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Activity Coefficients of NaCl in Fructose + Water at 298.15 K

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The mean ionic activity coefficients of NaCl in fructose + water mixtures were experimentally determined at 298.15 K from electromotive force measurements of the following electrochemical cell containing two ion-selective electrodes (ISE): Na−ISE|NaCl(m),fructose(w),H_2O(1−w)|Cl−ISE. The molality (m) varied between (0.005 and 3.5) mol kg^{-1}, while the mass fraction of fructose in the mixture (w) was 0, 0.1, 0.2, 0.3, and 0.4. The emf values were analyzed using different models which employed extended Debye−Hückel equations and those of Pitzer, Scatchard, and Sen for describing the variations in activity coefficients with concentration. Results obtained with the different models were in good agreement. The interaction parameters of each model were comparatively analyzed with those of other similar systems reported in the literature, and discussion is presented concerning their variation with properties of the medium, particularly the dielectric constant. The free energy of transfer of the NaCl from the water to the mixed solvent was determined and its variation with the composition of the solvent is discussed in terms of ion−ion and ion−solvent interactions. Also determined was the primary hydration number of the NaCl, which was compared with results from the literature. Finally, the parameters of interaction g_{ij} and salting constant k_s were estimated.

1. Introduction

It is well known that in recent decades there has been a marked increase in interest in the understanding of thermodynamic properties of multicomponent electrolytic systems, particularly for those which, due to their composition, are important in industrial, biological, or environmental terms.

Within these thermodynamic properties, the activity coefficients remain as one of the properties most often determined in areas as diverse as environmental chemistry (studies of wastewater pollution), chemical oceanography, metallurgy, petroleum, paper, and others fields. This is also true for studies related to the desalinization of seawater, crystallization of salts from natural brines, and recovery of geothermal energy, as well as applications of biochemical interest involving biological fluids which often consist of complex multicomponent electrolyte solutions.

Both activity coefficients and other related properties such as osmotic coefficients, solvent activity, and Gibbs free energy of the mixture (or of transfer) allow us to analyze the ion−solvent and ion−ion interactions occurring in the medium, as well as the structural implications played by the different components.

Within multicomponent systems, those of the type electrolyte + sugar + water are especially important for understanding the behavior of sugars in living organisms. Relatively few studies have been made, however, which contribute thermodynamic data on these systems, especially at high concentrations. Among these, the more notable are those of Morel et al.,[1−3] Wang et al.,[4−12] Hu et al.,[13,14] and Gregory and McTigue.[15] Of these studies, only one[8] (despite the importance of fructose) gives data for HCl + D-fructose + H_2O system.

D-Fructose, $C_6H_{12}O_6$ (levulose or fruit sugar), is widely used in the food industry. It is known to be the sweetest natural sugar, with relative sweetness of about 1.8 to 2 times that of sucrose and 2.5 times that of D-glucose.[16] For this reason, it is more widely employed than the other sugars in calorie-reduced food products.

Among the more notable physical properties of D-fructose is its high solubility in water at ambient temperature. This makes it difficult to recover by crystallization from fructose-rich aqueous syrups. Here, precise knowledge of the numerical values of activity coefficients in systems of this type are of special importance for the design and modeling of separation processes where phase equilibria are involved.

The present study includes the experimental determination of mean ionic activity coefficients in aqueous NaCl solutions containing fructose in an attempt to provide fundamental knowledge on ionic interactions in electrolyte + sugar + water solutions in relation to the structure and properties of the medium.

The molality of NaCl varied betwen (0.005 and 3.5) mol kg^{-1} mixed solvent, while the mass fractions of fructose studied were 0, 0.1, 0.2, 0.3, and 0.4. Measurements of electromotive force in the experiments were made using ion-selective electrodes (ISE), one for the sodium ion and one for the chlorine ion. The temperature was maintained constant at 298.15 K.

2. Experimental Section

D(−)-Fructose (Merck, for microbiology) was dried in vacuo at 340 K for 5 days before use. NaCl (Merck, pro analysis), was also dried in vacuo at 373 K for 5 d. Both were stored over silica gel in a desiccator and used without further purification. For each set of experiments (corresponding to a mass fraction of D-fructose), working solutions were obtained by adding successive known masses of solid NaCl to a solution previously prepared of D-fructose and double-distilled water ($k = 5 \times 10^{-7}$ S cm^{-1}). The precision of the molality was estimated to be about ±0.0001. The solutions were continually stirred with a magnetic stirrer.

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Table 1. Values of the Molality (m) and Electromotive Force (E) for the Cell Na−ISE|NaCl(m),Fructose(w),H_2O(1−w)|Cl−ISE and Ionic Mean Activity Coefficients (γ) Calculated for NaCl in the Different Fructose + H_2O Mixtures at 298.15 K

