

Activity Coefficients and Volumetric Properties for the NaI + Maltose + Water System at 298.15 K

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Activity coefficients for the NaI + maltose + water system at 298.15 K were determined by an electrochemical method. The Gibbs energy interaction parameter (g_{ES}) and salting constant (k_s) have also been calculated. Infinite dilution apparent molar volumes for maltose ($V_{\Phi,S}$) in aqueous NaI solution and those for NaI ($V_{\Phi,E}$) in aqueous maltose solution have been determined from density measurements as well as volumetric interaction parameters. The results are discussed in terms of the structural interaction model and the structural properties of anions.

Introduction

Interactions of electrolytes with saccharides are very important not only in exploration of the stability of polysaccharides in biological systems but also in the chemical industry of saccharides and the treatment of waste containing saccharides. The interactions between saccharides and electrolytes have been studied by solubility measurements,¹ spectroscopy (NMR,² FT-IR³), a gas–liquid equilibrium method,⁴ and ion selective electrodes (ISEs).^{5–7}

Maltose (4-*O*- α -D-glucopyranosyl- α -D-glucopyranoside) is a reducing disaccharide consisting of two glucose units linked by a glycosidic bond. It is a natural cell-protecting agent, as well as an energy reservoir in many organisms. This disaccharide is an essential component for maintaining cell viability. Iodine is a trace element necessary for the synthesis and metabolism of thyroid hormones.⁸ Therefore, information on the interactions between NaI and maltose can improve the understanding of ion interactions with maltose residues of biologically important compounds.

In our laboratory, thermodynamic properties for some electrolyte + saccharide + water systems have been studied.^{9,10} As a continuation, we report in this paper activity coefficients and volumetric properties for the NaI + maltose + water system at 298.15 K. The interactions between NaI and maltose in water are discussed.

Experimental Section

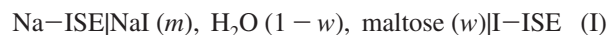
Chemicals. D-(+)-Maltose (BR, Fluka Chem. Co.) was dried under a vacuum to constant weight. Deionized water was redistilled in the presence of KMnO_4 . Using this method, pure water with a conductivity of $(1.0 \cdot 10^{-4} \text{ to } 1.2 \cdot 10^{-4}) \text{ S} \cdot \text{m}^{-1}$ at $T = 298.15 \text{ K}$ was obtained and used throughout this work.

NaI (AR, mass fraction purity > 99 %, Shanghai Chem. Co.) was recrystallized from ethanol and then dried under vacuum at $T = 343 \text{ K}$ to constant weight. All reagents were stored over P_2O_5 in desiccators. All solutions were prepared by weight.

Measurements of Cell Potentials. A sodium glass electrode (Na-ISE, Orion 8611BN) and an iodine ion selective electrode (I-ISE, Jiangsu Electroanalytical Instrument Co. model 303)

were used. Cell potentials were measured with a PH/ISE meter (Orion 920A+, with a resolution of 0.1 mV). In all measurements, the temperature of the sample solution was controlled at $T = (298.15 \pm 0.02) \text{ K}$.

The following electrochemical cells were set up to measure cell potentials for the ternary system⁶



where m and m_r are the molalities of NaI ($\text{mol} \cdot \text{kg}^{-1}$) in the working and reference solutions, defined as the number of moles of solutes per kilogram of the mixed solvent, and w is the mass fraction of maltose in the mixed solvent.

It should be recalled that the apparent standard cell potential (E^{0*}) includes the asymmetry potential of the electrode as $E^{0*} = E^0 + E^{\text{asym}} = E^0 + (\epsilon_{\text{Na}}^{\text{asym}} + \epsilon_{\text{I}}^{\text{asym}})$. Since E^{asym} tends to be a small and independent value for the composition of the solvent, we may suppose^{6,7} that $E_S^{0*} - E_W^{0*} \cong E_S^0 - E_W^0$. Therefore, the difference in cell potential between cells (I) and (II) can be written as $\Delta E = E(\text{II}) - E(\text{I})$ to eliminate the total asymmetry.

Measurement of Densities. Solution densities were measured with a vibrating digital densimeter (model DMA 60/602, Anton Paar, Austria). The temperature around the sample cells 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 within $\pm 0.005 \text{ K}$.

Each experiment series was carried out at a fixed maltose concentration. The mass fraction of maltose ranged from 0.05 to 0.25. The concentration of NaI was increased by the addition of solid NaI, ranging from about $(0.01 \text{ to } 0.20) \text{ mol} \cdot \text{kg}^{-1}$ for measurements of cell potentials. The concentration of NaI ranged from $(0.15 \text{ to } 1.00) \text{ mol} \cdot \text{kg}^{-1}$ for measurements of densities.

Results and Discussion

Activity Coefficients. According to Nernst–Nikolsky, the cell potential for 1:1 electrolytes can be expressed as⁵

$$E = E^{0*} + 2S \ln m_r \quad (1)$$

where E^{0*} is the apparent standard cell potential, which depends on the activity of the ions in the internal reference solution and

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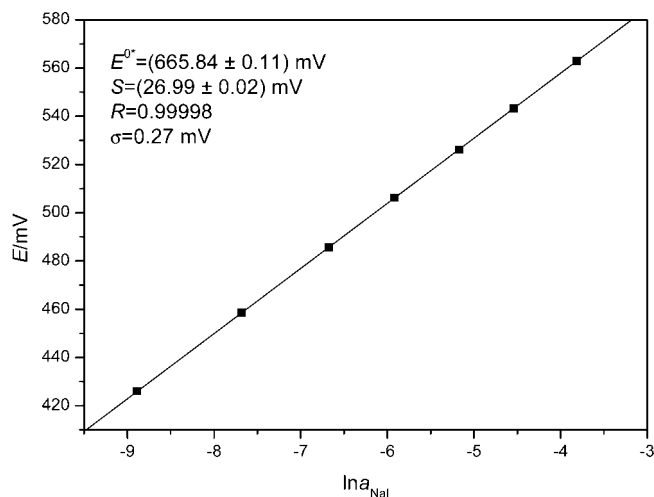


Figure 1. Calibration of the Na-ISE versus I-ISE in an aqueous solution of NaI at 298.15 K.

the types of the two ISEs; the constant S is the slope of the electrode response (assuming $S \approx S_{\text{Na}} \approx S_{\text{I}} \approx (S_{\text{Na}} + S_{\text{I}})/2$); and γ is the mean ionic activity coefficient of the electrolyte (NaI).

