Thermodynamics of the Interaction of HCl with D-Fructose in Water at 278.15−318.15 K

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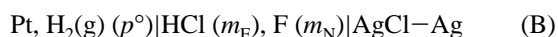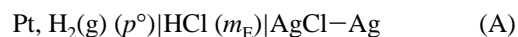
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Electromotive forces of the cells without liquid-junction, Pt, H_2(g) ($p°$)|HCl (m_E)|AgCl−Ag and Pt, H_2 (g) ($p°$))|HCl (m_E), F (m_N)|AgCl−Ag, have been measured at 10 K intervals from 278.15 to 318.15 K, where F stands for D-fructose, m_E = 0.01−0.1 mol kg^{-1}, and m_N = 0.1−0.5 mol kg^{-1}. The thermodynamic parameters of interaction, g_{EN}, h_{EN}, s_{EN}, and $c_{p,EN}$, of D-fructose with HCl in water have been evaluated, together with the standard transfer Gibbs free energies of HCl from water to aqueous D-fructose of various concentrations. In comparison with HCl−D-glucose, the g_{HCl-F}, h_{HCl-F}, and s_{HCl-F} values are smaller at most of the temperatures. The group additivity analysis was made in detail. The relationship between the hydration and stereochemistry of the sugars was discussed. The suggestion "H$^+$-induced structural changes" was developed and used to interpret the difference in interaction with HCl between D-fructose and D-glucose.

1. Introduction

This paper is part of a continuing study of the thermodynamics of the interaction between electrolyte (E) and a hydroxyl compound in water. In the previous papers of this series, the thermodynamic studies of ternary systems sugar [glucose (G), sucrose]−electrolyte−water[1] at 298.15 K and of the interaction of HCl with alcohol (ethanol, 2-propanol, 1,2-propanediol, glycerol, *tert*-butyl alcohol) in dilute aqueous solutions[2] at 278.15−318.15 K have been carried out. In the most recent paper[3] of this series, the thermodynamic parameters of the interaction of HCl with D-glucose in water was reported at 278.15−318.15 K. A comparison of the interaction parameters showed that g_{EN}, h_{EN}, and Ts_{EN} for the HCl−G pair are obviously higher than those for the MCl (alkali metal chlorides)−G pairs. The suggestion "H$^+$-induced structural changes" was made to interpret this feature. In this suggestion, it is assumed that the decyclization of glucose will contribute a positive value to g_{EN}, h_{EN}, and Ts_{EN} for the HCl−G pair. However, the reasons for the effect have not been investigated in detail. On the other hand, the group additivity parameters obtained from the HCl−alcohol−water systems[2] have been shown to be inapplicable to the HCl−G−water systems. We believe that this is related to carbohydrate stereochemistry. The relation between the hydration and stereochemistry of carbohydrates, especially when electrolyte is present, is very interesting but complicated. Therefore, the solution of these problems needs many new experimental data and theoretical efforts. In the present paper, we report the interaction parameters between HCl and D-fructose in water from 278.15 to 318.15 K at 10 K intervals. This should provide additional information on the interaction between HCl and D-fructose. On the basis of these and some published data, further theoretical analysis has been made.

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

$$\text{Pt, H}_2\text{(g) } (p°)|\text{HCl } (m_E)|\text{AgCl−Ag} \qquad \text{(A)}$$

$$\text{Pt, H}_2\text{(g) } (p°)|\text{HCl } (m_E),\ \text{F } (m_N)|\text{AgCl−Ag} \qquad \text{(B)}$$

at m_E(A) = m_E(B) were carried out at five temperatures, where F stands for D-fructose, m_E and m_N are the molalities of electrolyte (HCl) and nonelectrolyte (D-fructose), respectively, with respect to a kilogram of pure water, m_E = 0.01−0.1 mol kg^{-1}, and m_N = 0.1−0.5 mol kg^{-1}.

2. Experimental Section

D-Fructose (A. R., Shanghai Chemical Co.) was dried under vacuum at 343 K to constant weight, stored in a desiccator, and used without further purification. The specific conductivity of the deionized and redistilled water used in this work was (1.0−1.2) × 10^{-4} Ω^{-1} m^{-1} at room temperature. Purification and standardization of hydrochloric acid have been described elsewhere.[3]

The Ag−AgCl electrodes were prepared by the thermal-electrolytic method.[4] They were 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 those 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.[5] They are in excellent agreement with the literature values[6] within experimental error. The hydrogen electrodes were lightly coated with platinum black according to the method of Hills and Ives.[7] 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.[8] These cells were thermostated at each temperature with an accuracy of ±0.02 K. The other experimental apparatus and the experimental procedures were the same as those previously described.[3] The atmospheric pressure was measured by a barometer and was calibrated for temperature, height above sea level, and latitude. The vapor pressure data for 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.

