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Carbohydrate Research 328 (2000) 383–391

CARBOHYDRATE RESEARCH

Volumetric properties for the monosaccharide (D-xylose, D-arabinose, D-glucose, D-galactose)–NaCl–water systems at 298.15 K

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Received 10 December 1999; accepted 27 March 2000

Abstract

Densities have been measured for monosaccharide (D-xylose, D-arabinose, D-glucose and D-galactose)–NaCl–water solutions at 298.15 K. These data have been used to determine the apparent molar volumes of these saccharides and NaCl in the studied solutions. Infinite-dilution apparent molar volumes for the saccharides ($V^0_{\Phi,S}$) in aqueous NaCl and those for NaCl ($V^0_{\Phi,E}$) in aqueous saccharide solutions have been evaluated, together with the standard transfer volumes of the saccharides ($\Delta_t V^0_S$) from water to aqueous NaCl and of NaCl ($\Delta_t V^0_E$) from water to aqueous saccharide solutions. It is shown that the $\Delta_t V^0_S$ and $\Delta_t V^0_E$ values are positive and increase with increasing co-solute molalities. Volumetric parameters indicating the interactions of NaCl with saccharides in water have been obtained, respectively, by using transfer volumes of the saccharides and NaCl, and the resulting values are in good agreement with each other within experimental error. The interactions between saccharides and NaCl are discussed in terms of the structural interaction model and the stereochemistry of the saccharide molecules in water.

Keywords: Density; Apparent molar volume; NaCl; Monosaccharide; Volumetric interaction parameter

1. Introduction

The interaction between saccharide (S) and electrolyte (E) in aqueous solution is of great importance in biochemistry and biophysics [1]. Morel and co-workers [1,2] have carried out a series of investigations on the association of cations (Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+}, and Ga^{3+}) and some saccharides with a specific stereochemical structure. However, in their studies anionic and univalent cationic contributions and non-specific (no complexing) interactions of di- and trivalent cations with saccharides are all eliminated since these interactions are much weaker than the complexing interactions.

In previous work [3], we investigated the interactions of some monosaccharides (D-xylose, D-arabinose, D-glucose, D-galactose, and D-fructose) with HCl in water by using a standard electrochemical method. The results showed that the Gibbs free-energy parameters (g_{ES}) for the interaction between HCl and saccharide correlate linearly with the mean number [n(e-OH)] of equatorial hydroxy groups in molecules [3c]. Furthermore, the group interaction parameters were also evaluated based on the Savage–Wood group addi-

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0008-6215/00/$ - see front matter
PII: S0008-6215(00)00102-6

tivity principle and the stereochemistry of the saccharide molecule [3d]. Very recently, the interactions between these monosaccharides (except for D-fructose) and NaCl have been studied by the ion-selective electrode (ISE) technique [4]. It was found that the NaCl–saccharide interactions are obviously weaker than HCl–saccharide and also depend upon the stereochemistry of the monosaccharide molecules in water. To better understand the interactions of electrolyte (ions) with saccharide, it was deemed necessary to carry out a systematic and extensive study using additional experimental methods. As a continuation of previous work, we report here the volumetric properties for monosaccharide–NaCl–water systems. This should provide additional information on the interactions between saccharide and electrolyte in water.

2. Experimental

D-Xylose and D-galactose (Biochem. R., Shanghai chem. Co.) were recrystallized from water–EtOH mixtures. D-arabinose, anhyd D-glucose (A.R., Shanghai Chem. Co.) and sodium chloride (G.R., Jiangsu Chem. Co.) were used without further purification. All reagents were dried under vacuum at 333 K to constant weight and stored over P_2O_5 in desiccators. Distilled deionized water was used with a specific conductivity of $1.0–1.2 \times 10^{-4}$ S m^{-1} at 298 K.