Then, the difference in cell potential between cells (I) and (II) can be represented by

$$\Delta E = E(\text{II}) - E(\text{I}) = 2S \ln \frac{m_{\text{r}} \gamma_{\text{r}}}{m \gamma} \quad (2)$$

The activity coefficients of NaI in pure water were calculated by the empirical equation recommended by Hamer and Wu.¹¹ The experimental procedure has been elaborated in a previous work.¹² A very good linear relationship was obtained when E was plotted versus $2 \ln m \gamma$ using eq 1. The slope (S) obtained from least-squares analysis is 26.99 mV (theoretical value $RT/F = 25.69$ mV at 298.15 K), with a correlation coefficient of 0.99998. The calibration of the Na-ISE toward the I-ISE as a reference electrode is shown in Figure 1.

The γ_{r} and γ values for NaI in the maltose + water mixtures can be calculated from the Debye-Hückel extended equation which can be written as¹³

$$\log \gamma = -\frac{A|Z_+Z_-|\sqrt{I}}{1 + Ba\sqrt{I}} - \log(1 + 0.001vmM_S) + CI \quad (3)$$

where I is the ionic strength; a is the ion size parameter; C is the ion interaction parameter; v is the number of ions into which the electrolyte dissociates; M_S is the average molar mass of mixed solvent; and A and B are the Debye-Hückel constants, which are given by

$$A = 1.8247 \cdot 10^6 d^{1/2} / (\epsilon_r T)^{3/2} \text{ mol}^{-1/2} \cdot \text{dm}^{3/2} \cdot \text{K}^{3/2} \quad (4)$$

$$B = 50.2901 \cdot d^{1/2} / (\epsilon_r T)^{1/2} \text{ \AA}^{-1} \cdot \text{mol}^{-1/2} \cdot \text{dm}^{3/2} \cdot \text{K}^{1/2} \quad (5)$$

where d , ϵ_r , and T represent density, relative permittivity of the mixed solvent, and the thermodynamic temperature, respectively. Values of density and relative permittivity of the maltose + water mixtures were taken from the literature^{14,15} and are listed in Table 1.

Using eqs 2 and 3, values of γ_{r} , a , and C were obtained by least-squares analysis. These values with their standard deviations are listed in Table 2, as well as the standard deviation of the fit.

Table 1. Average Molar Mass, Relative Permittivity, Debye-Hückel, and Pitzer Parameters for the Different Maltose + Water Mixtures at 298.15 K

w	M_S	ϵ_r^a	d^b	A	B	A_Φ
0	18.015	78.38	0.997047	0.5100	0.3285	0.3915
0.05	18.911	76.66	1.016777	0.5325	0.3354	0.4087
0.10	19.900	74.77	1.037258	0.5583	0.3430	0.4286
0.15	20.999	73.52	1.058396	0.5784	0.3495	0.4440
0.20	22.226	72.80	1.080390	0.5931	0.3548	0.4553
0.25	23.606	71.11	1.103064	0.6208	0.3627	0.4765

^a Ref 14. ^b Ref 15.

Table 2. Parameters of the Debye-Hückel Equation in the Different Maltose + Water Mixtures at 298.15 K

w	γ_{r}	a Å	C kg·mol ⁻¹	σ mV
0	0.8146 ± 0.0016	4.13 ± 0.48	0.108 ± 0.029	0.1
0.05	0.8056 ± 0.0023	4.51 ± 0.63	0.079 ± 0.038	0.1
0.10	0.7957 ± 0.0018	3.39 ± 0.48	0.154 ± 0.037	0.1
0.15	0.7900 ± 0.0033	3.17 ± 0.86	0.187 ± 0.073	0.2
0.20	0.7739 ± 0.0012	4.69 ± 0.30	-0.061 ± 0.019	0.1
0.25	0.7649 ± 0.0009	3.61 ± 0.22	0.041 ± 0.018	0.1

Activity coefficients of NaI in maltose + water mixed solvents can also be evaluated from the Pitzer equation. For 1:1 electrolytes, the equation can be written as¹⁶

$$\ln \gamma = f_\gamma + B_\gamma m + C_\gamma m^2 \quad (6)$$

where

$$f_\gamma = -A_\Phi x \quad (7)$$

$$B_\gamma = 2\beta^0 + 2\beta^1 y \quad (8)$$

$$x = m^{1/2} / (1 + bm^{1/2}) + (2/b) \ln(1 + bm^{1/2}) \quad (9)$$

$$y = [1 - \exp(-\alpha m^{1/2})(1 + \alpha m^{1/2} - 0.5\alpha^2 m)] / (\alpha^2 m) \quad (10)$$

In the equations above, α and b are empirical parameters with values of 2.0 and 1.2, respectively.¹⁶ β^0 , β^1 , and C_γ are solute specific interaction parameters, and A_Φ is the Debye-Hückel constant for the osmotic coefficients defined by

$$A_\Phi = 1.4006 \cdot 10^6 d^{1/2} / (\epsilon_r T)^{3/2} \text{ mol}^{-1/2} \cdot \text{dm}^{3/2} \cdot \text{K}^{3/2} \quad (11)$$

In eq 6, the first term represents long-range electrostatic interactions, the second term short-range hard-core effects, and the third term interactions of three ions.

