interaction between solute molecules.[47] The value of the thermodynamic pair interaction parameters is the result of the competition between the two interactions. For the sodium halide−saccharide−water systems studied here, the total effects can be presented as a sum of three contributions: (a) partial dehydration of hydration shells of saccharide molecules, (b) partial dehydration of hydration shells of ions (including sodium cation and halide anions), and (c) direct interaction between saccharide molecules and sodium cation or halide anions.

Enthalpic Pair Interaction Parameters. *Enthalpic Parameters and Saccharide Stereochemistry.* In our case the effect (b) can be assumed as being constant,[48] so the observed differences in the enthalpic pair interaction parameters are connected with the variation of effects (a) and (c). In order to explain the dependence of the enthalpic pair interaction parameters for studied systems on saccharide stereochemistry, we tried to find some correlations between h_{ES} values and parameters that illustrate structural and electrostatic features of saccharides.

As mentioned by Piekarski and Tkaczyk,[48] some additional information about the factors that influence the h_{ES} parameters under discussion could be described by the Abraham−Kamlet−Taft equation[49] in the following form:

$$h_{ES} = (h_{ES})_0 + s\pi^* + a\alpha + b\beta + nV_S^0 \qquad (9)$$

where π^* refers to the polarity, α and β represent the donor-proton and acceptor-proton properties, respectively, V_S^0 is the limiting partial molar volume, and $(h_{ES})_0$ is an interaction parameter of a sodium halide with an infinitely small, uncharged and nonpolar molecule which neither forms hydrogen bonds nor influences, in any way, the water structure. Obviously, $s\pi^*$ indicates the direct interaction and $a\alpha$, $b\beta$, and nV_S^0 indicate the partial dehydration. Owing to the lack of these parameters describing the properties of saccharides in aqueous solution, it is difficult to get quantitive relationships between h_{ES} and these parameters in detail. However, some qualitative relationships could be found according to Piekarski's work.[48] It was reported that the $a\alpha$, $b\beta$, and nV_S^0 terms that illustrate the breaking of some saccharide−water and water−water hydrogen bonds give positive contributions to the h_{ES} values. That is to say, the partial dehydration of saccharide molecules is an endothermic process. However, this impact is counterbalanced by negative $s\pi^*$ terms resulting mostly from ion−dipole interactions.

Therefore, if the negative $s\pi^*$ terms provide more contributions than other terms, the h_{ES} parameters will be negative. Our results (Table 2) just show that the direct interaction is the main factor of all the interactions for sodium halide−saccharide−water systems.

Since the calorimetrical results only provide macroscopic information about the microscopic interactions, it is necessary to find another method to further understand the essence of these interactions. So we employed quantum chemical calculations to get some details of the direct interactions between saccharide molecules and sodium cation or halide anion. The results calculated are presented in Tables 3−5. For some systems it is possible that at T = 298 K multiple low energy conformers are present in aqueous solution. A comprehensive theoretical analysis for direct interaction of saccharides with ions is follows.

The theoretical results show that the direct interaction of saccharides with sodium cation is an exothermic process (Table 3), which is in agreement with the above analysis. The interaction of O with Na$^+$ has been determined to be ion−dipole interaction (70.58−85.30 kJ mol^{-1}), which is stronger than usual intermolecular interaction (<20 kJ mol^{-1}) but weaker than ionic bond.

Considering all of the Na$^+$−saccharid complexes, we suppose that each complex exists with the same probability, and then the

Table 3. Thermal Energies, Enthalpies, Free Energies, and Entropies of Direct Interaction between Aldopyranose and Sodium Cation in Gas Phase at 298.15 K

