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Fractional Walden Rule for Electrolytes in Supercooled Disaccharide Aqueous Solutions

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The electrical conductivity of CsCl, KCl, Bu₄NBr, and Bu₄NI was studied in stable and supercooled (metastable) sucrose and trehalose aqueous solutions over a wide viscosity range. The results indicate that large positive deviations from the Walden rule occur in these systems due to the higher tendency of the ions to move in water-rich regions, as previously observed for NaCl and MgCl₂. The electrical molar conductivity viscosity dependence can be described with a fractional Walden rule ($\Lambda\eta^\alpha = \text{constant}$), where α is a decoupling parameter which increases with ionic size and varies between 0.61 and 0.74 for all of the studied electrolytes. Using the electrical molar conductivity dependence of ion–ion interactions, an effective dielectric constant was calculated for a trehalose 39 wt% aqueous solution as a function of temperature. Above 278 K, the effective and the bulk solution dielectric constants are similar, but at lower temperatures, where the carbohydrate becomes less mobile than water, the effective dielectric constant approaches the dielectric constant of water. We also conclude that the solute–solvent dielectric friction contribution can be neglected, reinforcing the idea that the observed breakdown of the Walden rule is due to the existence of local microheterogeneities. The Walden plots for the studied ionic solutes show a decoupling similar to that found for the diffusion of water in the same solutions.

1. Introduction

Trehalose and sucrose have been widely used to preserve biomolecules under stress conditions.^{1–3} Combinations of sugars with electrolytes have been proved to have superior protective capacity than sugars alone.^{4–6} This observation can be explained considering that the presence of salts in water–saccharide systems modify important properties related to the cryoprotectant capacity of these media, such as water sorption and crystallization rate.^{7,8}

A dramatic increment in the viscosity of aqueous sugar mixtures is produced when these systems are cooled from the normal liquid region down to the supercooled regime. This increment should prevent deterioration reactions of preserved molecules by delaying molecular mobility. Therefore, considering that the rate of the processes taking place in such media, are often diffusion-controlled,⁹ the study of the diffusion of solutes in sugar aqueous solutions is of fundamental interest to the cryopreservation and food technologies.

The hydrodynamic equations such as the Walden Rule (eq 1),¹⁰ or the Stokes–Einstein equation (eq 2),

$$\Lambda^0\eta = \frac{z^2eF}{AR} \quad (1)$$

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$$\frac{D^0\eta}{T} = \frac{k_B}{AR} \quad (2)$$

(where Λ^0 is the molar conductivity at infinite dilution of a univalent electrolyte ($z = z_+ = |z_-|$), η is the viscosity of the solvent, e is the electron charge, F is the Faraday constant, $(1/R = 1/R_+ + 1/R_-)$ is the sum of the reciprocal radii of the ions, A is a constant whose value depends on the friction conditions (6π for stick and 4π for slip boundary conditions, respectively), D^0 is the diffusion constant at infinite dilution, k_B is the Boltzmann constant, and T is the temperature) are commonly used to predict the electrical molar conductivity or the diffusion coefficient of a solute in a solvent of viscosity η , using conductivity or diffusion data in another solvent.

Λ^0 and D^0 are related through the Nernst equation,¹¹

$$D^0 = \frac{k_BT\lambda_+\lambda_-^0}{eF\Lambda^0} \quad (3)$$

where λ_i^0 are the ionic limiting molar conductivities ($\Lambda^0 = \lambda_+^0 + \lambda_-^0$).

The viscosity of simple solvents can only be changed by varying the temperature. However, in binary mixtures such as polyol–water solutions, the viscosity can be changed by several orders of magnitude with temperature and concentration variations. Therefore, aqueous polyol mixtures represent a stringent test for the analysis of the validity of the hydrodynamic model, represented by eqs 1 and 2, in a wide viscosity range.

The effect of viscosity on the ionic mobility in binary aqueous solutions has been studied for more than one hundred years. Heber Green¹² was the first to analyze the effect of viscosity on the electrical conductivity of HCl and LiCl in sucrose aqueous solutions. Stokes and co-workers^{13–16} reanalyzed this effect during the fifties by measuring the conductivity of LiCl, KI, KClO₄, KBr, KNO₃, AgNO₃, MgCl₂, CaCl₂, LaCl₃, N(n-Am)₄I (tetra-*n*-amylammonium iodide) in sucrose 10 and 20 wt%, HCl in sucrose 10–40 wt%, and KCl in sucrose 10–60 wt% at 298.15 K. They also performed measurements for the same salts in aqueous mannitol 10 wt% and aqueous glycerol 10–20 wt% at 298.15 K. Similar studies were carried out by Treiner and Fuoss¹⁷ for tetra-alkyl-ammonium bromides and tetraphenyl-borate in acetonitrile-octacyanoethyl sucrose mixtures.