By combining eqs 2 and 6, we can get values of γ_{r} , β^0 , β^1 , and C_γ by least-squares analysis. Then parameters obtained are summarized in Table 3. Because the molality is not more than 0.2 mol·kg⁻¹, the fits with $C_\gamma = 0$ were also made. The results show that the parameter C_γ does not cause a notable improvement of the standard deviations of the fit. Thus, obtained parameters are also given in Table 3. It can be seen from Tables 2 and 3 that the γ_{r} values calculated using the two theories for each of the mixed solvents are in good agreement with each other. Activity coefficients and standard cell potentials (E^{0*}) of NaI in the mixed solvents were obtained from eqs 1 and 2 and summarized in Table 4.

In this work, an anion-ISE was used as a reference electrode, and a cation-ISE was used as a working electrode. Therefore, the standard Gibbs energy of transfer for an electrolyte from water to saccharide + water systems can be written as

$$\Delta_i G_{\text{E}}^{0m(\text{M})} = nF(E_{\text{S}}^0 - E_{\text{W}}^0) \quad (12)$$

where F is the Faraday constant, and E_{S}^0 and E_{W}^0 are the standard cell potentials of the electrolyte in saccharide + water and in pure water, respectively.

Table 3. Parameters of the Pitzer Equation for NaI in the Different Maltose + Water Mixtures at 298.15 K

w	γ_{r}	β^0 kg·mol ⁻¹	β^1 kg·mol ⁻¹	C_{γ} kg ² ·mol ⁻²	σ mV
0	0.8151 ± 0.0032	0.053 ± 0.398	0.403 ± 0.593	0.272 ± 1.208	0.1
	0.8145 ± 0.0015	0.142 ± 0.038	0.271 ± 0.081	--	0.1
0.05	0.8081 ± 0.0039	-0.352 ± 0.502	1.040 ± 0.746	1.402 ± 1.522	0.1
	0.8051 ± 0.0021	0.107 ± 0.055	0.362 ± 0.118	--	0.1
0.10	0.7958 ± 0.0037	0.179 ± 0.461	0.217 ± 0.691	0.067 ± 1.383	0.1
	0.7957 ± 0.0017	0.202 ± 0.044	0.184 ± 0.194	--	0.1
0.15	0.7903 ± 0.0069	0.179 ± 0.881	0.249 ± 1.314	0.188 ± 2.654	0.2
	0.7921 ± 0.0008	0.162 ± 0.020	0.335 ± 0.044	--	0.1
0.20	0.7719 ± 0.0021	0.139 ± 0.270	0.195 ± 0.403	-0.626 ± 0.814	0.1
	0.7733 ± 0.0010	-0.067 ± 0.028	0.501 ± 0.060	--	0.1
0.25	0.7651 ± 0.0019	0.006 ± 0.253	0.393 ± 0.378	0.194 ± 0.764	0.1
	0.7647 ± 0.0009	0.070 ± 0.024	0.297 ± 0.052	--	0.1

Table 4. Experimental Cell Potentials (E) and Ionic Mean Activity Coefficients (γ) for NaI in Different Mixed Solvents of Maltose + Water at 298.15 K

$w = 0$			$w = 0.05$			$w = 0.10$			$w = 0.15$			$w = 0.20$			$w = 0.25$		
$E^{0*} = 665.8$ mV			$E^{0*} = 668.7$ mV			$E^{0*} = 671.6$ mV			$E^{0*} = 674.9$ mV			$E^{0*} = 680.7$ mV			$E^{0*} = 684.5$ mV		
m^a	E^b	γ	m^a	E^b	γ	m	E	γ	m	E	γ	m	E	γ	m	E	γ
0.01316	426.0	0.8930	0.01175	422.7	0.8923	0.01358	432.7	0.8807	0.01312	434.0	0.8783	0.01349	440.9	0.8724	0.01332	443.7	0.8674
0.02488	458.5	0.8624	0.02471	461.0	0.8626	0.02606	465.7	0.8457	0.02600	468.7	0.8429	0.02493	471.9	0.8383	0.02451	474.3	0.8310
0.04250	485.6	0.8341	0.04301	488.8	0.8294	0.04321	491.1	0.8165	0.04238	493.2	0.8142	0.04387	500.0	0.8018	0.04212	501.1	0.7944
0.06373 ^c	506.2	0.8147	0.06493 ^c	509.5	0.8062	0.06399 ^c	510.9	0.7957	0.06450 ^c	514.3	0.7908	0.06363 ^c	518.1	0.7730	0.06443 ^c	522.0	0.7649
0.09519	526.2	0.7901	0.09454	528.3	0.7844	0.09643	531.1	0.7677	0.09360	532.8	0.7677	0.09297	536.6	0.7453	0.09474	540.6	0.7342
0.1335	543.2	0.7719	0.1337	545.6	0.7642	0.1337	547.5	0.7502	0.1326	550.2	0.7480	0.1338	554.0	0.7149	0.1337	557.1	0.7062
0.1974	563.0	0.7533	0.2002	565.9	0.7433	0.2010	568.0	0.7296	0.1999	570.8	0.7267	0.2003	572.9	0.6777	0.1997	576.3	0.6748

^a m in moles of NaI per kilogram of mixed solvents (kg·mol⁻¹). ^b E in mV. ^c Reference molality.

Table 5. Gibbs Energy Interaction Parameters (g_{ES}) and Salting Constants (k_{S}) for the Electrolyte + Maltose + Water Systems at 298.15 K

electrolyte	$2vg_{\text{ES}}$ J·kg·mol ⁻²	k_{S} kg·mol ⁻¹
NaCl	613 ^a	0.247
NaBr	277 ^b	0.112
NaI	43	0.017

^a Ref 20. ^b Ref 21.

