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Activity coefficients of NaCl in trehalose–water and maltose–water mixtures at 298.15 K

Felipe Hernández-Luis,* Eliseo Amado-González,† Miguel A. Esteso

Departamento de Química Física, Universidad de la Laguna, Tenerife, Spain

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Abstract

The ionic mean activity coefficients of NaCl in trehalose–water and maltose–water mixtures have been experimentally determined at 298.15 K from emf measurements by electrochemical cell containing ion selective electrodes (ISE):

Na-ISE|NaCl (m), sugar (Y%), H_2O ($100-Y$%)|Cl-ISE

The electrolyte molality (m) ranged between 0.01 and 3 mol kg^{-1}, approximately, and the weight percent (Y%) of sugar in the mixture of solvents between 0, 10, 20, 30 and 40%. The system is considered as an electrolyte in a mixture of solvents and the data have been analysed by using the Debye–Hückel and Pitzer equations. The results obtained with both equations are in quite agreement with each other. The variation of the fit parameter from both equations were studied relative to the change in the dielectric properties of the mixture of solvents. Standard free energy of transference were comparatively discussed in terms of ion–solvent, ion–ion interactions and the hydration of both the electrolyte and the sugar.

Keywords: Pitzer model; emf; Activity coefficients; Electrolytes; NaCl; Trehalose; Maltose; Ionic interaction

1. Introduction

There is renewed interest in the measurement of thermodynamic properties of electrolytes in mixtures of solvents. Activity coefficients are one of the most important thermodynamic properties used to analyse problems associated with the equilibria of systems in diverse areas such as environmental chemistry, geochemistry, industrial chemistry, as well as in the development of applied research work on biology, biochemistry and pharmaceutical industry.

Similar to other related values (osmotic coefficients, activity of solvents, excess free energy of mixture or transference) the activity coefficient gives us a way to analyse solvent–ion and ion–ion interactions in solutions, and it may give valuable information about the structural modifications of the different components.

Research on systems such as electrolyte–sugar–water is specially important in the study of the behaviour of sugars in metabolic processes of organisms. However, relatively few data are available concerning these systems, especially at high concentrations. The main research work in this line has been done by Morel and coworkers[1–3] and Wang and coworkers.[4–12]

Trehalose is a non-reducing disaccharide consisting of two glucose units linked by a glycosidic bond. Three such dimers are possible, including α–α, β–β and α–β, indicating the linkage configurations. Trehalose [α-D-glucopyranosyl-(1 → 1)-α-D-glucopyranoside] dimer, which from now on will be referred to as trehalose, is the dominant isomer of trehalose in nature. It is found in high relative concentrations in organisms such as certain plants, seeds and invertebrates adapted to endure drought conditions or low temperature[13,14] and to survive under complete dehydration[15–17] such as spores in fungi. Compared with other disaccharides, it is well-known that trehalose is highly effective as a bioprotector against cell and tissue damage resulting from freezing or

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* Corresponding author. Fax: +34-922-318514.

E-mail address: ffhelu@ull.es (F. Hernández-Luis).

† Universidad de la Laguna scientific visiting; present address: Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, AA 078 Bogotá, Colombia.

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dehydration processes.[18,19] Although it has received considerable attention in recent years, the role of trehalose as a cryoprotector against the freeze–drying cycle is not clear, but, it may be closely associated with the ability to modify the structure of water molecules around the solute.[20,21]

In the present study, the mean ionic activity coefficients of the NaCl in solutions containing trehalose and water have been determined experimentally in order to be more knowledgeable about the ionic interactions in electrolyte–sugar–water solutions and their relation with the structure and properties of aqueous solutions. The concentration of NaCl ranged between 0.01 and 3 mol kg^{-1}, and the percentages of trehalose studied were 0, 10, 20, 30 and 40% by weight. Similarly, maltose [α-D-glucopyranosyl-(1→4)-α-D-glucopyranoside] has the same shape and size as the trehalose molecule. Therefore, its aqueous solutions were also investigated in order to compare the influence of the structure of the mixture of solvents with the ionic interactions.

In order to obtain measures of electromotive force (emf), two ion selective electrodes (ISE) were used, one for the sodium ion and another for chloride ion. The temperature was kept constant at 298.15 K for all the studies.

2. Experimental

Trehalose dihydrate ($C_{12}H_{22}O_{11}\cdot 2H_2O$) and maltose monohydrate ($C_{12}H_{22}O_{11}\cdot H_2O$) were obtained from Sigma Chemical Co. and were used as received. Sodium chloride (Merck, pro analysi), was dried in vacuo at 373 K for 3 days. Both were stored over silica gel in a desiccator. All solutions were prepared by weight. For each set of experiments (corresponding to a wt.% of sugar) working solutions were obtained by adding successive solid weighed NaCl to a solution previously prepared of each sugar and bidistilled water ($\kappa < 5 \times 10^{-7}$ S cm^{-1}). The solutions were continually stirred with a magnetic stirrer.