Solution densities were measured with a vibrating tube digital density meter (Model DMA 60/602, Anton Paar, Austria), which has been described elsewhere [5,6]. The temperature around the density meter cell was controlled by circulating water from a constant-temperature bath (Schott, Germany). A CT1450 temperature controller and CK-100 ultracryostat were employed to maintain the bath temperature to within ± 0.005 K. The density meter was calibrated with pure water and dry air. The error in density was estimated to be $\pm 3 \times 10^{-6}$ g cm^{-3}.

In order to obtain the apparent molar volumes of saccharides and electrolyte (NaCl) in ternary solutions simultaneously from a single set of density data, the following experimental procedure was designed. (i) The molality for all solutions were defined as the number of moles of a solute per kg of pure water. (ii) All test solutions with given molalities were prepared by accurate weighing. The errors in molality are within $\pm 0.03\%$ for saccharides and $\pm 0.01\%$ for NaCl. In addition, the densities of binary solutions were determined accurately since they are basic data in calculating apparent molar volumes of the electrolyte and saccharides in ternary solutions.

3. Results and discussion

Apparent molar volumes.—The density data measured are given in Table 1. The apparent molar volumes of saccharides $V_{\Phi,S}$ and electrolyte (NaCl) $V_{\Phi,E}$ were, respectively, calculated by using the following equations [7]:

$$V_{\Phi,S} = \frac{M_S}{d} - \frac{(1000 + m_E M_E)(d - d_E)}{m_S d d_E} \quad (1)$$

$$V_{\Phi,E} = \frac{M_E}{d} - \frac{(1000 + m_S M_S)(d - d_S)}{m_E d d_S} \quad (2)$$

where M_E and M_S are the molar masses of electrolyte and saccharide, m_E and m_S are the molalities of electrolyte and saccharide with respective to 1 kg of pure water, and d, d_S and d_E are densities of saccharide–NaCl–water, saccharide–water and electrolyte–water solutions, respectively. It should be pointed out that as $m_E = 0$ for Eq. (1) and $m_S = 0$ for Eq. (2), d is reduced to the density of binary solution, and both d_S and d_E are reduced to the density of pure water. Thus calculated $V_{\Phi,E}$ and $V_{\Phi,S}$ values are also included in Table 1. It has been found that both plots of $V_{\Phi,S}$ against m_S and $V_{\Phi,E}$ against $m_E^{1/2}$ are linear. Therefore, infinite-dilution apparent molar volumes $V^0_{\Phi,S}$ and $V^0_{\Phi,E}$, which equal in value to the standard partial molar volumes (V^0_S and V^0_E), are obtained by least-squares weighing fitting experimental data to the following equations [8,9]:

$$V_{\Phi,S} = V^0_{\Phi,S} + S^*_S m_S \quad (3)$$

$$V_{\Phi,E} = V^0_{\Phi,E} + S^*_E m_E^{1/2} \quad (4)$$

where S^*_S and S^*_E are the experimental slopes. Weighing factor of V_Φ used in the regression

Table 1
Densities and apparent molar volumes of some monosaccharides and NaCl in NaCl–water, monosaccharide–water and monosaccharide–NaCl–water systems at 298.15 K