$w = 0$			$w = 0.1$			$w = 0.2$			$w = 0.3$			$w = 0.4$		
($X_{\text{Fru}} = 0.00000$)[a]			($X_{\text{Fru}} = 0.01099$)[a]			($X_{\text{Fru}} = 0.02439$)[a]			($X_{\text{Fru}} = 0.04109$)[a]			($X_{\text{Fru}} = 0.06250$)[a]		
m	$-E$		m	$-E$		m	$-E$		m	$-E$		m	$-E$	
mol·kg^{-1}	mV	γ	mol·kg^{-1}	mV	γ	mol·kg^{-1}	mV	γ	mol·kg^{-1}	mV	γ	mol·kg^{-1}	mV	γ
0.01993	47.62	0.873	0.01743	46.69	0.879	0.01691	50.86	0.872	0.005630	5.06	0.922	0.01238	50.30	0.867
0.03881	79.26	0.839	0.08484	119.75	0.768	0.03711	86.91	0.812	0.03496	89.90	0.798	0.03869	101.87	0.774
0.04500	86.13	0.829	0.1000	127.39	0.759	0.09270	128.74	0.745	0.07265	123.86	0.753	0.06059	122.15	0.739
0.05634	96.51	0.814	0.1822	155.04	0.720	0.1000	132.34	0.742	0.1000	138.46	0.731	0.09608	143.45	0.711
0.1000	122.99	0.775	0.2690	173.25	0.700	0.2300	170.44	0.687	0.1627	160.80	0.700	0.1000	144.86	0.702
0.1031	124.34	0.772	0.3569	186.27	0.683	0.3779	193.53	0.661	0.3047	189.79	0.664	0.2184	179.69	0.641
0.1339	136.20	0.752	0.4839	200.60	0.669	0.5000[b]	206.98	0.652	0.5000[b]	212.77	0.638	0.3676	204.26	0.620
0.2039	155.87	0.729	0.5000[b]	202.07	0.667	0.6334	218.27	0.644	0.6978	228.77	0.628	0.5000[b]	218.25	0.602
0.3519	181.34	0.700	0.6785	216.42	0.653	1.0798	244.40	0.634	1.1949	255.46	0.622	0.6956	234.06	0.592
0.4687	194.66	0.685	1.1146	241.31	0.651	1.3855	258.28	0.651	1.5993	272.41	0.651	1.2325	263.62	0.600
0.5000[b]	197.79	0.683	1.5483	258.61	0.661	1.6100	266.41	0.658	1.9524	283.53	0.665	1.8313	285.46	0.623
0.5978	206.08	0.673	2.3649	281.83	0.685	2.2827	286.68	0.694	2.3888	295.82	0.693	2.5874	307.13	0.677
0.8146	219.63	0.646	2.7759	291.98	0.714	2.8453	300.24	0.728	3.0071	311.05	0.745	3.3357	323.80	0.732
1.5150	251.98	0.660	3.5844	308.36	0.765	3.3396	311.57	0.776	3.4592	320.74	0.784	3.7493	334.14	0.799
2.3469	275.09	0.674												
3.3646	297.10	0.727												

[a] Mole fraction. [b] Molality of reference.

Na−ISE (mod. 6.0501.100) and Cl−ISE (mod. 6.0502.120) were obtained from Metrohm Corp. A double-wall vessel Metrohm cell was used to hold the electrodes and the solution. The temperature in the cell was maintained at (25.00 ± 0.02) °C using a Hetofrig model 04 PT thermoregulator and a platinum-resistance thermometer (Guildline model 9540) was used to record the temperature.

The emf measurements were carried out with a 614 Keithley Electrometer having an inner impedance greater than 5×10^{13} Ω with a resolution of ±0.1 mV. To obtain more precise emf readings, the 2-V analog output of the electrometer was connected to a Keithley model 197A Microvolt DMM with an input greater than 10^{12} Ω and resolution of ±0.01 mV.

Depending on the concentration of the NaF studied, and independent of the w of fructose, it was observed that, after approximately 45 min, the variation of the potential with time was very small (around 0.10−0.15 mV per 10−15 min.). The reading at this moment was considered to represent the cell in equilibrium.

3. Results

Activity coefficients values for NaCl in w fructose + (1 − w) water mixtures from $w = 0$ to 0.4 were determined from the *emf* measurements of galvanic cells without transference. The cell used were of the type

$$\text{Na−ISE}|\text{NaCl}(m),\text{fructose}(w),\text{H}_2\text{O}(1-w)|\text{Cl−ISE} \quad \text{(I)}$$

combined with that of the reference

$$\text{Na−ISE}|\text{NaCl}(m_\text{r}),\text{fructose}(w),\text{H}_2\text{O}(1-w)|\text{Cl−ISE} \quad \text{(II)}$$

to eliminate the asymmetry potential of the electrodes. In these cells, m and m_r are the molality of NaCl in the working and reference solutions, respectively. w is mass fraction of the fructose in the mixture.

Applying the equation of Nernst−Nikolsky to cells I and II and subtracting the following expression is obtained

$$\Delta E = E_\text{I} - E_\text{II} = -2k \log \frac{m\gamma}{m_\text{r}\gamma_\text{r}} \quad (1)$$

where E is the emf of the cell, $k = (\ln 10)RT/F$ is the theoretical Nernst slope, and γ and γ_r are the mean ionic activity coefficients of NaCl at molalities m and m_r, respectively. E values for different fructose + water mixtures as a function of the NaCl molalities are shown in Table 1.

Since the coefficients of activity of the NaCl in pure water are precisely known,[17] the values of E that appear in Table 1 for $w = 0$ allow calibration of the electrode system using expression 1. A very good linear relationship is obtained when plotting ΔE vs $-2 \log(m\gamma/m_r\gamma_r)$. The value obtained by applying least-squares regression analysis is $k = 58.07 \pm 0.09$ mV, with a standard deviation of 0.38 mV. This value of k differs from the theoretical value by about only 1.8%. This well exceeds acceptability criteria for a system containing two ISEs. In this calculation, it has been assumed that $k_{\text{Na}} \cong k_{\text{Cl}} \cong k \cong (k_{\text{Na}} + k_{\text{Cl}})/2$.[12]

To calculate γ values for different molalities of NaCl in the sugar + water mixture, it was important to determine the value of γ_r. For this, we employed different theoretical models to describe the variation of the activity coefficients with concentration.

