Thermodynamics of the Interacton of HCl with D-Glucose in Water at 278.15−318.15 K

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Electromotive forces of cells without liquid-junction Pt, H_2(g, $p°$)|HCl(m_E)|AgCl−Ag and Pt, H_2(g, $p°$)|HCl-(m_E),G(m_N)|AgCl−Ag, have been measured at 10 K intervals from 278.15 to 318.15 K, where G refers to D-glucose, m_E = 0.005−0.1 mol kg^{-1}, and m_N = 0.1−0.3 mol kg^{-1}. The thermodynamic parameters of interaction, f_{EN} (g_{EN}, h_{EN}, s_{EN} $c_{p,EN}$), of G with HCl in water have been evaluated. It appears that $g_{EN} > 0$, $h_{EN} > 0$, $Ts_{EN} > 0$, and $c_{p,EN} < 0$ at all five temperatures (except for Ts_{EN} at 318.15 K), and the values of g_{EN} vary slightly with temperature, whereas the values of h_{EN} and Ts_{EN} decrease rapidly from positive to negative with increasing temperature. By use of the values of $\Delta_t G°(H^+)$ reported by Wells and co-workers, the values of $g_{H^+−G}$ and $g_{Cl^−−G}$ have been obtained at 298.15 K. A comparison of the interaction parameters for the HCl−G pair with those for the MCl (alkali chlorides)−G pair shows that the g_{EN}, h_{EN}, and s_{EN} for the HCl−G pair are obviously higher than those for the MCl−G pair. These were interpreted in terms of the suggestion "H$^+$-induced structural changes". Furthermore, it has been shown that the group additivity parameters obtained from the HCl−alcohol−water systems is not applicable to the HCl−G−water system.

1. Introduction

Sugars are not only biologically important compounds but also typical nonelectrolytes (N) with hydrophilic hydroxyl groups, which are capable of hydrogen bonding.[1] Glucose (G) is one of the most important sugars and has been regarded as a typical hydrophilic nonelectrolyte resembling urea. So far, the thermodynamic properties of aqueous glucose solutions have been extensively studied[1,2] and reviewed.[3]

The interaction between sugar and electrolyte (E) in aqueous solutions is of great importance in biochemistry and has been closely looked at since Angyal's pioneering studies.[4] For example, Morel and co-workers[5] have made a systematic study of the interaction between cation and sugar. However, the primary aim for them was to study the complexing properties (so-called specific interactions) of various sugars with some cations. In these studies, anionic and univalent cationic contributions and no-specific (i.e. no complexing) interactions of di- and trivalent cations with some sugars (e.g., glucose) are all eliminated, and all studies were restricted to 298.15 K. Very recently, we have studied the thermodynamics of the interaction of HCl with alcohols[6] in water at 278.15−318.15 K and of ternary systems sugar (glucose, sucrose)−electrolyte−water[7] at 298.15 K. As part of the systematic study of the thermodynamics of interaction of electrolytes with hydroxyl compounds in water, we report here the interaction parameters between HCl and glucose in water from 278.15 to 318.15 K at 10 K intervals. This should provide additional information on the interaction between HCl and glucose in water.

Electromotive force (emf) measurements of the cells A and B without liquid-junction,

$$Pt, H_2(g, p°)|HCl(m_E)|AgCl−Ag \qquad (A)$$

$$Pt, H_2(g, p°)|HCl(m_E),G(m_N)|AgCl−Ag \qquad (B)$$
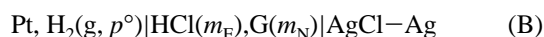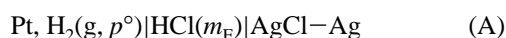
at m_E(A) = m_E(B) were carried out at five temperatures, where $p°$ = 101.325 kPa, m_E and m_N are the molalities of electrolyte (HCl) and nonelectrolyte (glucose), respectively, with respect

to a kilogram of pure water, m_E = 0.005−0.1 mol kg^{-1}, and m_N = 0.1−0.3 mol kg^{-1}.

2. Experimental Section

D-Glucose (A.R., anhydrous, Shanghai Chemical Co.) was dried under vacuum at 343 K to constant weight, stored in a desiccator, and used without further purification. Hydrochloric acid was prepared from the G.R. grade acid by distilling in an all-glass apparatus. Only the middle fraction was used. The stock solution of HCl was standardized gravimetrically by weighing silver chloride. The average difference among five replicate determinations was less than ±0.02%. The deionized water was distilled in an all-glass still, and its specific conductivity was (1.0−1.2) × 10^{-4} Ω^{-1} m^{-1}. All test solutions were prepared by weighing water, glucose, and the stock solution of HCl.