theoretical parameters	Na$^+$(β-Xyl)^{4}C$_1$	Na$^+$(β-Glc)^{4}C$_1$	Na$^+$(α-Ara)^{1}C$_4$	Na$^+$(β-Gal)^{4}C$_1$
species	[O1,O2]	[O1,O2]	[O1,O2]	[O1,O2]
ΔE/kJ mol^{-1}	−165.60	−156.77	−163.56	−156.34
ΔH/kJ mol^{-1}	−167.35	−158.13	−165.09	−157.57
ΔG/kJ mol^{-1}	−134.36	−125.96	−132.64	−125.62
ΔS/J mol^{-1} K^{-1}	−110.76	−137.82	−108.98	−107.27
species	[O2,O3]	[O2,O3]	[O2,O3]	[O2,O3]
ΔE/kJ mol^{-1}	−170.59	−163.92	−147.20	−164.83
ΔH/kJ mol^{-1}	−173.01	−165.97	−148.34	−166.80
ΔG/kJ mol^{-1}	−138.58	−132.35	−116.84	−133.38
ΔS/J mol^{-1} K^{-1}	−115.62	−134.52	−105.76	−112.22
species	[O3,O4]	[O3,O4]	[O3,O4]	[O3,O4]
ΔE/kJ mol^{-1}	−162.48	−156.61	−159.73	−162.17
ΔH/kJ mol^{-1}	−164.66	−158.33	−161.11	−163.88
ΔG/kJ mol^{-1}	−130.78	−125.55	−128.94	−131.05
ΔS/J mol^{-1} K^{-1}	−113.78	−134.03	−108.01	−110.21
species	[O4]	[O4,O6]	[O4,O5]	[O4,O5,O6]
ΔE/kJ mol^{-1}	−107.78	−171.45	−141.16	−205.25
ΔH/kJ mol^{-1}	−109.03	−173.28	−142.72	−207.51
ΔG/kJ mol^{-1}	−80.57	−140.73	−110.00	−171.60
ΔS/J mol^{-1} K^{-1}	−95.6	−130.31	−109.9	−120.57
species	[O1,O5]	[O1,O5,O6]	[O1,O5]	[O1,O5,O6]
species	−151.29	−183.87	−163.15	−187.76
ΔE/kJ mol^{-1}	−152.42	−183.92	−160.17	−188.73
ΔH/kJ mol^{-1}	−121.17	−154.84	−133.50	−156.81
ΔG/kJ mol^{-1}	−104.98	−132.91	−103.36	−107.15
ΔS/J mol^{-1} K^{-1}	9.9364	6.7733	6.1173	5.8616
species		[O6]		[O6]
ΔE/kJ mol^{-1}		−123.08		−123.82
ΔH/kJ mol^{-1}		−124.3		−125.33
ΔG/kJ mol^{-1}		−95.63		−95.59
ΔS/J mol^{-1} K^{-1}		−128.76		−99.88

average of interaction enthalpies follows the trend (Table 3) Na$^+$(β-Gal)^{4}C$_1$ (−168.30 kJ mol^{-1}) < Na$^+$(β-Glc)^{4}C$_1$ (−160.66 kJ mol^{-1}) < Na$^+$(α-Ara)^{1}C$_4$ (−155.49 kJ mol^{-1}) < Na$^+$(β-Xyl)^{4}C$_1$ (−153.29 kJ mol^{-1}). However, in fact, the probability increases with increasing interaction of those complexes. Taking the complexes with the lowest energies (Figure S1) into account, the trend is Na$^+$(β-Gal)^{4}C$_1$[O4,O5,O6] (−207.51 kJ mol^{-1}) < Na$^+$(β-Glc)^{4}C$_1$[O1,O5,O6] (−183.92 kJ mol^{-1}) < Na$^+$(β-Xyl)^{4}C$_1$ [O2,O3] (−173.01 kJ mol^{-1}) < Na$^+$(α-Ara)^{1}C$_4$[O1,O2] (−165.09 kJ mol^{-1}) (Table 3). The theoretical calculations of Na$^+$−aldopyranose complexes indicate that the enthalpy of interaction of Na$^+$ with aldopyranoses containing 4a−OH group (at C4 there is an axial OH) or 5−CH$_2$OH group (at C5 there is a CH$_2$OH group) is lower. In other words, the 4a−OH and 5−CH$_2$OH groups provide a negative contribution to the value of h_{ES}.

The direct interaction between saccharide and chloride anion is also an exothermic process (Table 4), which is similar to that

Table 4. Thermal Energies, Enthalpies, Free Energies, and Entropies of Direct Interaction between Aldopyranose and Chloride Anion in Gas Phase at 298.15 K