It was observed that for these systems the electrical molar conductivity at a given solution viscosity is bigger than the value predicted by eq 1, and its dependence on the solution viscosity can be expressed by a fractional Walden rule:

$$\Lambda\eta^\alpha = \text{constant} \quad (4)$$

where α is a decoupling constant close to 0.7. This modified Walden rule was first proposed to describe the conductivity viscosity dependence in molten salts.^{18,19}

In sucrose and trehalose aqueous mixtures, we have previously shown^{8,20} that eq 4 with $\alpha = 0.6–0.75$, describes the molar conductivity viscosity dependence of NaCl, LiCl, and MgCl₂ in the liquid and supercooled regimes. This behavior was ascribed to the presence of structural microheterogeneities in the solution, in such a way that small ions move in regions richer in water, having lower viscosity than that of the bulk solution. These heterogeneities play an important role in the delay produced in sugar crystallization when ionic solutes are added to water-saccharide matrices.⁸

For bigger ions, such as sucrose and trehalose borate esters, we observed²¹ that in the liquid regime eq 1 gives a correct description of the dependence of the anion molar conductivity (λ_-) with viscosity, in contrast to what was observed for simple salts: LiCl, NaCl, and MgCl₂. The validity of the hydrodynamic equations (SE equation, in this case) was also observed in the liquid regime for the diffusion of ferrocene methanol,²² a neutral probe, and fluorescein sodium salt^{23–25} in sucrose and trehalose aqueous solutions. However, in the supercooled regime the SE equation does not describe these solutes diffusion coefficients viscosity dependence, and a corrected equation, equivalent to eq 4,

$$\frac{D\eta^\alpha}{T} = \text{constant} \quad (5)$$

should be used to describe the diffusion coefficient viscosity relationship for $T < 1.3–1.5 T_g$ (with T_g being the glass transition temperature of the solution). The same behavior was observed by Ediger and co-workers for the self-diffusion of supercooled single-component glass-forming systems, such as 1,3-bis-(1-naphthyl)-5-(2-naphthyl)benzene ($\alpha\alpha\beta$ -TNB)²⁶ and *o*-terphenyl (OTP),²⁷ near the glass transition temperature, and for the diffusion of tetrace in supercooled ($\alpha\alpha\beta$ -TNB).²⁸

The decoupling observed between solute diffusion and solution viscosity close to the glass transition was ascribed to spatially heterogeneous dynamics in the supercooled regime, with a reduced decoupling temperature, T_g/T , determined by the solute–solvent size relationship and the solute–solvent interactions.

An exhaustive description of the dependence of solute mobility with size in supercooled disaccharide aqueous solutions has not been reported yet, and the differences observed for the mobility of the different solutes reported in the literature are still unexplained. Therefore, the aim of this work is to extend the available data on the mobility of ionic solutes in disaccharide aqueous solutions to solutes of higher size. We will discuss the effect of ionic size and charge in the decoupling index, α (eq 4), which gives the magnitude of the deviations to the Walden rule. For this purpose we measured the electrical conductivity of KCl, CsCl, Bu₄NBr (tetrabutylammonium bromide), Bu₄NI (tetrabutylammonium iodide) in stable and supercooled (meta-stable) sucrose and trehalose aqueous solutions and analyzed the dependence of α with ionic size and charge. Besides, some aspects related to the mobility viscosity decoupling, previously neglected, were considered in this work.

2. Experimental Section

2.1. Preparation of the Solutions. Aqueous disaccharide solutions were prepared with sucrose (Riedel de Haën), α , α -trehalose (Hayashibara), KCl, CsCl (Merck), Bu₄NBr, and Bu₄NI (Aldrich) and water deionized through a Millipore filter. All chemicals were used as received without further purification. Supercooled aqueous solutions were prepared by heating carefully the aqueous sugar mixtures until dissolution of the sugar, followed by rapidly cooling the homogeneous solutions down to the working temperature.

The conductivity of Bu₄NI in trehalose aqueous solutions was studied at a constant trehalose concentration (39.13 wt%) between 268.15 and 293.15 K for salt concentrations between 0.4 and 7.3 mmol.dm^{−3}, and the infinite dilution molar conductivity value was obtained by extrapolating the molar conductivity dependence with concentration to infinite dilution.

For the other salts, only one fixed salt concentration, between 5 and 17 mmol.dm^{−3}, was analyzed.

2.2. Conductivity Measurements. Conductivity measurements were performed as previously described.⁸ The solution resistance was measured with an AC bridge (Wayne Kerr 6425) in the frequency range 500–5000 Hz and the true resistance value was obtained by extrapolation of R vs ω^{-1} at infinite frequency.

For the conductivity measurements of Bu₄NI in trehalose 39.13 wt% a conventional glass cell with a mixing bulb and total volume of 500 cm³ was used. This cell, with a cell constant between 0.09828 cm^{−1} (268.15 K) and 0.09888 cm^{−1} (293.15 K), has been previously used for high precision conductivity determinations.²⁹ Another cell of smaller volume (30 cm³ approximately), with cell constant between 0.1002 cm^{−1} (248.15 K) and 0.0957 cm^{−1} (323.15 K), was used for the rest of the measurements. The cell constant values were determined by measuring the conductivity of standard solutions, KCl/water³⁰ above 273.15 K and KI/ethanol³¹ below this temperature.

The conductivity of the measured sugar/water/ionic solutions was corrected by the conductivity of the solvent: an aqueous sugar solution of the same disaccharide concentration as the studied ionic solution.

A thermostatted ethyleneglycol/water bath was used to control the temperature of the solutions within ± 0.05 K.