The Ag−AgCl electrodes were of the thermal−electrolytic type[8] aged in 0.1 mol kg^{-1} HCl(aq), which was deoxygenated by bubbling hydrogen. Three days after preparation, the finished electrodes were intercompared and the bias potentials were usually less than 0.05 mV. Only Ag−AgCl electrodes whose bias potential was less than 0.02 mV were used. Standard electrode potentials of Ag−AgCl in water were determined by Bates' method.[9] They are in excellent agreement with the values in the literature[10] within experimental error. The hydrogen electrodes were lightly coated with platinum black according to the method of Hills and Ives.[11] The high-purity hydrogen served as the source of hydrogen. The cells were of all-glass construction with four isothermal presaturators containing the test solution, as described by Yang et al.[12] These cells were thermostated at each temperature with an accuracy of ±0.02 K.

For a set of measurements, two Ag−AgCl electrodes were soaked overnight in the test solution. All measurements were made by two Ag−AgCl electrodes and two hydrogen electrodes. Equilibrium was reached about 3−5 h after the initiation of hydrogen bubbling. The criterion for the attainment of equilibrium was a reading steady to the nearest 0.05 mV for a period of about 1 h. The emfs of the cells were measured at 298.15, 278.15, 288.15, 298.15, 308.15, 318.15, and 298.15 K by a UJ-

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TABLE 1: Emfs (in mV) of Cells A and B for the HCl−Glucose−Water System from 278.15 to 318.15 K

		T (K)				
m_E (mol kg^{-1})	m_N (mol kg^{-1})	278.15	288.15	298.15	308.15	318.15
0.005 000	0.0000	0.491 99	0.495 90	0.498 80	0.501 50	0.503 56
	0.0997	0.491 23	0.495 24	0.498 37	0.501 00	0.502 99
	0.2000	0.490 87	0.494 62	0.497 77	0.500 38	0.502 40
0.010 000	0.0000	0.459 52	0.462 17	0.464 18	0.465 59	0.466 53
	0.0987	0.459 04	0.461 73	0.463 71	0.465 18	0.466 08
	0.2001	0.458 55	0.461 26	0.463 26	0.464 68	0.465 59
	0.2999	0.457 91	0.460 62	0.462 64	0.464 17	0.465 07
0.030 016	0.0000	0.409 35	0.410 16	0.410 44	0.410 12	0.409 33
	0.0998	0.408 95	0.409 80	0.410 08	0.409 81	0.409 00
	0.1999	0.408 39	0.409 29	0.409 66	0.409 42	0.408 61
	0.2801	0.407 90	0.408 82	0.409 18	0.408 93	0.408 15
0.049 99	0.0000	0.386 21	0.386 38	0.385 90	0.384 85	0.383 38
	0.1001	0.385 71	0.385 87	0.385 40	0.384 31	0.382 77
	0.1999	0.385 10	0.385 30	0.384 91	0.383 82	0.382 23
	0.3201	0.384 54	0.384 77	0.384 34	0.383 29	0.381 75
0.070 00	0.0000	0.371 16	0.370 71	0.369 66	0.368 09	0.366 03
	0.1002	0.370 63	0.370 23	0.369 21	0.367 63	0.365 54
	0.2005	0.370 16	0.369 75	0.368 76	0.367 21	0.365 17
	0.3001	0.369 69	0.369 29	0.368 29	0.366 77	0.364 68
0.100 00	0.0000	0.355 06	0.354 12	0.352 51	0.350 39	0.347 78
	0.1307	0.354 33	0.353 42	0.351 82	0.349 70	0.347 07
	0.2001	0.354 09	0.353 19	0.351 64	0.349 54	0.346 97
	0.3010	0.353 57	0.352 69	0.351 18	0.349 10	0.346 74

25-type potentiometer that was calibrated against a standard cell. A mirror-type galvanometer was used as a null detector. The three values at 298.15 K agreed to within 0.1 mV.

The atmospheric pressure was measured by a barometer and was calibrated for temperature, height above sea level, and latitude. The vapor pressure data of the test solutions at the experimental temperatures and molalities were obtained by Raoult's law. The observed emfs were corrected to the values at 101.325 kPa of hydrogen. The corrected emfs are listed in Table 1.