m_E (mol kg^{-1})	d (g cm^3)	$V_{\Phi,S}$ (cm^3 mol^{-1})	$V_{\Phi,E}$ (cm^3 mol^{-1})	m_E (mol kg^{-1})	d (g cm^3)	$V_{\Phi,S}$ (cm^3 mol^{-1})	$V_{\Phi,E}$ (cm^3 mol^{-1})
D-Xylose							
$m_X = 0.20000$ mol kg^{-1}				$m_X = 0.8000$ mol kg^{-1}			
0	1.007718	95.88		0	1.037296	96.09	
0.15000	1.013679	96.02	17.58	0.15000	1.042770	96.25	18.25
0.30000	1.019527	96.13	17.86	0.30000	1.048102	96.45	18.65
0.50000	1.027209	96.18	18.10	0.50000	1.055218	96.54	18.70
0.75000	1.036599	96.36	18.41	0.75000	1.063839	96.77	19.01
1.00000	1.045820	96.49	18.64	1.00000	1.072342	96.95	19.21
$m_X = 0.4000$ mol kg^{-1}				$m_X = 1.0000$ mol kg^{-1}			
0	1.017969	95.95		0	1.046402	96.17	
0.15000	1.023742	96.15	17.94	0.15000	1.051711	96.34	18.58
0.30000	1.029447	96.23	18.07	0.30000	1.056872	96.56	19.00
0.50000	1.036919	96.34	18.30	0.50000	1.063800	96.67	18.99
0.75000	1.046077	96.48	18.56	0.75000	1.072229	96.86	19.21
1.00000	1.055075	96.57	18.77	1.00000	1.080505	97.04	19.40
$m_X = 0.6000$ mol kg^{-1}				$m_X = 1.2000$ mol kg^{-1}			
0	1.027817	96.02		0	1.055195	96.22	
0.15000	1.033434	96.21	18.12	0.15000	1.060384	96.37	18.63
0.30000	1.038971	96.33	18.30	0.30000	1.065358	96.62	19.29
0.50000	1.046245	96.45	18.50	0.50000	1.072047	96.79	19.35
0.75000	1.055112	96.69	18.81	0.75000	1.080234	97.01	19.54
1.00000	1.063929	96.71	18.93	1.00000	1.088368	97.13	19.61
D-Arabinose							
$m_A = 0.20000$ mol kg^{-1}				$m_A = 0.8000$ mol kg^{-1}			
0	1.008224	93.31		0	1.039193	93.62	
0.15000	1.014171	93.53	17.69	0.15000	1.044628	93.84	18.56
0.30000	1.019992	93.79	18.01	0.30000	1.050005	93.99	18.66
0.50000	1.027654	93.94	18.24	0.50000	1.057034	94.20	18.90
0.75000	1.036997	94.38	18.56	0.75000	1.065528	94.61	19.33
1.00000	1.046183	94.68	18.79	1.00000	1.073940	94.90	19.54
$m_A = 0.4000$ mol kg^{-1}				$m_A = 1.0000$ mol kg^{-1}			
0	1.018967	93.40		0	1.048732	93.72	
0.15000	1.024729	93.64	18.03	0.15000	1.054037	93.91	18.65
0.30000	1.030398	93.81	18.25	0.30000	1.059267	94.06	18.81
0.50000	1.037828	94.04	18.50	0.50000	1.066069	94.31	19.15
0.75000	1.046876	94.46	18.85	0.75000	1.074364	94.65	19.51
1.00000	1.055783	94.79	19.08	1.00000	1.082515	94.97	19.76
$m_A = 0.6000$ mol kg^{-1}				$m_A = 1.2000$ mol kg^{-1}			
0	1.029266	93.54		0	1.057929	93.81	
0.15000	1.034876	93.74	18.20	0.15000	1.063116	93.97	18.69
0.30000	1.040385	93.91	18.44	0.30000	1.068182	94.14	19.02
0.50000	1.047616	94.12	18.68	0.50000	1.074842	94.34	19.27
0.75000	1.056397	94.51	19.06	0.75000	1.082850	94.72	19.74
1.00000	1.065051	94.82	19.29	1.00000	1.090797	95.01	19.96
D-Glucose							
$m_{GL} = 0.20000$ mol kg^{-1}				$m_{GL} = 0.8000$ mol kg^{-1}			
0	1.010386	112.10		0	1.046847	112.46	
0.15000	1.016304	112.33	17.70	0.15000	1.052175	112.69	18.65
0.30000	1.022110	112.53	17.97	0.30000	1.057396	112.69	18.92
0.50000	1.029699	112.87	18.29	0.50000	1.064309	113.12	19.05
0.75000	1.039022	113.19	18.57	0.75000	1.072694	113.48	19.37
1.00000	1.048140	113.62	18.82	1.00000	1.080934	113.81	19.60

