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

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Activity coefficients and volumetric properties for the NaBr + maltose + water system were determined at 298.15 K by cell potential and density measurements, respectively. The activity coefficients were evaluated respectively from the cell potential data using the Debye−Hückel and the Pitzer equations, and they are in quite agreement with each other. Infinite-dilution apparent molar volumes for maltose ($V^0_{\Phi,S}$) in aqueous NaBr and those for NaBr ($V^0_{\Phi,E}$) in aqueous maltose were evaluated, respectively. Free energy and volumetric interaction parameters (g_{ES} and v_{ES}) were also obtained. These results were discussed in terms of the stereochemistry of saccharide molecules and the group additivity model.

Introduction

Saccharides and their derivatives play a very important role in various biological systems. In recent years, the hydration characteristics of saccharides[1−4] and their interactions with electrolytes and nonelectrolytes[5−7] in aqueous media have developed a great deal of interests, due to their significant importance in several fields such as biology, biochemistry, catalysis, and pharmaceutical industry.

Maltose is a reducing disaccharide consisting of two glucose units linked by a glycosidic bond. It is widely used in the food industry. Recently, it has been realized that there are antigens (carbohydrates) on the surface of human red blood cell that determine the blood group of uniqueness. It has been already proved that disaccharides on the membrane can provide us some important information on the recognition and interactions between the cells. Therefore, it is very significant to study the interactions between electrolytes and maltose in water. However, the investigation in this field is seldom reported.[8]

Morel and co-workers[9,10] have carried out a series of investigations of the interaction between divalent and trivalent cations and some saccharides with a specific stereochemical structure. Recently, Hernandez-Luis et al.,[11,12] Jiang et al.,[13−15] and Banipal et al.[16,17] studied thermodynamic properties of some mono-, di-, and trisaccharides in aqueous electrolytic solutions by electrochemistry, microcalorimetry, and volumetry, respectively. In our previous work,[18−24] thermodynamic studies of some ternary electrolyte + saccharide + water systems have been carried out using galvanic cells and densimetry. As a continuation of this study, the activity coefficients and apparent molar volumes for the NaBr + maltose + water systems will be reported for a wide molality range at 298.15 K. Free energy and volumetric interaction parameters (g_{ES} and v_{ES}) will be also reported. The results will be discussed in terms of saccharide molecular stereochemistry and the group additivity model.

Experimental Section

Chemicals. D(+)-Maltose (BR, Fluka Chemical Co.) was dried under vacuum at 333 K to constant weight and stored over P_2O_5 in desiccators. Pure distilled deionized water was used with a specific conductivity of (1.0×10^{-4} to 1.2×10^{-4}) $S{\cdot}m^{-1}$ at 298.15 K.

NaBr (AR, >99.0 %, Shanghai Chemical Co.) was recrystallized from pure distilled deionized water and then dried under vacuum at 413 K to constant weight. It was also stored over P_2O_5 in desiccators.

Measurements of Activity Coefficients. A sodium-glass electrode (Orion 8611BN) and a bromide ion-selective electrode (Orion 9635BN) were used. A PH/ISE meter (Orion 920A) with a resolution of 0.1 mV was used to monitor the cell potential measurements, and details have been described elsewhere.[18,25] In all measurements, the temperature of the sample solution was controlled at (298.15 ± 0.02) K. To minimize the risk of the presence of concentration gradients in the cell, the solutions were continuously stirred with a magnetic stirrer.

The following cells were set up to measure cell potentials for the electrolyte + saccharide (non-electrolyte) + water systems:[11,25]

$$\text{Na−ISE} \mid \text{NaBr}\,(m),\ \text{H}_2\text{O}\,(1-w)\ \text{saccharide}\,(w), \mid \text{Br−ISE} \qquad \text{(I)}$$

$$\text{Na−ISE} \mid \text{NaBr}\,(m_r),\ \text{H}_2\text{O}\,(1-w)\ \text{saccharide}\,(w), \mid \text{Br−ISE} \qquad \text{(II)}$$

where m and m_r are respectively the molalities of NaBr in the working and reference solutions, defined as the number of moles of solutes per kilogram of the mixed solvent (saccharide + water), and w is the mass fraction of the species in the mixed solvent.

It should be recalled that the standard cell potential (E^{0*}) includes the asymmetry potential of the electrodes as

$$E^{0*} = E^0 + E^{\text{asym}} = E^0 + (\epsilon^{\text{asym}}_{\text{Na}} + \epsilon^{\text{asym}}_{\text{Cl}}) \qquad (1)$$

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Table 1. Experimental Cell Potentials (E) and Ionic Mean Activity Coefficients (γ) for NaBr in Different Mixed Solvents of Maltose + Water at 298.15 K