3. Thermodynamic Relations and Results

In the McMillan-Mayer [13] approach the excess thermodynamic functions are expressed in terms of pair and triplet interactions between the two solutes. We consider a solution of electrolyte and nonelectrolyte in a solvent of species water (W). The concentrations of E and N are expressed as the number of moles per kg of water. The total thermodynamic function of a solution containing 1 kg of water, m_N moles of N, and m_E moles of E, which dissociates into ν ions, is given by

$$F(m_N, m_E) = F°(m_N, m_E) + F^{EX}(m_N) + F^{EX}(m_E) + 2\nu f_{EN}m_E m_N + 3\nu^2 f_{EEN}m_E{}^2 m_N + 3\nu f_{ENN}m_E m_N{}^2 + ... \quad (1)$$

where $F°(m_N, m_E)$ is the total thermodynamic function of the ternary system when it is assumed that the ions are neutral particles and there are no interactions between the solutes. $F^{EX}(m_N)$ and $F^{EX}(m_E)$ are the excess functions of the binary N−W and E−W systems, respectively. f_{EN}, f_{ENN}, and f_{EEN} are pair and triplet interaction parameters that take into account all new sources of nonideality in the ternary system. For example, f_{EN} is a measure of the new interaction between N and E and of the corresponding decreases in the N−W and E−W interactions. In a dilute solution, pair interactions are the leading contribution to nonideality; higher-order terms are not too important. In fact, f_{EN} is the mean values of all the pair interaction parameters between N and each of the ions of a given electrolyte. For the $M_{\nu^+}X_{\nu^-}$−N pair, it follows that

$$f_{EN} = (\nu^+ f_{M^+-N} + \nu^- f_{X^--N})/\nu \quad (2)$$

where $\nu = \nu^+ + \nu^-$. For the transfer function of electrolyte from water to aqueous nonelectrolyte solution (W + N), we have from eq 2

$$\Delta_t F_E(W \rightarrow W + N) = F_E(m_N, m_E) - F_E°(m_E)$$

$$= 2\nu f_{EN}m_N + 6\nu^2 f_{EEN}m_E m_N + 3\nu f_{ENN}m_N{}^2 + ... \quad (3)$$

where both $F_E(m_E, m_N)$ and $F_E°(m_E)$ are the partial molal quantities of E.

In the particular case of Gibbs free energies, eq 3 is reduced to [14a,5c,6d]

$$\Delta_t G_E(W \rightarrow W + N) = -nF\Delta E$$

$$= \mu_E(m_E, m_N) - \mu_E°(m_E)$$

$$= 2\nu g_{EN}m_N + 6\nu^2 g_{EEN}m_E m_N + 3\nu g_{ENN}m_N{}^2 \quad (4)$$

where $\mu_E(m_E, m_N)$ and $\mu_E°(m_E)$ are the chemical potentials of E in E−N−W and E−W systems, respectively, F is the Faraday constant, and ΔE is the difference of the electromotive forces. In the present case, $\Delta E = E_A - E_B$. The higher order terms have been neglected in eq 4. As $m_E \rightarrow 0$, eq 4 is further reduced to

$$\Delta_t G_E°(W \rightarrow W + N) = 2\nu g_{EN}m_N + 3\nu g_{ENN}m_N{}^2 \quad (5)$$

When eq 4 is fit to the experimental data obtained in this paper using the least-squares routine, it is observed that g_{ENN} values are very small and that their deviations are large. Therefore, the interaction parameters were obtained from eq 4 in which the term containing g_{ENN} was neglected. These parameters are given in Table 2, together with their standard deviations and the standard deviation of the fit. It appears from Table 2 that g_{EEN} lacks precision because of experimental errors. However, this is not too important because we are interested principally in the pair interaction parameter, g_{EN}, which is most important in dilute solutions.

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TABLE 2: Free Energy Interaction Parameters for the HCl−Glucose−Water System from 278.15 to 318.15 K

T (K)	g_{EN} (J kg mol^{-2})	g_{EEN} (J kg^2 mol^{-3})	σ^a (mV)	R^b
278.15	129.1 ± 4.2	−16.8 ± 11.9	0.08	0.98
288.15	121.5 ± 4.1	−11.2 ± 11.6	0.08	0.98
298.15	116.7 ± 3.8	−14.3 ± 10.7	0.08	0.98
308.15	113.7 ± 5.4	−13.0 ± 15.0	0.11	0.96
318.15	117.3 ± 5.6	−15.2 ± 15.8	0.11	0.96

^{a} σ is the standard deviation of the fit. ^{b} R is the correlation coefficient.