For 1:1 electrolyte, the Debye−Hückel extended equation can be written as[18,19]

$$\log \gamma = -\frac{Am^{1/2}}{1 + Bam^{1/2}} + cm - \log(1 + 0.002mM) \quad (2)$$

where a represented the ion size parameters, c the ion-interaction parameter, and M the average molecular mass of mixed solvent. A and B represent the Debye−Hückel constant given by[18,19]

$$A = 1.824710^6 d^{1/2}/(\epsilon_\text{r}T)^{3/2}\ \text{kg}^{1/2}\ \text{mol}^{-1/2} \quad (3)$$

$$B = 50.2901 d^{1/2}/(\epsilon_\text{r}T)^{1/2}\ \text{kg}^{1/2}\ \text{mol}^{-1/2}\ \text{Å}^{-1} \quad (4)$$

where d stands for the density, ϵ_r the relative permittivity (static dielectric constant) of the solvent, and T the temperature. The density values were taken from Cerdeiriña et al.[20] The relative permittivity was estimated by applying the equation proposed by Hasted et al.[21] that establishes the linear dependence of the relative permittivity on the solute concentration and the values reported by Saito et

Table 2. Values of Average Molecular Mass (M), Relative Permittivity (ϵ_r), Densities (d), Debye–Hückel (A and B), and Pitzer (A_ϕ) Constants as a Function of the Mass Fraction and Mole Fraction of Fructose in the Mixture Fructose + Water at 298.15 K

w	X_{Fru}	M	ϵ_r	d/(g·cm^{-3})	A^a	B^b	$A_\phi{}^c$
0	0.00000	18.015	78.38	0.9971	0.5100	0.3285	0.3915
0.1	0.01099	19.797	76.40	1.0369	0.5403	0.3393	0.4147
0.2	0.02439	21.970	73.99	1.0796	0.5785	0.3518	0.4440
0.3	0.04109	24.678	70.97	1.1255	0.6286	0.3667	0.4825
0.4	0.06250	28.149	67.12	1.1745	0.6983	0.3852	0.5360

[a] In kg$^{1/2}$·mol$^{-1/2}$. [b] In kg$^{1/2}$·mol$^{-1/2}$·Å^{-1}. [c] In kg$^{1/2}$·mol$^{-1/2}$.

Table 3. Summary of the Values Obtained for the Parameters of the Debye–Hückel Equation in the Different Fructose + Water Mixture at 298.15 K

w	γ_r	a/Å	c/kg mol^{-1}	σ/mV
0	0.680 ± 0.003	3.8 ± 0.1	0.057 ± 0.002	0.38
0.1	0.668 ± 0.003	3.8 ± 0.1	0.067 ± 0.002	0.28
0.2	0.655 ± 0.003	3.6 ± 0.1	0.081 ± 0.002	0.36
0.3	0.639 ± 0.003	3.6 ± 0.1	0.087 ± 0.002	0.43
0.4	0.605 ± 0.004	3.5 ± 0.1	0.096 ± 0.003	0.55

al.[22] for the proportional constant, δ (concentration expressed in mole fraction, X_{Fru}).

The values used for d and ϵ_r as well as the Debye–Hückel constants, A and B, are listed in Table 2 together with the values of M (average molecular mass of mixed solvent).

By combination of eqs 1 and 2, the values of a, c, and γ_r can be optimized for each fructose + water mixture studied. These values with their standard deviations as well as the standard deviation of the fit are shown in Table 3.

Another way to evaluate the γ_r values is using the Pitzer equation. For 1:1 electrolyte, the Pitzer equation can be written as[23,24]

$$\ln \gamma = f^{\gamma} + B^{\gamma} m + C^{\gamma} m^2 \tag{5}$$

where

$$f^{\gamma} = -A_\phi \left[\frac{m^{1/2}}{1 + b m^{1/2}} + \frac{2}{b} \ln(1 + b m^{1/2}) \right] \tag{6}$$

$$B^{\gamma} = 2\beta^0 + \frac{2\beta^1}{\alpha^2 m} [1 - (1 + \alpha m^{1/2} - \alpha^2 m/2) \exp (\alpha m^{1/2})] \text{ kg}^{1/2} \text{ mol}^{-1/2} \tag{7}$$

In these equations α and b are assumed fixed parameters with values of 2.0 kg$^{1/2}$ mol$^{-1/2}$ and 1.2 kg$^{1/2}$ mol$^{-1/2}$, respectively,[23–25] 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

$$A_\phi = 1.400610^6 d^{1/2}/(\epsilon_r T)^{3/2} \text{ kg}^{1/2} \text{ mol}^{-1/2} \tag{8}$$

with all symbols having the usual meaning. In the last column of Table 2 are shown the A_ϕ values for the fructose + water system at 298.15 K.

By combination of eq 1 and eqs 5–7, the γ_r, β^0, β^1, and C^γ values can be optimized for each fructose + water mixture studied. These values are summarized in Table 4 together with their standard deviations, as well as the standard deviation of the fit.

Two further equations were employed in order to obtain a good estimation of γ_r. Here, for a 1:1 electrolyte, the Scatchard et al.[26,27] equation can be written as

$$\ln \gamma = \frac{1}{2} \left[\frac{2 S m^{1/2}}{1 + a m^{1/2}} + 2 a^{(1)} m + \frac{3}{2} a^{(2)} m^2 + \frac{4}{3} a^{(3)} m^3 + \frac{5}{4} a^{(4)} m^4 \right] \tag{9}$$

where $S = -3A_\phi$ and a, $a^{(1)}$, $a^{(2)}$, $a^{(3)}$, and $a^{(4)}$ are the characteristic interaction parameters of the model. Furthermore, the Sen et al.[28,29] equation can be written as

$$\log \gamma = A_1 m^{1/2} + A_2 m + A_3 m^{3/2} + A_4 m^2 + \cdots \tag{10}$$

where A_i, at a given temperature, represents parameters dependent on the relative permittivity, ϵ_r, and density, d; they should not be assumed a priori but rather obtained from the fit. This is one of the advantages of the latter method as compared with the others where it is necessary to know some parameters a priori which depend on the properties of the medium.