Table 1 (*Continued*)

m_E (mol kg^{-1})	d (g cm^3)	$V_{\Phi,S}$ (cm^3 mol^{-1})	$V_{\Phi,E}$ (cm^3 mol^{-1})	m_E (mol kg^{-1})	d (g cm^3)	$V_{\Phi,S}$ (cm^3 mol^{-1})	$V_{\Phi,E}$ (cm^3 mol^{-1})
$m_{GL} = 0.4000$ mol kg^{-1}				$m_{GL} = 1.0000$ mol kg^{-1}			
0	1.023108	112.22		0	1.057940	112.56	
0.15000	1.028799	112.51	18.16	0.15000	1.063097	112.79	18.90
0.30000	1.034433	112.65	18.26	0.30000	1.068149	113.01	19.17
0.50000	1.041755	112.97	18.59	0.50000	1.074797	113.26	19.38
0.75000	1.050758	113.30	18.85	0.75000	1.082976	113.54	19.58
1.00000	1.059563	113.68	19.10	1.00000	1.090974	113.84	19.79
$m_{GL} = 0.6000$ mol kg^{-1}				$m_{GL} = 1.2000$ mol kg^{-1}			
0	1.035259	112.32		0	1.068547	112.68	
0.15000	1.040772	112.56	18.35	0.15000	1.073544	112.89	19.12
0.30000	1.046176	112.80	18.63	0.30000	1.078460	113.08	19.32
0.50000	1.053281	113.05	18.86	0.50000	1.084904	113.33	19.55
0.75000	1.061926	113.47	19.20	0.75000	1.092799	113.63	19.80
1.00000	1.070499	113.72	19.36	1.00000	1.100549	113.92	20.01
D-Galactose							
$m_{GA} = 0.20000$ mol kg^{-1}				$m_{GA} = 0.8000$ mol kg^{-1}			
0	1.010672	110.65		0	1.047996	110.96	
0.15000	1.016612	110.78	17.56	0.15000	1.053315	111.21	18.73
0.30000	1.022405	111.04	17.95	0.30000	1.058557	111.41	18.90
0.50000	1.030032	111.20	18.20	0.50000	1.065502	111.58	18.98
0.75000	1.039289	111.85	18.60	0.75000	1.073814	112.04	19.43
1.00000	1.048452	112.07	18.80	1.00000	1.082045	112.38	19.66
$m_{GA} = 0.4000$ mol kg^{-1}				$m_{GA} = 1.0000$ mol kg^{-1}			
0	1.023676	110.77		0	1.059363	111.07	
0.15000	1.029420	110.93	17.81	0.15000	1.064491	111.33	19.12
0.30000	1.035004	111.19	18.26	0.30000	1.069570	111.52	19.20
0.50000	1.042412	111.31	18.42	0.50000	1.076309	111.68	19.22
0.75000	1.051316	111.89	18.88	0.75000	1.084329	112.13	19.70
1.00000	1.060157	112.19	19.09	1.00000	1.092301	112.46	19.91
$m_{GA} = 0.6000$ mol kg^{-1}				$m_{GA} = 1.2000$ mol kg^{-1}			
0	1.036118	110.85		0	1.070222	111.19	
0.15000	1.041656	11.05	18.20	0.15000	1.075205	111.42	19.24
0.30000	1.047043	111.31	18.62	0.30000	1.080098	111.64	19.47
0.50000	1.054151	111.57	18.85	0.50000	1.086595	111.84	19.54
0.75000	1.062816	111.96	19.17	0.75000	1.094435	112.19	19.88
1.00000	1.071349	112.28	19.38	1.00000	1.102115	112.54	20.14
NaCl–water							
0	0.997047			0.50000	1.017063		17.98
0.15000	1.003178		17.39	0.75000	1.026716		18.28
0.30000	1.009188		17.69	1.00000	1.036183		18.52