TABLE 3: Pair Interaction Parameters for the HCl−Glucose in Water from 278.15 to 328.15 K

T (K)	Ts_{EN} (J kg mol^{-2})	h_{EN} (J kg mol^{-2})	$c_{p,EN}$ (J kg mol^{-2} K^{-1})
278.15	264	393	−8.8
288.15	182	303	−9.1
298.15	94	210	−9.5
308.15	∼0	114	−9.8
318.15	−102	14	−10.1

The pair free energy interaction parameter g_{EN} was analyzed as a function of thermodynamic temperature T using a least-squares routine, and the best representation of the data was found to be[6b,d]

$$g_{EN} = a + bT + cT^2 \qquad (6)$$

The coefficients a = 1622.4 J kg mol^{-2}, b = −9.7882 J kg mol^{-2} K^{-1}, and c = 0.015 889 J kg mol^{-2} K^{-2} were obtained with a standard deviation of the fit of 1.0 J kg mol^{-2}.

The pair interaction parameters are related to each other in usual way.[14] From eq 6, it follows that

$$s_{EN} = -(b + 2cT) \qquad (7)$$

$$h_{EN} = a - cT^2 \qquad (8)$$

$$c_{p,EN} = -2cT \qquad (9)$$

By use of eqs 4, and 7−9, various pair interaction parameters at different temperatures were obtained. They are given in Table 3.

Friedman[15] defines salting constant k_S by the relationship

$$k_S = -(\partial \ln m_N / \partial m_E)_{\mu_N} \qquad (10)$$

where μ_N is the chemical potential of the nonelectrolyte in an aqueous solution of electrolyte. If both m_N and m_E are low, it can be deduced that[14a,6c]

$$RTk_S = 2\nu g_{EN} \qquad (11)$$

where R is gas constant. By use of eq 11, the values of k_S at different temperatures can be calculated.

4. Discussion

4.1. Temperature Dependence of the Pair Interaction Parameters. It appears from Table 2 that $g_{EN} > 0$ at the temperatures concerned. This means that glucose is being salted-out by HCl in water (thermodynamic repulsion). Similar phenomena have been found for the HCl−alcohol,[6] NaX−alcohol,[16] and alkali metal−alcohol[14a] pairs in water. Figure 1 shows that h_{EN} and Ts_{EN} decrease rapidly with increasing
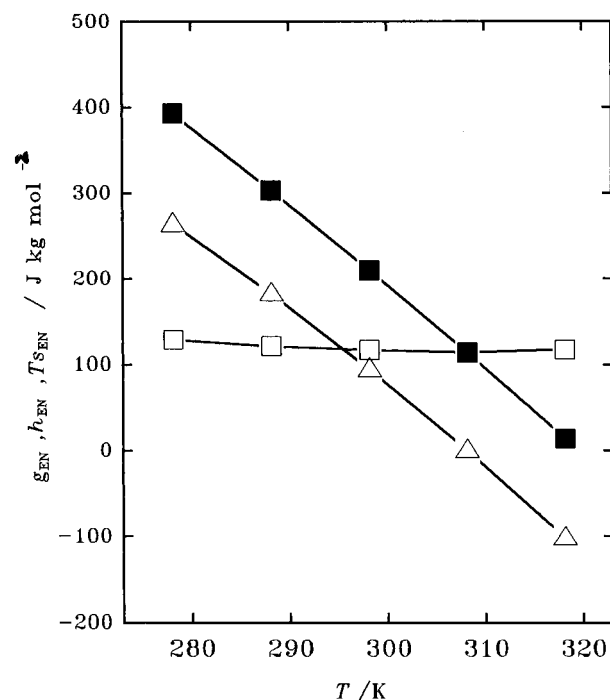
Figure 1. Temperature dependence of the interaction parameters for the HCl−glucose pair in water: □, g_{EN}; ■, h_{EN}; △, Ts_{EN}.

temperature, whereas g_{EN} is not sensitive to the temperatures used. Similar features also exist for the HCl−alcohol−water systems.[6]