3. Results and Discussion

3.1. Conductivity of Bu₄NI in Aqueous Trehalose 39.13 wt%. The electrical molar conductivity values of Bu₄NI in aqueous trehalose 39.13 wt%, between 268.15 and 293.15 K, are informed in Table 1 as a function of salt concentration. The

TABLE 1: Electrical Molar Conductivity of Bu₄NI in an Aqueous Trehalose Solution 39.13 wt%

<i>T</i> (K)	[Bu ₄ NI] (mmol.dm ⁻³)	<i>η</i> (mPa.s)	<i>Λ</i> (S.cm ² .mol ⁻¹)
293.15	0.5240	7.379	19.95
	1.732		19.48
	2.238		19.52
	3.591		19.20
	4.837		19.01
	5.919		18.90
	7.193		18.72
288.15	0.5250	9.153	16.84
	1.735		16.45
	2.242		16.48
	3.598		16.18
	4.846		16.05
	5.931		15.98
	7.207		15.84
283.15	0.5261	11.60	14.10
	1.738		13.84
	2.246		13.74
	3.605		13.57
	4.856		13.42
	5.942		13.36
	7.221		13.23
278.15	0.5271	15.06	11.55
	1.742		11.32
	2.251		11.30
	3.612		11.15
	4.865		11.08
	5.954		11.03
	7.235		10.89
273.15	0.5281	20.14	9.353
	1.745		9.173
	2.255		9.160
	3.619		9.045
	4.874		8.956
	5.965		8.927
	7.248		8.827
268.15	0.5291	27.84	7.387
	1.748		7.280
	2.259		7.252
	3.626		7.183
	4.883		7.104
	5.976		7.099
	7.262		6.994

measurements at 293.15 K correspond to equilibrium solutions and the ones below this temperature to supercooled solutions.

Table 1 includes the viscosity values of the solutions obtained by fitting, with the Génotelle equation, $\log \eta$ as a function of sugar concentration and temperature, with the corresponding fitting parameters reported in a recent work.³²

The molar concentration of the electrolyte, c , was calculated using the molal concentration and the density of the solutions. For this calculation experimental density data of trehalose aqueous mixtures were used.^{33,34} The effect of salt on the density and viscosity of the solution was neglected considering that the change in these properties due to electrolyte addition is smaller than the error obtained by fitting these properties as a function of sugar concentration and temperature.^{35–37}

At low electrolyte concentrations, Λ varies linearly with $c^{1/2}$, according to the Onsager law,¹¹

$$\Lambda = \Lambda^0 - A\sqrt{c} \quad (6)$$

with

$$A = \left[\frac{2.801 \cdot 10^6 q |z_+ z_-| \Lambda^0}{(\epsilon_s T)^{3/2} (1 + \sqrt{q})} + \frac{41.25 (|z_+| + |z_-|)}{\eta (\epsilon_s T)^{1/2}} \right] \quad (7)$$

where $q = 1/2$ for 1:1 electrolytes. Λ^0 was estimated by fitting the measured values of Λ , as a function of $c^{1/2}$, with a linear regression. The obtained results are reported in Table 2 together with calculated values of A (Onsager's slope).

As expected, Λ^0 increases with temperature due to the reduction in the solution viscosity. Figure 1 shows the Walden product for the electrical molar conductivity of the salt at infinite dilution as a function of viscosity. It can be observed that the molar conductivity does not decrease with the inverse of viscosity but depends on $\eta^{-\alpha}$, where $\alpha = 0.742 \pm 0.002$. As indicated in Figure 1, the infinite dilution molar conductivity of the salt in water at 298.15 K was included in the calculation of α .³⁸

As was mentioned in the Introduction, this behavior was previously observed in other polyol–water mixtures and it was explained considering that the ions move in regions richer in water, having lower viscosity than the bulk.^{8,20}

The values of α calculated with the experimental Λ determined in trehalose–water and water solutions at solute concentrations between 0.5 and 7.2 mmol.dm⁻³ agree, within the experimental error, with the value obtained using the values of Λ^0 obtained by extrapolation of Λ to infinite dilution. Therefore, it can be concluded that Λ values at small solute concentrations can be used to determine the values of α . This procedure will be adopted in the following part of the work and discussed in the next section.

Using the molar conductivity dependence on ionic concentration, and taking into account that the viscosity close to the ions (η^*) is given by $\eta^{0.742}$, a local dielectric constant (ϵ_s^*) can be estimated using eq 7 and the experimental values of A reported in Table 2. The obtained results are given in Table 3 and plotted in Figure 2. In this figure it can be observed that, at temperatures above 283.15 K, the calculated ϵ_s^* values agree with the static dielectric constant of a trehalose aqueous solution 40wt%.³⁹ However, at lower temperatures ϵ_s^* seems to be closer to the static dielectric constant of water.⁴⁰