By combination of eqs 1 and 8 or 1 and 9, the parameters representing each method may be optimized together the values of γ_r. These are shown in Table 5 together with those obtained from the other methods used. The values of the other adjustable parameters are not included, as they do not provide any additional significant information.

4. Discussion

Despite the broad range of concentrations studied, Table 3 shows that the Debye–Hückel equation permits making fits within the limits of error expected for these types of systems. An almost constant value of (3.7 ± 0.1) Å was obtained for the ion size parameter a, a value similar to that obtained by Wang et al.[6] for the glucose + water (3.5 ± 0.1) Å and sucrose + water (3.8 ± 0.1 Å) systems. Figure 1 shows parameter c as a function the inverse of the relative permittivity for the three systems, showing a tendency toward similarity. The values for ion-interaction parameter c representing the fructose + water and glucose + water[6] systems are very similar and slightly higher than those reported for the sucrose + water[6] system. It appears reasonable to suppose that this is related to the structure

Table 4. Summary of the Values Obtained for the Parameters of the Pitzer Equation in the Different Fructose + Water Mixture 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	0.682 ± 0.003	0.0794 ± 0.0104	0.2499 ± 0.0444	−0.0003 ± 0.0048	0.38
	0.682 ± 0.003	0.0788 ± 0.0018	0.2521 ± 0.0201		0.36
0.1	0.668 ± 0.003	0.1049 ± 0.0070	0.2286 ± 0.0351	−0.0063 ± 0.0031	0.30
	0.671 ± 0.003	0.0907 ± 0.0015	0.2905 ± 0.0207		0.34
0.2	0.654 ± 0.003	0.1290 ± 0.0102	0.2061 ± 0.0473	−0.0101 ± 0.0046	0.37
	0.658 ± 0.003	0.1070 ± 0.0021	0.2985 ± 0.0251		0.43
0.3	0.638 ± 0.004	0.1348 ± 0.0109	0.2825 ± 0.0527	−0.0086 ± 0.0048	0.44
	0.641 ± 0.004	0.1153 ± 0.0023	0.3663 ± 0.0275		0.48
0.4	0.605 ± 0.005	0.1451 ± 0.0138	0.3305 ± 0.0671	−0.0078 ± 0.0057	0.59
	0.608 ± 0.004	0.1265 ± 0.0025	0.4113 ± 0.0340		0.61

Table 5. Summary of the γ_r Values for NaCl Obtained for Different Methods in Fructose + Water Mixture at 298.15 K and Average Value, $\langle\gamma_r\rangle$

	D–H[a]		P3[a]		P2[a]		SC[a]		SE[a]		
w	γ_r	σ/mV	γ_r	σ/mV	γ_r	σ/mV	γ_r	σ/mV	γ_r	σ/mV	$\langle\gamma_r\rangle$
0	0.680 ± 0.003	0.38	0.682 ± 0.003	0.38	0.682 ± 0.003	0.36	0.682 ± 0.003	0.38	0.689 ± 0.012	0.40	0.683 ± 0.003
0.1	0.668 ± 0.003	0.28	0.668 ± 0.003	0.30	0.671 ± 0.003	0.34	0.664 ± 0.004	0.27	0.663 ± 0.008	0.27	0.667 ± 0.003
0.2	0.655 ± 0.003	0.36	0.654 ± 0.003	0.37	0.658 ± 0.003	0.43	0.650 ± 0.004	0.33	0.643 ± 0.008	0.31	0.652 ± 0.006
0.3	0.639 ± 0.003	0.43	0.638 ± 0.004	0.44	0.641 ± 0.004	0.48	0.638 ± 0.003	0.43	0.636 ± 0.009	0.50	0.638 ± 0.002
0.4	0.605 ± 0.004	0.55	0.605 ± 0.005	0.59	0.608 ± 0.004	0.61	0.599 ± 0.004	0.47	0.591 ± 0.010	0.45	0.602 ± 0.007

[a] D–H, Debye–Hückel; P3 and P2, Pitzer with 3 or 2 parameters, respectively; SC, Scatchard; SE, Sen.

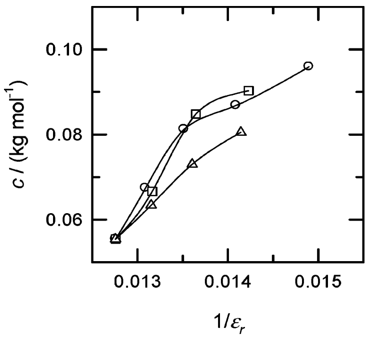

Figure 1. Plot of Debye–Hückel ion-interaction parameter c vs $1/\epsilon_r$. ○, fructose + water; □, glucose + water;[6] △, sucrose + water.[6]

of the sugar, since while the disaccharide sucrose, formed of one molecule of fructose linked to one of glucose, has a relatively stable configuration in dilute aqueous solution, the monosaccharide D-glucose reaches an equilibrium between two conformers (β-D-glucopyranose and α-D-glucofuranose), whereas the monosaccharide D-fructose presents five different forms in the same conditions of concentration in water (α-pyranose, β-pyranose, α-furanose, β-furanose, and open chain).