analysis is $(\delta V_\Phi)^{-2}$, where $\delta V_\Phi = -(M + 1000/m)\ \delta d/d^2$, δd is uncertainty of the solution density and is taken as a constant [8,9], M is the molar mass of solute, and m is the molality, respectively. The infinite-dilution apparent molar volumes thus obtained for the systems studied are given in Tables 2 and 3, respectively. Recent literature data [10] for D-xylose, D-arabinose, D-glucose, and D-galactose in water are also represented in Table 2. It is evident that these values are in good agreement (within experimental error) with those obtained in this work. In order to compare the standard partial molar volume of NaCl in water with the literature values, we also fitted the data on the NaCl–water system to the equation [11]:

$$V_{\Phi,E} = V^0_{\Phi,E} + 1.868 c_E^{1/2} + b_V c_E \quad (5)$$

where 1.868 is the theoretic slope, b_V the empirical constant, and c_E the molarity evaluated by

$$c_E = m_E d_E/(1 + 10^{-3} m_E M_E) \quad (6)$$

The resulting value is also given in Table 3. Obviously, agreement is quite good among these two values obtained from Eqs. (4) and (5) and that reported in the literature [11]. To the best of our knowledge, the standard partial molar volumes of these monosaccharides in aqueous NaCl and those of NaCl in the aqueous saccharide solutions are reported for the first time.

Volume of transfer.—Using values of $V^0_{\Phi,S}$ and $V^0_{\Phi,E}$ in Tables 2 and 3, standard transfer volumes for NaCl, $\Delta_t V^0_E$, from water to saccharide–water solutions and those for saccharides, $\Delta_t V^0_S$, from water to NaCl–water solutions were, respectively, calculated. It was shown that $\Delta_t V^0_S$ and $\Delta_t V^0_E$ increase with increasing molalities of NaCl and saccharides, respectively. These features can be interpreted in terms of the hydration model.

The standard partial molar volume, V^0_i, of an ion in solution can be broken down into the following terms [12a]:

$$V^0_i = V_i + V_c + V_r + V_e \quad (7)$$

Table 2
Infinite-dilution apparent molar volumes ($V^0_{\Phi,S}$/cm^3 mol^{-1}) of the monosaccharides in aqueous NaCl solutions and slopes (S^*_S/cm^3 kg mol^{-2}) of Eq. (3) at 298.15 K [a]

Saccharide	m_E (mol kg^{-1})					
	0	0.15000	0.30000	0.50000	0.75000	1.00000
Xylose	95.82 ± 0.01 (0.34 ± 0.01) 95.4 ± 0.3 [b] [10b] 96.45 ± 03 [10c] 95.60 [10d] 95.68 ± 0.09 [10e]	96.02 ± 0.03 (0.30 ± 0.04)	96.05 ± 0.02 (0.48 ± 0.02)	96.09 ± 0.02 (0.58 ± 0.02)	96.29 ± 0.04 (0.59 ± 0.05)	96.37 ± 0.05 (0.65 ± 0.06)
Arabinose	93.23 ± 0.02 (0.49 ± 0.02) 93.7 ± 0.3 [b] 94.2 ± 0.02 [10c] 93.2 [1][10b] 94.0 [10d] 93.43 ± 0.05 [10e]	93.50 ± 0.03 (0.40 ± 0.04)	93.68 ± 0.02 (0.39 ± 0.02)	93.89 ± 0.02 (0.39 ± 0.03)	94.32 ± 0.01 (0.33 ± 0.02)	94.65 ± 0.02 (0.31 ± 0.02)
Glucose	111.99 ± 0.01 (0.57 ± 0.01) 112.0 ± 0.1 [b] 111.79 [10f] 112.7 ± 0.1 [10c] 111.7 [10b] 111.3 [10g] 112.3 [10h] 111.99 [10i][10j] 111.91 ± 0.09 [10e]	112.27 ± 0.03 (0.52 ± 0.05)	112.49 ± 0.04 (0.50 ± 0.05)	112.77 ± 0.02 (0.47 ± 0.02)	113.20 ± 0.05 (0.35 ± 0.07)	113.56 ± 0.01 (0.30 ± 0.02)
Galactose	110.52 ± 0.02 (0.56 ± 0.02) 110.5 ± 0.3 [b] 111.1 ± 0.2 [10c] 110.2 [10b] 110.64 [10d] 110.29 ± 0.04 [10b]	110.70 ± 0.03 (0.62 ± 0.03)	110.97 ± 0.02 (0.56 ± 0.02)	111.13 ± 0.06 (0.58 ± 0.07)	111.74 ± 0.02 (0.38 ± 0.02)	112.02 ± 0.02 (0.44 ± 0.02)