Na-ISE (mod. 6.0501.100) and Cl-ISE (mod. 6.0502.120) were obtained from Metrohm company. A double wall vessel cell Metrohm was used to keep the electrodes and the solution. The temperature in the cell was constant within 25.00 ± 0.02 °C. A thermostated water line from a thermostat–cryostat Hetofrig model 04 PT was used and a platinum resistance thermometer (Guildline model 9540) to record the temperature.

The emf measurements were carried out with a 614 Keithley electrometer which has an inner impedance greater than 5×10^{13} Ω whose resolution is ±0.1 mV. To obtained 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.

3. Results

Activity coefficients values for NaCl in sugar–water mixtures (sugar: trehalose or maltose) from 0 to 40 wt.% sugar were determined from the emf measurements of galvanic cells without transference. The cell used were of type:

$$\text{Na-ISE}|\text{NaCl }(m),\ \text{sugar }(Y\%),\ H_2O\ (100 - Y\%)|\text{Cl-ISE} \tag{I}$$

combined with that of the reference

$$\text{Na-ISE}|\text{NaCl }(m_r),\ \text{sugar }(Y\%),\ H_2O\ (100 - Y\%)|\text{Cl-ISE} \tag{II}$$

to eliminate the asymmetry potential of the electrodes. In these cells, m and m_r are the molality of NaCl (mol kg/mixed-solvent) in the working and reference solutions, respectively. Y is the wt.% of the solvent in the mixture.

Applying the equation of Nernst–Nikolsky to the cells (I) and (II) and subtracting, the following expression is obtained:

$$\Delta E = E_I - E_{II} = -2k \log \frac{m\gamma}{m_r\gamma_r} \tag{1}$$

where E is the emf of 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 molality m and m_r, respectively. E values for different sugar–water mixtures as a function of the NaCl molalities are shown in Tables 1 and 2.

Since the coefficients of activity of the NaCl in pure water perfectly are known,[22] the values of E that appears in Table 1 for $Y = 0$, allow to carry out a calibration of the electrode system, using the expression (1). A very good linear relationship is obtained when it is plotted ΔE versus $-2\log(m\gamma/m_r\gamma_r)$. The obtained value by applying least-squares regression analysis is of $k = 58.11 \pm 0.03$ mV, being the correlation coefficient 0.999998 and the standard deviation 0.14 mV. This value of k differs only in 1.8%, approximately, from the theoretical value. This is more that acceptable for a system containing two ISEs. In this calculation, it has been assumed that $k_{Na} \cong k_{Cl} \cong k \cong (k_{Na} + k_{Cl})/2$.

In order to calculate γ values for different molalities of NaCl in the sugar–water mixture is necessary the knowledge of the γ_r value. These parameters were evaluated by using the Debye–Hückel or Pitzer equation.

For 1:1 electrolyte, the Debye–Hückel extended equation can be written as:[23,24]

$$\log \gamma = -\frac{A\sqrt{m}}{1 + Ba\sqrt{m}} + cm - \log(1 + 0.002mM) \tag{2}$$

being a the ion size parameters, c the ion-interaction

Table 1
Experimental E and γ values calculated for the NaCl in the mixture of trehalose–water at 298.15 K