$w = 0$			$w = 0.1$			$w = 0.2$			$w = 0.3$			$w = 0.4$		
m^a	E^b	γ	m^a	E^b	γ	m^a	E^b	γ	m^a	E^b	γ	m^a	E^b	γ
0.02164	233.3	0.8695	0.01407	218.2	0.8822	0.02068	242.3	0.8463	0.02014	248.8	0.8432	0.01962	256.3	0.8375
0.03604	258.0	0.8413	0.03335	259.8	0.8312	0.04055	275.2	0.8149	0.04149	283.2	0.7954	0.03753	286.4	0.7831
0.05120	274.9	0.8208	0.05453	283.3	0.8004	0.06514	297.8	0.7849	0.06943	307.5	0.7601	0.0686	314.5	0.7372
0.08452	298.9	0.7905	0.07099	295.9	0.7842	0.08851	312.3	0.7644	0.1000	324.7	0.7357	0.09662	330.5	0.7129
0.1000	306.9	0.7797	0.09038	307.4	0.7692	0.1000	318.1	0.7568	0.1941	356	0.6938	0.1000	332.4	0.7146
0.1367	321.7	0.7592	0.1000	312.2	0.7627	0.2333	358.2	0.7038	0.3517	384.5	0.6640	0.1250	343.1	0.7029
0.2183^c	344.1	0.7327	0.1187	320.4	0.7529	0.3710^c	380.6	0.6821	0.5000^c	401.9	0.6536	0.2011	365.5	0.6734
0.3541	367.4	0.7085	0.1328^c	325.8	0.7469	0.5000	395.1	0.6698	0.7099	419.8	0.6505	0.3260^c	388.6	0.6491
0.5000	384.5	0.6981	0.2268	351.2	0.7143	0.6916	411.6	0.6660	0.9003	432.2	0.6517	0.5000	409.6	0.6349
0.6292	395.8	0.6901	0.3726	375.0	0.6886	0.9004	425.4	0.6678	1.2008	448.2	0.6656	0.7110	427.7	0.6333
0.9041	414.3	0.6866	0.5000	389.4	0.6777	1.2021	441.1	0.6774	1.5002	461.3	0.6862	0.9029	440.4	0.6374
1.4220	438.6	0.6980	0.5628	395.3	0.6747	1.5002	453.9	0.6950	1.8007	472.7	0.7125	1.1999	456.5	0.6545
2.1551	462.9	0.7364	0.9125	420.0	0.6706	1.8000	464.9	0.7164	2.1005	482.9	0.7438	1.5005	469.9	0.6780
			1.4126	443.9	0.6873	2.1003	474.8	0.7433				1.8004	481.7	0.7098
			2.1170	468.3	0.7347							2.0999	492.2	0.7454

[a] m in moles of NaBr per kilogram of mixed solvents (mol kg^{-1}). [b] E in mV. [c] Reference molality.

Since E^{asmy} tends to be a small and independent value for the composition of the solvent, we may suppose[11,12] that

$$E_S^0{}^* - E_W^0{}^* \cong E_S^0 - E_W^0 \tag{2}$$

Therefore, the difference in cell potentials (ΔE) between cells I and II can be expressed as $\Delta E \cong E_I - E_{II}$ to eliminate the total asymmetry potential.

The experimental procedure has been elaborated in previous work.[18−21] A typical slope (k) of the electrodes response obtained by a least-squares regression analysis is 25.88 mV, with a correlation coefficient of 0.99999. Activity coefficients of NaBr in aqueous solutions were calculated by the empirical equation recommended by Hamer and Wu,[26] which are in good excellent agreement with the theoretical value (25.69 mV at 298.15 K) of the Nernst equation.

Measurement of Densities. Solution densities were measured with a vibrating digital densimeter (model DMA 60/602, Anton Paar, Austria), which has been described elsewhere.[22−24] The temperature around the sample cells were controlled by circulating water from a constant-temperature bath (Schott, Germany). A CT1450 temperature controller and CK-100 ultra-cryostat were employed to maintain the bath temperature within ± 0.005 K. The molality in density measurements is defined as the number of moles of a solute per kilogram of pure water.

Results and Discussion

Activity Coefficients of NaBr in Maltose + Water Mixtures. According to Cammann,[27] the difference in cell potential (ΔE) between cells I and II in a given solvent can be expressed by

$$\Delta E = E_I - E_{II} = 2k \log \frac{m\gamma}{m_r \gamma_r} \tag{3}$$

To calculate the activity coefficients of NaBr, the Debye−Hückel extended equation can be written as[28]

$$\log \gamma = -\frac{A\sqrt{m}}{1 + Ba\sqrt{m}} + Cm - \log(1 + 0.001\nu m M_S) \tag{4}$$

Table 2. Values for the 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	0.7327 ± 0.0008	4.09 ± 0.05	0.07019 ± 0.00097	0.09
0.1	0.7467 ± 0.0009	3.93 ± 0.05	0.08256 ± 0.00117	0.10
0.2	0.6816 ± 0.0014	4.00 ± 0.07	0.09014 ± 0.00165	0.15
0.3	0.6535 ± 0.0009	3.95 ± 0.05	0.10307 ± 0.00111	0.10
0.4	0.6493 ± 0.0024	4.02 ± 0.11	0.11580 ± 0.00280	0.28

where a is the ion size parameter, C is the ion−interaction parameter, ν is the number of ions into which the electrolyte dissociates, and M_S is the average molecular mass of mixed solvent. A and B represent the Debye−Hückel constant given by

$$A = 1.8247 \times 10^6 d^{1/2}/(\epsilon_r T)^{3/2} \text{ mol}^{-1/2}\cdot\text{dm}^{3/2}\cdot\text{K}^{3/2} \tag{5}$$

$$B = 50.2901 \times d^{1/2}/(\epsilon_r T)^{1/2} \text{ Å}^{-1}\cdot\text{mol}^{-1/2}\cdot\text{dm}^{3/2}\cdot\text{K}^{1/2} \tag{6}$$

where d represents the density (g cm^{-3}), ϵ_r is the relative permittivity of the solvent, and T is the thermodynamic temperature. The density values of maltose + water mixtures were taken from Eya et al.[29] The relative permittivities for maltose + water mixtures were taken from Matsuoka et al.[30] These values collected by Hernandez-Luis et al.[12] were used by us to calculate activity coefficients of NaBr in aqueous saccharides solutions.

Inserting eq 4 into eq 3, a least-squares analysis was used to determine the γ_r, a, and C values for each of the mixed solvents from the experimental ΔE values listed in Table 1. Thus obtained values are shown in Table 2, together with their standard deviations. It is interesting to find that the ion−interaction parameter C is linear with reciprocal of relative permittivity $1/\epsilon_r$, as shown in Figure 1.