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

		emf for given T (K)				
m_E (mol kg^{-1})	m_N (mol kg^{-1})	278.15 K	288.15 K	298.15 K	308.15 K	318.15 K
0.010 000	0.0000	0.459 49	0.462 18	0.464 13	0.465 61	0.466 57
	0.0929	0.459 01	0.461 88	0.463 83	0.465 22	0.466 07
	0.2300	0.458 70	0.461 47	0.463 39	0.464 75	0.465 53
	0.3601	0.458 32	0.461 15	0.463 02	0.464 46	0.465 25
	0.5012	0.457 85	0.460 66	0.462 61	0.463 97	0.464 75
0.030 000	0.0000	0.409 19	0.410 19	0.410 53	0.410 18	0.409 13
	0.1002	0.408 82	0.409 78	0.410 02	0.409 69	0.408 51
	0.2301	0.408 46	0.409 37	0.409 75	0.409 33	0.408 00
	0.3607	0.408 08	0.409 06	0.409 40	0.408 93	0.407 66
	0.5000	0.407 71	0.408 67	0.409 01	0.408 53	0.407 41
0.049 99	0.0000	0.386 21	0.386 39	0.385 88	0.384 87	0.383 23
	0.1002	0.385 78	0.386 08	0.385 52	0.384 40	0.382 68
	0.2301	0.385 25	0.385 59	0.385 00	0.383 79	0.382 02
	0.3701	0.384 82	0.385 12	0.384 61	0.383 44	0.381 59
	0.4997	0.384 60	0.384 56	0.384 17	0.383 07	0.381 34
0.100 0	0.0000	0.354 99	0.354 17	0.352 49	0.350 28	0.347 58
	0.1000	0.354 52	0.353 72	0.352 06	0.349 81	0.347 03
	0.2305	0.354 28	0.353 49	0.351 74	0.349 20	0.346 37
	0.3610	0.353 69	0.352 95	0.351 35	0.348 85	0.345 94
	0.5027	0.353 23	0.352 38	0.350 74	0.348 48	0.345 69

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

T (K)	g_{EN} (J kg^2 mol^{-2})	g_{EEN} (J kg^2 mol^{-3})	g_{ENN} (J kg^2 mol^{-3})	σ^a (mV)	R^b
278.15	90.6 ± 7.5	13.1 ± 8.6	-21.8 ± 10.9	0.10	0.98
288.15	73.8 ± 6.0	22.1 ± 7.0	-4.3 ± 8.8	0.08	0.99
298.15	83.0 ± 6.2	14.0 ± 7.2	-12.9 ± 9.0	0.08	0.98
308.15	104.4 ± 5.3	26.7 ± 6.1	-39.1 ± 7.7	0.07	0.99
318.15	137.2 ± 6.1	29.5 ± 7.0	-75.7 ± 8.8	0.08	0.99

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

3. Results

According to the McMillan−Mayer approach, the transfer Gibbs free energy of electrolyte from water (W) to aqueous nonelectrolyte solutions (W + N) may be expressed by[3,9]

$$\Delta_t G_E(W \to W + N) = \mu_E(m_E, m_N) - \mu^\circ_E(m_E)$$

$$= -nF\Delta E$$

$$= 2\nu g_{EN} m_N + 6\nu^2 g_{EEN} m_E m_N +$$
$$3\nu g_{ENN} m_N 2 \quad (1)$$

where $\mu_E(m_E, m_N)$ and $\mu^\circ_E(m_E)$ are, respectively, the chemical potentials of electrolyte in E−N−W and E−W systems, F is the Faraday constant, and ν is the number of ions into which the electrolyte dissociates. g_{EN}, g_{EEN}, and g_{ENN} are pair and triple interaction Gibbs free energy parameters that take into account all new sources of nonideality in the ternary system. ΔE is the difference of the emfs. In the present case, $\Delta E = E_B - E_A$ and the higher order terms have been neglected. These interaction parameters were obtained from least-squares analysis of the experimental data. They are given in Table 2, together with their standard deviations and the standard deviations of the fit. In the present paper, we are interested in the pair parameters which are most important in dilute solutions. The relation between g_{EN} and thermodynamic temperature T can be well-represented by the empirical equation[3]

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

Using a least-squares routine, the coefficients a = 6264.3 J kg mol^{-2}, b = −42.704 J kg mol^{-2} K^{-1}, and c = 0.073 693 J kg mol^{-2} K^{-2} were obtained with the standard deviation of the fit of 3.8 J kg mol^{-2}.