According to the McMillan–Mayer theory, the transfer Gibbs energy of an electrolyte from water to aqueous saccharide solutions can be expressed as¹⁷

$$\Delta_{\text{t}}G_{\text{E}}^{0m(\text{W})}(\text{W} \rightarrow \text{W} + \text{S}) = \mu^0(m_{\text{E}}, m_{\text{S}}) - \mu^0(m_{\text{E}}) = 2vg_{\text{ES}}m_{\text{S}} + 3vg_{\text{ESS}}m_{\text{S}}^2 + \dots \quad (13)$$

where g_{ES} and g_{ESS} are pair and triple Gibbs energy interaction parameters, respectively. $\mu^0(m_{\text{E}}, m_{\text{S}})$ and $\mu^0(m_{\text{E}})$ are the standard chemical potentials of the electrolyte in the saccharide + water system and pure water, respectively.

To evaluate the Gibbs energy interaction parameters, the standard transfer Gibbs energies of NaI ($\Delta_{\text{t}}G_{\text{E}}^{0m(\text{M})}$) on the m_{E}^{M} scale (in moles per kilogram of the mixed solvent) were first converted into those ($\Delta_{\text{t}}G_{\text{E}}^{0m(\text{W})}$) on the m_{E}^{W} scale (in moles per kilogram of pure water) through the use of the expression¹⁸

$$\Delta_{\text{t}}G_{\text{E}}^{0m(\text{W})} = \Delta_{\text{t}}G_{\text{E}}^{0m(\text{M})} - vRT \ln(1 + 0.001m_{\text{S}}M_{\text{S}}) \quad (14)$$

Thus, the g_{ES} values obtained from eq 13 are given in Table 5. According to Desnoyer,¹⁹ the relation of the salting constant (k_{S}) and pair Gibbs energy interaction parameter (g_{ES}) is:

$$RTk_{\text{S}} = 2vg_{\text{ES}} \quad (15)$$

The k_{S} values calculated from eq 15 are also included in Table 5, together with the values for other electrolytes reported in the literature.^{20,21}

As can be seen from the data in Table 5, the k_{S} and g_{ES} values decrease from Cl⁻ to I⁻. The values of k_{S} are positive, indicating that maltose is salted out by NaX (X stands for Cl, Br, and I) in water. This is possibly because the interactions between X⁻ and hydroxyl groups are stronger than those between Na⁺ and hydroxyl groups in maltose. The order of k_{S} and g_{ES} for electrolyte + maltose + water systems may be interpreted by the dispersive energy between maltose molecules and anions. The equation of dispersive energy between an ion and a molecule is expressed as²²

$$u_{\text{dispersive}} = \frac{-3\alpha_1\alpha_2h\nu_{01}\nu_{02}}{2(\nu_{01} + \nu_{02})r^6} \quad (16)$$

where r is the distance between the ion and the molecule; h is Planck's constant; α_1 is the polarizability of ions; ν_{01} is the eigenfrequency of ions in the perturbation state; and α_2 and ν_{02} have the same meanings for molecules as α_1 and ν_{01} do for ions.

From Cl⁻ to I⁻, the ionic radius and polarizability increase, and the dispersive energy becomes more negative. Therefore, the k_{S} and g_{ES} values are in this order: NaCl > NaBr > NaI. This shows that the dispersive energy between maltose molecules and anions determines the values of k_{S} . As shown in Figure 2, there is a good linear relation between k_{S} and $1/r^6$. This is consistent with the relation between u and $1/r^6$ (eq 16).

Apparent Molar Volumes. The measured density data are listed in Table 6. Apparent molar volumes of maltose ($V_{\Phi,\text{S}}$) and NaI ($V_{\Phi,\text{E}}$) were calculated, respectively, using the following equations²³

$$V_{\Phi,\text{S}} = \frac{M_{\text{S}}}{d} - \frac{(1000 + m_{\text{E}}M_{\text{E}})(d - d_{\text{E}})}{m_{\text{S}}dd_{\text{E}}} \quad (17)$$

$$V_{\Phi,\text{E}} = \frac{M_{\text{E}}}{d} - \frac{(1000 + m_{\text{S}}M_{\text{S}})(d - d_{\text{S}})}{m_{\text{E}}dd_{\text{S}}} \quad (18)$$

where M_{E} and M_{S} are the molar masses of NaI and maltose; m_{E} and m_{S} are the molalities of NaI and maltose per kilogram

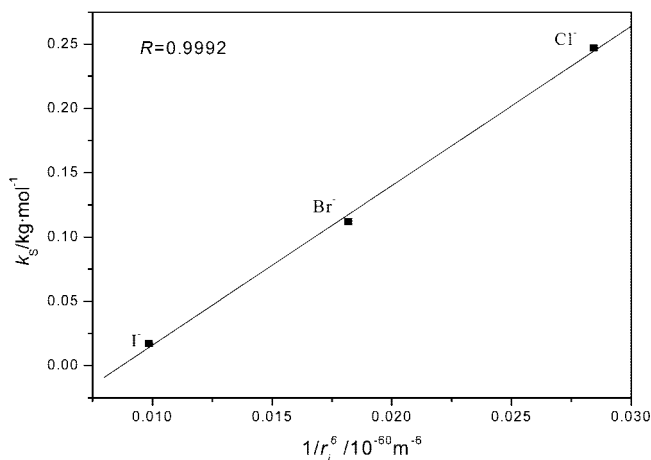


Figure 2. Plot of salting constants (k_s) versus reciprocal of the sixth power of the anion radius for the NaX + maltose + water systems.