theoretical parameters	Cl$^-$(β-Xyl)^{4}C$_1$	Cl$^-$(β-Glc)^{4}C$_1$	Cl$^-$(α-Ara)^{1}C$_4$	Cl$^-$(β-Gal)^{4}C$_1$
species	[O1,O2]	[O1,O2]	[O1,O2]	[O1,O2]
ΔE/kJ mol^{-1}	−116.42	−129.72	−114.16	−126.12
ΔH/kJ mol^{-1}	−118.96	−132.54	−116.84	−129.12
ΔG/kJ mol^{-1}	−85.64	−98.27	−83.40	−94.73
ΔS/J mol^{-1} K^{-1}	−111.75	−114.94	−112.15	−115.35
species	[O2,O3]	[O2,O3]	[O2,O3]	[O2,O3]
ΔE/kJ mol^{-1}	−104.76	−129.53	−119.77	−112.77
ΔH/kJ mol^{-1}	−106.76	−132.33	−122.70	−114.81
ΔG/kJ mol^{-1}	−76.79	−100.65	−89.95	−84.50
ΔS/J mol^{-1} K^{-1}	−100.51	−106.26	−109.83	−101.66
species	[O3,O4]	[O3,O4]	[O3,O4]	[O3,O4]
ΔE/kJ mol^{-1}	−93.31	−101.72	−90.92	−110.27
ΔH/kJ mol^{-1}	−94.80	−103.28	−92.38	−111.82
ΔG/kJ mol^{-1}	−65.95	−74.11	−62.02	−82.36
ΔS/J mol^{-1} K^{-1}	−96.78	−97.84	−101.85	−98.82
species	[O4]	[O4]	[O4]	[O4]
ΔE/kJ mol^{-1}	−85.5	−73.54	−69.83	−69.36
ΔH/kJ mol^{-1}	−86.56	−74.40	−70.52	−69.43
ΔG/kJ mol^{-1}	−58.92	−45.97	−42.83	−42.56
ΔS/J mol^{-1} K^{-1}	−92.71	−95.35	−92.88	−90.10
species	[O1]	[O1]		[O1]
ΔE/kJ mol^{-1}	−96.78	−108.84		−106.03
ΔH/kJ mol^{-1}	−98.27	−110.56		−107.87
ΔG/kJ mol^{-1}	−69.68	−81.59		−78.79
ΔS/J mol^{-1} K^{-1}	−95.89	−97.16		−97.53

between saccharide and sodium cation. However, the major interaction of saccharide with Cl$^-$ is considered as hydrogen bonding interaction. Since the distance of H and Cl$^-$ in O−H⋯Cl$^-$ is less than 3.0 Å^{50} (the sum of the van der Walls radii) and the bond angle of O−H⋯Cl is more than 150°, this hydrogen bond is classified as medium (the value of bond energy is in the range 25−40 kJ mol^{-1}).[51] Especially, the weak interaction of Cl$^-$ with H (−CH) also plays a significant role in this system.[52]

When the probability of each complex existing in the discussed system is assumed to be equal, the average of the interaction enthalpies follows the trend (Table 4) Cl$^-$(β-

Glc)^{4}C$_1$ (−110.62 kJ mol^{-1}) < Cl$^-$(β-Gal)^{4}C$_1$ (−106.61 kJ mol^{-1}) < Cl$^-$(β-Xyl)^{4}C$_1$ (−101.07 kJ mol^{-1}) < Cl$^-$(α-Ara)^{1}C$_4$ (−100.61 kJ mol^{-1}). This trend is not exactly in conformance with the interaction enthalpies of complexes with the lowest energies (Figure S2), i.e., Cl$^-$(β-Glc)^{4}C$_1$ (−132.54 kJ mol^{-1}) < Cl$^-$(β-Gal)^{4}C$_1$ (−129.12 kJ mol^{-1}) < Cl$^-$(α-Ara)^{1}C$_4$ (−122.70 kJ mol^{-1}) < Cl$^-$(β-Xyl)^{4}C$_1$ (−118.96 kJ mol^{-1}) (Table 4). Nevertheless, those results still indicate that the interaction enthalpy between Cl$^-$ and aldopyranoses is larger when aldopyranoses contain 4e−OH (at C4 there is an equatorial OH) group or 5−CH$_2$OH group. As a consequence, the 4e−OH and 5−CH$_2$OH groups give a negative contribution to h_{ES} for Cl$^-$−saccharide complexes.

Considering that the interaction between saccharide and Cl$^-$ is much weaker than that between saccharide and Na$^+$, 4a−OH group generally provides a more negative contribution to h_{ES} than 4e−OH group. Combining with the results of theoretical calculations, the direct interaction between saccharide and sodium halide should follow the order β-D-galactopyranose-^{4}C$_1$ > β-D-glucopyranose-^{4}C$_1$ > α-D-arabinopyranose-^{1}C$_4$ ≈ β-D-xylopyranose-^{4}C$_1$. However, in aqueous sodium halide solution, the values of h_{ES} follow the order: β-D-galactopyranose-^{4}C$_1$ > α-D-arabinopyranose-^{1}C$_4$ > β-D-glucopyranose-^{4}C$_1$ > β-D-xylopyranose-^{4}C$_1$. Noticeably, the agreement between theoretical calculation and experimental data for the aldopyranoses studied here is not very good. In our case, the effect of partial dehydration of ions can be assumed as being constant,[48] in all probability, the discrepancy is caused by the partial dehydration of saccharides. This result is consistent with Petton's conclusion.[40]

