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Activity coefficients for NaCl–monosaccharide (D-glucose, D-galactose, D-xylose, D-arabinose)–water systems at 298.15 K

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Abstract

Electrochemical cells with a sodium ion selectivity electrode (Na–ISE) versus a chloride ion selectivity electrode (Cl–ISE) as a reference electrode were used to determine the activity coefficients for NaCl–monosaccharide (D-glucose, D-galactose, D-xylose, and D-arabinose) systems in water at 298.15 K. A comparison of the results thus obtained was made with those determined by another electromotive force (emf) method. It is shown that agreement is excellent. The Gibbs free energy parameters of the interactions between these sugars and NaCl in water were evaluated together with the parameter C_1(CHOH, exo), indicating the interaction of the exocyclic CHOH group of saccharide molecules and NaCl. The results suggested that the interactions of these monosaccharides with NaCl are controlled mostly by the dominant conformer of their molecules in water. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Activity coefficients; NaCl; Monosaccharide; Ion selectivity electrode; Interaction

1. Introduction

Numerical values of activity coefficients of a chemical species are a reflection of the interactions between the components in a system. Accurate measurements and correlation of activity coefficients for the saccharide (S)–electrolyte–(E)–water systems are very valuable for the design of equilibrium-based separation processes. On the other hand, the investigation of the interactions of saccharide with electrolyte is helpful for understanding the behavior and biological function of saccharides in biological systems [1]. However, few data for the electrolyte–saccharide–water systems have been reported [2].

Electrochemical methods can deal directly with the thermodynamic properties of solutions containing electrolytes. Thus, electrochemical cells have become an essential tool for experimental studies and have been widely used for the measurements of the thermodynamic properties of electrolytic solutions. For example, galvanic cells were applied to measure mean activity coefficients of electrolyte solutions [3]. The introduction of ion-selective electrodes (ISEs) has remarkably broadened the range of electrolytes that can be studied by this potentiometric technique. A cation ISE combined with an Ag–AgX (X = Cl, Br and I) electrode has been successfully applied to determine the mean activity coefficients in bi-

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nary and ternary systems [4]. Recently, Vera and co-workers used cells with two ISEs, a cation and an anion ISE, versus a double-junction reference electrode, to measure the activity coefficients for electrolyte–amino acid–water systems [5]. The following cells were set up to measure the thermodynamic properties of the electrolyte–saccharide (non-electrolyte)–water systems in this work:

$$\text{cation ISE}|\text{electrolyte } (m_E)|\text{anion ISE} \qquad \text{(I)}$$

$$\text{cation ISE}|\text{electrolyte } (m_E), \text{ saccharide } (m_S)|\text{anion ISE} \qquad \text{(II)}$$

where m_E and m_S are, respectively, the molalities of electrolyte and saccharide defined as the number of moles of solutes per kg of pure water. This is an elegant way of overcoming the liquid-junction potential.

In previous work [6,7], thermodynamic studies of some saccharide–electrolyte–water ternary systems have been carried out in our laboratory using galvanic cells [6] and cells with a cation ISE versus Ag–AgCl reference electrode [7]. As a continuation of this study, the activity coefficients of NaCl at 298.15 K in water–NaCl–monosaccharide (D-glucose, D-galactose, D-xylose, D-arabinose) systems were measured at a wide molality range in this work. The activity coefficients of these monosaccharides in the ternary systems were evaluated. The differences between the interactions of NaCl with these monosaccharides were discussed in terms of their stereochemistry.

2. Experimental

D-Galactose, D-xylose and D-arabinose (Biochem. R., Shanghai Chem. Co.) were recrystallized from water–EtOH mixtures. These purified saccharides and anhydrous D-glucose (AR, Shanghai Chem. Co.) and sodium chloride (GR, > 99.95%, Shanghai Chem. Co.) were 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 $1.0–1.2 \times 10^{-4}$ S m^{-1} at 298 K.

A sodium-glass electrode (model 312) and a chloride ion-selective electrode (model 301) were obtained from Jiangsu Electroanalytic Instrument factory. A PH/ISE meter (Shanghai Rex Instrument Factory, model PXSJ–216) with a resolution of 0.1 mV was used to monitor the electromotive force (emf) measurements. It has two inputs with BNC (Bayonet Neil–Concelman) connectors for the indicator ISEs and two inputs for reference electrodes. Since we wanted to use an ISE as a reference electrode, a BNC pin-tip adapter was connected to the reference ISE and connected to the reference input. The apparatus used in this work was similar to that described by Haghtaiab and Vera [8]. In all measurements, the temperature of the sample solution was held at 298.15 ± 0.02 K. The conditioning procedure for the electrodes was followed exactly according to the manufacture's instructions. All the instruments were grounded prior to and during the experiments. In order to minimize the risk of the presence of concentration gradients in the cell, the solutions were continuously stirred with a magnetic stirrer.