These phenomena can be interpreted in terms of the structural interaction and electrostatic models described in previous papers.[6b,e] The interactions between glucose and HCl should include four types of interactions: H$^+$−R (alkyl groups, hydrophobic), Cl$^-$−R, H$^+$−O (OH, C=O, and −O− groups, hydrophilic), and Cl$^-$−O. The interaction of the H$^+$−O pair, which is mainly electrostatic (attractive) in nature, contributes a negative value to h_{EN} and g_{EN}. This interaction should be stronger than that of the H$^+$−R pair, which is mainly structural interaction (dehydration, structural breaking effect) and contributes a positive value to h_{EN}, s_{EN}, and g_{EN}. Obviously, the signs of the contributions of the G−H$^+$ pair to interaction parameters are mainly controlled by the interaction of the H$^+$−O pair. On the other hand, the interaction of the Cl$^-$−R pair, in which structural interaction is the leading part, contributes a positive value to h_{EN} and s_{EN}. This interaction, as suggested by Desnoyers and co-workers,[14a] decreases rapidly with temperature. The interaction of the Cl$^-$−O pair, which is mainly electrostatic (repulsive) and does not vary significantly with temperature, contributes a positive value to h_{EN}, s_{EN}, and g_{EN}. Therefore, the values of g_{EN} for the Cl$^-$−G, even for the HCl−G, are determined by the interaction of the Cl$^-$−O pair, i.e., the value of g_{EN} is mainly determined by the electrostatic interaction. These are in agreement with the suggestion of Kelley and Lilley[17] that the experimental free-energy pair-interaction parameters are fairly well represented by the electrostatic interaction only. Based on these ideas, the experimental results observed in this work can be easily understood.

Heat capacity is a very sensitive probe for studying structural interactions.[14b] The negative values mean that the interaction of glucose with HCl in water results in a reduction in structure of the solutions.

4.2. Interaction Parameters between Ions and Glucose. Using the spectrophotometric solvent-sorting method, Wells and co-workers[18] obtained free energies of transfer of H$^+$, $\Delta_t G°$-

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TABLE 4: Pair Free Energy Interaction Parameters (in J kg mol^{-2}) between Ion and Glucose (G) at 298.15 K

HCl$-$G	H$^+$$-$G	Cl$^-$$-$G	Na$^+$$-$G	K$^+$$-$G
117[a]	-93[b]	338[b]	-234[d]	-288[d]
113[b]				
123[c]				

[a] This work. [b] Obtained by fitting eq 5 to data of $\Delta_t G_{HCl}$, $\Delta_t G_{H^+}$ and $\Delta_t G_{Cl^-}$ in ref 19 from water to water$-$glucose mixtures. [c] Calculated from eq 2. [d] Calculated from eq 2 using data in ref 5d.
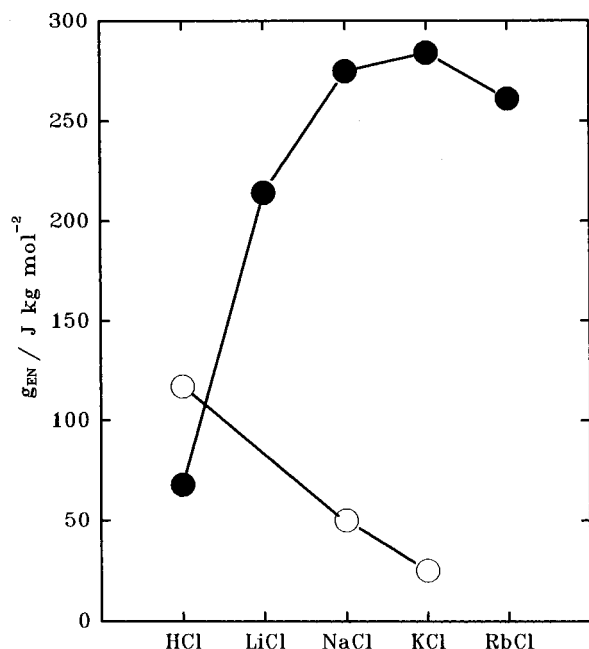
Figure 2. Dependence of g_{EN} on cations in water at 298.15 K: ○, MCl$-$G pair, from this work (HCl$-$G) and ref 5d (others); ●, MCl$-$TBA pair, from ref 6e. (M = H, Li, Na, K, Rb; TBA = *tert*-butyl alcohol; G = glucose).

(H$^+$), from water to water$-$glucose mixtures at 298.15 K (on the mole fraction scale). Furthermore, using the standard potentials, $E°$, determined by Williams et al.,[19] they calculated the values of $\Delta_t G°$(HCl) at 5, 10, 20, and 30% D-glucose. The values of $\Delta_t G°$(Cl$^-$) were then obtained from

$$\Delta_t G°(Cl^-) = \Delta_t G°(HCl) - \Delta_t G°(H^+) \quad (12)$$

By fitting eq 5 to the data of standard free energies of transfer (concentration scale converted), the values of g_{HCl-G}, g_{H^+-G}, and g_{Cl^--G} were obtained and given in Table 4. It appears that three values of g_{HCl-G} listed in this table are very close. On the other hand, data in Table 4 show that the interaction of the Cl$^-$$-$G pair contributes a relative large positive value to g_{HCl-G}, whereas that of the H$^+$$-$G pair contributes a negative value. These confirm our suggestions above.