Regarding the Pitzer equation, Table 4 shows that, although the concentration of electrolyte is greater than 2.0 mol kg^{-1}, consideration of parameter C^{γ} does not cause a notable improvement of the standard deviations of the fit. As is well known in Pitzer thermodynamic treatments of electrolyte solutions, the electrostatic term is a constant for all electrolytes of the same valence type and does not take into consideration the differences in the solvation of the ions, ionic sizes, and the distance of closest approach. The second virial coefficient is a complicated function of many interactions and β^0 and β^1 parameters, which govern the coefficient, absorbed the effect of these factors. In Figure 2 the β^0 and β^1 values obtained for the fit are plotted against the reciprocal of relative permittivity of the three sugar + water mixtures which are being compared. It is interesting to note that both β^0 (which can be identified with the total binary ionic interactions) and β^1 (which can be identified with the interactions between un-like-charged ions) become linear with $1/\epsilon_r$. This is the typical profile observed with 1:1 electrolytes[6,23,30] both in water as mixed solvents as amply documented by Gupta.[30]

As can be noted from Table 5, the values of γ_r obtained by all the methods are in good agreement with each other. The last column shows the calculated mean values, where a maximum uncertainty value of about 1% can be noted.

With these mean values for γ_r, values for γ have been calculated which appear in Table 1 for each molality of NaCl and percentage of fructose studied. Despite the wide molality range studied, the standard deviation of the activity coefficients between our values and those reported in the literarure[17] was calculated to be ±0.004 in pure water, which shows very good agreement between both series of data. We have assumed that the other percentages have a similar uncertainty.

Figure 3 is an example of the dependence of log γ vs $m^{1/2}$ at various percentages of sugar in the solvent mixture. For all systems explored, these curves show a comparable trend and their typical minimum shifts toward lower log g values as the percentage of sugar increases (relative permittivity of the solvent mixture decrease). It is also observed that the greatest difference in log γ in comparison with its value in pure water is for mass fraction 0.3 in glucose, while the 0.1 of fructose has little influence on the value of log γ. The values for the sucrose + water system are intermediate between those of the fructose + water and glucose + water systems.

The standard free energy of transference, ΔG_t^0 (or "medium effect"), is probably one of the magnitudes most commonly used for the understanding of differences in behavior between a dissolved solute in a pure solvent and that of a mixture of solvents. As is well known, this parameter is defined as the difference between the standard free energies per mole of electrolyte in a pure solvent (usually water) and another pure or mixed solvent and

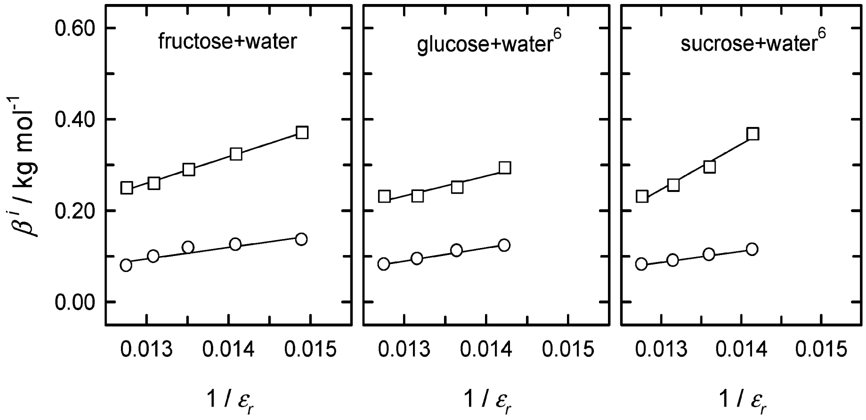

Figure 2. ○, β^0; □, β^1 for NaCl in sugar + water mixtures at 298.15 K as a function of inverse of relative permittivity.

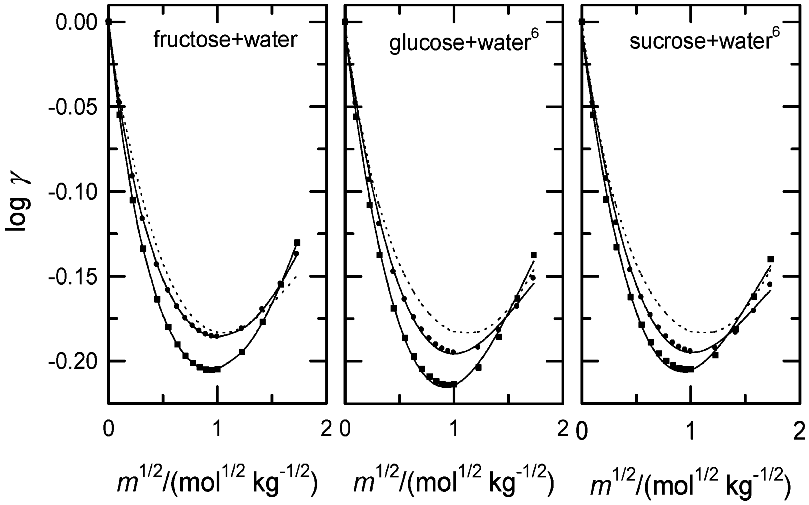

Figure 3. Plot of log γ vs $m^{1/2}$ for NaCl in sugar + water at 298.15 K. Dashed line, $w = 0$; ●, $w = 0.1$; ■, 0.3.