It can be seen from Table 2 that the difference in enthalpic interaction parameter between the NaCl−glucose−water system and NaCl−xylose−water system is 58 J kg mol^{-2}, which is close to that between NaCl−galactose−water system and NaCl−arabinose−water system (53 J kg mol^{-2}). The same phenomenon can also be observed for NaBr−saccharide−water system and NaI−saccharide−water systems. This reveals that the negative contribution of 5−CH$_2$OH group to $2vh_{ES}$ in the ternary systems is extremely small. Additionally, the experimental values in Table 2 also show that the difference in enthalpic interaction parameter between NaCl−arabinose−water system and NaCl−xylose−water system (542 J kg mol^{-2}) is close to that between NaCl−galactose−water system and NaCl−glucose−water system (542 J kg mol^{-2}). This can be attributed primarily to the different stereostructures of saccharide molecules in aqueous solution. The 4−OH groups of β-D-glucopyranose and β-D-xylopyranose are equatorial, whereas they are axial in β-D-galactopyranose and α-D-arabinopyranose molecules. It is well-known that e−OH group is more readily hydrated than a−OH group for saccharide molecules in aqueous solution. As a result, glucose and xylose fit into the structure of water better than galactose and arabinose.[53−56] Then glucose and xylose need more energy to break the hydration structure during the dehydration process. Therefore, the partial dehydration process of monosaccharides with 4e−OH group gives a more positive contribution to $2vh_{ES}$ than monosaccharides with 4a−OH. Furthermore, their contributions are numerically far greater than 5−CH$_2$OH group.

Owing to the complicated conformers of D-fructose and sucrose in aqueous solution, it is a formidable task to clear up the direct interactions between sodium halide and fructose or sucrose through quantum chemical calculation. So some earlier

theoretical results are employed to explain the enthalpic parameters $2vh_{ES}$ of fructose and sucrose. For fructose, the preferred conformation in aqueous solution is β-D-fructopyranose-$^1C_4$ (57%).[57] Considering 1a−OH and 1−CH$_2$OH groups, the direct interaction of fructose with sodium halide is likely to be stronger than in arabinose. For sucrose, because of the multiple −OH groups, the direct interaction is likely to be much stronger than in monosaccharides. However, their experimental $2vh_{ES}$ values were different with our conjectures. This must be attributed to the different partial dehydration process of fructose and saccharides.

It has been regarded that the partial dehydration process is accompanied by overlap of the solvation cospheres of the solute molecules, resulting in a partial destruction of the solvation cosphere (solvent−solvent interactions) and a weakening of the solute−solvent interactions.[47] Thus a further discussion regarding partial dehydration of saccharide molecules is presented below.

The enthalpic pair parameter h_{SS} in Table 1 could provide useful information about the interaction between hydrated saccharide molecules in aqueous solution. It was proposed that most of the nonassociating solutes can be phenomenologically divided into three groups according to the signs of the self-interaction parameters:[58]

prevailingly hydrophobic solutes	$g_{XX} < 0$; $Ts_{XX} > h_{XX} > 0$
hydrophilic (urea-like) solutes	$g_{XX} < 0$; $h_{XX} < Ts_{XX} < 0$
hydrophilic (sucrose-like) solutes	$g_{XX} > 0$; $h_{XX} > Ts_{XX} > 0$

The second set encloses hydrophilic solutes that perturb the ordered local structure of water, essentially because their orienting effect is not compatible with an ice-like organization of water. The third set encloses essentially oligosaccharides, in which the dominant interaction is probably solute−solvent interaction. There is no doubt that xylose, glucose, arabinose, and galactose ($h_{SS} < 0$) are urea-like solutes, whereas fructose and sucrose ($h_{SS} > 0$) are sucrose-like solutes (Table 1). Consequently, the different dominant interactions in the process of partial dehydration are chiefly responsible for the differences in the enthalpic interaction parameters $2vh_{ES}$ in different aqueous saccharide solutions.

For aldopyranose, if a weak hydration occurs at the interface between these aldopyranose molecules and bulk water, it must consist of at least two layers of molecules. The first layer, in contract with aldopyranose, because of the strongly oriented dipolar interaction, must maintain memory of the aldopyranose framework. The molecules of this layer can interact, only to a limited extent, between themselves, and consequently this interaction must be less than that in bulk water. Moreover, the water molecules in the next layer not only interact with the first layer, but also interact with the water molecules in bulk water. For those reasons, in the partial dehydration process of aldopyranose molecules, the relaxation of water molecules to bulk water from the second layer is mainly responsible for the thermodynamic interaction parameters.[59] To be specific, the interaction enthalpies of aldopyranoses with the same ions, to a large extent, depend on the solvent−solvent interaction (water−water), which contributes to the so-called solvent reorganization term, rather than the solvent−solute interaction or direct solute−solute interaction.