Each set of experiments was performed at a fixed electrolyte concentration, ranging from 0.01 to 1.0 mol kg^{-1}, and the concentration of saccharides was increased by addition of solid saccharide from 0.1 up to 1.6 mol kg^{-1} or higher. The choice of molality ranges of electrolyte and saccharides was based mainly on the operation condition of the electrodes, the solubility of saccharides and their dissolution rate. For example, the dissolution rate of D-galactose is slow, especially in concentrated solution, compared with the other three saccharides. Thus, its maximum molality was selected to be 1.6 mol kg^{-1}. Otherwise, the time required to reach equilibrium would be longer for each set of experiments so that the reliability of data measured would decrease. All the solutions were based on molality with respect to 1 kg of pure water. The molalities in all the test solutions were accurate to about 0.02 wt.% for NaCl and 0.2 wt.% for saccharides. The readings of the potentiometer were made only when the drift was less than 0.1 mV for 10 min. For each set of experiments, the two electrodes were allowed to stay in aq NaCl solution for 1–2 h so that the stability of the potentials could be ascertained. After a certain mass of saccharides was added, the solution was allowed to reach equilibrium. The time required for a stable potential reading was found to be 10–30 min. To ascertain the stability of the electrodes during a set of experiments, after the cell potential with the last sample solution was measured, the electrodes were transferred into a binary NaCl–water solution that had the same NaCl molality as the solution just measured. The two emf values in the NaCl–water solutions agreed to within 0.3 mV. Some experiments such as 0.01 (the most diluted) and 1.0 mol kg^{-1} (the most concentrated) of NaCl were replicated three times, and the data reported are the average of the replicates that agreed to within 0.3 mV. For each set of experiments, the electrodes were calibrated by measuring the emf of cell I (binary system). The slope S of the electrode response was determined using activity coefficients of NaCl calculated by the empirical equation recommended by Hamer and Wu [9]. The typical value of slope S for the electrode obtained by linear regression analysis of the experimental points was 25.57 ± 0.03 mV with a correlation coefficient of 0.99996. It is in excellent agreement with the theoretical value (25.69 mV at 298 K) of the Nernst equation. For all experiments, the experimental slopes were found to be constant within experimental error. Therefore, an average of several experimental slopes was used in the calculation for each saccharide.

3. Results and discussion

According to Nikolsky [10], the potential of an ISE can be expressed by

$$E = E' \pm (S_i/Z_i) \ln a_i \tag{1}$$

where a_i is the activity of ion i. The constant E' is the emf of the measuring circuit of the ISE. It depends on the activity of the ions in the inner solution and on the type of internal reference electrode of the ISE. The constant S_i refers to the slope of the electrode responsive to ion i, and Z_i is the charge number of ion i.

Then, for cells I and II, assuming $S \cong S_+ \cong S_- \cong (S_+ + S_-)/2$ leads to

$$E^{\mathrm{I}} = E^{\mathrm{I}\prime} + S\left(\frac{Z_+ + Z_-}{\nu Z_+ Z_-}\right)\ln a_{\mathrm{E}}^{\mathrm{I}} \tag{2}$$

$$E^{\mathrm{II}} = E^{\mathrm{II}\prime} + S\left(\frac{Z_+ + Z_-}{\nu Z_+ Z_-}\right)\ln a_{\mathrm{E}}^{\mathrm{II}} \tag{3}$$

where E^{I} and E^{II} are emfs of cells I and II, respectively. $E^{\mathrm{I}\prime} = E^{\mathrm{II}\prime} = E'_+ - E'_-$. a_{E} is the activity of electrolyte defined as

$$a_{\mathrm{E}} = (m_\pm \gamma_\pm)^\nu \tag{4}$$

where $m_\pm$ and $\gamma_\pm$ are mean ionic molality and activity coefficients of the electrolyte relative to unity at infinite dilution of NaCl in pure water. $\nu = \nu_+ + \nu_-$, where ν_+ and ν_- are the stoichiometric numbers of cation and anion.