0%			10%			20%			30%			40%		
m	$-E$	γ	m	$-E$	γ	m	$-E$	γ	m	$-E$	γ	m	$-E$	γ
0.03173	64.78	0.8452	0.01230	27.76	0.8903	0.06696	117.34	0.7777	0.1403	161.63	0.6900	0.03831	108.99	0.7928
0.06378	97.48	0.8037	0.06800	107.96	0.7889	0.1361	148.82	0.7140	0.2332	183.63	0.6415	0.06001	128.74	0.7485
0.1364	132.63	0.7543	0.1002	126.25	0.7692	0.1985	166.02	0.6882	0.2915	193.40	0.6229	0.09007	147.11	0.7177
0.2000	150.50	0.7328	0.1252	136.62	0.7560	0.3000	184.48	0.6564	0.4500	212.60	0.5903	0.1150	157.95	0.6967
0.2033	151.31	0.7324	0.2442	167.37	0.7128	0.3917	196.56	0.6387	0.5008	217.33	0.5825	0.1435	167.74	0.6780
0.4271	185.58	0.6876	0.3001	176.92	0.7008	0.5136	209.43	0.6286	0.6562	230.30	0.5748	0.1900	180.60	0.6605
0.5967	201.58	0.6757	0.3763	187.45	0.6886	0.7410	226.61	0.6123	0.8428	242.17	0.5662	0.2421	191.60	0.6447
0.7500	212.19	0.6634	0.4781	199.02	0.6816	0.8946	235.98	0.6107	1.0000 [a]	250.54	0.5633	0.3301	205.47	0.6223
1.0000 [a]	226.07	0.6550	0.6761	215.16	0.6636	1.0000 [a]	241.43	0.6086	1.0115	251.09	0.5630	0.4299	217.26	0.6036
1.2500	237.14	0.6525	0.8489	226.34	0.6596	1.0068	241.95	0.6108	1.2533	261.70	0.5607	0.5200	226.10	0.5945
1.5175	246.89	0.6520	1.0000 [a]	234.25	0.6549	1.1500	248.41	0.6077	1.4000	267.29	0.5607	0.6208	234.49	0.5880
1.7500	254.59	0.6586	1.0851	238.46	0.6560	1.3097	254.91	0.6069	1.6001	274.31	0.5638	0.7100	240.79	0.5825
2.0799	264.21	0.6704	1.3367	249.04	0.6567	1.5682	264.33	0.6109	1.7592	279.40	0.5672	0.8336	248.90	0.5826
2.2924	269.51	0.6756	1.5349	256.83	0.6674	1.7223	269.78	0.6197	1.9790	286.59	0.5814	0.9300	255.06	0.5900
2.4200	272.77	0.6827	1.7500	262.72	0.6578	1.9698	277.01	0.6253	2.2351	293.60	0.5915	1.0000 [a]	259.36	0.5975
2.5605	276.22	0.6909	1.8722	266.23	0.6592	2.1790	282.72	0.6329	2.4598	299.45	0.6035	1.7488	289.11	0.6160
2.9502	284.78	0.7105	2.1564	274.23	0.6706	2.4047	288.72	0.6459	2.7012	305.36	0.6178	2.1987	302.32	0.6365
			2.5100	283.82	0.6967	2.7643	297.69	0.6712	2.9760	311.79	0.6370	2.5680	312.17	0.6624
						2.9998	303.24	0.6904	3.0002	312.42	0.6398	2.9373	321.39	0.6952

Units: moles NaCl/kg mixed-solvent for m; mV for E.

[a] Reference molality.

Table 2
Experimental E and γ values calculated for the NaCl in the mixture of maltose–water at 298.15 K

10%			20%			30%			40%		
m	$-E$	γ	m	$-E$	γ	m	$-E$	γ	m	$-E$	γ
0.03040	70.09	0.8428	0.1336	146.35	0.7238	0.02810	79.49	0.8183	0.03833	99.00	0.7852
0.1137	131.13	0.7547	0.1890	162.59	0.7058	0.06323	117.13	0.7665	0.09415	140.77	0.7313
0.1718	150.79	0.7378	0.2700	178.51	0.6773	0.1340	150.90	0.7061	0.1889	172.58	0.6845
0.2943	175.47	0.7023	0.4082	196.94	0.6454	0.1772	164.06	0.6931	0.2722	189.61	0.6656
0.4178	192.03	0.6867	0.5534	211.22	0.6318	0.2767	183.92	0.6578	0.3691	204.06	0.6535
0.5839	207.73	0.6707	0.6600	219.63	0.6258	0.3425	193.96	0.6484	0.4401	211.96	0.6412
0.6872	215.62	0.6663	0.7749	227.24	0.6197	0.4309	204.34	0.6330	0.5271	220.17	0.6297
0.8395	226.03	0.6704	0.9368	236.53	0.6162	0.5681	217.34	0.6212	0.6121	227.56	0.6278
1.0000 [a]	235.02	0.6725	1.0000 [a]	239.48	0.6120	0.7051	227.17	0.6081	0.7105	234.62	0.6220
1.0750	238.58	0.6713	1.1699	246.87	0.6056	0.7631	230.77	0.6035	0.8261	242.01	0.6194
1.2010	244.04	0.6695	1.3265	253.18	0.6052	0.8819	237.52	0.5969	1.0000 [a]	251.22	0.6141
1.3150	248.70	0.6706	1.4752	258.73	0.6075	1.0000 [a]	243.39	0.5913	1.0261	252.63	0.6154
1.5001	255.84	0.6772	1.6345	263.96	0.6081	1.0667	246.49	0.5894	1.2120	260.34	0.6070
1.7003	262.48	0.6815	1.7937	268.13	0.6019	1.2703	254.94	0.5852	1.4134	268.07	0.6067
1.8568	266.93	0.6815	2.0014	274.45	0.6114	1.4001	259.87	0.5854	1.6170	275.16	0.6103
2.2073	276.77	0.6967	2.2178	280.12	0.6173	1.5618	265.35	0.5850	1.8506	282.27	0.6139
2.3772	281.52	0.7108	2.3890	284.21	0.6215	1.7552	271.59	0.5890	2.0806	289.12	0.6254
2.5286	285.39	0.7215	2.6200	289.37	0.6277	1.9123	276.04	0.5905	2.2546	293.70	0.6320
2.6891	289.15	0.7309	2.8369	293.77	0.6325	2.0090	278.67	0.5921	2.4680	298.68	0.6372
2.8526	292.70	0.7392	3.0820	298.74	0.6424	2.1836	283.17	0.5955	2.6401	302.45	0.6419
3.0676	297.34	0.7536				2.4189	288.64	0.5992	2.7970	305.91	0.6488
						2.7001	294.81	0.6066			
						2.8636	298.11	0.6106			