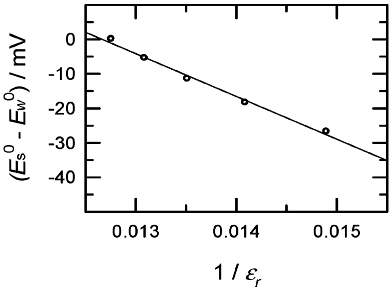

Figure 4. Test of the Born condition for the variation of $(E_S^0 - E_W^0)$ on the inverse of relative permittivity for the mixed solvents.

Table 6. Values of Standard Gibbs Energy of Transference, ΔG_t^0/(kJ mol^{-1}), for NaCl in Different Sugar + Water Mixtures at 298.15 K

w	fructose + water	glucose + water[5]	sucrose + water[4]
0	0.00	0.00	0.00
0.1	0.53	0.65	0.62
0.2	1.11	1.39	1.39
0.3	1.78	2.20	2.17
0.4	2.59	(2.89)[a]	(2.87)[a]

[a] Extrapoled value.

represents the change in solvation at infinite dilution when the solute is transferred from one solvent to another. Considering the ions to be rigid spheres with radius r_+ and r_-, in a uniform dielectric medium, ΔG_t^0 can be calculated by using the well-known expression of Born

$$\Delta G_t^0 = -nF(E_s^0 - E_w^0) = -\frac{Ne^2}{2}\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{11}$$

where s and w stand for solvent mixture and pure water, respectively, and all the other symbols have their usual meaning. To calculate ΔG_t^0, it is necessary to know the values of the standard potential of the cell for each percentage studied. These may be obtained beginning with values for E, m, and γ as listed in Table 1 and applying the expression

$$E = E^{0*} - 2k \log m\gamma \tag{12}$$

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

$$E^{0*} = E^0 + E^{\mathrm{asym}} = E^0 + (\epsilon_{\mathrm{Na}}^{\mathrm{asym}} + \epsilon_{\mathrm{Cl}}^{\mathrm{asym}}) \tag{13}$$

Since E^{asym} tends to be a small and independent value for the composition of the solvent, we may suppose[31,32] that $(E_s^0{*} - E_w^0{*}) \cong (E_s^0 - E_w^0)$. It is seen from eq 11 that the plot of $(E_s^0 - E_w^0)$ against $1/\epsilon_r$ should be a straight line. In effect, Figure 4 demonstrates this relation, where a correlation index of 0.9995 is obtained, having a standard deviation of less than 1 mV.

Once $(E_s^0 - E_w^0)$ has been evaluated, the values for ΔG_t^0 are then calculated. These values appear in Table 6 for the fructose + water system together with those obtained from literature references for the glucose + water[5] and sucrose + water[4] systems. It is notable in all cases that the values of ΔG_t^0 become more positive with increasing percentages of sugar, which shows that the transference of NaCl from water to the water−sugar mixtures studied here is a not spontaneous process.

Since ΔG_t^0 is fundamentally related to the changes in solvation undergone by the electrolyte in the presence of the sugar, it is of interest to calculate the hydration number of the NaCl in each case. For this we used the equation of Feakins and French[33] which allows calculation of the primary hydration number of the electrolyte based on the dependency which exists between the standard potential of the cell and the logarithm of the weight fraction of water in the mixture according to

$$\Delta E^0 = E_s^0 - E_w^0 = n_{\mathrm{hyd}} k \log w \tag{14}$$

Figure 5 shows a plot of ΔE^0 vs $-k \log w$ where an excellent correlation is observed and is linear in all cases. The values found for n_{hyd} were 2.1 ($r = 0.9999$) for the fructose + water mixture, 2.5 ($r = 0.9999$) for glucose + water, and 2.5 ($r = 0.9996$) for sucrose + water. These values of n_{hyd} are somewhat low compared with those obtained from the literature,[33−35] which varied between 4.0 and 8.0 depending on the measurement method employed. Though the relation between the hydration and stereochemistry of carbohydrates, especially when electrolyte is present, is highly complicated,[8] the explanation for the low hydration of NaCl in the presence of sugars may be due to the competition for hydration between sugars and NaCl. According to Mathlouthi,[16,36] with sucrose for example, the hydration number may vary between 1 and 21 depending on authors and methods, with the most probable values being from 5 to 6 H_2O molecules per sucrose molecule. With glucose and fructose, there is slight difference, with about 2.7 for

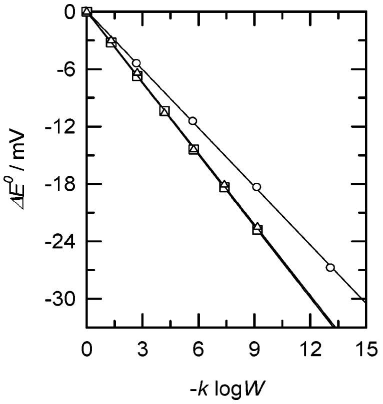

Figure 5. Variation of standard emf with weight fraction of water for: ○, fructose + water; □, glucose + water;[5] and △, sucrose + water[6] at 298.15 K.

glucose and 3.2 for fructose. Basing the hydration number on the ratio of H_2O molecules per OH on the periphery of the sugar, glucose and sucrose seem comparable, whereas fructose has a higher hydration number. This higher affinity of fructose for water is well known[16,36] and may explain that n_{hyd} for NaCl would be slightly less in fructose + water than in glucose + water or sucrose + water and, thus, that ΔG_t^0 may also be slightly less for the fructose + water mixture than for the glucose + water and sucrose + water mixtures. The differences are not very large given that, despite a high affinity, it is also known that although fructose retains a higher number of water molecules around its molecule, this water of hydration is more mobile and might be exchanged with bulk water easily.