Enthalpic Parameters and Anions. When we assume the cation Na$^+$ plays approximately the same role in each system, the interaction of anions with saccharide in aqueous solution is chiefly responsible for the differences in interaction parameters of different sodium halides with the same saccharide (in Table 2). As previously mentioned, the direct interaction between saccharide molecules and ions is the major part of all interactions for studied systems. Thus, theoretical calculation was employed to obtain more details of the direct interaction between saccharide and Br$^-$, and the results are presented in Table 5.

Table 5. Thermal Energies, Enthalpies, Free Energies, and Entropies of Direct Interaction between Monosaccharide and Bromide Anion in Gas Phase at 298.15 K

theoretical parameters	Br$^-$(β-Xyl)$^4C_1$	Br$^-$(β-Glc)$^4C_1$	Br$^-$(α-Ara)$^1C_4$	Br$^-$(β-Gal)$^4C_1$
species	[O1,O2]	[O1,O2]	[O1,O2]	[O1,O2]
ΔE/kJ mol^{-1}	−100.34	−113.09	−97.82	−109.72
ΔH/kJ mol^{-1}	−102.28	−115.27	−99.95	−112.1
ΔG/kJ mol^{-1}	−69.97	−82.13	−67.32	−78.71
ΔS/J mol^{-1} K^{-1}	−108.37	−111.17	−109.43	−112.01
species	[O2,O3]	[O2,O3]	[O2,O3]	[O2,O3]
ΔE/kJ mol^{-1}	−80.19	−112.08	−102.56	−95.71
ΔH/kJ mol^{-1}	−81.6	−114.25	−104.85	−97.16
ΔG/kJ mol^{-1}	−52.54	−83.72	−73.17	−67.74
ΔS/J mol^{-1} K^{-1}	−97.48	−102.43	−106.28	−98.66
species	[O3,O4]	[O3,O4]	[O3,O4]	[O3,O4]
ΔE/kJ mol^{-1}	−77.68	−85.38	−75.97	−79.46
ΔH/kJ mol^{-1}	−78.54	−86.36	−76.91	−79.99
ΔG/kJ mol^{-1}	−51.43	−58.98	−47.16	−50.86
ΔS/J mol^{-1} K^{-1}	−90.92	−91.85	−99.78	−97.72
species	[O4]	[O4]	[O4]	[O4]
ΔE/kJ mol^{-1}	−73.07	−61.42	−58.43	−57.15
ΔH/kJ mol^{-1}	−73.7	−61.74	−58.72	−56.93
ΔG/kJ mol^{-1}	−46.89	−34.72	−31.8	−30.37
ΔS/J mol^{-1} K^{-1}	−89.92	−90.61	−90.28	−89.1
species	[O1]	[O1]		[O1]
ΔE/kJ mol^{-1}	−83.44	−94.59		−92.09
ΔH/kJ mol^{-1}	−84.54	−95.93		−93.52
ΔG/kJ mol^{-1}	−56.78	−67.72		−65.43
ΔS/J mol^{-1} K^{-1}	−93.12	−94.6		−94.2

Because the direct interaction between X$^-$ and saccharide is essentially a hydrogen bonding interaction, it is determined by the electronegativity of anions. Then the value of interaction enthalpies between saccharides and anions decreases from Cl$^-$ to I$^-$ with decreasing electronegativity of anions (Cl$^-$ = 3.0, Br$^-$ = 2.8, I$^-$ = 2.5).[60] Our theoretical calculations are consistent with this result. It is obvious that the interaction enthalpies between Br$^-$ and saccharide molecules are smaller than those between Cl$^-$ and saccharide molecules, and their differences range from 12.86 to 31.83 kJ mol^{-1} (Tables 4 and 5). Similar contributions of 4−OH and 5−CH$_2$OH groups can also be observed for the Br$^-$−saccharide−water system. Unfortunately, the theoretical results of direct interaction between saccharide and anions are opposite to the experimental order $2vh_{ES}$ (NaCl) > $2vh_{ES}$ (NaBr) > $2vh_{ES}$ (NaI). In other words, the direct interaction is not responsible for the variation of enthalpic parameters.