4.3. Comparison of the Interaction Parameters for the HCl$-$Glucose Pair with Those for the MCl$-$Glucose Pair. It is very interesting to note that the value of g_{HCl-G} is notably higher than those of g_{MCl-G} (M = Na$^+$ and K$^+$). However, the values of $g_{HCl-TBA}$ (TBA = *tert*-butyl alcohol) are much lower than those of $g_{MCl-TBA}$[6e] (see Figure 2). The latter was interpreted in a previous paper.[6e] How is the former interpreted?

Using the values of g_{NaCl-G}, g_{KCl-G}, and g_{Cl^--G}, we have calculated the values of g_{Na^+-G} and g_{K^+-G}, which are also given in Table 4. Obviously, the difference between g_{HCl-G} and g_{MCl-G} results from the difference in interaction between HCl$-$O and MCl$-$O pairs, especially that between H$^+$$-$O and M$^+$$-$O pairs.

As mentioned above, both g_{H^+-G} and g_{M^+-G} are negative, which results from the comparative stronger electrostatic attractions of these ions with the groups containing oxygen (OH, C=O, and $-$O$-$). It has been shown that glucose exists in aqueous solutions as an equilibrium mixture of various isomers (structural isomers and stereoisomers). The equilibria concerning the cyclic structures and chain structures are presented by

α-D-glucose (36.4 %) $\rightleftharpoons$
 chain D-glucose (0.01%) $\rightleftharpoons$ β-D-glucose (63.6%) (I)

A cyclic isomer is more stable than a chain one. H$^+$(aq) interacts more strongly with the C=O group in a chain glucose molecule than with other oxygen atoms ($-$OH, $-$O$-$). It is possible, as suggested by Wells and co-workers,[18] that a H$^+$ ion and a glucose molecule form a stable glucose$-$H$^+$(aq) ion. If this is true, equilibria I will be broken. The shift of various equilibria (many isomers) will occur. For example, cyclic structures will be transferred into chain structures (called "H$^+$-induced structural changes"). This leads to two main results: (1) the decyclization will contribute a positive value to g_{EN}, h_{EN}, and Ts_{EN} for the HCl$-$glucose pair; (2) the interaction of Cl$^-$ with G becomes more strong and gives a more positive contribution to g_{EN}, h_{EN}, and Ts_{EN}. A similar process would not occur in the interaction of M$^+$ with G because of the large volume of hydrated M$^+$ ions. This is the probable reason that g_{HCl-G} is more positive than g_{MCl-G}. Williams et al.[19] suggested that a possible reaction or rearrangement of a glucose molecule occurs under the experimental condition based on the fact that the attainment of equilibrium in cell B needs a longer time than that in the cell A. This is in agreement with our suggestion above, since the equilibria between α- and β-structures, and five- and six-membered rings are slowly established,[20] especially when the concentration of chain isomer is very low.

As far as enthalpy and entropy parameters for the MCl$-$G pairs are concerned, only h_{KCl-G} has been reported in the literature.[5e] The s_{KCl-G} parameters can be calculated from

$$h_{EN} = g_{EN} + Ts_{EN} \quad (13)$$

Figure 3 shows that the h_{HCl-G} and Ts_{HCl-G} values are much larger than those for the NaCl$-$G pair, whereas no similar trend exists between MCl$-$alcohol and HCl$-$alcohol pairs in water.[6e] According to the suggestion (H$^+$-induced structural changes) above, this can be easily interpreted.

4.4. Group Additivity Analysis. The Savage$-$Wood group additivity model[2d] has been successfully applied to the non-electrolyte$-$nonelectrolyte pairs in water (e.g., urea, alcohols, sugars, and animo acids[21,22]) and to the electrolyte$-$nonelectrolyte pairs in water.[23] This model was used by us for the HCl$-$alcohol$-$water systems[6] to obtain free energy interaction parameters for the HCl$-$OH and HCl$-$CH$_2$ pairs, and the values of $g_{HCl-alcohol}$ calculated from these group parameters are in good agreement with experimental values. An attempt was made to calculate g_{HCl-G} from these group parameters (assuming that g_{HCl-OH} equals to g_{HCl-O}). Results showed that the calculated value of g_{HCl-G} is much smaller than the experimental value. Similar results have been reported by Tasker and Wood[21] for the interactions of nonelectrolyte$-$nonelectrolyte. Using the group additivity parameters calculated from the pair parameters between urea, alcohols, sugars, and amino acids, they obtained the values of h_{S-S} (S = sugar). However, these calculated values are more negative than the experimental values. We believe that this results possibly from the cyclic structures of sugar, the groups of which lost partly relative independent character, i.e., there are interactions between the adjacent groups