TABLE 3: Pair Interaction Parameters for HCl−Fructose in Water from 278.15 to 318.15 K

T (K)	Ts_{EN}^a (J kg mol^{-2})	h_{EN}^a (J kg mol^{-2})	$c_{p,EN}^a$ (J kg mol^{-2} K^{-1})
278.15	476 ± 186	564 ± 190	-41.0 ± 8.9
288.15	68 ± 107	146 ± 107	-42.5 ± 9.2
298.15	-369 ± 56	-286 ± 56	-44.0 ± 9.5
308.15	-836 ± 114	-734 ± 115	-45.5 ± 9.9
318.15	-1333 ± 212	-1196 ± 208	-47.0 ± 10.2

^{a} Standard deviations were estimated by Please's method.[11]

Using the equations[3,9a,10],

$$s_{EN} = -(b + 2cT) \quad (3)$$

$$h_{EN} = a - cT^2 \quad (4)$$

$$c_{p,EN} = -2cT \quad (5)$$

values of pair interaction entropic, enthalpic and isobaric capacity parameters (s_{EN}, h_{EN}, $c_{p,EN}$) were obtained and given in Table 3. The standard deviations for these interaction parameters were estimated by Please's method.[11] They are also included in Table 3.

The salting constant, k_s, defined by Friedman[12] can be calculated by[2c,9a]

$$RTk_s = 2\nu g_{EN} \quad (6)$$

at both m_N and m_E being low, where R is the gas constant.

Using eq 1 and the interaction parameters in Table 2, the standard transfer Gibbs free energies of HCl, $\Delta_t G_{HCl}^\circ$, have been evaluated from water to aqueous D-fructose at various concentrations. These values are given in Table 4.

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TABLE 4: Standard Transfer Gibbs Free Energies of HCl, $\Delta_t G_{HCl}°$ (J mol^{-1}), from Water to Aqueous D-Fructose at Different Concentrations

	$\Delta_t G_{HCl}°$ for given $m_N{}^a$ (mol kg^{-1})			
T (K)	0.1 mol kg^{-1}	0.2 mol kg^{-1}	0.3 mol kg^{-1}	0.5 mol kg^{-1}
278.15	35	67	97	149
288.15	29	58	86	141
298.15	32	63	93	147
308.15	39	74	104	150
318.15	50	92	124	161

[a] Molality is expressed as the number of moles per kg of pure water.
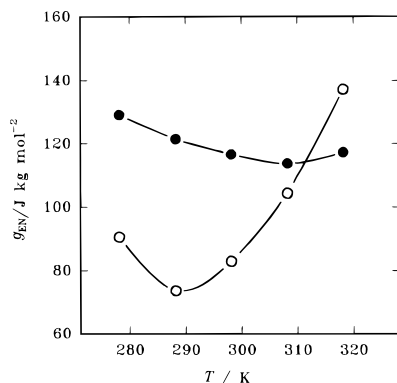
Figure 1. Temperature dependence of g_{EN} for HCl−fructose and HCl−glucose pairs in water: ○, $g_{HCl−fructose}$; ●, $g_{HCl−glucose}$.
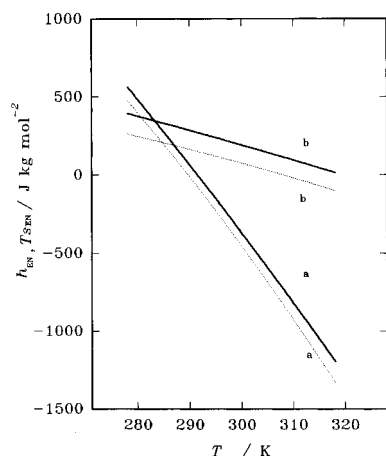
Figure 2. Temperature dependence of h_{EN} (solid lines) and Ts_{EN} (dashed lines) for HCl−fructose and HCl−glucose pairs in water: a, HCl−fructose pair; b, HCl−glucose pair.