It is well-known that all the halide anions are structure breakers except F$^-$.[61] In aqueous solutions, when anions and

hydrated saccharide molecules approach each other, the various interactions of X^- with saccharide molecules may cause some water molecules to be squeezed out from the hydration shells of saccharide into water. In this process, water molecules need to absorb some energy to overcome the weak interactions of their surrounding molecules. This leads to an increase in enthalpy and makes a positive contribution to the observed h_{ES} values. For anions, since their ionic radii increase from Cl^- to I^- (Cl^- = 0.90 Å, Br^- = 1.14 Å, I^- = 1.35 Å),[60] the destructive effects on the hydration shells of saccharide molecules increase from Cl^- to I^- as well. Then the positive contributions to the $2vh_{ES}$ parameter should follow the order $Cl^- < Br^- < I^-$. Obviously, this conclusion is still opposite to the experimental order $2vh_{ES}$ (NaCl) > $2vh_{ES}$ (NaBr) > $2vh_{ES}$ (NaI).

Therefore, the experimental results are most likely connected with an energetic effect of the partial dehydration of hydrated X^-. This effect could be energetically more unfavorable for Cl^- compared with Br^- and I^- owing to the more exothermic hydration enthalpy of Cl^- ($\Delta H_{solv}(Cl^-)$ = −1470.1 kJ mol^{-1}; $\Delta H_{solv}(Br^-)$ = −1438.7 kJ mol^{-1}; $\Delta H_{solv}(I^-)$ = −1397.7 kJ mol^{-1}).[62] As a result, the positive contribution of partial dehydration of anions should follow the order $Cl^- > Br^- > I^-$. Moreover, the average difference in the theoretical direct interaction enthalpies between saccharide and different anions is 18.41 kJ mol^{-1} (Tables 4 and 5), which is smaller than the difference between different anion hydration enthalpies (31.4 kJ/mol). It also demonstrates that partial dehydration of the hydrated anion is responsible for the variations of $2vh_{ES}$ parameter.

It is clear from the above analyses that the interactions of saccharides with cation and anion are essentially ion−dipole interaction and hydrogen bonding interactions, respectively. Since those two interactions are stronger in studied systems rather than partial dehydration of ions and saccharide molecules, the sign of enthalpic pair interaction parameter $2vh_{ES}$ is determined by the direct interactions between saccharides and ions. However, no matter the interactions occurring between different saccharides and the same ion or occurring between different ions and the same saccharide, the differences in direct interaction enthalpies between saccharide molecules and ions are fairly small. As a consequence, it is the partial dehydration of saccharides or anions that is chiefly responsible for the difference in value of interaction enthalpic parameters in their interaction process.

Entropic Pair Interaction Parameters. *Entropic Parameters and Saccharide Stereochemistry.* Similar to the enthalpic pair interaction parameters, the change of entropy can also be attributed to (a) partial dehydration of hydration shells of saccharide, (b) partial dehydration of hydration shells of ions, and (c) direct interaction between saccharide and ions. The theoretical results of direct interaction entropies between saccharides and ions are presented in Tables 3−5. It is evident that the contribution of direct interaction entropy to s_{ES} is negative. Since the differences in those interaction entropies are small, little information of different function groups can be reliably inferred. Curiously, the interaction entropy of glucose with Na^+ is no doubt lower than in all other aldopyranoses. It is possible that the difference between interaction entropies for different saccharides is attributed primarily to the partial dehydration of saccharide. Because the interaction entropy is much more intricate than enthalpy, the analysis is carried out from two aspects.

For the NaCl−aldopyranose−water systems studied, the entropic parameters $2vTs_{ES}$ follow the trend D-arabinose < D-galactose < D-xylose < D-glucose. The difference in entropic parameters between xylose and glucose is 20 J kg mol^{-2}, while the difference between arabinose and galactose is 61 J kg mol^{-2}. It means 5−CH_2OH group provides a positive contribution to the entropic parameter of aldopyranose. The differences in entropic parameters between two pentoses (arabinose and xylose) and two hexoses (galactose and glucose) are 268 and 309 J kg mol^{-2}, respectively. It is easy to see that 4a−OH group of monosaccharide provides a more negative contribution to the entropic parameter than 4e−OH group for the NaCl−aldopyranose−water systems.

For the NaBr−aldopyranose−water systems studied, the entropic parameters $2vTs_{ES}$ follow the trend D-galactose < D-arabinose < D-glucose < D-xylose, which is different from NaCl system. The entropic parameters of xylose and arabinose are respectively 22 and 73 J kg mol^{-2} higher than those of glucose and galactose, which indicates a negative contribution of −CH_2OH group to entropy. This is quite different from the contribution of −CH_2OH group for NaCl−aldopyranose−water systems. The entropic parameters $2vTs_{ES}$ of xylose and glucose are 436 and 497 J kg mol^{-2} higher than those of arabinose and galactose, respectively. Similar to NaCl system, the 4a−OH group of monosaccharide gives a more negative contribution to the entropic parameter than 4e−OH group. For the aldopyranose in aqueous sodium iodine solution, the situation is much the same as that in aqueous sodium bromide solution.