Table 6. Densities and Apparent Molar Volumes of Maltose and NaI in the NaI + Water, Maltose + Water, and NaI + Maltose + Water Systems at 298.15 K

m_E $\text{mol} \cdot \text{kg}^{-1}$	d $\text{g} \cdot \text{cm}^{-3}$	$V_{\Phi,S}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	V_S $\text{cm}^3 \cdot \text{mol}^{-1}$	$V_{\Phi,E}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	V_E $\text{cm}^3 \cdot \text{mol}^{-1}$
$w = 0.05$					
0.0000	1.016777	210.08	210.25	--	35.64
0.1500	1.033092	210.49	210.49	36.10	36.09
0.3000	1.049173	210.88	210.76	36.31	36.36
0.5000	1.070302	211.21	211.09	36.50	36.63
0.7500	1.096243	211.65	211.54	36.67	36.90
1.0000	1.121646	212.25	211.10	36.84	37.13
$w = 0.10$					
0.0000	1.037258	210.22	210.78	--	35.90
0.1500	1.052884	210.65	211.02	36.39	36.63
0.3000	1.068298	211.00	211.28	36.57	36.93
0.5000	1.088541	211.44	211.59	36.77	37.23
0.7500	1.113389	211.86	212.03	36.97	37.52
1.0000	1.137722	212.29	211.50	37.16	37.77
$w = 0.15$					
0.0000	1.058434	210.57	211.37	--	36.31
0.1500	1.073337	211.04	211.62	36.76	36.97
0.3000	1.088046	211.32	211.86	36.93	37.24
0.5000	1.107386	211.72	212.16	37.09	37.51
0.7500	1.131116	212.14	212.56	37.29	37.78
1.0000	1.154387	212.50	211.94	37.46	38.01
$w = 0.20$					
0.0000	1.080438	210.82	212.03	--	36.67
0.1500	1.094605	211.19	212.29	37.11	37.33
0.3000	1.108584	211.50	212.51	37.30	37.61
0.5000	1.126969	211.91	212.79	37.47	37.88
0.7500	1.149568	212.32	213.17	37.63	38.15
1.0000	1.171686	212.76	212.43	37.83	38.38
$w = 0.25$					
0.0000	1.103065	211.33	212.79	--	37.09
0.1500	1.116471	211.66	213.05	37.50	37.68
0.3000	1.129711	211.94	213.25	37.65	37.93
0.5000	1.147136	212.36	213.50	37.79	38.17
0.7500	1.168534	212.71	213.86	37.98	38.42
1.0000	1.189561	213.13	212.99	38.12	38.62
$w = 0.30$					
0.0000	1.126587	211.73	213.65	--	37.45
0.1500	1.139223	211.99	213.92	37.83	38.02
0.3000	1.151702	212.27	214.10	37.99	38.26
0.5000	1.168125	212.61	214.32	38.14	38.49
0.7500	1.188325	213.01	214.64	38.30	38.72
1.0000	1.208181	213.37	213.63	38.43	38.92

of pure water; and d , d_S , and d_E are densities of maltose + NaI + water, maltose + water, and NaI + water solutions, respectively. These obtained values are also included in Table

6. $V_{\Phi,S}$ and $V_{\Phi,E}$ are found to be linear functions of m_S and $m_E^{1/2}$ for each solute studied, respectively. Therefore, infinite dilution apparent molar volumes ($V_{\Phi,S}^0$ and $V_{\Phi,E}^0$), which are equal to the standard partial molar volumes (V_S^0 and V_E^0) were obtained from least-squares analysis using the following equations^{24,25}

$$V_{\Phi,S} = V_{\Phi,S}^0 + S_S^* m_S \quad (19)$$

$$V_{\Phi,E} = V_{\Phi,E}^0 + S_E^* m_E^{1/2} \quad (20)$$

where S_S^* and S_E^* are the experimental slopes. The weighing factor of V_{Φ} used in the regression analysis is $(\delta V_{\Phi})^{-2}$, where $\delta V_{\Phi} = -(M + 1000/m)\delta d/\delta d^2$; δd is the uncertainty of the solution density and is taken as a constant;^{24,25} M is the molar mass of solute; and m is the molality. The infinite dilution apparent molar volumes for the systems studied are given in Tables 7 and 8. In addition, the $V_{\Phi,E}^0$ values were also obtained by fitting the equation²⁷

$$V_{\Phi,E} = V_{\Phi,E}^0 + 1.868 c_E^{1/2} + b_V c_E \quad (21)$$

where 1.868 is the theoretical slope; b_V is the empirical constant; and c_E is the molarity ($\text{mol} \cdot \text{dm}^{-3}$) evaluated by

$$c_E = m_E d_E / (1 + 10^{-3} m_E M_E) \quad (22)$$

Thus, values obtained of $V_{\Phi,E}^0$ (NaI) are also given in Table 8. Obviously, the agreement is good among the two values of $V_{\Phi,E}^0$ (NaI) from eqs 20 and 21 and the one reported in the literature.²⁸

Partial molar volumes of maltose (V_S) and NaI (V_E) at each composition were calculated, respectively, by

$$V_S = \left[\frac{\partial (V_{\Phi,S} m_S)}{\partial m_S} \right]_{T,P} = V_S^0 + 2 S_S^* m_S \quad (23)$$

$$V_E = \left[\frac{\partial (V_{\Phi,E} m_E)}{\partial m_E} \right]_{T,P} = V_E^0 + 1.5 S_E^* m_E^{1/2} \quad (24)$$

and are also given in Table 6. Their standard deviations, $\sigma(V_S)$ and $\sigma(V_E)$, can be evaluated from the equations

$$\sigma(V_S) = [\sigma(V_{\Phi,S}^0)^2 + \{2 m_S \sigma(S_S^*)\}^2]^{1/2} \quad (25)$$

$$\sigma(V_E) = [\sigma(V_{\Phi,E}^0)^2 + \{1.5 m_E \sigma(S_E^*)\}^2]^{1/2} \quad (26)$$

In most cases, $\sigma(V_S)$ and $\sigma(V_E) < 0.15 \text{ cm}^3 \cdot \text{mol}^{-1}$.