Subtracting Eq. (2) from Eq. (3) and rearranging gives

$$\ln\left(\frac{\gamma_\pm^{\mathrm{II}}}{\gamma_\pm^{\mathrm{I}}}\right) = \frac{E^{\mathrm{II}} - E^{\mathrm{I}}}{S}\left(\frac{Z_+ Z_-}{Z_+ + Z_-}\right) \tag{5}$$

This equation allows one to calculate the ratio of $\gamma_\pm^{\mathrm{II}}$ to $\gamma_\pm^{\mathrm{I}}$ at the same molality of electrolyte from the emfs measured in cells II and I.

Mean activity coefficients of NaCl.—Using Eq. (5) and the values of S, the emf data measured experimentally were converted into the ratios of the mean activity coefficients of NaCl in the presence of saccharide to those in the absence of saccharide at the same NaCl molality. The results are given in Tables 1–4. The standard deviations of the ratios are evaluated to be within ± 0.004.

In order to analyze the experimental data obtained, a procedure similar to that suggested by Scatchard [11] and adopted by Lilley and co-workers [4a] and Vera and co-workers [5] was used. For the systems studied in this work, we have

$$\begin{aligned}\nu \ln\left(\frac{\gamma_\pm^{\mathrm{II}}}{\gamma_\pm^{\mathrm{I}}}\right) &= C_1 m_{\mathrm{S}} + C_2 m_{\mathrm{E}} m_{\mathrm{S}} + C_3 m_{\mathrm{S}}^2 + C_4 m_{\mathrm{E}}^2 m_{\mathrm{S}} \\ &\quad + C_5 m_{\mathrm{E}} m_{\mathrm{S}}^2 + C_6 m_{\mathrm{S}}^3\end{aligned} \tag{6}$$

where C_n are parameters indicating pair, triple and quadruple interactions between the saccharide molecules and ions of electrolyte, and higher-order terms have been neglected (see also below). The values of C_n were obtained from a least-squares analysis of the experimental data. The results thus evaluated are presented in Table 5, together with the standard deviation of the fit. To examine the effect of the number of parameters on the quality of the fit and to compare the contribution of these parameters, Eq. (6) with fewer parameters was also used to fit the experimental data. The results of the fit using an equation with four parameters are also presented in Table 5. It can be seen from the standard deviations that the quality of the fit using the four-parameter equation is slightly poorer than that of the six-parameter equation. This shows that the fifth and sixth terms in Eq. (6) make a relatively small contribution to the ratios of mean activity coefficients compared with the other terms. In fact, quadruple and higher-order interactions (C_4, C_5...) can be ignored when the concentration of saccharide is not very high. For example, the three-parameter equation can work very well in dilute solution, as shown by the results (given also in Table 5) from this equation using data ranging from 0 to 1.0 mol kg^{-1} of m_S. It is interesting to note that the number of parameters used for the fitting only slightly affects the value of C_1. Particularly, the C_1 values from the six-parameter equation in a wide molality range and the three-parameter equation in a relative dilution solution agree to within 0.003 kg mol^{-1} for all four systems. It should be mentioned that the selection of the number of parameters depends on two factors. One is the molality ranges studied. The number of

Table 1
The ratios of the mean ionic activity coefficients of NaCl in the presence and absence of D-glucose at different molalities of NaCl and D-glucose at 298.15 K

m_{glucose} (mol kg^{-1})	$\gamma^{\text{II}}_{\pm}/\gamma^{\text{I}}_{\pm}$ for given m_{NaCl} (mol kg^{-1})					
	0.01	0.1	0.3	0.5	0.7	1.0
0.1	1.006	1.006	1.004	1.004	1.004	1.002
0.3	1.014	1.014	1.010	1.010	1.008	1.006
0.5	1.024	1.020	1.018	1.016	1.012	1.012
0.7	1.028	1.028	1.024	1.020	1.018	1.016
1.0	1.042	1.038	1.030	1.026	1.026	1.024
1.3	1.053	1.049	1.040	1.034	1.032	1.028
1.6	1.067	1.061	1.046	1.040	1.040	1.034
2.0	1.082	1.074	1.057	1.053	1.049	1.042
2.5	1.102	1.089	1.065	1.061	1.057	1.049
3.0	1.117	1.102	1.082	1.072	1.067	1.057
3.5	1.130	1.117	1.093	1.080	1.074	1.067
4.0	1.141	1.128	1.104	1.091	1.082	1.074

Table 2
The ratios of the mean ionic activity coefficients of NaCl in the presence and absence of D-galactose at different molalities of NaCl and D-galactose at 298.15 K