[a] Values of S^*_S are represented in parentheses. Data are evaluated from Eq. (3).
[b] The best values suggested by Golberg and Tewari [10a].

Table 3
Infinite-dilution apparent molar volumes ($V^0_{\Phi,E}$/cm^3 mol^{-1}) of NaCl in aqueous monosaccharides solutions and slopes (S^*_E/cm^3 kg mol^{-2}) of Eq. (4) at 298.15 K [a]

Saccharide	m_S (mol kg^{-1})						
	0	0.20000	0.4000	0.6000	0.8000	1.00000	1.2000
Xylose	16.69 ± 0.01 (1.83 ± 0.01) 16.67 ± 0.01 [b] 16.62 [c]	16.87 ± 0.03 (1.77 ± 0.04)	17.23 ± 0.10 (1.53 ± 0.13)	17.56 ± 0.06 (1.39 ± 0.09)	17.71 ± 0.12 (1.49 ± 0.17)	18.19 ± 0.16 (1.19 ± 0.21)	18.70 ± 0.38 (0.92 ± 0.52)
Arabinose		16.98 ± 0.04 (1.81 ± 0.05)	17.22 ± 0.09 (1.85 ± 0.12)	$17.38 \pm 0.08)$ $(1.91 \pm 0.11$	17.60 ± 0.19 (1.95 ± 0.20)	17.74 ± 0.11 (2.03 ± 0.17)	17.81 ± 0.09 (2.17 ± 0.12)
Glucose		16.97 ± 0.02 (1.85 ± 0.03)	17.33 ± 0.13 (1.77 ± 0.18)	17.74 ± 0.05 (1.63 ± 0.07)	17.93 ± 0.11 (1.67 ± 0.15)	18.38 ± 0.04 (1.41 ± 0.05)	18.48 ± 0.04 (1.52 ± 0.06)
Galactose		16.86 ± 0.08 (1.95 ± 0.11)	17.07 ± 0.12 (2.03 ± 0.16)	17.62 ± 0.10 (1.77 ± 0.13)	17.77 ± 0.25 (1.88 ± 0.33)	18.10 ± 0.33 (1.81 ± 0.45)	18.40 ± 0.20 (1.71 ± 0.27)

[a] Values of S^*_E are represented in parentheses. Data are evaluated from Eq. (4).
[b] From Eq. (5). $b_V = 0.002$ cm^3 dm^3 mol^{-2}.
[c] Ref. [11].

where V_i is the intrinsic volume, V_c the cavity volume, V_r the solvent–structure reaction volume, and V_e the electrostriction volume. The sum of the final three terms can be regarded as the apparent electrostriction volume, ΔV_e [12], viz.:

$$\Delta V_e = V^0_i - V_i \quad (8)$$

The ΔV_e has a large negative value [12]. As the molality of saccharide increases, the partial dehydration of Na^+ and Cl^- will take place compared with that in water. Since the saccharide molecules have less polarity and larger volume than water, their electrostriction effect by the ions is weaker than that of water. Consequently, the ΔV_e value will become less negative with increasing molality of saccharides. This is possibly the reason for the fact that $\Delta_t V^0_E$ increases with increasing molalities of saccharides.

