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Thermodynamics of the interaction of HCl with D-arabinose in water at 278.15–318.15 K

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Abstract

The thermodynamic parameters of interaction of HCl with D-arabinose in water were determined from electromotive force measurements from 278.15 to 318.15 K. The standard Gibbs free energies of transfer of HCl from water to aqueous solutions of 5, 10, and 15 wt.% of D-arabinose were evaluated. The group interaction Gibbs free-energy parameters ($G_{\mathrm{HCl-CH_2}}$, $G_{\mathrm{HCl-OH}}$, $G_{\mathrm{HCl-}e\mathrm{-OH}}$, $G_{\mathrm{HCl-}a\mathrm{-OH}}$, and $G_{\mathrm{HCl-O}}$) for the HCl–sugar (or alcohol)–water systems were evaluated and discussed in terms of the Savage–Wood group additivity principle and the stereochemistry of sugars, where –OH, –*e*-OH and –*a*-OH stand respectively for alcohol-, equatorial- and axial-hydroxyl groups. Of the five group interactions, the HCl–*e*-OH interaction contributes a large positive value to the pair interaction Gibbs free-energy parameters of HCl with sugars, whereas the contributions of the HCl–*a*-OH and HCl–O interactions are very small.

Keywords: Thermodynamics; D-Arabinose; HCl; Group additivity; Axial-, equatorial-hydroxyl groups

1. Introduction

The group additivity principle proposed by Savage and Wood [1] has been widely applied to the interactions of nonelectrolyte–nonelectrolyte (N) pairs [2,3] and of electrolyte (E)–nonelectrolyte pairs in water [4]. However, this principle failed to predict the pair molecular interaction parameters for systems containing sugars (S). For example, Tasker and Wood [2b] obtained some group additivity enthalpy parameters H_{ij} from the pair molecular interaction parameters h_{AB} between urea, alcohols, sugars and amino acids. But the calculated values of h_{AB} for sugars from these group parameters are much smaller than the experimental ones. Even the signs of the calculated and experimental values are opposite for some sugars. The calculated values of h_{AB} for sugars from the group parameters by Barone and co-workers [3a] have the same signs as the experimental, but all hexoses or pentoses have the same calculated values. Obviously, this is because the difference of their stereochemistry was not considered. These cases have also been noted in our previous work [5].

To rationalize the hydration characteristics of sugars, some concepts have been used such as hydration numbers [6], the anomeric effect [7], and the ratio of axial (*a*-) versus equatorial hydroxyl (*e*-OH) groups [8]. Uedaira and Uedaira [9] suggested that any properties which depend on the sugar hydration will correlate well with the number of *e*-OH groups *n*(*e*-OH) in sugar molecules. They have confirmed the suggestion for some properties such as diffusion coefficients [9a] and

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partial molar heat capacities [9b] of some mono-, di-, and trisaccharides in water. In our recent work [10], a linear relationship was observed between the Gibbs free-energy parameters of HCl with sugars, $g_{\mathrm{HCl-S}}$, and $n(e\text{-OH})$. However, the contributions of a-OH groups were not considered.

As part of a continuing study of the thermodynamics of the interaction of electrolytes with hydroxyl compounds, this work reports the interaction parameters for the HCl–D-arabinose (A) pair in water at 278.15–318.15 K. This will provide additional information on the interaction between HCl and sugar in water. In addition, the contributions of a-OH and e-OH groups are calculated and discussed in terms of the group additivity principle and the stereochemistry of sugars. These group parameters could possibly be used to predict the interactions of HCl with some sugars and related compounds.

2. Experimental

D-Arabinose (AR) was dried under vacuum at 333 K to constant weight and stored over P_2O_5 in a desiccator. Deionized water was distilled in an all-glass apparatus. The resulting water had a specific conductivity of $(1.0–1.2)\times 10^{-4}\ \Omega^{-1}\ \mathrm{m}^{-1}$ at room temperature. Purification and standardization of HCl have been described elsewhere [5].

The AgCl–Ag electrodes were of the thermal-electrolytic type [11]. They were aged in 0.1 mol kg^{-1} HCl (aq), which was deoxygenated by bubbling hydrogen. The finished electrodes were intercompared 3 days after preparation and the bias potentials were usually less than 0.05 mV. Only those AgCl–Ag electrodes whose bias potentials were less than 0.02 mV were used. Standard potentials of these electrodes in water, determined by Bates' method [12], are in excellent agreement with the literature values [13] within experimental error. The hydrogen electrodes were lightly coated with platinum black in terms of Hills and Ives' method [14]. 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. [15]. These cells were thermostated at each temperature with an accuracy of ±0.02 K. The other experimental apparatus and experimental procedures were the same as previously described [5].