$m_{\text{galactose}}$ (mol kg^{-1})	$\gamma^{\text{II}}_{\pm}/\gamma^{\text{I}}_{\pm}$ for given m_{NaCl} (mol kg^{-1})				
	0.01	0.05	0.1	0.5	1.0
0.1	0.998	0.998	1.000	1.000	1.000
0.3	0.996	0.996	0.998	0.998	1.000
0.5	0.994	0.996	0.996	0.998	0.998
0.7	0.992	0.994	0.996	0.996	0.998
1.0	0.990	0.992	0.994	0.994	0.996
1.3	0.989	0.990	0.992	0.994	0.996
1.6	0.989	0.990	0.992	0.994	0.996

Table 3
The ratios of the mean ionic activity coefficients of NaCl in the presence and absence of D-xylose at different molalities of NaCl and D-xylose at 298.15 K

m_{xylose} (mol kg^{-1})	$\gamma^{\text{II}}_{\pm}/\gamma^{\text{I}}_{\pm}$ for given m_{NaCl} (mol kg^{-1})			
	0.01	0.1	0.5	1.0
0.1	1.006	1.006	1.004	1.004
0.3	1.021	1.016	1.012	1.012
0.5	1.031	1.027	1.020	1.016
0.7	1.043	1.035	1.029	1.021
1.0	1.058	1.045	1.039	1.031
1.3	1.069	1.058	1.051	1.039
1.6	1.080	1.070	1.060	1.045
2.0	1.095	1.084	1.068	1.056
2.5	1.114	1.101	1.082	1.068
3.0	1.134	1.121	1.095	1.076

parameters used in the fit should increase with increasing molality because the contributions of higher-order terms increase in this case. The other is the characteristics of the interactions between solute species. The terms indicating no weak interactions should be considered. On the other hand, if too many parameters were used, the reliability will decrease as the number of data points decreases. Consequently, more parameters and experimental data points are required when the molality range of solutes is wider and the interaction between solute species is stronger.

It can be seen from Tables 1 and 3 that for a given NaCl molality, the $\gamma^{\text{II}}_{\pm}/\gamma^{\text{I}}_{\pm}$ ratio (positive) increases with increasing molality of glucose and xylose. The increase is larger at lower NaCl molalities. On the contrary, the $\gamma^{\text{II}}_{\pm}/\gamma^{\text{I}}_{\pm}$ ratio (negative), as seen from Table 2, decreases with increasing molality of galactose, and the trend is stronger at lower NaCl molalities. In particular, the $\gamma^{\text{II}}_{\pm}/\gamma^{\text{I}}_{\pm}$ ratio, as seen from Table 4, changes from increase to decrease with increasing arabinose molality. On the other hand, the dependence of the $\gamma^{\text{II}}_{\pm}/\gamma^{\text{I}}_{\pm}$ ratios on the molality of glucose and xylose are stronger than on that of galactose and arabinose. This will be further discussed below.

Comparison of mean activity coefficients of NaCl.—Stokes [12] has made a comparison of mean activity coefficients of NaCl in the NaCl–sucrose–water system from isopiestic [13] and emf measurements using an Na ISE versus Ag–AgCl as the reference electrode [7c]. Good agreement was obtained. Wang and co-workers (WLL) [7c] have reported the activity coefficients of NaCl in glucose–water mixtures. This enables us to compare two sets of data obtained using different electrodes.

As done by Stokes [12], first, the molalities and activity coefficients of NaCl were converted for two scales using the following relations

$$m = 100m^{*}/(100 - Y) \tag{7}$$

$$\begin{aligned}\exp[\Delta EF/(2RT)] &= m^{*}_{\text{ref}}\gamma^{*}_{\text{ref}}/(m^{*}\gamma^{*})\\ &= m_{\text{ref}}\gamma_{\text{ref}}/(m\gamma)\end{aligned} \tag{8}$$

where m^{*} and γ^{*} are the WLL molality defined as moles of NaCl per kg of saccharide–water mixtures, and the WLL activity coefficient is defined relative to unity at infinite dilution of NaCl in a given mixed solvent.

Table 4
The ratios of the mean ionic activity coefficients of NaCl in the presence and absence of D-arabinose at different molalities of NaCl and D-arabinose at 298.15 K

$m_{\text{arabinose}}$ (mol kg^{-1})	$\gamma^{\text{II}}_{\pm}/\gamma^{\text{I}}_{\pm}$ for given m_{NaCl} (mol kg^{-1})				
	0.01	0.05	0.1	0.5	1.0
0.3	1.004	1.002	1.002	1.002	1.002
0.5	1.004	1.004	1.004	1.002	1.002
0.7	1.006	1.006	1.002	1.002	1.000
1.0	1.006	1.002	1.000	1.000	0.998
1.3	1.004	1.002	1.000	0.998	0.994
1.6	1.004	1.000	0.998	0.996	0.994
2.0	1.002	0.998	0.996	0.994	0.882
2.5	1.000	0.996	0.994	0.992	0.990