In previous discussion, the partial dehydration of saccharide includes two processes: the relaxation of water molecules from hydrated saccharide to bulk water and the reorganization of those water molecules. It is easy to realize that the solute−solvent entropy change is positive whereas the reorganization entropy (arising from solvent−solvent energy fluctuation) is negative. The results of theoretical calculations have indicated that the interaction between water and 4e−OH or 5−CH_2OH group is stronger than 4a−OH or 5−H group. As a result, their solute−solvent interaction entropy must be more positive. Then the entropic parameters of aldopyranoses should follow the trend D-glucose > D-xylose > D-galactose > D-arabinose (the contribution of 4e−OH group is much greater than 5−CH_2OH group), which matches the experimental results for the NaCl−aldopyranose−water systems well. For fructose, the 1a−OH group provides a more negative contribution to entropy than arabinose, and for sucrose, more e−OH groups represent more positive contributions to interaction entropies between sucrose and ions in water. This is fairly different from that of saccharides in sodium bromide or sodium iodide solutions, which will be discussed later in more detail.

Entropic Parameters and Anions. Compared with the enthalpic parameters, the relationship of entropic parameters and anions is more complicated. When the effect of Na^+ for different sodium halide is considered as a constant, the interaction between anion and saccharide in water is chiefly responsible for the entropic parameters. Previous analysis has shown that the partial dehydration of saccharide gives more positive contributions to entropic parameters, rather than direct interaction between saccharide and anion which provides less negative contributions. Here we discuss the other two contributions to entropic parameters, including partial dehydrations of different anions and partial dehydrations of the same saccharide caused by different anions.

In order to interpret partial dehydrations of different anions, the concept of "structure entropy" is introduced. As is well-known, in aqueous solutions, hydration shells with determinate water molecule order are formed around dissolved anions, and mutual interactions between anions may cause some water molecules to be squeezed out from the hydration shells into the solvent and reorganized again.[63] Since those interactions are not strong enough to destroy the primary hydration structure of the "iceberg", the partial desolvation effect can only destroy the secondary hydration layer structure, leading to a positive contribution to entropy. This entropy change resulting from the structural breakage of water in this region is called the "structure entropy". According to the results calculated by Huang's equation,[64] the structure entropies of Cl^-, Br^-, and I^- are 42.7, 58.2, and 74.9 $J\ K^{-1}\ mol^{-1}$, respectively. Consequently, the partial dehydrations of the anions contribute negative values to the entropic parameters, and the contributions follow the trend $Cl^- < Br^- < I^-$.

The contribution coming from partial dehydration of saccharide caused by Cl^- to the entropic parameter has been discussed before. However, for the sodium halide—saccharide—water systems, since the negative reorganization entropies increase with increasing ionic radii of anions, the positive interaction entropy changes caused by the partial dehydration of the same saccharide molecule decrease. Therefore, compared with the NaCl—saccharide—water systems, the contribution of solute—solvent interaction entropy to the entropic parameter is further reduced due to the reorganization entropy for the NaBr—saccharide—water systems, resulting in an increasing contribution of direct interaction between NaBr and saccharide. Then the contribution of $5-CH_2OH$ group is negative to entropy, and the entropic parameters of glucose, xylose, and fructose are higher in sodium bromide solution than in sodium chloride solution. For the NaI—saccharide—water systems, because the positive solute—solvent interaction entropies are counterbalanced by more negative reorganization entropies, the partial dehydration of I^- plays a significant role among all of the interaction entropies. In brief, the different predominant interaction entropies are apparently responsible for the complicated changes of entropic parameters.

Generally speaking, the entropy pair parameters of interaction between saccharide and sodium halide in aqueous solution are more complicated than enthalpic pair parameters, because they apparently depend on the different dominant interactions in the partial dehydration process of saccharides or ions. To be exact, virtually little entropy coming from the cancellation of solute—solvent interaction entropy changes and reorganization in dehydration process is the ultimate cause of complicated entropic parameters.