The V^0_S is the sum of the intrinsic volume and the volume contribution due to saccharide–solvent interactions (solvation) [13]

$$V^0_S = V_i + V_{solv} \quad (9)$$

The hydration shells of saccharide molecules decrease with increasing NaCl molality since both Na^+ and Cl^- are strongly hydrated. Due to electrostatic attraction with Na^+, the hydration of OH, C=O, and –O– groups on saccharide molecules are dominant in aqueous NaCl solutions and contribute a positive value to V^0_S. This leads to a positive and increasing $\Delta_t V^0_S$ with increase of NaCl molality. We have also noted that Cabani et al. [14] evaluated a value of hydration volume ΔV_{hydr} (OH) of -0.67 cm^3 mol^{-1} for the OH group using group additivity analysis based on various experimental data of alcohol, saccharide, etc. Although the dehydration of OH groups on saccharide molecules is different from those on alcohol molecules arising from the effect of stereochemistry, an average of ΔV_{hydr} (OH) values for saccharides should be negative. A detailed discussion for the interaction of NaCl with the saccharides will be given in the next section.

Volumetric interaction parameters.—The transfer volume $\Delta_t V_{\Phi,S}$ of a saccharide at molality m_S from water to a solution of electrolyte at molality m_E can be expressed as [7,15]

$$\Delta_t V_{\Phi,S} = V_{\Phi,S}(m_S,m_E) - V_{\Phi,S}(m_S) = 2\upsilon v_{ES} m_E + 3\upsilon^2 v_{EES} m_E^2 + 3\upsilon v_{ESS} m_E m_S + \ldots \quad (10)$$

where υ is the number of ions into which the electrolyte dissociates, v_{ES}, v_{EES} and v_{ESS} are pair and triplet interaction parameters. Simi-

larly, by considering the transfer of the electrolyte from water to the saccharide solutions, one has

$$\Delta_t V_{\Phi,E} = V_{\Phi,E}(m_E,m_S) - V_{\Phi,S}(m_E) = 2\upsilon v_{ES} m_S + 3\upsilon^2 v_{EES} m_S m_E + 3\upsilon v_{ESS} m_S^2 + \ldots \quad (11)$$

For the standard molar volume, i.e., $m_S \to 0$ for Eq. (10) and $m_E \to 0$ for Eq. (11), it immediately follows that

$$\left(\frac{\partial \Delta t V_S^0}{\partial m_E}\right)_{mE=0} = \left(\frac{\partial \Delta t V_E^0}{\partial m_S}\right)_{mS=0} = 2\upsilon v_{ES} \quad (12)$$

The pair volumetric interaction parameter v_{ES}, which indicates the E–S interaction at infinite dilution and is of theoretical importance, is then readily measurable from each of the standard transfer volumes. The interaction parameters are least-squares obtained from Eqs. (10) and (11), respectively. As an example, the resulting parameters from these two equations for the xylose–NaCl–water system are represented in Table 4. It is evident that agreement is very good between values of the volumetric interaction parameters evaluated from different equations, particularly for pair-interaction parameters, within experimental error. This further verified the relations (Eqs. (10)–(12)) experimentally. Therefore, the average volumes for each parameter obtained from the two equations are taken as experimental values.

When $m_S \to 0$ and $m_E \to 0$, Eqs. (10) and (11) can be, respectively, written as

$$\Delta_t V^0_{\Phi,S}/m_E = 2\upsilon v_{ES} + 3\upsilon^2 v_{EES} m_E + \ldots \quad (13)$$

$$\Delta_t V^0_{\Phi,E}/m_S = 2\upsilon v_{ES} + 3\upsilon v_{ESS} m_S + \ldots \quad (14)$$

Obviously, the plots of $\Delta_t V_{\Phi,S}$ versus m_E and $\Delta_t V_{\Phi,E}$ versus m_S enable the interaction parameters to be obtained. However, we prefer to determine these parameters by Eqs. (10) and (11) because smaller errors should be involved in the derivation of these parameters from these equations.

On the basis of the group additivity model [16], the pair interactions between electrolyte and saccharide can be divided into four types: cation–R (alkyl group), anion–R, cation–O (OH, C=O, and –O–), and anion–O. The intrinsic volumes of ions and groups can be considered to be independent on their interactions. Accordingly, the v_{ES} value arises mainly from the change in hydration shells of these ions and groups (structural interaction).