The Pitzer equations based on a semiempirical theory of statistical mechanics have been used successfully for representing the activity coefficients of electrolytes in mixed solvents. For 1:1 electrolyte, the equations derived by Pitzer[31] are given by

$$\ln \gamma = f_\gamma + B_\gamma m + C_\gamma m^2 \tag{7}$$

where

$$f_\gamma = -A_\Phi x$$

$$B_\gamma = 2\beta^0 + 2\beta^1 y$$

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

Table 3. Values for the Parameters of the Pitzer Equation 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	0.7323 ± 0.0010	0.1103 ± 0.0053	0.2402 ± 0.0181	−0.00731 ± 0.00336	0.09
	0.7336 ± 0.0009	0.0988 ± 0.0010	0.2769 ± 0.0077	0[a]	0.10
0.1	0.7471 ± 0.0010	0.1181 ± 0.0058	0.2937 ± 0.0192	−0.00198 ± 0.00372	0.10
	0.7475 ± 0.0007	0.1151 ± 0.0009	0.3032 ± 0.0070	0[a]	0.09
0.2	0.6827 ± 0.0015	0.1197 ± 0.0083	0.3745 ± 0.0290	0.00391 ± 0.00536	0.14
	0.6826 ± 0.0011	0.1255 ± 0.0013	0.3489 ± 0.0103	0[a]	0.14
0.3	0.6537 ± 0.0008	0.1442 ± 0.0048	0.4084 ± 0.0166	−0.00089 ± 0.00304	0.08
	0.6545 ± 0.0007	0.1426 ± 0.0008	0.4043 ± 0.0062	0[a]	0.08
0.4	0.6488 ± 0.0027	0.1637 ± 0.0156	0.5060 ± 0.0549	−0.00156 ± 0.00999	0.27
	0.6474 ± 0.0019	0.1618 ± 0.0024	0.5354 ± 0.0193	0[a]	0.25

[a] The Pitzer equation with $C_\gamma = 0$ (i.e., C_γ was omited).

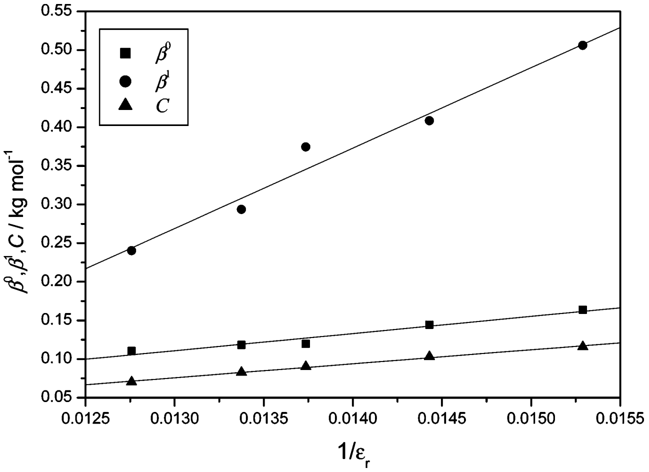

Figure 1. Plots of β^0, β^1, and Debye−Hückel ion−interaction parameter C vs $1/\epsilon_r$.

and

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

In the equations above, α and b are empirical parameters, and A_Φ is the Debye−Hückel constant for the osmotic coefficients defined by

$$A_\Phi = 1.4006 \times 10^6 d^{1/2}/(\epsilon_r T)^{3/2}\ \mathrm{mol^{-1/2}\cdot dm^{3/2}\cdot K^{3/2}} \quad (8)$$

It has been shown by Koh et al.[32] that the same values of α and b for aqueous solutions could be used for the methanolation water mixtures without greatly affecting the standard deviation of the fit. Therefore, α and b were used as fixed parameters with values of 2.0 and 1.2 (kg$^{1/2}$·mol$^{-1/2}$), respectively. The values for A_Φ were also obtained from the literature.[12]

Using eqs 3, 7, and 8, the γ_r, β^0, β^1, and C_γ values were optimized for each saccharide + water system. These values are summarized in Table 3, together with their standard deviations and the standard deviations of the fit. Since the molality is not more than 2.0 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 were also summarized in Table 3.

According to the Pitzer theory, the second virial coefficient is a complicated function of many interactions, and controlled by β^0 and β^1 parameters. Values of β^0 and β^1 are positive in maltose + water mixtures, indicating a net repulsive force in short-range interactions and positive second virial coefficients. This is the typical profile observed with 1:1 electrolytes in aqueous solutions.[33] Furthermore, it is observed also that both β^0 and β^1 are vary linear with the reciprocal of relative permittivity for saccharide + water mixtures (see Figure 1).

As can be seen from Tables 2 and 3, the values γ_r obtained from the two theoretical models for each of the mixed solvents are in good agreement with each other. Therefore, the mean of two γ_r values for a given solvent was used to calculate the γ for NaBr in this solvent from eq 3. They are also included in Table 1. In the concentration range studied, both of the activity coefficients obtained from our experimental values are in quite agreement with those reported by Hamer and Wu[26] in pure water.