4. Discussion

4.1. Temperature Dependence of the Pair Interaction Parameters and Comparison between HCl−D-Fructose and HCl−D-Glucose. The temperature dependence of pair interaction parameters for HCl−glucose and HCl−fructose pairs is shown in Figures 1 and 2. It can be seen that values of $g_{HCl−F}$ are smaller than those of $g_{HCl−G}$ from 278.15 up to 312 K and values of Ts_{EN} and h_{EN} for HCl−fructose are smaller than those for HCl−glucose from 318.15 down to 284 K. Compared with the HCl−D-glucose pair, the effect of temperature on the parameters g_{EN}, Ts_{EN}, and h_{EN} is stronger for the HCl−fructose pair.

Bernal and van Hook[13] determined the isobaric expansion coefficients [$(\partial V_{2,\phi}°/\partial T)_p$] and the isentropic compressibility ($k_{s,2,\phi}°$) of solutions of a number of carbohydrates from 288.15 to 328.15 K. They found that both of the values for glucose at

TABLE 5: Group Additivity Parameters in Water at 298.15 K

group		H_{kl}/(J kg mol^{-2})		
k	l	ref 16[b]	ref 15d[c]	ref 15c[d]
CH$_2$	CH$_2$	43 ± 4	42.8 ± 9.4	34.50 ± 7.51
OH	OH	−1 ± 8	−54[a]	−66.6[a]
O	O	−138 ± 27	−110.8 ± 59.5	
O	OH	−95 ± 10		
CH$_2$	OH	10 ± 8	51.0 ± 21.2	
CH$_2$	O	77 ± 9		
CHOH	CHOH	20[a]	−7.4 ± 6.3	−13.88 ± 6.53
CH$_2$	CHOH	31[a]	27.9 ± 8.3	44.0 ± 6.53

[a] Evaluated by linear combination of the other parameters; for example, $H_{CHOH−CHOH} = {}^1/_4 H_{CH_2−CH_2} + H_{CH_2−OH} + H_{OH−OH}$. [b] Evaluated through the fitting of about 50 h_{ij} experimental values (25 sugars; 17 alcohols, ketones, and ethers) using only three arbitrarily chosen groups: CH$_2$, O, and OH. [c] Derived from nearly 100 data (11 sugers; 20 alcohols). Chosen groups: CH$_2$, O, and CHOH. [d] Derived from 23 alcohols. Chosen groups: CH$_2$, O, and CHOH.

298.15 K are lower than those for fructose. This phenomenon, as noted by Bernal and van Hook, suggests that glucose hydration responds to temperature in a significantly different fashion than does fructose.

In addition, Figure 1 shows that a minimum in $g_{HCl−G}$ (about 115 J kg mol^{-1}) takes place at about 308 K, whereas a minimum in $g_{HCl−F}$ (77.7 J kg mol^{-1}) occurs at about 290 K. The minimum in k_s can also be obtained from eqs 2 and 6: 0.176 kg mol^{-1} at 320 K for D-glucose and 0.129 kg mol^{-1} at 292 K for D-fructose. Desnoyers et al.[14a] predicted from the scaled particle theory[14b] that the minimum in k_s for E(NaCl, CsCl)−alcohol (methanol, ethanol)−water systems is at about 323 K, and the experimentally observed value is at 333 K. In a previous paper,[2e] a minimum in k_s (0.03 kg mol^{-1}) was observed at 322 K for the HCl−2-propanol−water system.

4.2. Group Additivity Analysis. In a recent paper,[3] we noted that the Savage−Wood group additivity model[15] cannot be used to predict the values of $g_{HCl−s}$ (s = sugar) from the group parameters obtained experimentally from HCl−alcohol−water systems. A similar phenomenon has been found by Tasker and Wood[16] for nonelectrolyte−water binary systems: the calculated h_{ss} values for some monosaccharides from the group parameters, which were obtained by a fit of the experimental data for sugars, alcohols, ketones, and others,[16d] are always less (mostly negative) than the experimental values (positive). Further discussion will be made as follows.