Units: moles NaCl/kg mixed-solvent for m; mV for E.
[a] Reference molality.

parameter and M the average molecular mass of mixed solvent. A and B are the Debye–Hückel constant given by:

$$A = 1.8247 \times 10^6 d^{1/2}/(\varepsilon_r T)^{3/2} \quad \text{kg}^{1/2}\ \text{mol}^{-1/2} \tag{3}$$

$$B = 50.2901 \times d^{1/2}/(\varepsilon_r T)^{3/2} \quad \text{kg}^{1/2}\ \text{mol}^{-1/2}\ \text{Å} \tag{4}$$

where d, ε_r and T stands for the density, relative permittivity (static dielectric constant) of the solvent and the temperature, respectively. The density values were taken from Elias and Elias[25] for the trehalose–water system and of Eya and coworkers[26] for the maltose–water system. The relative permittivity for both sugar–water mixtures were taken from Matsuoka and coworkers.[27]

The values used for d and ε_r as well as the Debye–Hückel constant, A and B, are listed in Table 3 together with the values of M.

By combining Eqs. (1) and (2) the values of a, c and γ_r can be optimized for each mixture sugar–water studied. These values with their standard deviations as well as the standard deviation of the fit are shown in Table 4.

Another way to evaluate the γ_r values is using the Pitzer equation. For 1:1 electrolyte, the Pitzer equation can be written as:[28,29]

$$\text{In}\ \gamma = f^{\gamma} + B^{\gamma} m + \mathring{A} m^2 \tag{5}$$

where

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

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

In these equations α and b are assumed fixed parameters with values of 2.0 and 1.2, respectively;[28–30] β^0, β^1 and $\mathring{A}$ are solute-specific interaction parameters and A_{ϕ} is the Debye–Hückel constant for the osmotic coefficients defined by:

$$A_{\phi} = 1.4006 \times 10^6 d^{1/2}/(\varepsilon_r T)^{3/2} \quad \text{kg}^{1/2}\ \text{mol}^{-1/2} \tag{8}$$

having all symbols the usual meaning. In the last column of the Table 3 are shown the A_{ϕ} values for the each sugar–water system at 298.15 K.

By combining Eqs. (1), (5)–(7) the γ_r, β^0, β^1 and $\mathring{A}$ values can be optimized for each mixture sugar–water studied. In Table 5 are summarised these values together with their standard deviations as well as the standard deviation of the fit.

Table 3
Values of average molecular mass, relative permittivity, densities, Debye–Hückel and Pitzer constants as a function of the weight percentage of sugar in the of mixtures trehalose–water and maltose–water at 298.15 K

Y%	M	ε_r	d	A	B	A_ϕ
0	18.015	78.38	0.9971	0.5100	0.3285	0.3915
Trehalose–water						
10	19.900	75.60	1.0376	0.5492	0.3412	0.4216
20	22.226	73.50	1.0819	0.5850	0.3534	0.4490
30	25.168	70.50	1.1288	0.6361	0.3685	0.4883
40	29.007	68.40	1.1786	0.6802	0.3823	0.5221
Maltose–water						
10	19.900	74.77	1.0374	0.5583	0.3431	0.4286
20	22.226	72.80	1.0808	0.5931	0.3549	0.4553
30	25.168	69.30	1.1275	0.6523	0.3715	0.5007
40	29.007	65.40	1.1776	0.7272	0.3908	0.5582

Table 4
Summary of the values obtained for the parameters of the Debye–Hückel equation in the different trehalose–water and maltose–water mixtures at 298.15 K

Wt.%	γ_r	a (Å)	c (kg mol^{-1})	σ (mV)
0	0.6521 ± 0.0024	3.78 ± 0.12	0.0577 ± 0.0019	0.23
Trehalose–water				
10	0.6539 ± 0.0031	4.32 ± 0.16	0.0553 ± 0.0027	0.31
20	0.6059 ± 0.0026	3.06 ± 0.08	0.0804 ± 0.0019	0.23
30	0.5611 ± 0.0025	2.58 ± 0.07	0.0938 ± 0.0018	0.19
40	0.5978 ± 0.0022	3.14 ± 0.08	0.1004 ± 0.0020	0.27
Maltose–water				
10	0.6713 ± 0.0026	4.33 ± 0.10	0.0641 ± 0.0013	0.22
20	0.6091 ± 0.0031	3.78 ± 0.10	0.0556 ± 0.0015	0.20
30	0.5901 ± 0.0018	4.09 ± 0.07	0.0529 ± 0.0012	0.20
40	0.6147 ± 0.0033	5.09 ± 0.13	0.0561 ± 0.0016	0.27