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

$$\mathrm{Pt},\ \mathrm{H_2}\ (g,\ p^\circ)\,|\,\mathrm{HCl}\ (m_{\mathrm{HCl}})\,|\,\mathrm{AgCl–Ag} \qquad (\mathrm{A})$$

$$\mathrm{Pt},\ \mathrm{H_2}\ (g,\ p^\circ)\,|\,\mathrm{HCl}\ (m_{\mathrm{HCl}}),\ \mathrm{A}\ (m_{\mathrm{A}})\,|\,\mathrm{AgCl–Ag} \qquad (\mathrm{B})$$

at $m_{\mathrm{HCl}}\ (\mathrm{A}) = m_{\mathrm{HCl}}\ (\mathrm{B})$ were carried out at 10 K intervals from 278.15 to 318.15 K, where $p^\circ = 101.325$ kPa, m_{HCl} and m_{A} are the molalities of HCl and D-arabinose, respectively, with respect to 1 kg of pure water. In order to obtain accurate pair interaction parameters, which indicate the interactions between E and N at infinite dilution, measurements were made in dilute solutions, i.e., $m_{\mathrm{HCl}} = 0.01–0.15$ mol kg^{-1}, $m_{\mathrm{A}} = 0.2–0.8$ mol kg^{-1}. The observed emfs were corrected to the values at 101.325 kPa of hydrogen. These corrected emfs are listed in Table 1.

3. Results and discussion

The Gibbs free energies of transfer of electrolyte from water (W) to aqueous nonelectrolyte solutions (W + N) may be expressed as [5]:

$$\begin{aligned}\Delta_t G_{\mathrm{E}}\ (\mathrm{W}\rightarrow\mathrm{W}+\mathrm{N}) &= -nF\Delta E\\ &= 2\nu g_{\mathrm{EN}}m_{\mathrm{N}} + 6\nu^2 g_{\mathrm{EEN}}m_{\mathrm{E}}m_{\mathrm{N}}\\ &\quad + 3\nu g_{\mathrm{ENN}}m_{\mathrm{N}}^2 \qquad (1)\end{aligned}$$

where n and F have their usual meaning, ΔE is the difference of the emfs. In the present case, $\Delta E = E_{\mathrm{B}} - E_{\mathrm{A}}$ at $m_{\mathrm{E}}\ (\mathrm{A}) = m_{\mathrm{E}}\ (\mathrm{B})$; 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 are taken into account for all new sources of nonideality in the ternary system. The higher terms have been neglected in Eq. (1). The interaction Gibbs free-energy parameters for the HCl–D-arabinose–water system were least-squares obtained and are given in Table 2.

Table 1
Emfs (mV) of the cells A and B for the HCl–D-arabinose–water system from 278.15 to 318.15 K

m_{HCl} (mol kg^{-1})	m_A (mol kg^{-1})	T (K)				
		278.15	288.15	298.15	308.15	318.15
0.010000	0.0000	0.45948	0.46211	0.46417	0.46564	0.46647
	0.2032	0.45898	0.46156	0.46358	0.46489	0.46563
	0.4014	0.45877	0.46102	0.46312	0.46437	0.46504
	0.6078	0.45848	0.46092	0.46272	0.46404	0.46476
	0.7889	0.45839	0.46085	0.46260	0.46391	0.46455
0.030000	0.0000	0.40962	0.41045	0.41040	0.41006	0.40910
	0.2036	0.40898	0.40974	0.40972	0.40919	0.40811
	0.3900	0.40869	0.40938	0.40935	0.40871	0.40763
	0.5924	0.40848	0.40921	0.40885	0.40829	0.40715
	0.7881	0.40817	0.40894	0.40860	0.40778	0.40670
0.05000	0.0000	0.38630	0.38636	0.38581	0.38468	0.38301
	0.2001	0.38571	0.38576	0.38504	0.38373	0.38195
	0.3962	0.38516	0.38507	0.38430	0.38290	0.38122
	0.6149	0.38497	0.38490	0.38398	0.38256	0.38068
	0.8019	0.38454	0.38444	0.38363	0.38221	0.38030
0.10000	0.0000	0.35508	0.35408	0.35238	0.35024	0.34749
	0.1918	0.35437	0.35327	0.35141	0.34923	0.34630
	0.4073	0.35366	0.35256	0.35056	0.34814	0.34524
	0.6040	0.35333	0.35210	0.35002	0.34746	0.34461
	0.7862	0.35314	0.35186	0.34990	0.34735	0.34446
0.15000	0.0000	0.33675	0.35518	0.33297	0.33016	0.32683
	0.1921	0.33604	0.33439	0.33204	0.33299	0.32543
	0.3781	0.33550	0.33351	0.33139	0.32796	0.32472
	0.5953	0.33480	0.33300	0.33055	0.32713	0.32391
	0.7984	0.34443	0.33254	0.33001	0.32669	0.32333