The values of enthalpic group parameters {H_{kl}} in Table 5 were obtained respectively from different subsets of data (see the notation of Table 5). The values of a given {H_{kl}} are substantially in agreement with one another (except the discussed case of {$H_{OH−OH}$} and related quantities). Interestingly, we note that the {$H_{OH−OH}$} values from different fits tend to be less negative with an increase in the rate $n_{sugar}/n_{alcohol}$ (0, 11/20, 25/17) of the number of data on sugars and alcohols in a given fit. The calculated h_{ss} values from the group parameters in column 4 are less than the experimental values. If the {$H_{OH−OH}$} value in column 5 was used to predict the h_{ss} values, the results would be even less than the experimental values. This shows that the {$H_{OH−OH}$} value in column 5 is the worst one among the three values for describing the interaction in water between the OH groups on different sugar molecules. On this basis, the {$H_{OH−OH}$} values can be assumed as an indication of an almost ideal behavior of the OH groups of the sugars in water, but the same is not true for the OH groups on the polyols.

The above analysis shows that the differences between sugar and alcohol are mainly attributed to the OH groups.

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4.3. Hydration and Stereochemistry of Sugars. The differences between sugar and alcohol have been roughly discussed on the basis of the group additivity model, but it is evident that this model cannot be used for the discrimination or prediction of the differences among the properties of the isomers.[16] These differences are especially important in biological functions and are not negligible. They seem to be correlated with the hydration and stereochemistry of the sugars.

Some hydration models have been so far proposed to rationalize the data of sugars in water.[17–22] Galema and co-workers[22] suggested that the OH groups on sugar molecules are structure breakers. We believe that the break effect of these OH groups is weaker than those on alcohol molecules resulting from the specific structure of saccharides which fit into the structure of water. Moreover, the fit into the structure of water depends particularly on the stereochemistry of saccharide, as observed by Barone[17] and Galema and co-workers.[22] The more the OH groups on saccharide molecules fit into the water structure, the less they break the water structure. In terms of these suggestions, not only the differences in thermodynamic parameters among isomers and those between D-fructose and D-glucose[13,17,23] can be interpreted, but also the argument about "structure-making" and "structure-breaking" for aqueous saccharide solutions can be intervened. The methylene and methenyl groups (hydrophobic) on saccharide molecules are generally considered to be structure-makers. The OH groups on the same molecules are weak structure-breakers. At a given condition, an alternative effect is possibly striking.

In the recent paper,[3] we suggested a so-called "H^+-induced structural change" model to explain the differences in interaction between HCl−glucose and HCl−alcohol pairs. This model has been further confirmed by the very recent study of Serianni and colleagues.[24] On the basis of this model and the hydration model of sugars mentioned above, we can easily understand why the decyclization of sugar will contribute a positive value to g_{EN}, h_{EN}, and Ts_{EN}. Obviously, the decyclization will dispel the compatibility between the OH groups on ring sugar molecules and the three-dimensional hydrogen-bonded structure of water. This is equivalent to breaking the structure of water. This effect depends on the stereochemistry of sugars and the percentage composition of equilibrium mixtures in water, especially that of the dominant conformer. The dominant conformer, β-glucopyranose (1e2e3e4e5e, 64% at 298.15 K), of D-glucose fits into the water structure more than the dominant conformer, β-fructopyranose (1e2a3e4e5a, 57% at 309 K), of D-fructose.[25,26] The decyclization of β-glucopyranose will contribute a more positive value to h_{EN} and Ts_{EN} than does β-fructopyranose. This is possibly a main reason for the fact that $h_{HCl−G}$ and $Ts_{HCl−G}$ are larger than $h_{HCl−F}$ and $Ts_{HCl−F}$, respectively, at the temperatures studied except below 280 K. Compared with $g_{HCl−F}$, the higher values of $g_{HCl−G}$ (from 278.15 to 312 K) are due to the difference in the effect of decyclization of β-glucopyranose and β-fructopyranose. The effect of the transformation of the OH groups caused by the decyclization will decrease with increasing temperature. In addtion, the effect for D-fructose depends more on temperature than that for D-glucose,[13] so that the reduction of h_{EN} and Ts_{EN} for HCl−D-fructose is more rapid than those for HCl−D-glucose. The negative h_{EN} and Ts_{EN} at higher temperatures (see Figure 2) seem to show that the signs of these parameters have been governed by the interaction of the $H^+−O$ pair.

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