Table 5
Values of the parameters of Eq. (6) [a]

	C_1 (10^{-2})	C_2 (10^{-2})	C_3 (10^{-2})	C_4 (10^{-2})	C_5 (10^{-2})	C_6 (10^{-2})	δ [b]	$m_{S,max}$ [c]
Glucose	9.054	−7.985	−0.7097	3.755	0.2886	0.03233	0.0021	4.0
	8.463	−7.095	−0.4099	3.755			0.0024	4.0
	8.873	−3.846	−1.1116				0.0018	1.0
Galactose	−1.798	2.289	−0.3665	−0.7494	−0.4791	0.4289	0.0010	1.6
	−2.061	1.676	0.4295	−0.7494			0.0011	1.6
	−1.848	1.090	0.1990				0.0010	1.0
Xylose	12.199	−6.981	−2.161	2.465	0.4246	0.2825	0.0025	3.0
	10.774	−6.002	−0.883	2.465			0.0029	3.0
	12.442	−4.525	−2.380				0.0027	1.0
Arabinose	2.776	−2.651	−2.435	1.070	0.3931	0.5082	0.0015	2.5
	1.192	−1.895	−0.548	1.070			0.0020	2.5
	2.778	−1.154	−2.160				0.0013	1.0

[a] Units: $(\text{mol kg}^{-1})^{-1}$ for C_1; $(\text{mol kg}^{-1})^{-2}$ for C_2 and C_3; $(\text{mol kg}^{-1})^{-3}$ for C_4, C_5 and C_6.

[b] δ is the standard deviation of the fit to Eq. (8) defined as $[\Sigma(\text{calcd. ratio} - \text{expl. ratio})^2/(\text{number of data points} - \text{number of parameters used})]^{1/2}$.

[c] $m_{S,max}$ is the maximum molality used to fit. Unit, mol kg^{-1}.

The subscript 'ref' refers to the reference molality (0.1 mol kg^{-1}). Y is the percentage of saccharide in the mixed solvent. The comparison between the results from two emf methods shows that the agreement is within 0.005 for most data measured in the molality ranges of NaCl and glucose. A comparison is shown in Fig. 1.

Activity coefficients of saccharides.—Application of the cross-differential relation [3] to Eq. (6) gives

$$\ln(\gamma_S^{II}/\gamma_S^{I}) = C_1 m_E + (1/2)C_2 m_E^2 + 2C_3 m_E m_S + (1/3)C_4 m_E^3 + C_5 m_E^2 m_S + 3C_6 m_E m_S^2 \qquad (9)$$

where γ_S^{II} and γ_S^{I} are the activity coefficients (relative to unity at infinite dilution of saccharide in pure water) of saccharide in the NaCl–saccharide–water and saccharide–water systems at the same NaCl molalities, respectively.

Figs. 2–5 represent, respectively, the dependence of the ratios $(\gamma_S^{II}/\gamma_S^{I})$ of the activity coefficients for the saccharides in the presence and absence of NaCl on the molalities of NaCl and saccharides. Solid lines are obtained from Eq. (9). It can be seen from Figs. 2 and 4 that for a given glucose or xylose molality, the $\gamma_S^{II}/\gamma_S^{I}$ ratio increases with increasing NaCl molality. The increase is larger at lower glucose and xylose molalities. However, for a given galactose molality, $\gamma_S^{II}/\gamma_S^{I}$ decreases at lower and increases slowly at higher galactose molality with increasing NaCl molality, as shown in Fig. 3. In contrast to galactose, the $\gamma_S^{II}/\gamma_S^{I}$ for a given arabinose molality increases at lower and decreases at higher arabinose molalities with increasing NaCl molality, but this decreasing trend becomes smaller at higher arabinose molality (see Fig. 5).