4. Discussion

By comparing Tables 4 and 5 it is seen that, within experimental error, the obtained γ_r applying the different methods are in good agreement with each other. In spite of the high concentration range studied, the Debye–Hückel equation adequately fits the results with an average standard deviation of ±0.23 mV. The closet approach parameter a usually has values between 3.4 ± 0.7 Å for the trehalose–water system, and 4.2 ± 0.5 Å for the maltose–water system. The ionic interaction parameter c increases with the percentage of sugar in the trehalose–water mixture, while in the maltose–water mixture it is maintained practically constant. Fig. 1 shows a plot of c versus the reciprocal of relative permittivity, as it is a good predictor of linear dependence.

With respect to the equation of Pitzer, in Table 5, it can be seen that though the concentration range was greater than 2 mol kg^{-1},[28,30] the consideration of parameter $\mathring{A}$ does not predict a notable improvement in the standard deviations of the fits. On average, this deviation is ±0.22 mV with two parameters and ±0.20 mV with three parameters.

As it is known, in the Pitzer thermodynamic treatment of electrolyte solutions, the electrostatic term is a constant for all electrolytes of same valence type and it does not take into consideration the differences in the solution of the ions, ionic sizes or the distance of closet approach. The second virial coefficient is a complicated function of many interactions, where β^0 and β^1 are the parameters that govern this coefficient. In Fig. 2, the obtained β^0 and β^1 values of the fit are plotted against the reciprocal of relative permittivity for the different sugar–water mixtures. 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 unlike-charged ions) change linearly with $1/\varepsilon_r$. This is the typical profile observed for 1:1 electrolytes[6,28,31,32] with water as one of the solvents in the mixture. Although in the Pitzer thermodynamic treatment there is no explicit dependence of β^0 on relative permittivity of the solvents, it was found[32] that the radial distribution function at hard-core contact (g_{+-}, g_{++} and g_{--}) was a function of the relative permittivity, which may be the cause of the variation of β^0. On the other hand, in the discussion of hard-core effects on osmotic and activity coefficients in terms of the Debye–Hückel theory, Pitzer[28,29,32] has pointed out that β^1 would be a function of κ^2 that involves the reciprocal of relative permittivity. Thus, the linear dependence of β^1 on $1/\varepsilon_r$ observed in this study is reasonable.

It is also interesting to note that the Debye–Hückel ion-interaction parameter c is numerically close to β^0

Table 5
Summary of the values obtained for the parameters of the Pitzer equation in the different trehalose–water and maltose–water mixtures at 298.15 K

Wt.%	γ_r	β^0 (kg mol^{-1})	β^1 (kg mol^{-1})	C^γ (kg^2 mol^{-2})	σ (mV)
0	0.6580 ± 0.0014	0.0658 ± 0.0038	0.3146 ± 0.0178	0.00699 ± 0.00188	0.11
	0.6549 ± 0.0015	0.0798 ± 0.0010	0.2553 ± 0.0113		0.15
Trehalose–water					
10	0.6558 ± 0.0035	0.0785 ± 0.0012	0.3806 ± 0.0496	0.00293 ± 0.00069	0.29
	0.6550 ± 0.0028	0.0838 ± 0.0022	0.3618 ± 0.0215		0.29
20	0.6093 ± 0.0038	0.1057 ± 0.0083	0.1967 ± 0.0428	−0.00193 ± 0.00390	0.23
	0.6105 ± 0.0027	0.1017 ± 0.0013	0.2160 ± 0.0174		0.24
30	0.5617 ± 0.0045	0.1233 ± 0.0078	0.0896 ± 0.0471	−0.00538 ± 0.00350	0.20
	0.5671 ± 0.0031	0.1114 ± 0.0012	0.1560 ± 0.0192		0.21
40	0.5943 ± 0.0025	0.1642 ± 0.0089	0.1649 ± 0.0371	−0.01815 ± 0.00456	0.24
	0.6003 ± 0.0026	0.1293 ± 0.0017	0.2989 ± 0.0206		0.32
Maltose–water					
10	0.6720 ± 0.0031	0.1003 ± 0.0067	0.3564 ± 0.0336	−0.00389 ± 0.00318	0.22
	0.6743 ± 0.0026	0.0922 ± 0.0010	0.3933 ± 0.0148		0.23
20	0.6112 ± 0.0044	0.0898 ± 0.0074	0.3124 ± 0.0435	−0.00465 ± 0.00335	0.20
	0.6157 ± 0.0030	0.0796 ± 0.0012	0.3675 ± 0.0181		0.21
30	0.5918 ± 0.0017	0.0837 ± 0.0048	0.4579 ± 0.0225	−0.00046 ± 0.00243	0.16
	0.5920 ± 0.0013	0.0828 ± 0.0008	0.4617 ± 0.0098		0.16
40	0.6156 ± 0.0025	0.0798 ± 0.0066	0.7707 ± 0.0309	0.00768 ± 0.00034	0.19
	0.6121 ± 0.0023	0.0946 ± 0.0012	0.7078 ± 0.0150		0.22