Assuming $c_{p,EN}$ (pair interaction isobaric heat capacity parameter) to be independent of temperature, the relationship between g_{EN} and thermodynamic temperature T is given by the following equation:

$$g_{EN} = aT + b - cT \ln T \tag{2}$$

The coefficients $a = -29.992$ J kg mol^{-2} K^{-1}, $b = 1080.2$ J kg mol^{-2}, and $c = -4.68001$ J kg mol^{-2} K^{-1} were least-squares obtained for the HCl–D-arabinose pair, with the standard deviation of the fit of 2.2 J kg mol^{-2} and the correlation coefficient of 0.997.

The pair interaction parameters are related to each other in the usual way [16]. From Eq. (2), it follows that:

$$s_{EN} = -a + c + c \ln T \tag{3}$$

$$h_{EN} = b + cT \tag{4}$$

$$c_{p,EN} = c \tag{5}$$

Values of s_{EN} and h_{EN}, which are pair interaction entropic and enthalpic parameters for HCl–D-arabinose, respectively, were calculated from these equations and are given in Table 3. The $c_{p,EN}$ $(=c)$ is the averaged pair interaction isobaric heat capacity parameter in the temperature range considered.

The salting constant, k_S, defined by Friedman [17] can be obtained from [16,18,19]:

$$RTk_S = 2\nu g_{EN} \tag{6}$$

with both m_N and m_E being low. The k_S values for the HCl–D-arabinose–water system were obtained and are also given in Table 3.

The standard Gibbs free energies of transfer, $\Delta_t G_{HCl}{}^{\circ w}$, of HCl from water to aqueous solutions of 5, 10 and 15 wt.% of D-arabinose can be calculated from Eq. (1) when m_{HCl} tends to zero. It is worthwhile to note that $\Delta_t G_{HCl}{}^{\circ w}$ is based on the molal concentration scale, defined as the number of moles of HCl

Table 2
Interaction free-energy parameters for the HCl–D-arabinose–water system from 278.15 to 318.15 K

T (K)	g_{EN} (J kg mol^{-2})	g_{EEN} (J kg^2 mol^{-3})	g_{ENN} (J kg^2 mol^{-3})	δ[a] (mV)	R[b]
278.15	64 ± 5	42.6 ± 3.4	-24.9 ± 4.3	0.11	0.98
288.15	77 ± 4	49.2 ± 3.0	-33.5 ± 3.7	0.09	0.99
298.15	86 ± 5	49.8 ± 3.9	-33.0 ± 4.9	0.12	0.99
308.15	104 ± 5	66.0 ± 3.9	-43.2 ± 4.9	0.12	0.99
318.15	118 ± 6	57.3 ± 4.6	-49.9 ± 5.7	0.12	0.98

[a] δ is the standard deviation of the fit.

[b] R is the correlation coefficient.

per kg of pure water. The relationship between the standard Gibbs free energies of transfer expressed in different concentration scales is given by the following equation[1]:

$$\Delta_t G^\circ_{HCl} = \Delta_t G_{HCl}{}^{\circ w} + \nu RT \ln(1 + 0.001\ m_N M_N) \qquad (7)$$

where $\Delta_t G^\circ_{HCl}$ is based on the usual molal concentration scale with respect to a 1 kg water–sugar mixture instead of pure water, M_N is the molecular mass of the nonelectrolyte (sugar). The calculated values are presented in Table 4.

It can be seen from Table 2 that $g_{HCl-A} > 0$ at all five temperatures. This means that D-arabinose is being salted out by HCl in water. Similar to g_{HCl-X} (X stands for D-xylose), g_{HCl-A} also increases with increasing temperature, but it is more sensitive than g_{HCl-X}. On the other hand, it is noted that $g_{HCl-A} < g_{HCl-X}$ at 278.15–318.15 K. Obviously, this is due to the difference of their stereochemistry since both of them are aldopentoses.