Apparent Molar Volume. The density data are listed in Table 4. Apparent molar volumes of maltose ($V_{\Phi,S}$) and NaBr ($V_{\Phi,E}$) were calculated respectively from[34]

$$V_{\Phi,S} = \frac{M_S}{d} - \frac{(1000 + m_E M_E)(d - d_E)}{m_S d d_E} \quad (9)$$

$$V_{\Phi,E} = \frac{M_E}{d} - \frac{(1000 + m_S M_S)(d - d_S)}{m_E d d_S} \quad (10)$$

where M_E and M_S are the molar masses of electrolyte (NaBr) and saccharide (maltose); m_E and m_S are the molalities of electrolyte and saccharide; and d, d_S, and d_E are densities of NaBr + maltose + water, maltose + water, and NaBr + water solutions, respectively. The results were also included in Table 4. It has been observed that both plots of $V_{\Phi,S}$ versus m_S and $V_{\Phi,E}$ versus $m_E{}^{1/2}$ are very linear. Therefore, infinite-dilution apparent molar volumes ($V^0_{\Phi,S}$ and $V^0_{\Phi,E}$), which are equal in value to the standard partial molar volumes (V^0_S and V^0_E), were obtained by least-squares weighted fitting experimental data to the following equations:[35,36]

$$V_{\Phi,S} = V^0_{\Phi,S} + S^*_S m_S \quad (11)$$

$$V_{\Phi,E} = V^0_{\Phi,E} + S^*_E m_E{}^{1/2} \quad (12)$$

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 $\delta V_\Phi = -(M + 1000/m)\,\delta d/d^2$, δd is uncertainty of the solution density and is taken as a constant,[35,36] M is the molar mass of solute. The resulting values of $V^0_{\Phi,S}$ and $V^0_{\Phi,E}$ for the studied systems are given in Tables 5 and 6, respectively. To compare the standard molar volume of NaBr in water with the literature values, we fit also the data for the NaBr + water system to[37,38]

$$V_{\Phi,E} = V^0_{\Phi,E} + 1.868 c_E^{1/2} + b_\nu c_E \quad (13)$$

where 1.868 is the theoretic slop, b_ν is the empirical

Table 4. Densities and Apparent Molar Volumes of Maltose and NaBr in the NaBr + Water, Maltose + Water, and NaBr + Maltose + Water Systems at 298.15 K

m_E	d	$V_{\Phi,S}$	V_S	$V_{\Phi,E}$	V_E
mol·kg^{-1}	g·cm^{-3}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}
		$w = 0.05$			
0.0000	1.016777	210.08	210.20		23.89
0.1500	1.028017	210.42	210.47	24.63	24.88
0.3000	1.039071	210.92	210.69	24.98	25.29
0.5000	1.053636	211.38	211.03	25.22	25.70
0.7500	1.071562	211.88	211.48	25.45	26.11
1.0000	1.089133	212.74	211.94	25.70	26.46
		$w = 0.10$			
0.0000	1.037258	210.22	210.76		24.19
0.1500	1.048020	210.49	211.01	24.86	25.17
0.3000	1.058636	210.72	211.23	25.10	25.58
0.5000	1.072590	211.04	211.56	25.36	25.98
0.7500	1.089712	211.59	211.98	25.68	26.39
1.0000	1.106594	212.00	212.40	25.87	26.73
		$w = 0.15$			
0.0000	1.058434	210.57	211.38		24.55
0.1500	1.068682	210.85	211.61	25.19	25.48
0.3000	1.078771	211.14	211.83	25.52	25.86
0.5000	1.092043	211.52	212.15	25.80	26.25
0.7500	1.108457	211.83	212.54	25.94	26.63
1.0000	1.124555	212.23	212.92	26.14	26.95
		$w = 0.20$			
0.0000	1.080438	210.82	212.08		24.75
0.1500	1.090193	211.05	212.29	25.38	25.76
0.3000	1.099795	211.29	212.50	25.69	26.18
0.5000	1.112402	211.64	212.81	26.01	26.60
0.7500	1.127962	212.00	213.16	26.23	27.01
1.0000	1.143206	212.46	213.51	26.49	27.36
		$w = 0.25$			
0.0000	1.103065	211.33	212.87		24.97
0.1500	1.112279	211.55	213.06	25.75	26.02
0.3000	1.121381	211.76	213.27	25.95	26.46
0.5000	1.133332	212.05	213.56	26.23	26.89
0.7500	1.147991	212.46	213.86	26.56	27.32
1.0000	1.162431	212.86	214.17	26.78	27.69
		$w = 0.30$			
0.0000	1.126587	211.73	213.78		25.65
0.1500	1.135245	211.95	213.94	26.19	26.54
0.3000	1.143777	212.18	214.14	26.45	26.92
0.5000	1.154975	212.50	214.42	26.76	27.28
0.7500	1.168783	212.87	214.67	27.00	27.65
1.0000	1.182390	213.24	214.93	27.18	27.96

constant, and c_E (in mol·dm^{-3}) is the molarity evaluated by

$$c_E = m_E d_E/(1 + 10^{-3} m_E M_E) \tag{14}$$

The resulting value is also given in Table 5. Obviously, agreement is quite good among the values from different equations and that reported in the literature.[23,37,38]

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

$$V_S = \left[\frac{\partial(V_{\Phi,S} m_S)}{\partial m_S}\right]_{T,p} = V^0_{\Phi,S} + 2 m_S S^*_S \tag{15}$$

$$V_E = \left[\frac{\partial(V_{\Phi,E} m_E)}{\partial m_E}\right]_{T,p} = V^0_{\Phi,E} + 1.5 m_E S^*_E \tag{16}$$

and given also in Table 4. The standard deviations, $\sigma(V_S)$ and $\sigma(V_E)$, were evaluated from

$$\sigma(V_S) = [\sigma(V^0_{\Phi,S})^2 + \{2 m_S \sigma(S^*_S)\}^2]^{1/2} \tag{17}$$

$$\sigma(V_E) = [\sigma(V^0_{\Phi,E})^2 + \{1.5 m_E \sigma(S^*_E)\}^2]^{1/2} \tag{18}$$