In agreement with Desnoyers et al.,[37,38] the transference free energy can be written

$$\Delta G_t(W \rightarrow W+S) = 2\nu g_{SE} m_S + 3\nu g_{SSE} {m_S}^2 + 3\nu^2 g_{SEE} m_E m_S + ... \quad (15)$$

for the electrolyte E and

$$\Delta G_t(W \rightarrow W+E) = 2\nu g_{SE} m_E + 3\nu^2 g_{SEE} {m_E}^2 + 3\nu g_{SSE} m_E m_S + ... \quad (16)$$

for the sugar S, with m_E and m_S the molalities of NaCl and fructose defined per kg of pure water; n is the number of ions into which E dissociates, and g_{ij} and g_{ijk} are pair and triplet interaction parameters.

For standard functions, the higher terms in m_S or m_E on the right-hand side of eqs 15 and 16 vanish.[38] Thus for the electrolyte we obtain

$$\Delta G_t^0 = -nF(E_S^0 - E_W^0) = 2\nu g_{SE} m_S + 3\nu^2 g_{SSE} {m_S}^2 + ... \quad (17)$$

At a low concentration of sugar, a least-squares regression of $\Delta G_{t,X}^0/m_s$ against m_s yields[4,38] a value of g_{SE}. $\Delta G_{t,X}^0$ is the transference free energy on the mole fraction scale, namely[4]

$$\Delta G_{t,x}^0 = \Delta G_{t,m}^0 + \nu RT \ln(18.015/M) \quad (18)$$

According to the approach of Desnoyer et al.,[40,41] the salting constant k_s can be related to g_{SE} through the expression

$$RTk_s = 2\nu g_{SE} \quad (19)$$

Before calculating k_s, the values of g_{SE} obtained from the regression were converted[4,5] to the scale of molality (in reference to 1 kg of pure water) using the Masterton et al. equations.[39] In Table 7 are listed values of $2\nu g_{SE}$ and k_S for the fructose + water system together with those taken from the literature on other sugars.[4,5,12] In all the cases, it is verified that $-0.7 \le k_s \le 0.7$.[40] It can be seen from the k_s values that in all the systems except NaCl−galactose−water[12] the sugars have a *salting-out* effect.

Table 7. Free-Energy Interaction Coefficients g_{SE} for Some NaCl + Sugar Pairs and Salting Constants k_s in Water at 298.15 K

sugar	$2\nu g_{SE}$/J kg mol^{-2}	k_s/kg mol^{-1}
fructose	12	0.005
sucrose[a]	288	0.116
glucose[b]	207	0.084
glucose[c]	218	0.088
xylose[c]	293	0.118
arabinose[c]	55	0.022
galactose[c]	−47	−0.019

[a] Reference 4. [b] Reference 5. [c] Reference 12.

Literature Cited

(1) Morel, J.-P.; Lhermet, C. Interactions entre les Cations et les Sucres. I. *Can. J. Chem.* **1985**, *63*, 2639−2643.

(2) Morel, J.-P.; Lhermet, C.; Morel-Desrosier, N. Interactions between Cations and Sugars. IV. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2567−2571.

(3) Rongere, P.; Morel-Desrosier, N.; Morel, J.-P. Interactions between Cations and Sugar VIII. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2771−2777.

(4) Wang, J.; Liu, W.; Bai, T.; Lu, J. 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.

(5) Wang, J.; Zeng, L.; Liu, W.; Lu, J. A Thermodynamics of the Ternary System Water + Glucose + Electrolyte at 298.15 K. *Termochim. Acta* **1993**, *224*, 261−269.

(6) Wang, J.; Liu, W.; Fan, J.; Lu, J. 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.

(7) Zhuo, K.; Wang, J.; Zhou, J.; Lu, J. Thermodynamics of the Interaction of HCl with D-Glucose in Water at 278.15−318.15 K. *J. Phys. Chem. B* **1997**, *101*, 3447−3451.

(8) Zhuo, K.; Wang, J.; Cao, Y.; Lu, J. 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.

(9) Wang, J.; Zhuo, K.; Zhang, Q.; Yan, Z.; Wang, H. 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.

(10) Wang, J.; Zhuo, K.; Zhang, Q.; Lu, J.; Thermodynamics of the Interaction of HCl with D-Xylose in Water at 278.15−318.15 K. *Can. J. Chem.* **1999**, *77*, 232−236.

(11) Zhuo, K.; Wang, J.; Zhang, Q.; Yan, Z.; Lu, L. Thermodynamics of the Interaction of HCl with D-Arabinose in Water at 278.15−318.15 K. *Carbohydr. Res.* **1999**, *316*, 26−33.

(12) Zhuo, K.; Wang, J.; Wang, H. Activity Coefficients for NaCl-Monosaccharide (D-Glucose, D-Galactose, D-Xylose, D-Arabinose)-Water System at 298.15 K. *Carbohydr. Res.* **2000**, *325*, 46−55.

(13) Hu, Y.-F. Application of Mckay and Perring Equations of the Activity Coefficients of Electrolytes in Two Aqueous Nonelectrolyte-Electrolyte Systems at 298.15 K. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 913−914.

(14) Hu, Y.-F.; Liu, Y.-H.; Sun, S.-P. Isopiestic Studies on the Systems {NaCl + $BaCl_2$ + $Mannitol_{(sat)}$(aq)} and {NaCl + Glycine + $Mannitol_{(sat)}$(aq)} at the Temperature 298.15 K. *J. Chem. Thermodyn.* **2000**, *32*, 341−347.