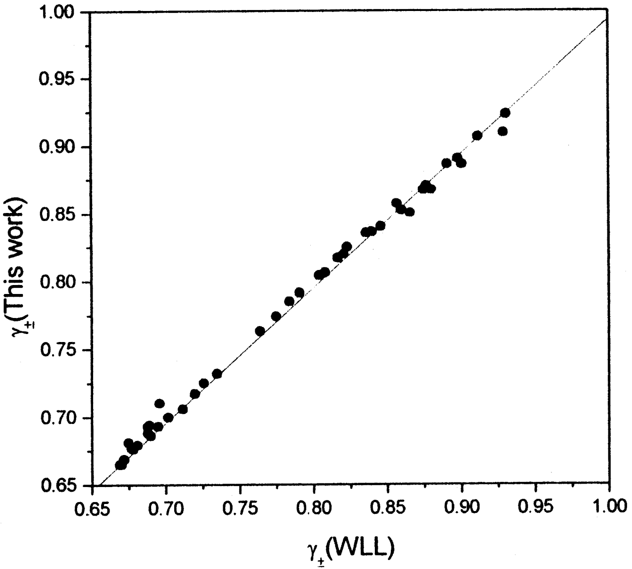

Fig. 1. Comparison of the mean activity coefficients obtained by Wang et al. $\gamma_{\pm}$(WLL) with those reported in this work $\gamma_{\pm}$(this work).

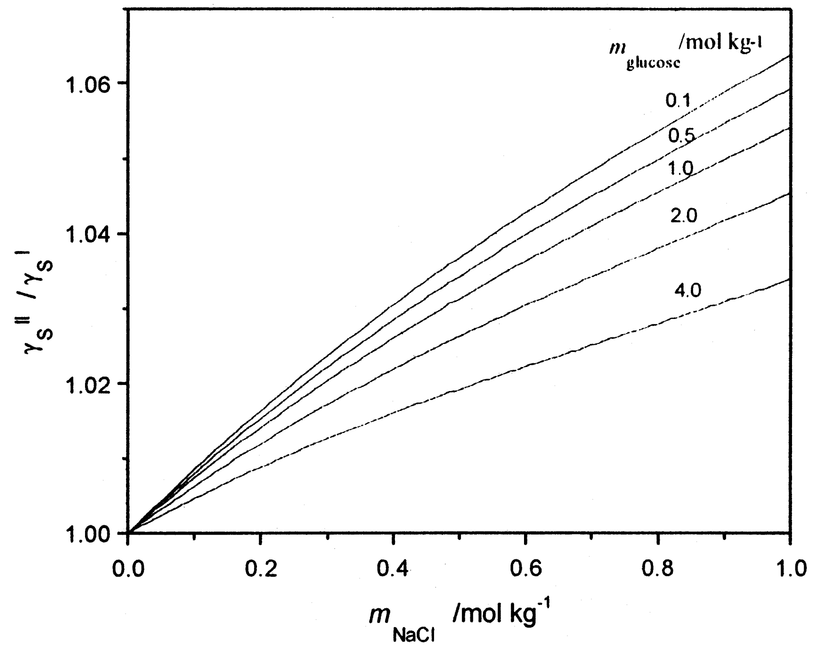

Fig. 2. Dependence of the ratio ($\gamma_S^{II}/\gamma_S^{I}$) of the activity coefficients of D-glucose in the presence and absence of NaCl on the molalities of NaCl and D-glucose at 298.15 K.

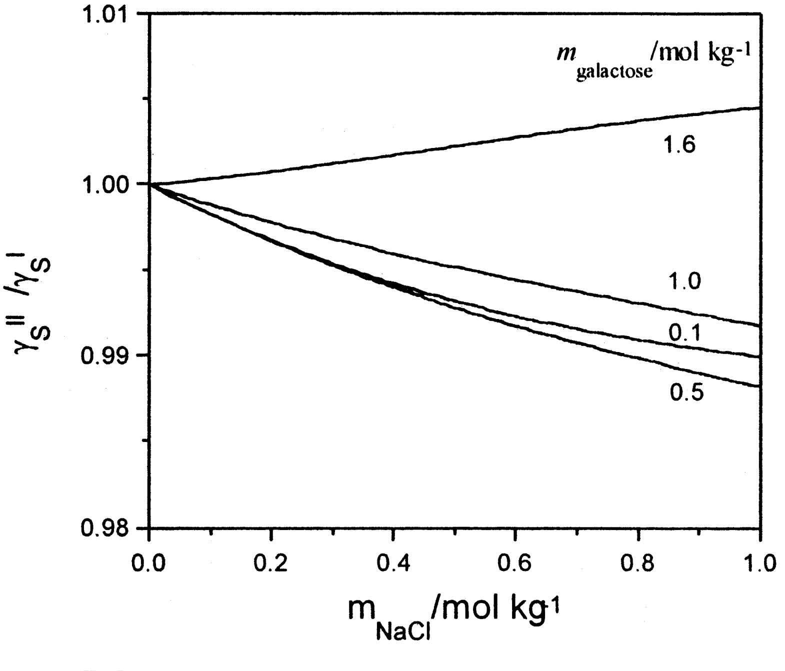

Fig. 3. Dependence of the ratio ($\gamma_S^{II}/\gamma_S^{I}$) of the activity coefficients of D-galactose in the presence and absence of NaCl on the molalities of NaCl and D-galactose at 298.15 K.