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

Interaction of Electrolytes with Saccharides in the Ternary Systems. The standard free energy of transfer is an important index of the difference in interactions of ion or electrolyte with two different solvents. The free energy of transfer for electrolyte from water (W) to aqueous saccharide solutions (W + S) can be expressed as[18]

$$\Delta_t G^0_E(\mathrm{W} \rightarrow \mathrm{W} + \mathrm{S}) = \mu^0_E(m_E, m_S) - \mu^0_E(m_E) = nF(E^0_S - E^0_W) \tag{19}$$

where F is the Faraday constant, μ^0_E is the standard chemical potential of the electrolyte, and E^0_S and E^0_W are the standard cell potentials of electrolyte in E + S + W and in E + W systems, respectively, which were obtained by extrapolating the function

$$E = E^0 + 2k \log m\gamma \tag{20}$$

Figure 2 shows the variation of standard free energy of transfer for NaBr with mole fraction of maltose (X) in the mixed solvents. $\Delta_t G^0_E$ for NaBr increases positively with increasing the proportion of maltose, implying that the thermodynamic stabilization decreases in the mixed solvents. Similar trends were observed for the transfer of some electrolytes from water to aqueous solutions of some mono- and disaccharides.[12,39] This results partly from Born-type electrostatic effects arising from decreasing dielectric constant of the mixed solvents, and partly from chemical

Table 5. Infinite-Dilution Apparent Molar Volumes ($V^0_{\Phi,S}$) of Maltose in Aqueous NaBr Solutions and Slopes (S^*_S) of Equation 11 at 298.15 K

m_E/mol kg^{-1}	0	0.1500	0.3000	0.5000	0.7500	1.0000
$V^0_{\Phi,S}$/cm^3 mol^{-1}	209.70 ± 0.06 210.07[a]	209.98 ± 0.05	210.21 ± 0.08	210.56 ± 0.08	211.04 ± 0.13	211.52 ± 0.15
S^*_S/cm^3 kg mol^{-2}	1.63 ± 0.08	1.58 ± 0.07	1.57 ± 0.11	1.54 ± 0.11	1.45 ± 0.18	1.36 ± 0.20

[a] Ref 4.

Table 6. Infinite-Dilution Apparent Molar Volumes ($V^0_{\Phi,E}$) of NaBr in Aqueous Maltose Solutions and Slopes (S^*_E) of Equation 12 at 298.15 K

m_S/mol kg^{-1}	0.0000	0.15376	0.32460	0.51554	0.73035	0.97380	1.25203
$V^0_{\Phi,E}$/cm^3 mol^{-1}	23.58 ± 0.002 23.61[a]	23.89 ± 0.06	24.19 ± 0.04	24.55 ± 0.04	24.75 ± 0.05	24.97 ± 0.07	25.65 ± 0.07
S^*_E/cm^{3}kg mol^{-2}	−0.133 ± 0.003	1.71 ± 0.08	1.69 ± 0.05	1.60 ± 0.05	1.74 ± 0.07	1.81 ± 0.10	1.54 ± 0.09

[a] Ref 23.

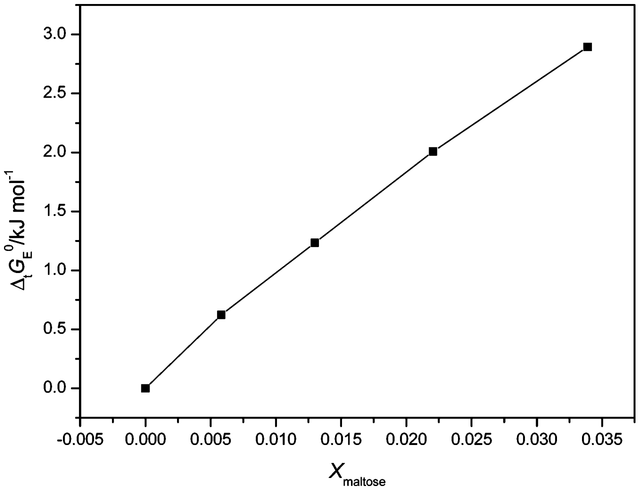

Figure 2. Variation of $\Delta_t G_E^0$ for NaBr as a function of molar fraction of maltose in the maltose + water mixture.

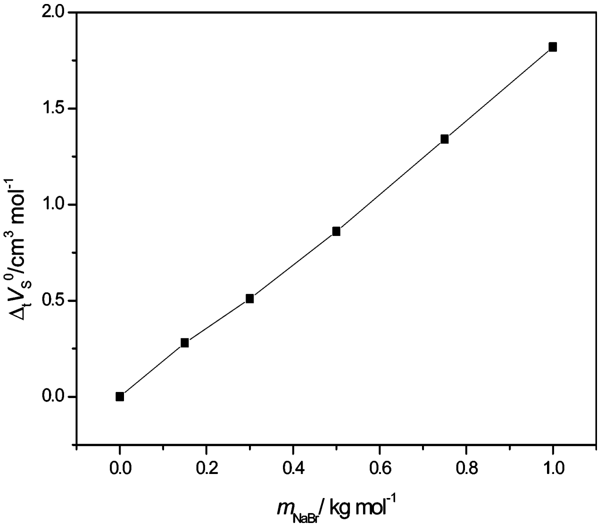

Figure 3. Variation of standard transfer volumes ($\Delta_t V_S^0$) of maltose from water to aqueous NaBr solutions with the molalities of NaBr.

effects arising from solvent acidity−basicity, preferential solvation, and structural aspects of the mixed solvents.