Particularity and Significance of Hydration Entropy of Glucose in Water. As mentioned previously, the differences in interaction entropies for different saccharides with a given ion in aqueous solutions is partly attributed to the direct interactions of saccharides with the ion and partial dehydration of the saccharide molecules. Obviously, the experimental entropic interaction parameters for each sodium halide—glucose—water system are obviously higher than those for other aldopyranose systems (Table 2). Meanwhile, the theoretical direct interaction entropy between glucose and Na^+ is distinctly lower than that between other aldopyranoses and Na^+ (Table 3). Then there is no doubt that the positive contribution from partial dehydration of glucose molecules is much lager than that from partial dehydration of other

aldopyranose molecules. That is to say, glucose has the lowest interaction entropy with water molecules among all of the monosaccharides. This is of great significance to higher species especially human beings, because glucose not only maintains the stability of its hydrated structure, but also brings a more ordered solution environment in biological systems. Perhaps this is one of the reasons why glucose plays an important role in living organisms rather than other monosaccharides.

Enthalpy—Entropy Compensation Phenomenon. In many chemical processes, there is a linear relationship between the enthalpy change and entropy change. This phenomenon is known as the enthalpy—entropy compensation. It was first found by Constable[65] and observed in many cases, ranging from gases or aqueous solutions of small molecules to large biomolecules. Because the compensation relationship lies outside the normal realm of thermodynamics, it is often called the extrathermodynamic relationships.

In this work, we also find a linear relationship between the enthalpic parameters and entropic parameters for the NaBr—aldopyranose—water systems (Figure 2). This is possibly
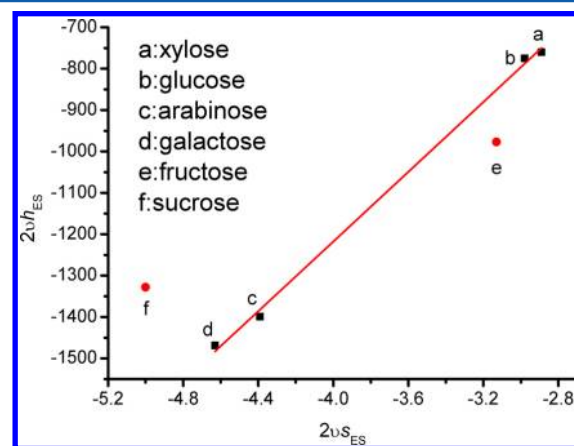

Figure 2. Correlation between $2vh_{NaBr-S}$ and $2vs_{NaBr-S}$ at 298.15 K.

attributed to different predominant interactions in different systems. As above-mentioned, there are two processes that occur during the solvation of solute, i.e., the interaction of solvent with solute molecules and the formation of the solvation cospheres (solvent reorganization). Yu and Karplus[66] have shown theoretically that the solvent—solvent interaction term is offset exactly by a corresponding term in the entropy. That is to say, in the process of hydration, the contributions of enthalpy and entropy coming from the environmental solvent interactions are usually compensated, resulting in a constant of free energy. If this part of enthalpy and entropy is substantial or even much larger than that contributed from solute—solvent interaction, a net enthalpy—entropy compensation effect will be observed.[67] In NaBr—saccharide—water systems, the variations of enthalpy and entropy are both chiefly responsible for partial dehydration of saccharides, yet only in aldopyranose systems, the predominant interaction is the solvent reorganization rather than the solute—solvent interaction. While, unlike aldopyranose, the enthalpic and entropic parameters of fructose and sucrose have no significant linear relationship.

■ CONCLUSION

The combination of results from calorimetric determinations and theoretical calculations reveals the essence of the

thermodynamic interactions occurring between electrolytes and saccharides in aqueous solutions. Though the direct interaction between saccharides and ions is dominant for saccharide–electrolyte–water systems, the partial dehydration of anions or saccharide molecules in their interaction process is chiefly responsible for the difference in thermodynamic interaction parameters. In fact, it is the stereochemistry of saccharide molecules that lead to the difference between interactions of different saccharides with given electrolytes. On the other hand, the anions directly influence their interactions with saccharides through their partial dehydration and indirectly affect the partial dehydration of saccharides. The enthalpy–entropy compensation relationship observed here confirms further that the difference in value of interaction entropic parameters between saccharides and ions depends primarily on the solvent–solvent (water–water) interaction in aqueous aldopyranose solution, whereas it depends primarily on the solvent–solute interaction in aqueous fructose/sucrose solution. Interestingly, we have noticed that the hydration entropy of glucose is lower than that of other monosaccharides, and therefore glucose should maintain the stability and order of biological systems more effectively than other monosaccharides. Perhaps this is a reason why glucose plays an important role in the living body rather than other monosaccharides.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental values of dilution enthalpies and mixing enthalpies (Tables S1–S4), dipole moments (Tables S5 and S6), structure information (Figures S1 and S2), and Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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