Interactions of NaCl with saccharides and their stereochemistry.—According to the McMillan–Mayer theory, the transfer Gibbs free energy of electrolyte (say NaCl) from water (W) to aqueous saccharide solutions (W + S) may be expressed by [6,14,15]

$$\begin{aligned}\Delta_t G_E(W \rightarrow W + S) &= \mu_E(m_E, m_S) - \mu_E^0(m_E) \\ &= \nu RT \ln(\gamma_\pm^{II}/\gamma_\pm^{I}) \\ &= 2\nu g_{ES} m_S + 6\nu^2 g_{EES} m_E m_S + 3\nu g_{ESS} m_S^2 \\ &\quad + 12\nu^3 g_{EEES} m_E^2 m_S + 12\nu^2 g_{EESS} m_E m_S^2 \\ &\quad + 4\nu g_{ESSS} m_S^3 \qquad (10)\end{aligned}$$

where $\mu_E(m_E, m_S)$ and $\mu_E^0(m_E)$ are the chemical potentials of electrolyte in E–S–W and E–W

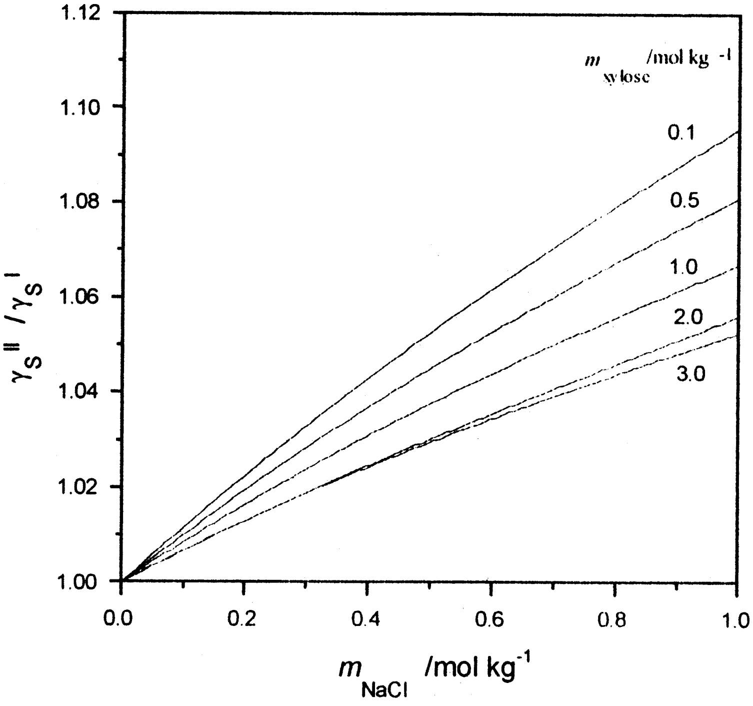

Fig. 4. Dependence of the ratio $(\gamma_S^{II}/\gamma_S^{I})$ of the activity coefficients of D-xylose in the presence and absence of NaCl on the molalities of NaCl and D-xylose at 298.15 K.

systems, respectively. The parameters such as g_{ES}, g_{EES} and g_{EEES} are pair, triple and quadruple interaction Gibbs free-energy parameters that are taken into account for all new sources of non-ideality in the ternary system. Here, the higher-order terms have been neglected. This relation has been used to analyze the interactions of electrolytes and non-electrolytes in water by some authors [6,14,15]. For example, Zhuo and co-workers [6] used it to treat the interactions of HCl with some saccharides. Comparison of this equation with Eq. (6) gives

$$RTC_1 = 2\nu g_{ES} \quad (11)$$

and other parameters in Eq. (10) have the corresponding relations to the parameters in Eq. (6). Additionally, as both m_S and m_E approach zero, rearrangement of Eq. (9) gives

$$\ln (\gamma_S^{II}/\gamma_S^{I})/m_E = C_1 = k_S \quad (12)$$

where k_S is the salting constant. Therefore, C_1 represents the pair interaction between NaCl and saccharide at infinite dilution and provides some insight for the development of theoretical models. The C_1 values presented in Table 5 indicate that NaCl has salt-out effects for glucose, xylose and arabinose and a salt-in effect for galactose in water.