Standard transfer volumes for NaBr ($\Delta_t V_E^0$), from water to maltose + water solutions and those for maltose ($\Delta_t V_S^0$) from water to NaBr + water solutions were calculated, respectively. Plots of $\Delta_t V_S^0$ versus the molality of NaBr and $\Delta_t V_E^0$ versus maltose were represented in Figures 3 and 4, respectively. As shown in Figures 3 and 4, the values of $\Delta_t V_S^0$ and $\Delta_t V_E^0$ for the NaBr + maltose + water system are positive and increase with increasing molalities of NaBr and maltose. Similar features have been noted also for the NaCl (or NaBr) + monosaccharide + water systems.[22,23] This can be interpreted in terms of the structural interaction model proposed by Desnoyers et al.[40] and the hydration model by Conway.[41] According to the models, the Na^+−O (O stands for OH, C=O, and −O groups) interaction [hydrophilic (+)−hydrophilic (−) interaction] should contribute a positive value to volume since the dehydration of Na^+ and O group will enhance the structure of water. On the other hand, it was concluded that this interaction is predominant.[23]

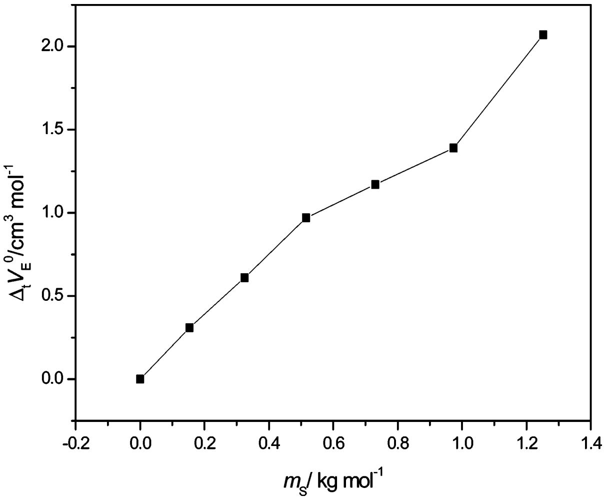

Figure 4. Variation of standard transfer volumes ($\Delta_t V_E^0$) of NaBr from water to aqueous maltose solutions with the molalities of the maltose.

On the basis of the McMillan−Mayer theory, the transfer free energy of electrolyte from water to aqueous saccharide solutions can be expressed as[18]

$$\Delta_t G_E^0(\mathrm{W} \rightarrow \mathrm{W} + \mathrm{S}) = \mu_E^0(m_E, m_S) - \mu_E^0(m_E) = 2\nu g_{ES} m_S + 3\nu g_{ESS} {m_S}^2 + ... \quad (21)$$

Similarly, volumetric interaction parameters can be obtained by separately fitting experimental data to the following equations:[23]

$$\Delta_t V_{\Phi,S} = V_{\Phi,S}(m_S, m_E) - V_{\Phi,S}(m_S) = 2\nu v_{ES} m_E + 3\nu^2 v_{EES} {m_E}^2 + 3\nu v_{ESS} m_E m_S + ... \quad (22)$$

$$\Delta_t V_{\Phi,E} = V_{\Phi,E}(m_E, m_S) - V_{\Phi,E}(m_E) = 2\nu v_{ES} m_S + 3\nu^2 v_{EES} m_S m_E + 3\nu v_{ESS} {m_S}^2 + \cdots \quad (23)$$

The parameters g_{ES} and g_{ESS} are pair and triple free energy interaction parameters, and v_{ES} and v_{EES} are pair and triple volumetric interaction parameters, respectively. $\Delta_t V_{\Phi,S}$ is the transfer volumes of maltose at molality m_S from water to a NaBr solution at molality m_E, and $\Delta_t V_{\Phi,E}$ is that of NaBr at molality m_E to a solution of maltose at m_S.

For evaluating the free energy interaction parameters, the standard free energies of NaBr ($\Delta_t G_E^{0m(M)}$) on the $m_E{}^M$ scale (in moles per kilogram of mixed solvent) were first converted into those ($\Delta_t G_E^{0m(W)}$) on the $m_E{}^W$ scale (in moles per kilogram of pure water) through the use of the expression[42]

$$\Delta_t G_E^{0m(W)} = \Delta_t G_E^{0m(M)} - \nu RT \ln(1 + 0.001 m_S M_S) \quad (24)$$

then values of g_{ES} were obtained by fitting these converted data to eq 21 and are listed in Table 7. The salting constant (k_S) was also calculated by[43]

$$k_S = 2\nu g_{ES}/RT \quad (25)$$

Thus the obtained values of k_S are also included in this table, together with the values for other saccharides reported in the literature.

Volumetric interaction parameters obtained least-squares from eqs 22 and 23 are in good agreement with each other

Table 7. Free Energy Interaction Parameters (g_{ES}) for the NaBr/NaCl−Saccharide Pairs and Salting Constants (k_S) in Water at 298.15 K

saccharide−NaX	$2\nu g_{ES}$/J·kg·mol^{-2}	k_S/kg·mol^{-1}
maltose−NaBr	277	0.112
maltose−NaCl[a]	613	0.247
glucose−NaBr[b]	114	0.046
galactose−NaBr[b]	−89	−0.036
xylose−NaBr[b]	102	0.041
sucrose−NaBr[b]	164	0.066

[a] Ref 12. [b] Ref 47.

Table 8. Volumetric Interaction Parameters and Their Standard Deviations for the NaBr + Saccharide + Water Systems at 298.15 K

	$2\nu v_{ES}$	$3\nu v_{ESS}$	$3\nu^2 v_{EES}$	σ^b
saccharide	cm^3·mol^{-2}·kg	cm^3·mol^{-3}·kg^2	cm^3·mol^{-3}·kg^2	cm^3·mol^{-1}
maltose	1.770 ± 0.053	−0.286 ± 0.039	0.078 ± 0.05	0.05
glucose[a]	1.620 ± 0.040	−0.237 ± 0.031	−0.194 ± 0.036	0.05

[a] Ref 23. [b] Standard deviation of the fit.