The models indicating structural interactions have been proposed and used by some authors, such as Friedman and Krishnan [17], Desnoyers et al. [18], and Franks et al. [19]. According to these models, only the cation–O interaction gives a positive contribution, whereas the other three types of interactions have negative contributions to v_{ES}. Evidently, the signs of v_{ES} (NaCl–S) are controlled by the Na^+–O interactions.

Both xylose and arabinose are pentoses; thus, the difference in their v_{ES} values should arise from their stereochemistry. Their dominant conformations in water are 1e2e3e4e and 1e2e3e4a, respectively. Based on the conclu-

Table 4
Volumetric interaction parameters for NaCl–saccharide–water systems at 298.15 K [a]

Saccharide	$2\upsilon v_{ES}$ ($cm^3\ mol^{-2}\ kg$)	$3\upsilon v_{ESS}$ ($cm^3\ mol^{-3}\ kg^2$)	$3\upsilon^2 v_{EES}$ ($cm^3\ mol^{-3}\ kg^2$)	σ [d] ($cm^3\ mol^{-1}$)
Xylose	0.920 ± 0.068	0.333 ± 0.056	-0.380 ± 0.052	0.07
	0.862 ± 0.047 [b]	0.379 ± 0.031 [b]	-0.370 ± 0.048 [b]	0.04 [b]
	0.977 ± 0.088 [c]	0.278 ± 0.081 [c]	-0.389 ± 0.065 [c]	0.09 [c]
Arabinose	1.422 ± 0.052	-0.257 ± 0.043	0.067 ± 0.045	0.05
Glucose	1.748 ± 0.041	-0.261 ± 0.029	-0.193 ± 0.040	0.04
Galactose	1.437 ± 0.095	-0.021 ± 0.077	-0.047 ± 0.083	0.09

[a] Average of values from Eqs. (10) and (11).
[b] From Eq. [10].
[c] From Eq. [11].
[d] Standard deviation of the fit.

sions drawn by Galema et al. [20] and Barone et al. [21], the former fits into the structure of water better than the latter. The dehydration of the latter [OH(4a)] contributes a more positive value to v_{ES} than the former [OH(4e)]. Consequently, the more positive v_{ES} value for NaCl–arabinose pair than for NaCl–xylose pair can be understood easily. Based on this idea, the differences in g_{ES} between these saccharides have been interpreted successfully [3,4]. Unfortunately, the difference in v_{ES} between D-galactose (dominant conformation is 1e2e3e4a) and D-glucose (1e2e3e4e) is contrary with this suggestion. At the present time, we cannot formulate a satisfactory explanation for this phenomenon. To examine whether similar a feature exists for other electrolytes and saccharides and to model the saccharide–electrolyte interactions, further work is underway.

4. Conclusions

Based on a careful experimental design, the density data for monosaccharide (D-xylose, D-arabinose, D-glucose and D-galactose)–NaCl–water systems, combined with data for the related binary systems, have been employed to calculate infinite-dilution apparent molar volumes of the monosaccharides and NaCl. This enables us to obtain some information on the solvation of both electrolyte (ions) in aqueous monosaccharide and saccharide in aqueous NaCl solutions.

Volumetric interaction parameters for monosaccharide–NaCl have been evaluated by using transfer volumes of the monosaccharides and those of NaCl. Values thus obtained are in good agreement with each other. Theoretic relations presented by Eqs. (10)(12) are further verified experimentally.

It seems that the differences in volumetric interaction parameters for the monosaccharide–NaCl–water systems cannot be well interpreted in terms of the stereochemistry of the saccharides. In this regard, it is necessary to carry our more work both experimentally and theoretically.

Acknowledgements

Financial support from the National Natural Science Foundation of China (Grant 29573102) and the Science Foundation of Henan Province is gratefully acknowledged.

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