Volumetric properties of ternary electrolyte–nonelectrolyte–water systems can be expressed as^{23,29}

$$\Delta_t V_{\Phi,S} = V_{\Phi,S}(m_S, m_E) - V_{\Phi,S}(m_S) = 2\nu_{ES} m_E + 3\nu_{EES}^2 m_E^2 + 3\nu_{ESS} m_E m_S + \dots \quad (27)$$

$$\Delta_t V_{\Phi,E} = V_{\Phi,E}(m_E, m_S) - V_{\Phi,E}(m_E) = 2\nu_{ES} m_S + 3\nu_{EES}^2 m_E m_S + 3\nu_{ESS} m_S^2 + \dots \quad (28)$$

where $\Delta_t V_{\Phi,S}$ and $\Delta_t V_{\Phi,E}$ are, respectively, the transfer volumes of a saccharide at molality m_S from water to a solution of electrolyte at molality m_E and of an electrolyte at molality m_E from water to a solution of saccharide at m_S . ν_{ES} , ν_{EES} , and ν_{ESS} indicate pair and triple volumetric interaction parameters between electrolytes and saccharides, respectively. These interaction parameters were respectively obtained from least-squares analysis by eqs 27 and 28, and they are in agreement with each other. Thus, their average values which can be considered as experimental values are listed in Table 9.

According to the structural hydration interaction model,³⁰ the interactions between NaX and maltose can be classified as follows: (1) cation–hydrophobic ($\text{Na}^+ - \text{R}$, R represents alkyl

Table 7. Infinite Dilution Apparent Molar Volumes ($V_{\Phi,S}^0$) of Maltose in Aqueous NaI Solutions and Slopes (S_S^*) of Equation 19 at 298.15 K

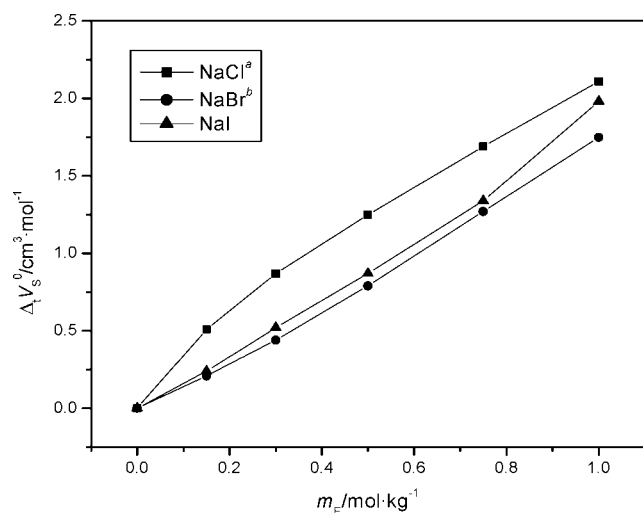
$m_E/\text{mol}\cdot\text{kg}^{-1}$	0	0.1500	0.3000	0.5000	0.7500	1.0000
$V_{\Phi,S}^0/\text{cm}^3\cdot\text{mol}^{-1}$	209.77 ± 0.05 210.07 ^a	210.01 ± 0.05	210.29 ± 0.06	210.64 ± 0.05	211.11 ± 0.05	211.75 ± 0.07
$S_S^*/\text{cm}^3\cdot\text{kg}\cdot\text{mol}^{-2}$	1.55 ± 0.07	1.56 ± 0.06	1.52 ± 0.08	1.47 ± 0.07	1.41 ± 0.06	1.15 ± 0.09

^a Ref 26.**Table 8. Infinite Dilution Apparent Molar Volumes ($V_{\Phi,S}^0$) of NaI in Aqueous Maltose Solutions and Slopes (S_S^*) of Equation 20 at 298.15 K**

w	0	0.05	0.10	0.15	0.20	0.25
$V_{\Phi,E}^0/\text{cm}^3\cdot\text{mol}^{-1}$	35.43 ± 0.01 35.07 ± 0.05 ^a 35.14 ^b	35.64 ± 0.02	35.90 ± 0.02	36.31 ± 0.03	36.67 ± 0.03	37.09 ± 0.02
$S_S^*/\text{cm}^3\cdot\text{kg}\cdot\text{mol}^{-2}$	1.13 ± 0.01	1.20 ± 0.03	1.25 ± 0.03	1.13 ± 0.04	1.14 ± 0.04	1.02 ± 0.03

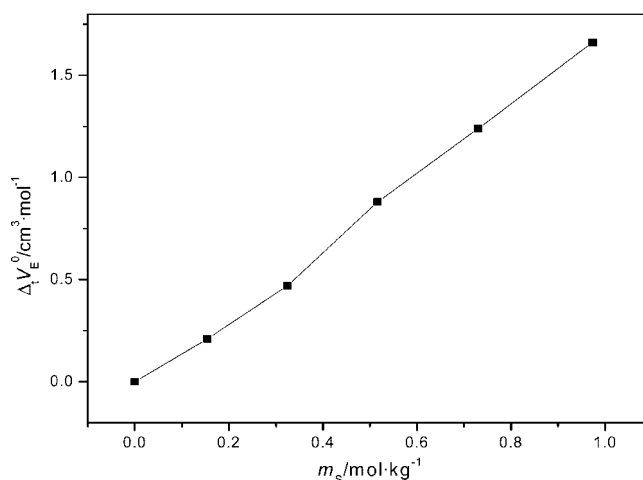
^a Obtained from eq 21. ^b Ref 28.**Table 9. Volumetric Interaction Parameters and Their Standard Deviations for Electrolyte + Maltose + Water Systems at 298.15 K**