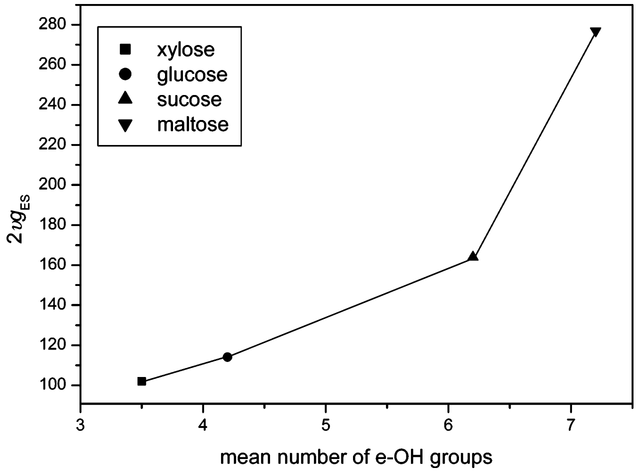

Figure 5. Relations between the free energy pair interaction parameters and the mean number of e-OH groups for the NaBr + saccharide + water systems at 298.15 K.

within experimental error. Therefore, mean values of them are given in Table 8.

Maltose is a combination of two glucose units connected by a glycosidic linkage. If a maltose molecule is regarded as a simple sum of two glucose units, then the following relations should be expected $v_{E-maltose}$ (or $g_{E-maltose}$) ≈ $2v_{E-glucose}$ (or $g_{E-glucose}$) on the basis of the group additivity model.[44] However, these do not agree with the experimental results. As shown in Tables 7 and 8, $g_{E-maltose}$ (277/4) > $2g_{E-glucose}$ (228/4), $v_{E-maltose}$ (1.77/4) ≈ $v_{E-glucose}$ (1.62/4). This indicates that the contribution of the interactions of NaBr with glycosidic linkage (−O−) in maltose to g_{ES} is larger than that with two hydroxy groups in glucose, and the contributions to volumetric interaction parameters are out of accord with the group additivity model.

Compared with the NaCl + maltose + water system,[12] $g_{NaCl-maltose}$ (613/4) > $g_{NaBr-maltose}$ (277/4). For a given saccharide, the free energy interaction parameters are dependent on the properties of ions (from Cl$^-$ to I$^-$). It has been observed that the g_{ES} values decrease from Cl$^-$ to I$^-$ for the electrolyte (NaCl, NaBr and NaI) + saccharide + water systems.[47] This has been interpreted in terms of dispersion forces between ions and saccharide molecules.[47]

As pointed out by Grover and Ryall,[45] salting out is essentially an electrostatic effect. We believe that the interaction between Br$^-$ and −O− will contributes a much larger positive value to g_{ES} than that between Br$^-$ and −OH. However, maltose has a larger cavity volume compared with glucose, which is available to accommodate Br$^-$ (a large negative contribution to volume). This is a possible reason for the fact $v_{E-maltose} \ll 2v_{E-glucose}$.

Uedaira and Uedaira[46] suggested that the effects of −OH groups are dominant in hydration of saccharide molecules. Wang et al.[39] also found that the interactions between electrolytes and saccharides are controlled mainly by the mean number of e-OH (equatorial hydroxyl group) and g_{ES} has a linear relationship with the mean number of e-OH in saccharide molecules. In a given electrolyte (say NaBr), it appears that g_{ES} increases linearly with the mean number of e-OH groups but the g_{ES} value for maltose is higher than that expected from the line (see Figure 5).

Literature Cited

(1) Galema, S. A.; Blandamer, M. J.; Engberts, J. B. F. N. Stereochemical aspects of the hydration of carbohydrates, kinetic medium effects of monosaccharides of a water cataluzed hydrolysis reaction. *J. Am. Chem. Soc.* **1990**, *112*, 9665−9666.
(2) Barone, G.; Castronuovo, G.; Doucos, D.; Elia, V.; Mattla, C. A. Excess enthalpies of aqueous solutions of monosaccharides at 298.15 K: pentoses and 2-deoxy sugars. *J. Phys. Chem.* **1983**, *87*, 1931−1937.
(3) Miyajima, K.; Sawada, M.; Nakagaki, M. Studies on aqueous solutions of saccharides. II. Viscosity *B*-coefficients, maltose, and maltotriose in aqueous solutions. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1954−1957.
(4) 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.
(5) Chatterjee, J. P.; Basumallick, I. N. Thermodynamics of transfer of electrolytes and lons from water to aqueous solutions of polyhydroxy compounds. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3107−3110.
(6) Jasra, R. V.; Ahluwalia, J. C. Enthalpies and heat-capacities of transfer of some sugars from water to aqueous urea solutions. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 1303−1309.
(7) Gregory, R. E.; McTigue, P. T. Gibbs energies of transfer of several alkali-metal chlorides from water to sucrose-water mixtures using streaming amalgam eletrodes. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 451−455.
(8) Dash, J. K.; Chakrabortty, M.; Chakravortty, V. Viscosity, conductance and acoustic studies on lanthanum(III) chloride in water and maltose-water mixed solvent system. *J. Mol. Liq.* **2000**, *84*, 215−222.
(9) Morel-Desrosier, N.; Lhermet, C.; Morel, J. P. Interactions between cations and sugars. Part 7. Gibbs energies, enthalpies and entropies of association of trivalent lanthanide cations with ribose in water at 298.15 K. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1223−1228.
(10) Rongere, P.; Morel-Desrosier, N.; Morel, J. P. Interactions between cations and sugars. Part 8. Gibbs energies, enthalpies and entropies of association of divalent and trivalent metal cations with xylitol and glucitol in water at 298.15 K. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2771−2777.
(11) 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.
(12) Hernández-Luis, F.; Amado-Gonzalez, E.; Esteso, M. A. Activity coefficients of NaCl in trehalose-water and maltose-water mixtures at 298.15 K. *Carbohydr. Res.* **2003**, *338*, 1415−1424.
(13) Jiang, Y. C.; Gao, S. Y.; Xia, S. P.; Hu, M. C.; Wang, J. J.; Zhuo, K. L. The enthalpy and entropy interaction parameters of cesium chloride with saccharides (D-glucose, D-galactose, D-xylose and D-arabinose) in water at T = 298.15 K. *J. Chem. Thermodyn.* **2003**, *35*, 493−501.
(14) Jiang, Y. C.; Gao, S. Y.; Xia, S. P.; Wang, J. J.; Zhuo, K. L.; Hu, M. C. Thermodynamics parameters of the interaction of CsCl with monosaccharide (D-glucose, D-galactose, D-xylose, and D-arabinose) in water at T = 298.15 K. *J. Chem. Thermodyn.* **2002**, *34*, 1959−1973.
(15) Jiang, Y. C.; Gao, S. Y.; Xia, S. P.; Hu, M. C.; Wang, J. J.; Lu, Y.; Zhuo, K. L. The enthalpy and entropy interaction parameters of cesium chloride with saccharides (D-glucose, D-fructose and sucrose) in water at 298.15 K. *Thermochim. Acta* **2003**, *400*, 37−42.
(16) Banipal, P. K.; Banipal, T. S.; Ahluwalia, J. C. Partial molar heat capacities and volumes of transfer of some saccharides from water