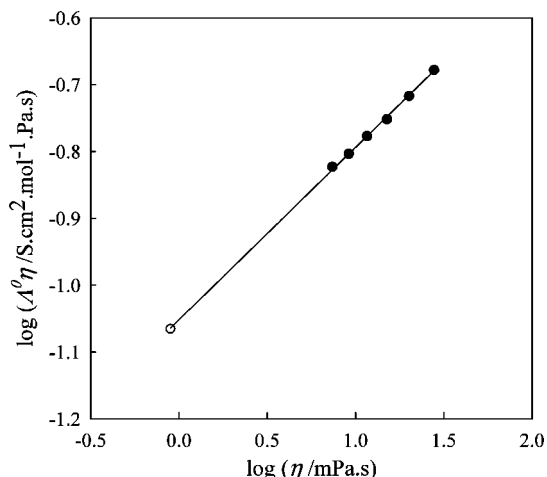
A simple interpretation of these results is as follows. The ionic mobility behaves, all over the range of temperature, as expected from eq 4, which accounts for the viscosity dependence determined by the heterogeneities around the charged solutes (alternatively, this could be seen as preferential water solvation). On the other hand, the local dielectric constant senses the mobility of the binary solvent molecules at larger distances from the ions. Thus, above 280 K the effective dielectric constant is essentially that of the bulk solution, while at lower temperatures, where the saccharide molecules become less mobile than the water molecules, the effective dielectric constant tends to the values of bulk water.

For this estimation, ionic association was neglected because of the size of the iodide and tetrabutylammonium ions and the relatively high dielectric constant of an aqueous trehalose solution 40 wt%.³⁹

3.2. Conductivity of KCl, CsCl, and Bu₄NBr in Sucrose Aqueous Solutions. The electrical molar conductivities of KCl, CsCl, and Bu₄NBr (4–17 mmol.dm⁻³) in sucrose aqueous solutions are listed in Table 4. Solutions of constant sucrose concentration were studied. Viscosity variations were attained by changing the temperature. All of the electrical conductivity values obtained for KCl and Bu₄NBr correspond to the supercooled regime, whereas for CsCl only half of the conduc-

TABLE 2: Electrical Molar Conductivity of Bu₄NI in an Aqueous Trehalose Solution 39.13 wt% at Infinite Dilution and Onsager's Slopes as a Function of Temperature

<i>T</i> (K)	Λ^0 (S.cm ² .mol ⁻¹)	<i>A</i> (S.cm ² .mol ^{-3/2} .dm ^{3/2})
293.15	20.37 ± 0.06	-19.4 ± 0.9
288.15	17.18 ± 0.05	-15.9 ± 0.9
283.15	14.41 ± 0.02	-14.0 ± 0.3
278.15	11.77 ± 0.03	-10.0 ± 0.5
273.15	9.53 ± 0.02	-8.2 ± 0.3
268.15	7.54 ± 0.02	-6.0 ± 0.4

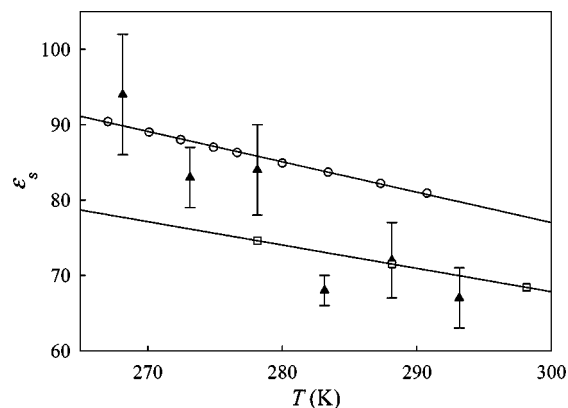
**Figure 1.** Walden product of Bu₄NI at infinite dilution in trehalose aqueous solutions: (●) trehalose 39.13 wt% at different temperatures (this work), (○) infinite dilution ionic conductivity in water at 298.15 K.³⁸ The line corresponds to the fit performed with eq 4.**TABLE 3: Experimental and Effective Static Dielectric Constants of a Trehalose Aqueous Solution 39.13 wt% as a Function of Temperature**

<i>T</i> (K)	ϵ_s (ref 37)	ϵ_s^*
293.15	69.9	67 ± 4
288.15	71.5	72 ± 5
283.15	73.1	68 ± 2
278.15	74.6	84 ± 6
273.15	76.0	83 ± 4
268.15	77.5	94 ± 8

tivity data are in this region of the supplemented phase diagram. Table 4 includes the viscosity values of the solutions obtained by fitting, with the Génotelle equation, $\log \eta$ as a function of sugar concentration and temperature, with the corresponding parameters we have recently reported.³² The fitting parameters correspond to the viscosity calculation where the residues which deviate more than three standard deviations were excluded from the analysis.

The salt molar concentration was determined from the molal concentration and the density of the solution, calculated from reported density data.⁴¹

Figure 3 shows the Walden products for the electrical conductivity values determined for the three salts. This graph includes the conductivity of the salts in water at 298.15 K at a solute concentration similar to the analyzed in the sucrose solutions. Again, we can observe that eq 4 describes the dependence of the electrical molar conductivity with solution viscosity. The decoupling constant, α , obtained for the three studied electrolytes, together with the values obtained for previous measurements of LiCl, NaCl, and MgCl₂ in aqueous sucrose and trehalose,^{8,20} are reported in Table 5. For LiCl, NaCl, and MgCl₂, α was recalculated using viscosity values calculated