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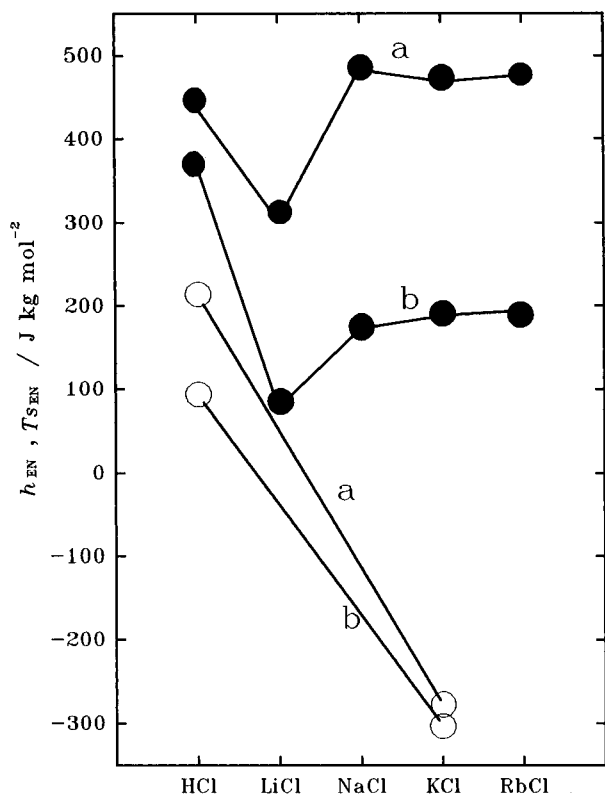
Figure 3. Dependence of h_{EN} (a) and Ts_{EN} (b) on cations in water at 298.15 K. Symbols are as for Figure 2 [h_{EN} from ref 6e (MCl–TBA) and ref 5e (others); Ts_{EN} were calculated from the equation $g_{EN} = h_{EN} - Ts_{EN}$].

in the same sugar molecule and steric hindrance to the interactions of groups in a molecule with groups in another molecule. Obviously, it is very interesting to get a better model for representing the interactions between sugar and electrolyte. To do this, it is necessary to obtain sufficient experimental data. Work on this is in progress.

References and Notes

(1) Miyajima, K.; Sawada, M.; Nakagaki, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1620, 1954.

(2) (a) Taylar, J. B.; Rowlinson, J. S. *Trans. Faraday Soc.* **1955**, *51*, 1183. (b) Stokes, R. H.; Robinson, R. A. *J. Phys. Chem.* **1966**, *70*, 2126. (c) Barone, G.; Cacace, P.; Castronuovo, G.; Elia, V. *Carbohydr. Res.* **1981**, *91*, 101. (d) Savage, J. J.; Wood, R. H. *J. Solution Chem.* **1976**, *5*, 733. (e) Bernal, P. J.; Van Hook, W. A. *J. Chem. Thermodyn.* **1986**, *18*, 955. (f) Daldrup, N.; Schönert, H. *J. Chem. Soc., Faraday Trans. 1* **1988**,*84*, 2553. (g) Bonner, O. D.; Cerutti, P. J. *J. Chem. Thermodyn.* **1976**, *8*, 105.

(3) (a) Goldberg, R. N.; Tewari, Y. B. *J. Phys. Chem. Ref. Data* **1989**, *18*, 809. (b) Barnoe, G. *Thermochim. Acta* **1990**, *162*, 17. (c) Franks, F. *Pure Appl. Chem.* **1987**, *59*, 1189.

(4) Angyal, S. J. *Aust. J. Chem.* **1972**, *25*, 1957.