	$2vv_{ES}$ $\text{cm}^3\cdot\text{mol}^{-2}\cdot\text{kg}$	$3vv_{ESS}$ $\text{cm}^3\cdot\text{mol}^{-3}\cdot\text{kg}^2$	$3v^2v_{EES}$ $\text{cm}^3\cdot\text{mol}^{-3}\cdot\text{kg}^2$	σ $\text{cm}^3\cdot\text{mol}^{-1}$
NaCl ^a	2.764 ± 0.062	−0.523 ± 0.046	−0.494 ± 0.058	0.06
NaBr ^b	1.770 ± 0.053	−0.286 ± 0.039	0.078 ± 0.050	0.05
NaI	1.815 ± 0.035	−0.257 ± 0.026	0.042 ± 0.033	0.04

^a Ref 32. ^b Ref 21.**Figure 3.** Variation of standard transfer molar volumes ($\Delta_t V_{\Phi,S}^0$) of maltose from water to aqueous electrolyte solutions with the molalities of electrolytes at 298.15 K. ^a Ref 32. ^b Ref 21.

groups); (2) anion–hydrophobic (X^- –R); (3) cation–hydrophilic (Na^+ –O, O represents OH, C=O, and –O– groups); and (4) anion and hydrophilic (X^- –O). Types (1), (2), and (4) contribute negative values to volume, whereas type (3) contributes a positive value to volume. It has been concluded that type (3) is predominant.²⁸ In addition, the increase in concentration of NaX (maltose) makes type (3) interactions stronger, so the $\Delta_t V_{\Phi,S}^0$ ($\Delta_t V_{\Phi,E}^0$) values are positive and increase just as can be seen from Figures 3 and 4.

For a given saccharide, the ν_{ES} values should be in the order $NaCl > NaBr > NaI$ in electrolyte + saccharide + water systems.³¹ In addition, it was observed in our previous work that the values of ν_{ES} are in the order $\nu_{NaCl-S} > \nu_{NaBr-S} > \nu_{NaI-S}$ for the NaX + glucose + water systems.^{29,31,33} But as represented in Figure 3, the $\Delta_t V_{\Phi,S}^0$ values for maltose are in this order: $NaCl > NaI > NaBr$ for the NaX + maltose + water systems. Similarly, the ν_{NaBr-S} value is smaller than the ν_{NaCl-S} and ν_{NaI-S} values for maltose, indicating that ν_{ES} and $\Delta_t V_{\Phi,S}^0$ are not dependent on the volumes of anions. Why are the ν_{ES}

**Figure 4.** Variation of standard transfer molar volumes ($\Delta_t V_{\Phi,S}^0$) of NaI from water to aqueous maltose solution with the molalities of maltose at 298.15 K.

values for NaX with maltose in this order? One possible reason is that there are several conformers of maltose in different electrolyte solutions,³⁴ and the interactions between anions and different conformers of maltose are different. Another possible reason is that there are two linkage torsion angles in maltose molecules.³⁵ Br^- can approach to the linkage torsion angles, and Br^- is smaller than I^- so that the linkage torsion angles (considered as cavity volumes) near the ring are available to accommodate Br^- (a large negative contribution to volume) according to Conway.³⁶ It can be observed that the ν_{ESS} values for the NaX + maltose + water systems are negative and increase from Cl^- to I^- .

Literature Cited

- (1) Chatterjee, J. P.; Basumallick, I. N. Thermodynamics of transfer of electrolytes and ions from water to aqueous solutions of polyhydroxy compounds. *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 3107–3110.
- (2) Symons, M. C. R.; Benvow, J. A.; Pelmore, H. J. Interactions between calcium ions and a range of monosaccharides studied by hydroxy-proton resonance spectroscopy. *J. Chem. Soc. Faraday Trans.1* **1984**, *80*, 1999–2016.
- (3) Tian, W.; Yang, L. M.; Xu, Y. Z.; Weng, S. F.; Wu, J. G. Sugar interaction with metal ions. FT-IR study on the structure of crystalline galactaric acid and its K^+ , NH_4^+ , Ca^{2+} , Ba^{2+} , and La^{3+} complexes. *Carbohydr. Res.* **2000**, *324*, 45–52.
- (4) Shalae, E. Y.; Franks, F. Equilibrium phase diagram of the water–sucrose–NaCl system. *Thermochim. Acta* **1995**, *255*, 49–61.
- (5) Hernández-Luis, F.; Amado-Gonzalez, E.; Estes, M. A. Activity coefficients of NaCl in trehalose–water and maltose–water mixtures at 298.15 K. *Carbohydr. Res.* **2003**, *338*, 1415–1424.
- (6) Hernández-Luis, F.; Grandoso, D.; Lemus, M. Activity coefficients of NaCl in fructose + water at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 668–674.