**Figure 2.** Effective static dielectric constants calculated from eq 7 for a trehalose aqueous solution 39.13 wt% as a function of temperature, with $\eta^* = \eta^{0.742}$ (▲). The static dielectric constants of aqueous trehalose 40 wt%³⁹ (□), and pure water⁴⁰ (○) are also shown. The lines correspond to linear fits of the static dielectric constants of trehalose 40 wt% and water as a function of temperature.**TABLE 4: Electrical Molar Conductivities of KCl, CsCl, and Bu₄NBr in Aqueous Sucrose Solutions as a Function of Temperature and Composition**

<i>T</i> (K)	Sucrose (wt%)	$\log \eta$ /mPa.s	<i>c</i> _{salt} ^a (mM)	Λ (S.cm ² .mol ⁻¹)
253.86	75.10	6.10	KCl (17)	0.01295
263.81		5.16		0.04439
273.71		4.43		0.1254
254.95		3.39		0.6953
263.44	61.08	2.92	CsCl (11)	1.281
273.36		2.48		2.436
283.18		2.13		4.181
293.18		1.83		6.656
303.06	68.38	1.59	CsCl (11)	9.955
310.40		1.43		12.98
317.96		1.29		16.59
254.52		4.51		0.1416
259.48	75.93	4.13	CsCl (14)	0.2257
266.35		3.69		0.4092
274.45		3.25		0.7598
282.37		2.89		1.294
289.40	76.27	2.62	Bu ₄ NBr (4.9)	1.973
297.36		2.34		3.023
305.40		2.11		4.436
312.34		1.92		5.986
251.72	76.27	6.60	CsCl (14)	0.006024
259.10		5.80		0.01615
264.03		5.35		0.03002
270.95		4.80		0.06501
277.86	76.27	4.33	Bu ₄ NBr (4.9)	0.1292
285.52		3.89		0.2531
258.30		5.98		0.006456
263.79		5.46		0.01283
268.55	76.27	5.06	Bu ₄ NBr (4.9)	0.02291
273.78		4.68		0.04017
283.67		4.05		0.1015
293.21		3.56		0.2269
308.69	76.27	2.91		0.6293

^a The reported salt concentration corresponds to 293.15 K. The molar concentrations at other temperatures were calculated with the corresponding density data.

with the Génotelle³² equation as previously mentioned. Data of NaCl in trehalose supercooled solutions reported by Longinotti et al.⁸ were discarded from this analysis since the salt concentration in these determinations was bigger than the average concentrations analyzed in other measurements.

Miller et al.²⁰ have previously found a similar decoupling index α for NaCl in three different disaccharide (sucrose, maltose and trehalose) aqueous solutions ($\alpha = 0.64 \pm 0.02$). However, this value increases for monosaccharides and glycerol aqueous mixtures, taking values of 0.78 and 0.91 for glucose

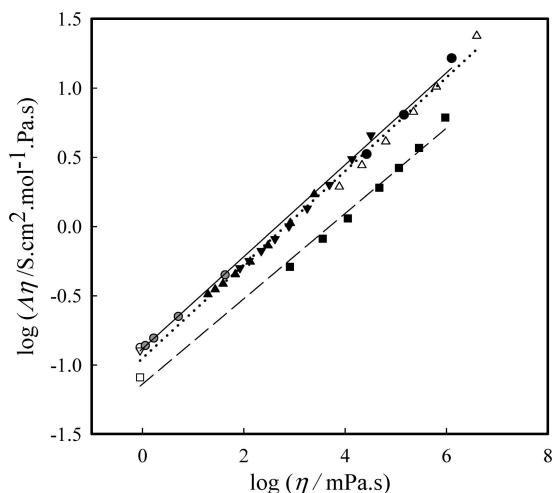


Figure 3. Walden product of KCl, CsCl, and Bu₄NBr in stable and supercooled sucrose aqueous solutions as a function of viscosity: (●) KCl (17 mmol.dm⁻³) in sucrose 75.10 wt% at different temperatures (this work); (○) KCl (infinite dilution) in water at 298.15 K;³⁸ (grey circles) KCl (infinite dilution) in sucrose 10–60 wt% at 298.15 K;¹⁴ (▲) CsCl (11 mmol.dm⁻³) in sucrose 61.08 wt% at different temperatures (this work); (▼) CsCl (11 mmol.dm⁻³) in sucrose 68.38 wt% (this work); (△) CsCl (14 mmol.dm⁻³) in sucrose 75.93 wt% (this work); (▽) CsCl (12 mmol.dm⁻³) in water at 298.15 K;³⁸ (■) Bu₄NBr (4.9 mmol.dm⁻³) in sucrose 76.27 wt% at different temperatures (this work); (□) Bu₄NBr (4.9 mmol.dm⁻³) in water at 298.15 K.³⁸ The lines correspond to the fits performed with eq 4 for KCl (solid line), CsCl (dotted line) and Bu₄NBr (dashed line).