(5) (a) Morel, J. P.; Lhermet, C. *Can. J. Chem.* **1985**, *63*, 2639. (b) Morel, J. P.; Lhermet, C.; Morel-Desrosiers, N. *Can. J. Chem.* **1986**, *64*, 996. (c) Maestre Alvarez, A.; Morel-Desrosiers, N.; Morel, J. P. *Can. J. Chem.* **1987**, *65*, 2656. (d) Morel, J. P.; Lhermet, C.; Morel-Desrosiers, N. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2567. (e)Morel-Desrosiers, N.; Morel, J. P. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 3461. (f) Morel-Desrosiers, N.; Lhermet, C.; Morel, J. P. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2173. (g) Morel-Desrosiers, N.; Lhermet, C.; Morel, J. P. *J. Chem. Chem. Soc., Faraday Trans.* **1993**, *89*, 1223. (h) Rongere, P.; Morel-Desrosiers, N.; Morel, J. P. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2771. (i) Israeli, Y.; Morel, J. P.; Morel-Desrosiers, N. *Carbohydr. Res.* **1994**, *263*, 25. (j) Israeli, Y.; Lhermet, C.; Morel, J. P.; Morel-Desrosiers, N. *Carbohydr. Res.* **1996**, *289*, 1.

(6) (a) Zhuo, K.; Wang, J.; Lu, Y.; Lu, J. *Acta Chim. Sin. (Chin. Ed.)* **1994**, *52*, 461. (b) Zhuo, K.; Wang, J.; Lu, J. *Acta Chim. Sin. (Chin. Ed.)* **1996,** *54*, 175. (c) Zhuo, K.; Wang, J.; Lu, J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 41. (d) Zhuo, K.; Wang, J.; Liu, W.; Lu, J. *Chin. J. Chem.* **1996**, *22*, 193. (e) Zhuo, K.; Wang, J.; Lu, J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3361. (f) Zhuo, K.; Wang, J.; Liu, W.; Lu, J. *A Collection of Papers of the First Youth Academic Symposium of Henan Province*; Chinese Science and Technology Press: Beijing, 1995; p 107.

(7) (a) Wang, J.; Liu, W.; Bai, T.; Lu, J. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1741. (b) Wang, J.; Zeng, L.; Liu, W.; Lu, J. *Thermochim. Acta* **1993**, *224*, 261. (c) Wang, J.; Liu, W.; Fan, J.; Lu, J. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3281.

(8) Bates, R. G. *Determination of pH*; John Wiley and Sons Inc.: New York, 1964; p 281.

(9) Bates, R. G.; Robinson, R. A. *J. Solution Chem.* **1980**, *9*, 455.

(10) White, D. R.; Bates, R. G.; Robinson, R. A. *J. Solution Chem.* **1980**, *9*, 457.

(11) Hills, G. J.; Ives, D. J. G. *Reference Electrodes*; Ives, D. J. G., Janz, G. J., Eds.; Academic Press: New York, 1960; p 107.

(12) Yang, J.; Men, D.; Liang, C.; Zhang, L.; He, L.; Sun, A. *J. Phys. Chem.* **1989**, *93*, 7248.

(13) McMillan, W. G.; Mayer, J. E. *J. Chem. Phys.* **1945**, *13*, 276.

(14) (a) Perron, G.; Joly, D.; Desnoyers, J. E.; Avedikian, L.; Morel, J. P. *Can. J. Chem.* **1978**, *56*, 552. (b) De Visser, C.; Perron, G.; Desnoyers, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 5894.

(15) (a) Friedman, H. L. *J. Solution Chem.* **1972**, *1*, 387. (b) Friedman, H. L. *The Physics and Chemistry of Aqueous Ionic Solutions*; Bellissent-Funel, M. C., Noilson, G. W., Eds.; D. Reidel Publishing Co.: Dordrecht, 1987; p 61.

(16) Piekarski, H. *Can. J. Chem.* **1986**, *64*, 2127.

(17) Kelley, B. P.; Lilley, T. H. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2771.

(18) Halawani, K. H. M.; Wells, C. F. *Thermochim. Acta* **1989**, *155*, 57.

(19) Williams, J. P.; Knight, S. B.; Crockford, H. D. *J. Am. Chem. Soc.* **1950**, *72*, 1127.

(20) Symons, M. C. R.; Benbow, J. A.; Pelmore, H. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1999.

(21) Tasker, I. R.; Wood, R. H. *J. Solution Chem.* **1982**, *11*, 295, 481, 729.

(22) Abate, V.; Baron, G.; Castronuovo, G.; Elia, V.; Savino, V. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 759.

(23) (a) Piekarski, H. *Can. J. Chem.* **1983**, *61*, 2203; **1986**, *64*, 2127. (b) Piekarski, H.; Tkaczyk, M. *Thermochim. Acta* **1987**, *112*, 377*; J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3661. (c) Cheek, P. J.; Gallardo-Jimenez, M. A.; Lilley, T. H. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3435. (d) Davis, K. G.; Gallardo-Jimenez, M. A.; Lilley, T. H. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2901. (e) Gallardo-Jimenez, M. A.; Lilley, T. H. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2909.