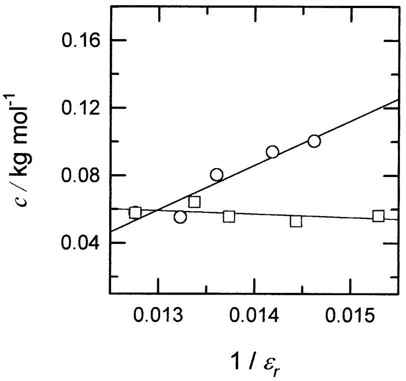

Fig. 1. Plot of Debye–Hückel ion-interaction parameter c vs. $1/\varepsilon_r$ (○) trehalose–water and (□) maltose–water.

for each sugar–water mixture such as it occurs in the systems containing NaCl in glucose–water and sucrose–water studied by Wang and coworkers.[6]

To calculate the γ values summarised in Tables 1 and 2, the following average values of γ_r were used: 0.6550, 0.6549, 0.6086, 0.5633 and 0.5975 for 0, 10, 20, 30 and 40% weight of trehalose and 0.6550, 0.6725, 0.6120, 0.5913 and 0.6141 for the same percentages of maltose. In the molality range studied, the standard deviation of the activity coefficient between our values and those reported in the literature[22] was calculated to be ±0.002 in pure water, which shows the good agreement between both series of data.

In Fig. 3, is plotted log γ versus $m^{1/2}$ with different sugar–water mixtures. A decrease of log γ of NaCl with decreasing relative permittivity of the mixed solvent (increasing in wt.% of sugar) is clear, and it must be related to the ion–solvent interactions. This effect is more pronounced in the system containing trehalose, and furthermore, a greater shift is observed in the typical minimum toward lower values of m.

As has been pointed out, the solutions of trehalose in water have been widely studied by different authors with the purpose of understanding their peculiar behaviour. Thus, for example, Magazu and coworkers,[21] have used three different techniques and have analysed the results of ultrasonic data, photon correlation spectroscopy and viscosity measurements. As it can be seen from the results of this study the hydration properties of trehalose solutions are quite complex. They concluded that the mixing process is not ideal and that the water–trehalose interaction strength decreases with increasing concentration. Similarly, for maltose, Nikam and coworkers[33] have also measured acoustical properties both in pure water and in aqueous NH_4Cl solution. Interesting conclusions were given regarding the hydration of the sugar and the influence due to the presence of ions.

It would be interesting to verify how this hydration of the sugar affects the hydration of solute, in this case the NaCl. The equation of Feakins and French[34,35] was used in order to analyse these effects. This equation allowed obtaining the primary hydration number of the

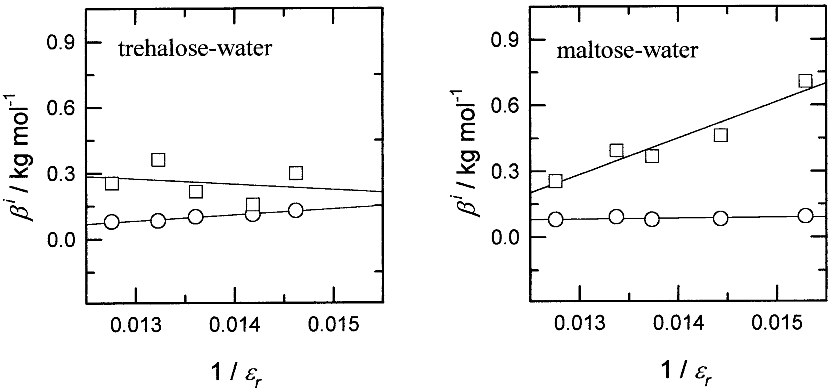

Fig. 2. (○) β^0 and (□) β^1 for NaCl in trehalose–water and maltose–water mixtures at 298.15 K as a function of inverse of relative permittivity.

electrolyte from the dependency between the standard potential of the cell and the logarithm of the weight fraction of the water in the mixture according to the following equation:

$$E^\circ_s - E^\circ_w = n_{hydr} k \log w \tag{9}$$

where s and w represent mixed solvent and water, respectively, n_{hydr} is the primary hydration number, and w is the weight fraction of water.

To estimate the standard potentials, the values of E, m and γ compiled in Tables 1 and 2 were substituted in the equation of Nernst–Nikolsky applied to cell (I) and written as:

$$E = E^{\circ *} - 2k \log m\gamma \tag{10}$$

where $E^{\circ *}$ is the apparent standard potential of the cell and contains the potential of asymmetry of both selective electrodes, namely:

$$E^{\circ *} = E^\circ + \varepsilon^{asym}_{Na} + \varepsilon^{asym}_{F} \tag{11}$$

As the condition of Born suggests, a linear variation of the standard potential with the inverse of the dielectric constant is observed for both systems as is shown in the Fig. 4.