TABLE 5: Decoupling Constant, eq 4, for the Molar Conductivity of Electrolytes in Sucrose and Trehalose Aqueous Solutions

Disaccharide	Electrolyte	α
Sucrose	NaCl	0.636 ± 0.006
	KCl	0.668 ± 0.006
	CsCl	0.662 ± 0.006
	Bu ₄ NBr	0.69 ± 0.01
	MgCl ₂	0.698 ± 0.007
Trehalose	LiCl	0.61 ± 0.02
	NaCl	0.622 ± 0.003
	Bu ₄ NI	0.742 ± 0.002
	MgCl ₂	0.719 ± 0.005

and glycerol, respectively. The observation made by these authors in disaccharide-water solutions was confirmed in this work, where the differences observed in the decoupling index of the studied electrolytes in sucrose and trehalose aqueous solutions can be attributed to the charge and size of the electrolytes, playing the structure of the disaccharide a secondary role.

It can be noted in Table 5 that the values of α obtained for the different electrolytes in disaccharide water solutions increase with ionic size. The same behavior was previously observed by Stokes and Stokes¹⁵ for the conductivity of HCl, KCl, KClO₄, N(n-Am)I in aqueous sucrose in a more limited viscosity range, where α takes values of 0.68, 0.682, 0.76, and 0.83, for the mentioned salts, respectively. For cations of higher charge these authors observed an increase of α with ionic charge. Thus, α takes values of 0.78, 0.78, and 0.81 for MgCl₂, CaCl₂, and LaCl₃, respectively. The same behavior was observed in this work for MgCl₂ over an extended viscosity range in comparison to 1:1 electrolytes.

The hydrodynamic radius of Bu₄N⁺, obtained with eq 1 for the molar conductivity of the ion in water at 298.15 K, is 0.471 nm for stick boundary condition.²⁹ This value is similar to the

crystallographic radius (0.494 nm).⁴² We have previously determined,²² using electrochemical methods with microelectrodes, that the hydrodynamic radius of ferrocene methanol (a neutral probe) in water at 298.15 K is 0.31 ± 0.03 nm for stick boundary condition, a value slightly larger than that determined by Miao et al.⁴³ (0.275 ± 0.04 nm), and close to the ones determined in sucrose aqueous solutions well above the glass transition.²² The averaged hydrodynamic radius of disodium fluorescein in water^{44–47} is 0.51 nm for stick boundary condition, in very good agreement with the value reported in dilute sucrose solutions (0.49 ± 0.15 nm).²³ Considering the similar radii of Bu₄N⁺, ferrocene methanol and fluorescein, the differences observed in the mobility viscosity dependence of Bu₄NI and Bu₄NBr in disaccharide aqueous solutions, in comparison to that of ferrocene methanol and fluorescein anion, are remarkable. For the ionic salts, Bu₄NI and Bu₄NBr in trehalose and sucrose aqueous solutions, respectively, $\Lambda^0\eta$ deviates from eq 1 even in the stable liquid region, well above T_g . On the other hand, the diffusion of ferrocene methanol and fluorescein is well described by the SE equation at reduced temperatures (T_g/T) below 0.75 and 0.65, respectively. The difference observed between these solutes can be explained considering that the viscosity dependence of the molar conductivity for the salts Bu₄NI and Bu₄NBr is mainly determined by the behavior of the smaller anionic species, as we concluded previously for the analysis of the electrical conductivity of sodium borate and its corresponding trehalose ester in concentrated borate-trehalose aqueous solutions.²¹ In stable solutions, the molar conductivity of the borate-trehalose ester is well described by the Walden rule. However, the total conductivity of sodium borate in trehalose aqueous mixtures, where the principal contributions to the conductivity are determined by the ester and sodium ions, is given by eq 4 with $\alpha = 0.62$, being in this case the ion Na⁺ responsible for the breakdown of the Walden rule.

In the same way, we can conclude that the effect of the smaller iodide and bromide ions on the molar conductivity of Bu₄NI and Bu₄NBr in trehalose and sucrose aqueous solutions determine the breakdown of the Walden rule in these systems, even when these anions are bulkier than Na⁺ ions. Even more, the effect of the anion size in the α value can be observed when comparing the Bu₄N⁺ salts, where α is bigger for the iodide in comparison with the smaller bromide counterion.

3.3. Dielectric Friction in Disaccharide Water Solutions.

Equation 1 has been used to define hydrodynamic ionic radii in water and other simple liquids, while its limitations, for small ions, have been recognized leading to corrections which account for the ion–solvent dielectric friction.

Zwanzig⁴⁸ developed a dielectric friction model and obtained an expression for the molar conductivity viscosity dependence that predicts a decrease in the Walden product, $\Lambda^0\eta$, with decreasing ionic size, as observed experimentally. However, the disagreement found between the values obtained from the experiments and those calculated with the theory is big, giving theory molar conductivity values smaller than the experimental ones. Hubbard and Onsager⁴⁹ developed the most complete continuum theory of ionic friction by solving the Navier–Stokes hydrodynamic equations. Wolynes⁵⁰ formulated the simplest form of this theory, where the total friction (ζ) is given by the following equation:

$$\frac{1}{\zeta} = \int_R^\infty \frac{dr}{4\pi r^2 \eta(r)} = \frac{\lambda}{z^2 e F} \quad (8)$$

with

$$\eta(r) = \eta \left(1 + \frac{R_{\text{HO}}^4}{r^4} \right) \quad (9)$$

R being the ionic radius and R_{HO} being the Hubbard Onsager radius defined as:

$$R_{\text{HO}}^4 = \frac{\tau e^2 (\epsilon_s - \epsilon_\infty)}{64 \pi^2 \eta \epsilon_0 \epsilon_s^2} \quad (10)$$

with ϵ_s being the static dielectric constant, ϵ_∞ being the infinite frequency dielectric constant, ϵ_0 being the permittivity of vacuum, and τ being the relaxation time of the solvent. This theory yields molar conductivity values of alkyl-ammonium ions that coincide with the experimental data, but overestimates the molar conductivity values of small ions. Bagchi and Biswas⁵¹ developed a model that includes the ultrafast solvation and allows describing the ionic conductivities of small ions in water and other simple solvents. Unfortunately, the calculation of the friction using this model requires detailed information of the dynamics of the solvent, which is not available for the aqueous sugar mixtures analyzed in this work.