We also see from Table 3 that all the s_{HCl-A} and h_{HCl-A} values are negative, and become more negative with increasing temperature. These phenomena can partially be interpreted in terms of the models developed and used in our previous papers [5,18,19]. The interactions between sugar and HCl could be roughly divided into four types of interactions: H^+–R (alkyl groups), Cl^-–R, H^+–O (OH, C=O, and –O–) and Cl^-–O. Two of them (Cl^-–R and H^+–O) are important. The electrostatic (attractive) interaction of H^+–O contributes a negative value to h_{EN} and s_{EN}, whereas the interaction of Cl^-–R, in which the structural interaction is the leading part, contributes a positive to h_{EN} and s_{EN}. The negative values of h_{EN} and s_{EN} observed experimentally are possibly because the contribution of the H^+–O interaction is larger than that of Cl^-–R. The signs of h_{EN} and s_{EN} are determined by the electrostatic interaction of H^+–O. The structural interaction decreases sharply with increasing temperature. On the contrary, the electrostatic interaction is not sensitive to temperature. Therefore, the values of h_{EN} and s_{EN} become more negative with increasing temperature.

The additivity principle is often used in chemical thermodynamics to separate the contributions of groups of atoms from the molecular properties. According to the additivity principle of Savage and Wood [1], the pair interaction Gibbs free-energy parameter, g_{HCl-N}, can simply be expressed as the sum of the interaction parameters of HCl with all possible functional groups of N. The resulting equation is:

$$g_{HCl-N} = \Sigma\, n_i G_{HCl-i} \qquad (8)$$

where n_i is the number of type i group on a nonelectrolyte molecule, G_{HCl-i} is the parame-

Table 3
Pair interaction parameters for HCl–D-arabinose in water from 278.15 to 318.15 K

T (K)	Ts_{EN} (J kg mol^{-2})	h_{EN} (J kg mol^{-2})	k_S (kg mol^{-1})
278.15	−286	−222	0.111
288.15	−344	−268	0.129
298.15	−403	−315	0.139
308.15	−464	−362	0.162
318.15	−527	−409	0.178

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[1] This equation can be derived from the relation $\mu_E = \mu^\circ_E + RT \ln a_E$.

Table 4
Standard Gibbs free energies of transfer of HCl from water to aqueous D-arabinose solutions (J mol^{-1})

T (K)	wt.% of D-arabinose					
	5		10		15	
	A[a]	B[a]	A	B	A	B
278.15	71	309	108	595	94	846
288.15	83	329	118	623	84	863
298.15	96	350	146	669	131	937
308.15	114	377	166	706	131	964
318.15	129	400	185	743	141	1001

[a] A and B stand for $\Delta_t G_{HCl}{}^{ow}$ and $\Delta_t G^{\circ}_{HCl}$, respectively (see text).

ter representing the interaction of HCl with each group i of the nonelectrolyte molecule.

According to the assumption of Savage and Wood [1], for C, CH, and CH_3, we consider here the interaction of HCl with hydroxyl compounds (alcohols and sugars) using only three arbitrarily chosen groups: $-CH_2-$, –OH, and –O–. To describe the difference in stereochemistry among various sugar molecules, the –OH groups are divided into three classes: e-OH, a-OH, and alcohol-OH group (which includes the exocyclic OH group of the pyranose and furanose molecules) since the –OH groups have been found to have different hydration characteristics [5,8]. The –O– groups in pyranose and furanose rings and glycosidic linkage are assumed to be equivalent. In addition, dioxane and 2-methoxyethanol are also chosen in order to evaluate the G_{HCl-O} value.

On the other hand, in order to calculate the number of a- and e-OH groups in sugar molecules, we recall the simplified assumption by Lemieux [20] that the number of quasi-equatorial OH groups in a molecule for α- and β-furanoses is regarded to be 1.25. On the basis of this and the percentage ratio of isomers in aqueous solutions [21], the n(e-OH) and n(a-OH) were calculated for the hydroxyl compounds concerned. The resulting values are given in Table 5. It is necessary to point out that the exocyclic OH groups were not regarded as e-OH or a-OH groups in this work. This is different from the approaches described in the literature [9] and in our previous paper [10] where the exocyclic OH groups in equatorial- and axial-groups (say CH_2OH) were regarded as e- and a-OH groups, respectively. At the same time, it was also assumed, as suggested by Wood [1], that $CH = 0.5CH_2$ and $CH_3 = 1.5CH_2$, while the tetrasubstituted carbons were not considered. These assumptions have been widely used in the literature. The number of the groups for some hydroxyl compounds are reported in Table 5.