to aqueous sodium chloride solutions at $T = 298.15$ K. *J. Chem. Thermodyn.* **2002**, *34*, 1825−1846.

(17) Banipal, P. K.; Banipal, T. S.; Ahluwalia, J. C.; Lark B. S. Partial molar heat capacities and volumes of transfer of some saccharides from water to aqueous urea solutions at $T = 298.15$ K. *J. Chem. Thermodyn.* **2000**, *32*, 1409−1432.

(18) 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.

(19) Zhuo, K. L.; Wang, J. J.; Zhou, J. G.; Lu, J. S. Thermodynamics of the interacton of HCl with D-glucose in water at 278.15−318.15 K. *J. Phys. Chem. B* **1997**, *101*, 3447−3451.

(20) Zhuo, K. L.; Wang, J. J.; Cao, Y. L.; Lu, J. S. Thermodynamics of the interaction of HCl with D-fructose in water at 278.15−318.15 K. *J. Phys. Chem. B* **1998**, *102*, 3574−3577.

(21) 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.

(22) 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.

(23) 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.

(24) 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.

(25) Wang, J. J.; Liu, W. B.; Fan, J.; Lu, J. S. Mean activity coefficient of NaCl in glucose-water and sucrose-water mixtures at 298.15 K. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3281−3285.

(26) 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*, 1047−1099.

(27) Cammann, K. *Working with Ion-Selective Electrodes*; Springer-Verlag: Berlin, 1979.

(28) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworth: London, 1959.

(29) Eya, H.; Mishima, K.; Nagatani, M.; Iwai, Y.; Arai, Y. Measurement and correlation of solubilities of oxygen in aqueous-solutions containing glucose, sucrose and maltose. *Fluid Phase Equilib.* **1994**, *97*, 201−209.

(30) Matsuoka, T.; Okada, T.; Murai, K.; Koda, S.; Nomura, H. Dynamics and hydration of trehalose and maltose in concentrated solutions. *J. Mol. Liq.* **2002**, *99*, 317−327.

(31) Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **1973**, *77*, 268−277.

(32) Koh, D. S. P.; Khoo, K. H.; Chan, C. Y. The application of the Pitzer equations to 1−1 electrolytes in mixed-solvents. *J. Solution Chem.* **1985**, *14*, 635−651.

(33) Pitzer, K. S.; Mayorga, G. Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolutes with one or both ions univalent. *J. Phys. Chem.* **1973**, *77*, 2300−2308.

(34) Visser, C. De; 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.

(35) 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.

(36) 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.

(37) Millero, F. J. In *Structure and Transport Processes in Water and Aqueous solutions*; Horne, R. A., Ed.; Wiley-Iterscience: New York, 1971; Chapter 15.

(38) Millero, F. J. Molar volumes of electrolytes. *Chem. Rev.* **1971**, *71*, 147−176.

(39) Wang, J.; Zeng, L.; Liu, W.; Lu, J. A thermodynamic study of the ternary system water + glucose + electrolyte at 298.15 K. *Thermochim. Acta* **1993**, *224*, 261−269.

(40) Desnoyers, J. E.; Joly, M.; Perron, G.; Jolicoeur, C. Apparent molal volumes of alkali halides in water at 25 degrees, influence of structural hydration interactions on concentration dependence. *J. Phys. Chem.* **1969**, *73*, 3346−3351.

(41) Conway, B. E. *Ionic Hydration in Chemistry and Physics*; Elsevier: Amserdam, The Netherlands, 1980.

(42) Zhuo, K. L. Thermodynamic pair interaction parameters on various concentration scales. *J. Phys. Chem. B* (in press).

(43) 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.

(44) Savage, J. J.; Wood, R. H. Enthalpy of dilution of aqueous mixtures of amides, sugars, urea, ethylene glycol, and pentaerytheitol at 25-degrees C. *J. Solution Chem.* **1976**, *5*, 733−750.

(45) Grover, P. K.; Ryall, R. L. Critical appraisal of salting-out and its implications for chemical and biochemical sciences. *Chem. Rev.* **2005**, *105*, 1−10.

(46) Uedaira., H.; Uedaira, H. Sugar-water interaction from diffusion measurements. *J. Solution Chem.* **1985**, *14*, 27−34.

(47) Zhuo, K. L. Studies on thermodynamics of the interaction between electrolyte and saccharide in water. Ph.D. Thesis, Lanzhou Institute of Chemical Physics, The Chinese Academy of Sciences, 2000; pp 40−62.

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