Since the asymmetry potentials are not very large and they are independent of the composition of the solvent, it is verified that:[31,36]

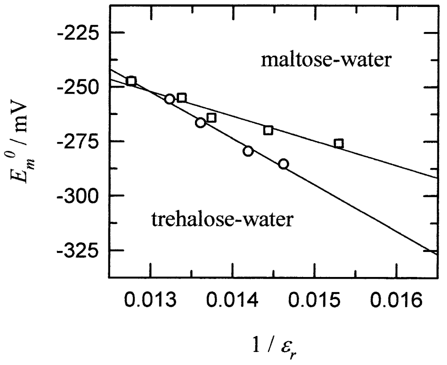

Fig. 4. Test of the Born equation for the variation of standard emf, E°_m, on the inverse of relative permittivity for the mixed solvents.

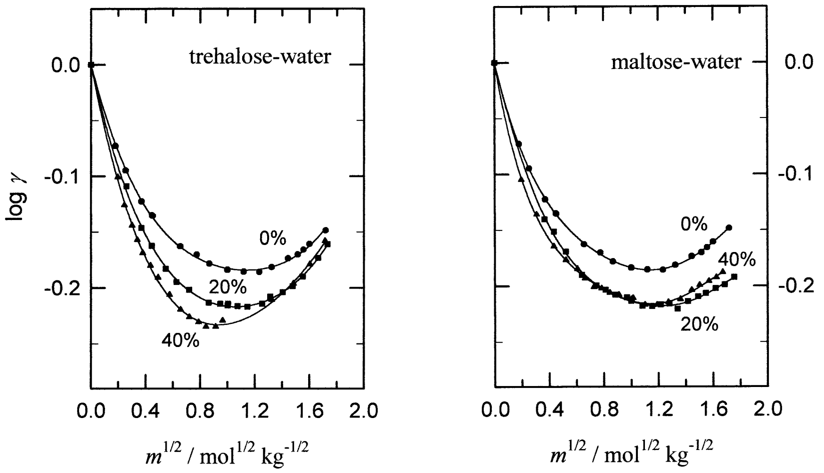

Fig. 3. Plot of log γ vs. $m^{1/2}$ for NaCl in trehalose–water and maltose–water mixtures at 298.15 K.

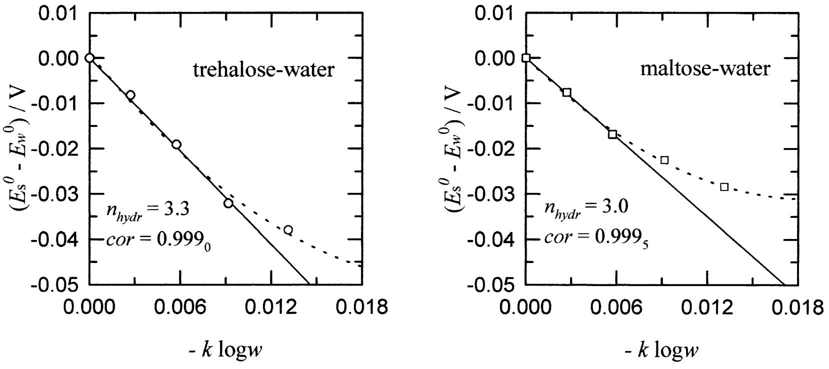

Fig. 5. Variation of standard emf with weight fraction of water at 298.15 K.

$$E_s^{\circ *} - E_w^{\circ *} \cong E_s^\circ - E_w^\circ \quad (12)$$

In Fig. 5, a plot of $E_s^\circ - E_w^\circ$ versus a function of the composition of the mixture according to Eq. (9), shows an excellent linear correlation in both cases. The values obtained for n_{hyd} are very similar: 3.3 ($r = 0.9990$) for the trehalose–water system and 3.0 ($r = 0.9995$) for the maltose–water system. Through a similar analysis with the data of Wang and coworkers for NaCl in glucose–water[5] and sucrose–water[4] is obtained 2.6 ($r = 0.9999$) and 2.6 ($r = 0.9996$), respectively. These values of $n_{\text{hyd}} \approx 3$ for NaCl are slightly small compared with those collected in the bibliography[37,38] and that ranged between 4 and 8 according to the measurement method employed. One must have in mind that the derivation of Eq. (9) roughly implies an ideal model for the solutions. Though the relation between the hydration and stereochemistry of the carbohydrates is very complicated, especially when there are electrolytes present,[8] a low hydration of NaCl in the presence of sugars might be found when there is competition between sugars and NaCl for the water molecules. The similarity found between the values of n_{hyd} would suppose that the hydration of the four sugars is very similar as in the observations of Liu and coworkers[39] who assert that the general hydration behaviour observed in trehalose–water does not differ dramatically from that of maltose or sucrose though it is possible that the small differences found in the simulations of these sugars are sufficient to account for their differing antidessicant properties; the mechanism remains unclear. However, Matsuoka and coworkers[27] indicate that trehalose is more strongly hydrated than other saccharides, such as glucose, xylose, sucrose, maltose and raffinose, this large hydration being responsible for the special characteristics of trehalose.