By fitting the data in Table 5 to Eq. (8), the group interaction parameters were obtained with a standard deviation of the fit of 9 J kg mol^{-2}. These parameters are given in column 2 of Table 6 along with their standard deviations. For comparison, the calculated values of g_{HCl-N} from these group parameters are also given in column 8 of Table 5. It is evident that these calculated values are in agreement with the experimental values presented in column 7 of Table 5. The agreement was also seen from Fig. 1. Meanwhile, we fit only the data of eight alcohols to Eq. (8), the right side of which is reduced to two terms (G_{HCl-CH_2} and G_{HCl-OH}), the G_{HCl-CH_2} and G_{HCl-OH} values were obtained and are given in column 4 of Table 6. The results show that the values from the two fits are substantially identical. This further confirms that the approach can work well.

It can be seen from Table 6 that both the values of $G_{HCl-a\text{-}OH}$ and G_{HCl-O} are small and have large deviations, which are possibly because the interactions of a-OH and –O– with HCl are weaker than with other groups in these molecules. Thus, we neglected their contributions and fit all experimental data in Table 5 to Eq. (8), the right side of which, in this case, has only three terms (G_{HCl-CH_2}, G_{HCl-OH}, and $G_{HCl-e\text{-}OH}$). The results so obtained, listed in column 3 of Table 6, are quite in agreement with those listed in column 2 of Table 6 (obtained from the fit to five group interaction parameters); even the deviations of the parameters of the former are smaller. This seems to indicate that: (a) the two terms can be neglected in this case and (b) the contribution of e-OH groups is the leading part among all the groups on sugar molecules. This enabled us to understand the fact that there exists a linear relationship between some properties of sugars and $n(e\text{-OH})$, such as diffusion coefficients [9a], partial molar capacities [9b], and pair interaction Gibbs free-energy parameters of HCl with sugars [10]. On the other hand, the excellent consistency among the results from the three fits for the HCl–CH_2 and HCl–OH pairs seems to show that the characteristics of the alkyl (R) and OH (exo) groups on sugar molecules are similar to those on alcohol molecules when these groups interact with HCl in water.

The signs of G_{HCl-CH_2} and G_{HCl-OH} and their temperature dependence have been discussed in terms of the structure and electrostatic models [5,18,19]. The dehydration of CH_2 (which is a structure maker [22]) is the leading contribution of the interaction of the HCl–CH_2 (H^+–CH_2 and Cl^-–CH_2) pair. Thus, values of G_{HCl-CH_2} are positive. On the contrary, the interactions of the HCl–OH (H^+–OH and Cl^-–OH) pair are mainly electrostatic, in which the thermodynamic attraction of H^+ with OH is the leading part, thus contributing a negative value to g_{HCl-N}. The very small change in G_{HCl-OH} at the temperature range from 278.15 to 318.15 K has been observed previously [23d], whereas the values of G_{HCl-CH_2} vary rapidly with temperature. This confirms that the interaction of HCl–OH is mainly electrostatic since the electrostatic interactions are not sensitive to temperature.

Table 5
Experimental and calculated values of g_{HCl-N} for the HCl–hydroxyl compound–water systems at 298.15 K

Hydroxyl compound[a]	n_{CH_2}	n_{OH}	$n_{e\text{-OH}}$	$n_{a\text{-OH}}$	n_O	g_{HCl-N} (J kg mol^{-2})		δ[c]
						Expt	Calcd[b]	
Methanol	1.5	1	0	0	0	11[d]	14	−3
Ethanol	2.5	1	0	0	0	23[e]	26	−3
1-Propanol	3.5	1	0	0	0	34[d]	39	−5
2-Propanol	3.5	1	0	0	0	30[f]	39	−9
1,2-Propanediol	3	2	0	0	0	26[g]	27	−1
Glycerol	2.5	3	0	0	0	18[h]	15	3
1-Butanol	4.5	1	0	0	0	51[d]	52	−1
tert-Butanol	4.5	1	0	0	0	68[i]	52	16
2-Methoxyethanol	3.5	1	0	0	1	31[d]	38	−7
Dioxane	4	0	0	0	2	55[d]	50	5
D-Glucose	3.5	1	3.6	0.4	1	117[j]	105	12
D-Galactose	3.5	1	2.7	1.3	1	76[k]	91	−15
D-Arabinose	3	0	2.6	1.4	1	86[l]	89	−3
D-Xylose	3	0	3.7	0.3	1	105[m]	106	−1
D-Fructose	3.5	1.4	1.7	1.9	1	83[n]	72	11
Sucrose	7	3	4.2	0.8	3	146[o]	148	−2