(15) Gregory, R. E.; McTigue, P. T. Gibbs Energies of Transfer of Several Alkali-Metal Chlorides from Water to Sucrose-Water Mixtures Using Streaming Amalgam Electrodes. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 451−455.

(16) Mathlouthi, M. Relationship between the Structure and the Properties of Carbohydrates in Aqueous Solutions: Solute−Solvent Interactions and the Sweetness of D-Fructose, D-Glucose and Sucrose in Solution. *Food Chem.* **1984**, *13*, 1−16.

(17) Hamer, W. J.; Wu, Y.-C., Osmotic Coefficients and Mean Activity Coefficients of Uni-Univalent Electrolytes in Water at 25 °C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047−1099.

(18) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworth: London, 1959.

(19) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*; Reinhold: New York, 1958.

(20) Cerdeiriña, C. A.; Carballo, E.; Tovar, C. A.; Romaní, L. Thermodynamic Properties of Aqueous Carbohydrate Solutions. *J. Chem. Eng. Data* **1997**, *42*, 124−127.

(21) Hasted, J. B.; Ritson, D. M.; Collie, C. H. Dielectric Properties of Aqueous Ionic Solutions. **1948**, *16*, 1−21.

(22) Saito, A.; Miyawaki, O.; Nakamura, K. Dielectric Relaxation of Aqueous Solution with Low-Molecular-Weight Nonelectrolytes and Its Relationship with Solution Structure. *Biosci. Biotech. Biochem*. **1997**, *61*, 1831−1835.

(23) Pitzer, K. S. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem*. **1973**, *77*, 268−277.

(24) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*; CRC Press: Boca Raton, Florida, 1991.

(25) Koh, D. S. P.; Khoo, K. H.; Chan, C.-Y. The Application of the Pitzer Equation to 1−1 Electrolytes in Mixed Solvents. *J. Solution Chem*. **1985**, *14*, 635−651.

(26) Scatchard, G. The Excess Free Energy and Related Properties of Solutions Containing Electrolytes. *J. Am. Chem. Soc.* **1968**, *90*, 3124−3129.

(27) Wu, Y. C.; Rush, R. M.; Scatchard, G. Osmotic and Activity Coefficients for Binary Mixtures of Sodium Chloride, Sodium Sulphate, Magnesium Sulphate, and Magnesium Chloride in Water at 25°. I. Isopiestic Measurements on the Four Systems with Common Ions. *J. Chem. Phys.* **1968**, *72*, 4048−4053.

(28) Sen, B.; Johnson, D. A.; Roy, R. N. Computation of Standard Potential by a Polynomial Curve-Fitting Program. *J. Phys. Chem*. **1967**, *71*, 1523−1525.

(29) Roy, R. N.; Vernon, W. Standard Potentials of the Silver−Silver Chloride Electrode in *tert*-Butyl Alcohol-Water Mixtures and the Thermodynamics of Solutions of Hydrochloric Acid at Different Temperatures. *J. Chem. Soc.* **1971**, 1242−1246.

(30) Gupta, A. R. Thermodynamics of Electrolytes in Mixed Solvents. Application of Pitzer's Thermodynamic Equations to Activity Coefficients of 1:1 Electrolytes in Methanol−Water Mixtures. *J. Chem. Phys.* **1979**, *83*, 2986−2990.

(31) Bald, A. Potentiometric and Conductometric Studies of NaI Solutions in Water + 2-Propanol Mixtures at 298.15 K. *J Electroanal. Chem*. **1993**, *352*, 29−41.

(32) Hernández-Luis, F.; Vázquez, M. V.; Esteso, M. A. Activity Coefficients of NaF Methanol−Water and Ethanol−Water at 298.15 K. *J. Mol. Liq.* **2003**, *108*, 283−301.

(33) Feakins, D.; French, C. M. Standard Potentials in Aqueous Organic Media: A General Discussion of the Cell H_2(Pt)|HCl|AgCl−Ag. *J. Chem. Soc.* **1957**, 2581−2589.

(34) Basili, A.; Mussini, P. R.; Mussini, T.; Rondinini, S. Thermodynamics of the Cell:{Na_XHg_{1-x}|NaCl(m)|AgCl|Ag} in (Methanol + Water) Solvent Mixtures. *J. Chem. Thermodym*. **1996**, *28*, 923−933.

(35) Bockris, J. O'M.; Reddy, A. K. *Modern Aspect of Electrochemistry*; Plenum: New York, 1970; Vol. 1.

(36) Mathlouthi, M. Personal communication.

(37) Desnoyers, J. E.; Perron, G.; Morel, J.-P.; Avédikian, L. *Chemistry and Physics of Aqueous Gas Solutions*; Adams, W. A., Ed.; The Electrochemical Society; Pricenton: New York, 1975.

(38) Perron, G.; Joly, D.; Desnoyers, J. E.; Avédikian, L.; Morel, J.-P. Thermodynamics of the Salting Effect; Free Energies, Enthalpies, Entropies, Heat Capacities, and Volumes of the Ternary Systems Electrolyte-Alcohol-Water at 25 °C. *Can. J. Chem*. **1978**, *56*, 522−559.

(39) Masterton, W. L.; Bolocofsky, D.; Lee, T. P. Ionic Radii from Scaled Particle Theory of the Salt Effect. *J. Phys. Chem*. **1971**, *75*, 2809−2815.

(40) Long, F. A.; McDevit, W. F. Activity Coefficients of Nonelectrolyte Solutes in Aqueous Salt Solutions. *Chem. Rev*. **1952**, *51*, 119−169.

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