A usual way of analysing thermodynamic properties of a ternary system of this type is in terms of transference functions. The transference free energy can be written:[40]

$$\Delta G_t(\mathrm{W} \rightarrow \mathrm{W + S}) = 2vg_{\mathrm{SE}}m_{\mathrm{S}} + 3vg_{\mathrm{SSE}}m_{\mathrm{S}}^2 + 3v^2g_{\mathrm{SEE}}m_{\mathrm{E}}m_{\mathrm{S}} + \cdots \quad (13)$$

for the electrolyte (E) and:

$$\Delta G_t(\mathrm{W} \rightarrow \mathrm{W + E}) = 2vg_{\mathrm{SE}}m_{\mathrm{E}} + 3v^2g_{\mathrm{SEE}}m_{\mathrm{E}}^2 + 3vg_{\mathrm{SSE}}m_{\mathrm{E}}m_{\mathrm{S}} + \cdots \quad (14)$$

for the sugar (S), with m_{E} and m_{S} the molalities of NaCl and trehalose or maltose defined per kg of pure water, v 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_{N} or m_{E} on the right-hand side of Eqs. (13) and (14) vanish.[40] Thus, for the electrolyte we obtain:

$$\Delta G_t^\circ = -nF(E_{\mathrm{S}}^\circ - E_{\mathrm{W}}^\circ) = 2vg_{\mathrm{SE}}m_{\mathrm{S}} + 3v^2g_{\mathrm{SSE}}m_{\mathrm{S}}^2 + \cdots \quad (15)$$

Fig. 6 shows the variation of ΔG_t° of the electrolyte with the mole fraction of sugar in mixed solvent. For the sake of comparison, the corresponding values of NaCl in water–sucrose[4] and water–glucose[5] are included. As the concentration of sugar increases, the transference free energy becomes increasingly positive, indicating possible increase in destabilization and decrease in hydration of the electrolyte in the sugar–water system[4,5]

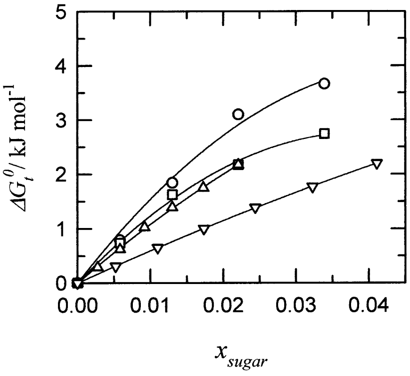

Fig. 6. Variation of ΔG_t° for the NaCl as a function of mole fraction of sugar in sugar–water mixture. (○) Trehalose; (□) maltose; (△) sucrose; (▽) glucose.

as consequence of the increase in the hydration of the sugar. The hydration order would be trehalose > maltose > glucose > sucrose, which is in agreement with the affirmations of Matsuoka and coworkers.[27]

At a low concentration of sugar, a least-square regression of $\Delta G^{\circ}_{t,X}/m_S$ against m_S yields[4,40] a value of g_{SE}. $\Delta G^{\circ}_{t,X}$ is the transference free energy on the mole fraction scale, namely:[4]

$$\Delta G^{\circ}_{t,X} = \Delta G^{\circ}_{t,m} + \nu RT \ln(18.015/M) \tag{16}$$

According to the approach of Desnoyers and coworkers[40,41] the salting constant k_s can be related to g_{SE} through the expression:

$$RTk_S = 2\nu g_{SE} \tag{17}$$

Before calculating k_s, the values of g_{SE} obtained from the regression were converted[4,5] to the scale of molality using the Masterton and coworkers.[42] In Table 6 are listed values of $2\nu g_{SE}$ and k_s for the trehalose–water and maltose–water systems together with those taken from the literature on other sugars.[4,5,12] In all the cases, it is verified that $-0.7 \leq k_s \leq 0.7$.[43] 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. Trehalose and maltose have very larger salting-out effects compared with the other sugars. It is also known that the interactions sugars–electrolytes are mainly controlled by the stereochemistry of the sugar.[12] It may be necessary to carry out a more exhaustive experimental study of these interactions, including their variations with temperature, before reaching verifiable conclusions. Our research group is currently carrying on related investigations which are in progress and are on the way to publication.

Table 6
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})
Trehalose	681	0.275
Maltose	613	0.247
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] Ref. 4.

[b] Ref. 5.

[c] Ref. 12.

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