Although glucose and galactose are hexoses and xylose and arabinose are pentoses, the C_1 value for glucose is approximately that for xylose, and both the absolute values of C_1 for galactose and aribinose are very small. The values for the former are markedly larger than

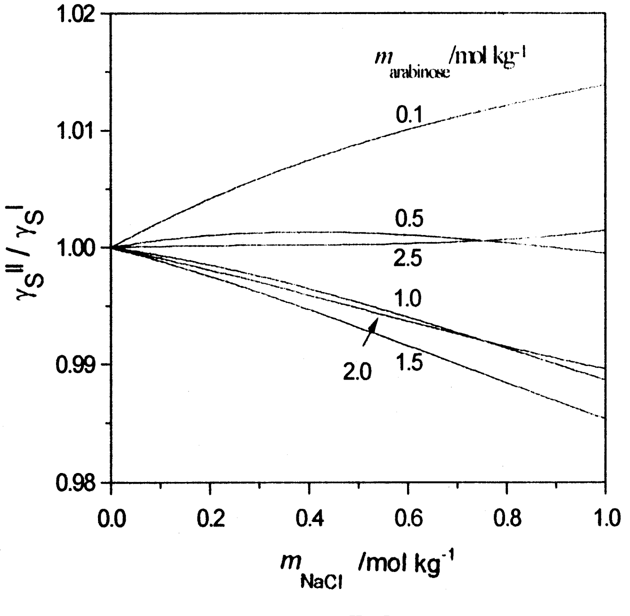

Fig. 5. Dependence of the ratio $(\gamma_S^{II}/\gamma_S^{I})$ of the activity coefficients of D-arabinose in the presence and absence of NaCl on the molalities of NaCl and D-arabinose at 298.15 K.

for the latter. Similar features have been found for the HCl–saccharide–water systems [6]. Evidently, these features arise from the difference in their stereochemistry.

Based on the studies of kinetic medium effects and volumetric properties of saccharides, Galema et al. [16] concluded that the hydration of a saccharide is mostly dependent on the relative position of the OH-4 in conjunction with its next nearest neighbor (the OH-2) in the pyranose ring (dominant conformer). The conformers with an axial OH-4 and equatorial OH-2 are the least compatible with the three-dimensional hydrogen-bonded structure of water. Similar conclusions were also made by Barone et al. [17]. The dominant conformation of D-glucose and D-xylose in water is 1e2e3e4e, whereas that of D-galactose and D-arabinose is 1e2e3e4a. Therefore, D-glucose and D-xylose fit better into the structure of water than D-galactose and D-arabinose. The hydrogen bonds of the former with water are stronger than those of the latter. Evidently, the dehydration of D-glucose and D-xylose should require more energy than that of D-galactose and D-arabinose as they interact with NaCl in water. Consequently, the C_1 values for glucose and xylose are larger than those for galactose and arabinose.

It is very interesting to note that the difference (-0.031 kg mol^{-1}) between C_1 (glucose) and C_1 (xylose) is almost equal to that (-0.046 kg mol^{-1}) between C_1 (galactose) and C_1 (arabinose). The average (-0.039 kg mol^{-1}) of these two differences can be considered to be the value of C_1(CHOH, exo), i.e., the contribution of the exocyclic CHOH group to C_1 in the chair ring of saccharide molecules. That is to say the interaction of saccharide with NaCl can be divided into group contributions, where a hexose molecule is divided into a ring and exocyclic CHOH group. The negative C_1(CHOH, exo) value means that the interaction between (CHOH, exo) and NaCl in water is thermodynamically attractive. These group parameters are possibly used to predict the interactions of polysaccharides with NaCl in water.

4. Conclusions

Activity coefficient data for the NaCl–monosaccharide (D-glucose, D-xylose, D-galactose and D-arabinose)–water systems were measured using electrochemical cells with an Na ISE versus Cl ISE as the reference electrode. Comparison of the thus measured results with those obtained by another type of cell using Ag–AgCl as the reference electrode shows quite good agreement. This means that the method used in this work is reliable and should lend itself to application in many ternary systems containing electrolytes. However, the measured data for the systems in which the electrolyte–nonelectrolyte interactions are very weak, such as NaCl–galactose and NaCl–arabinose, may have larger relative error.

The C_1 parameter in Eq. (6) is also the salting constant. It can be seen from the C_1 values that D-glucose and D-xylose have larger salt-out effects, whereas D-arabinose only has a small salt-out effect and D-galactose has a small salt-in effect by NaCl. The interactions of these monosaccharides with NaCl in water are mainly controlled by their stereochemistry. The C_1(CHOH, exo) value was evaluated and shows that the interaction of an exocyclic CHOH group in the chair conformation with NaCl contributes a negative value to C_1 for the NaCl–saccharide–water systems at 298.15 K.

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