Considering that some of the ions studied in this work are small in comparison to the solvent molecules, the dielectric friction should be considered in the description of the conductivity viscosity dependence of these solutes. Therefore, it is important to analyze the magnitude of the dielectric friction to evaluate if the deviations observed in eq 1 can be explained by this additional friction. Consequently, in order to test this hypothesis we calculated the Walden product, using the model proposed by Hubbard and Onsager (eq 8), for the conductivity data of NaCl in trehalose aqueous solutions reported by Miller et al.²⁰ This system was the only one analyzed in this work since the data of ϵ_s , ϵ_∞ , and τ , required for the calculation of R_{HO} (eq 10), were only available for aqueous trehalose.³⁹ What is more, according to the theory, this salt would have the largest dielectric friction among the studied salts in this work. Therefore, it represents a stringent test to our analysis. Table 6 summarizes the obtained results. The reported values of $\Lambda^0 \eta(r)$ correspond to the hydrodynamic radius of NaCl obtained in water at 298.15 K ($R = 0.062$ nm) and to the crystallographic radius ($R = 0.073$ nm) of the salt. The reported values of R_{HO} were calculated by fitting, with a linear equation, $\log R_{\text{HO}}$ as a function of $\log \eta$ for trehalose aqueous solutions 20–50 wt% between 278.15 and 308.15 K.

In Table 6 it can be observed that $\Lambda^0 \eta(r)$, where $\eta(r)$ is the viscosity corrected by the dielectric friction, also increases with solution viscosity. This increment can be described by eq 7 with $\alpha = 0.665 \pm 0.004$ and $\alpha = 0.671 \pm 0.004$ for $R = 0.073$ nm and $R = 0.062$ nm, respectively. These values of α are 7–8% bigger than that reported previously (Table 5), where the dielectric friction was neglected. Thus, although taking the dielectric friction into account reduces the magnitude of the deviations to the Walden rule for the conductivity of NaCl in trehalose aqueous solutions, it does not explain the magnitude of the observed deviations. Therefore, this analysis reinforces the idea of the existence of local microheterogeneities in the solution, where the ions move in regions richer in water. Considering that the magnitude of the dielectric friction for bigger ions such as Bu_4N^+ and I^- is smaller, the dielectric friction can not explain the values of α reported in Table 5 for Bu_4NI or Bu_4NBr .

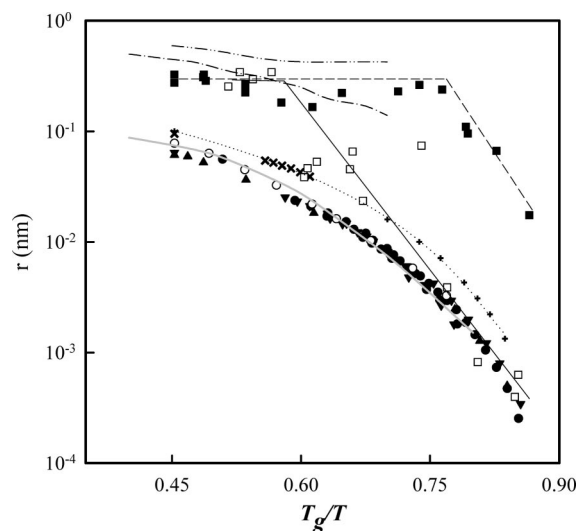


Figure 4. Hydrodynamic radii of ferrocene methanol (■), NaCl (●), KCl (▲), CsCl (▼), and Bu_4NBr (+) in sucrose aqueous solutions and fluorescein disodium anion (□), NaCl (○), and Bu_4NI (×) in trehalose aqueous solutions. The solid, dashed, and dotted lines are a visual guide to the eye for the behavior of fluorescein disodium anion, ferrocene methanol, and Bu_4NBr - Bu_4NI , respectively. The experimental data by Rampp et al.⁵² are also plotted for the diffusion of: trehalose in trehalose aqueous solutions (— · —); sucrose in sucrose aqueous solutions (— · —); and water in these disaccharide aqueous solutions (solid grey line).