[a] With an exception of dioxane, which was chosen to evaluate the HCl–O interaction parameter (see text).
[b] Calculated from the group parameters in column 2 of Table 6.
[c] $\delta = g_{HCl-N}$ (expt) $- g_{HCl-N}$ (calc).
[d] Evaluated from the $\Delta_t G_{HCl}{}^{\circ c}$ (based on the molarity scale) values in Ref. [26]: values of $\Delta_t G_{HCl}{}^{\circ c}$ were transformed into those of $\Delta_t G_{HCl}{}^{\circ w}$, and were then fitted to Eq. (1), the right side of which, in this case, has only two terms since the third term is zero.
[e] Ref. [23c].
[f] Ref. [18].
[g] Ref. [23a].
[h] Ref. [23b].
[i] Ref. [19].
[j] Ref. [5a].
[k] Ref. [27].
[l] This work.
[m] Ref. [10].
[n] Ref. [5b].
[o] Predicted from the experimental values for the glucose–HCl and sucrose–electrolyte pairs (see Ref. [28]).

Table 6
Pair group interaction Gibbs free-energy parameters derived from pair molecular interaction parameters for the HCl–hydroxyl compound–water systems at 298.15 K

	G_{HCl-i}/(J kg mol^{-2})		
HCl–*i*	1[a]	2[b]	3[c]
HCl–CH_2	13.0 ± 1.5	12.9 ± 1.2	12.6 ± 1.4
HCl–OH	-6.0 ± 2.9	-5.8 ± 2.7	-5.6 ± 3.2
HCl–*e*-OH	18.2 ± 2.3	18.6 ± 1.5	
HCl–*a*-OH	2.6 ± 4.9		
HCl–O	-1.0 ± 4.2		

[a] From the fit of all experimental data in Table 5. The standard deviation of the fit (σ) is 9 J kg mol^{-2}.

[b] From the fit of all experimental data in Table 5 but the contributions of the HCl–*a*-OH and HCl–O interactions were neglected. $\sigma = 8$ J kg mol^{-2}.

[c] From the fit of only data of alcohols in Table 5. $\sigma = 9$ J kg mol^{-2}.

trostatic interactions are not sensitive to temperature.

We now focus attention on the interaction of HCl with an *e*-OH group. A larger positive value of $G_{HCl-e\text{-}OH}$ seems to support the suggestion that an *e*-OH group is more favorable than an *a*-OH group on the formation of hydrogen bonding with water molecules in aqueous solution [24]. Based on the fact that pairs of alternate *e*-OH groups have distances corresponding to these of two OH groups in a tetrahedral arrangement of water molecules, Barone et al. [3a] concluded that these *e*-OH groups can promote the formation of labile cages of water molecules. Galema and coworkers [25] also came to a similar conclusion from a study of kinetic medium effects and volumetric properties of sugars. At the same time, they found that the presence of an *a*-OH group reduces this capability. If these suggestions are correct, then the interactions of HCl and *e*-OH should lead to a break, in part, of the hydrogen bonds of *e*-OH with water molecules. This is a possible reason why $G_{HCl-e\text{-}OH}$ has a large positive value.

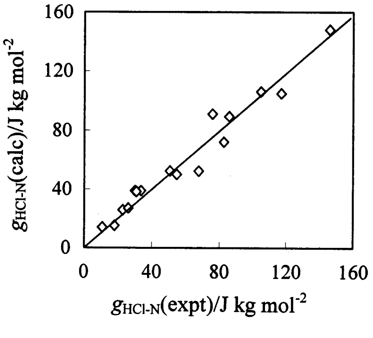

Fig. 1. Plot of g_{HCl-N} (expt) against g_{HCl-N} (calcd) for the HCl–hydroxyl compound–water systems at 298.15 K.

Finally, it should be mentioned that the percentages of each isomer of sugars depend both on the solvent (or mixture of solvents) and on the composition. However, the pair interaction parameters (say g_{EN}) are a measure of the change in the thermodynamic function as two molecules (ions) from infinite separation to some finite small distance. It is evident that the value of g_{HCl-S} depends both on the percentages of isomers of sugar in infinite dilute solution and on the hydration of HCl. The presence of HCl could lead to a change in the percentages of the isomers of sugars. In fact, the contribution of this change is a part of g_{HCl-S}.

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