- (7) Hernández-Luis, F.; Galleguillos, H. R.; Vazquez, M. V. Activity coefficients of NaF in (glucose + water) and (sucrose + water) mixtures at 298.15 K. *J. Chem. Thermodyn.* **2004**, *36*, 957–964.
- (8) Maier, J.; van Steeg, H.; van Oostrom, C.; Paschke, R.; Weiss, R. E.; Krohn, K. Iodine deficiency activates antioxidant genes and causes DNA damage in the thyroid gland of rats and mice. *Biochim. Biophys. Acta* **2007**, *1773*, 990–999.
- (9) Wang, J. J.; Liu, W. B.; Bai, T. C.; Lu, J. S. Standard Gibbs energies of transfer of some electrolytes from water to aqueous sucrose solutions at 298.15 K. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 1741–1744.
- (10) Zhuo, K. L.; Wang, Y. P.; Liu, Q.; Zhang, H. H.; Wang, J. J. Thermodynamic and conductivity properties of $\text{Cd}(\text{NO}_3)_2$ in monosaccharide (D-glucose, D-galactose, D-xylose, D-ribose). *J. Solution Chem.* **2006**, *35*, 753–768.
- (11) Hamer, W.; Wu, Y. Osmotic coefficients and mean activity coefficients of uni-univalent electrolytes in water at 25 °C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047–1068.
- (12) Zhuo, K. L.; Wang, J. J.; Wang, H. Q. Activity coefficients for NaCl–monosaccharide (D-glucose, D-galactose, D-xylose, D-arabinose)–water Systems at 298.15 K. *Carbohydr. Res.* **2000**, *325*, 46–55.
- (13) Wang, J. J.; Liu, W. B.; Fan, J.; Lu, J. S. Mean activity coefficients of NaCl in glucose–water and Sucrose–water mixtures at 298.15 K. *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 3281–3285.
- (14) Eya, H.; Mishima, K.; Nagatani, M.; Arai, Y. Measurement and correlation of solubilities of oxygen in aqueous solutions containing glucose, sucrose and maltose. *Fluid Phase Equilib.* **1994**, *97*, 201–209.
- (15) Matsouka, T.; Okada, T.; Murai, K. Dynamics and hydration of trehalose and maltose in concentrated solutions. *J. Mol. Liq.* **2002**, *98–99*, 317–327.
- (16) Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **1973**, *77*, 268–277.
- (17) Wang, J. J.; Zhuo, K. L.; Zhang, Q. F.; Yan, Z. N.; Wang, H. Q. Thermodynamics of the Interaction of HCl with D-galactose in water at 278.15–318.15 K. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3359–3363.
- (18) Zhuo, K. L. Thermodynamic pair interaction parameters on various concentration scales. *J. Phys. Chem. B* **2005**, *109*, 7460–7462.
- (19) Perron, G.; Joly, D.; Desnoyers, J. E.; Avedikian, L.; Morel, J. P. Thermodynamics of salting effect-free-energies, enthalpies, entropies, heat-capacities, and volumes of ternary-systems electrolyte–alcohol–water at 25-degrees C. *Can. J. Chem.* **1978**, *56*, 552–559.
- (20) Conway, B. E.; Novak, D. M. *Chemistry and Physics of Aqueous Gas Solution*; Adams, W. A., Eds.; The Electrochemistry Society: Princeton, NJ, 1975; p 115.
- (21) Zhuo, K. L.; Zhang, H. H.; Wang, Y. P.; Liu, Q.; Wang, J. J. Activity coefficients and volumetric properties for NaBr and maltose in water at 298.15 K. *J. Chem. Eng. Data* **2005**, *50*, 1589–1595.
- (22) Zhuo, K. L. Studies on thermodynamics of the interaction between electrolyte and saccharide in water. Ph.D. Thesis, Ph.D. Lanzhou Institute of Chemical Physics, The Chinese Academy of Sciences, 2000; pp 40–62.
- (23) Visser, C. D.; Perron, G.; Desnoyers, J. E. Volumes and heat capacities of ternary aqueous systems at 25°C. Mixtures of urea, tert-butyl alcohol, dimethylformamide, and water. *J. Am. Chem. Soc.* **1977**, *99*, 5894–5900.
- (24) Hedwig, G. R. Thermodynamics properties of peptide solutions. 3. Partial molar volumes and partial molar heat-capacities of some tripeptides in aqueous-solution. *J. Solution Chem.* **1988**, *17*, 383–397.
- (25) Zielenkiewicz, W.; Perlovich, G. L.; Nikitina, G. E.; Semeykin, A. S. Volumetric properties of tetraphenylporphine, their metallocomplexes and some substituted tetraphenylporphines in benzene solution. *J. Solution Chem.* **1996**, *25*, 135–153.
- (26) Banipal, P. K.; Banipal, T. S.; Lark, B. S.; Ahluwalia, J. C. Partial molar heat capacities and volumes of some mono-, di- and trisaccharides in water at 298.15, 308.15 and 318.15 K. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 81–87.
- (27) Millero, F. J. Molar volumes of electrolytes. *Chem. Rev.* **1971**, *71*, 147–176.
- (28) Harder, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed.; Reinhold: NY, 1958; pp 397.
- (29) Zhuo, K. L.; Wang, J. J.; Wang, H. Q.; Yue, Y. K. Densities, apparent molar volumes, and interaction parameters for the monosaccharide (D-xylose, D-arabinose, D-glucose, D-galactose)–NaBr–water systems at 298.15 K. *Z. Phys. Chem.* **2001**, *215*, 561–573.
- (30) Desnoyers, J. E.; Arel, M.; Jolicour, G. Apparent molal volumes of alkali halides in water at 25 deg. Influence of structural hydration interactions on the concentration dependence. *J. Phys. Chem.* **1969**, *73*, 3346–3351.
- (31) Zhuo, K. L.; Wang, J. J.; Zheng, H. H.; Xuan, X. P.; Zhao, Y. Volumetric parameters of interaction of monosaccharides (D-xylose, D-arabinose, D-glucose, D-galactose) with NaI in water at 298.15 K. *J. Solution Chem.* **2005**, *34*, 155–170.
- (32) Zhang, H. H. Activity coefficient and volumetric properties for electrolyte–disaccharide–water systems. MS. Thesis, Henan Normal University, 2005; pp 26–45.
- (33) Zhuo, K. L.; Wang, J. J.; Yue, Y. K.; Wang, H. Q. Volumetric properties for the monosaccharide (D-xylose, D-arabinose, D-glucose, D-galactose)–NaCl–water systems at 298.15 K. *Carbohydr. Res.* **2000**, *328*, 383–391.
- (34) Cesaro, A. In *thermodynamic data for biochemistry and biotechnology*; Franks, Ed.; Springer: Berlin, 1986; Vol. 2.
- (35) French, A. D.; Kelterer, A. M.; Johnson, G. P.; Dowd, M. K. B3LYP/6–31G, RHF/6–31G and MM3 heats of formation of disaccharide analogs. *J. Mol. Struct.* **2000**, *556*, 303–313.
- (36) Conway, B. E. *Ionic Hydration in Chemistry and Physics*; Elsevier: Amsterdam, The Netherlands, 1980.

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