TABLE 6: Dielectric Friction Calculation for the Electrical Molar Conductivity of NaCl in Aqueous Trehalose Solutions at 298.15 K²⁰ Using the Model Proposed by Hubbard and Onsager

(Trehalose) wt%	η (mPa.s)	R_{HO} (pm)	$\log \Lambda^0 \eta(r) / \text{S.cm}^2.\text{Pa.s.mol}^{-1}$	
			$R = 0.073$ nm	$R = 0.062$ nm
0.00	0.8937	150.0	−0.696	−0.634
19.98	1.765	140.7	−0.630	−0.568
34.98	4.382	129.2	−0.514	−0.454
45.00	10.36	119.2	−0.403	−0.346
53.95	29.73	108.0	−0.265	−0.211
58.98	64.31	100.5	−0.154	−0.103
64.96	206.7	90.06	0.012	0.058
70.96	1004	77.67	0.226	0.263
74.97	4087	68.10	0.449	0.479

The dielectric friction model proposed by Zwanzig⁴⁸ was not considered in this work because it sharply overestimates the dielectric friction contribution for small ions.

3.4. Decoupling in Disaccharide Supercooled Solutions.

In this section a comparison between the decoupling observed for the different ionic solutes analyzed in this work in aqueous disaccharide matrices will be given. In Figure 4, the effective hydrodynamic radius of the solutes, calculated assuming the validity of the hydrodynamic eqs 1 and 2, are plotted as a function of the T_g -scaled inverse temperature. Despite the fact that the hydrodynamic radius has not physical meaning, except in the region where the hydrodynamic equations are obeyed, it gives an idea of the T_g/T region where these equations are valid. It can be observed that the magnitude of the decoupling is very similar for all alkaline chlorides and takes place at temperatures well above T_g . The behavior for the bulky tetrabutylammonium salts looks similar to the one observed for smaller ions although, as expected, the effective radii of these ions are larger. Because both, anion and cation, contribute to the electrical conductivity, the decoupling for tetrabutylammonium salts can be influenced mainly by the smaller iodide and bromide counterions. This assumption is supported by the behavior of the effective

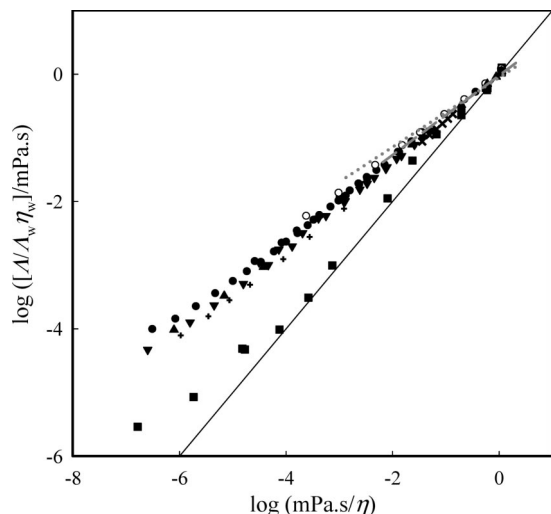


Figure 5. Modified Walden plots for ionic and non ionic solutes in trehalose and sucrose solutions. The symbols used are the same as in Figure 4. The solid line represents the ideal behavior and the gray dashed and dotted lines correspond to the diffusion data of water in sucrose and trehalose aqueous solutions respectively, reported by Ramp et al.⁵² Systems above the ideal line have supermobility whereas those below this line have submobility.

hydrodynamic radius of the fluorescein anion, whose diffusion coefficient in trehalose was measured recently.²⁵ It can be observed in Figure 4 that for this bulky ion, the Stokes–Einstein equation is obeyed over a narrow range of T_g/T , with a decoupling similar to that of the other ions when the temperature decreases. On the other hand, the range of validity of the Stokes–Einstein equation extends over a wide range of T_g/T for a neutral solute, as can be observed in Figure 4 for ferrocenemethanol.

We have included in Figure 4 the effective hydrodynamic radius of water, trehalose and sucrose, calculated from the diffusion data of each component in aqueous disaccharide mixtures, assuming the validity of the SE relationship.⁵² It is remarkable that the self-diffusion of the disaccharides seems to obey the classical hydrodynamic model, while water exhibits the same behavior as the ions. This reinforces the idea that, in the stable and supercooled regimes, the mobility of the ions is coupled to the water mobility, which in turn is decoupled from the disaccharide one.

Finally, we plotted the same results in the way of a modified Walden plot for a better comparison of the decoupling constants of the ionic and nonionic solutes having different hydrodynamic radii. This modified Walden plot allows the comparison of ionic and nonionic solutes because it considers that in the limit of zero disaccharide concentration eq 1 is valid with $R = R_w$, the effective radius in water. Therefore, when eq 4 is used to describe the viscosity dependence of the conductivity in saccharide aqueous solutions it results that:

$$\log\left(\frac{\Lambda}{\Lambda_w \eta_w}\right) = \alpha \log(\eta^{-1}) \quad (11)$$

The Walden product $\Lambda_w \eta_w$ in water gives a measurement of R_w^{-1} and, consequently, normalizes the plot for solutes of different sizes. A similar analysis is valid for the diffusion coefficients of solutes in systems which obey eq 5 by changing the ratio $\Lambda/\Lambda_w \eta_w$ by $D/D_w \eta_w$.

The modified Walden plots observed in Figure 5 clearly indicate that all the ionic salts fall on a common line on the superionic side of the Walden plot (above the ideal line, $\alpha = 1$), with an averaged decoupling constant $\alpha = 0.66 \pm 0.04$. On the other hand, the data for the neutral ferrocene-methanol lie on the ideal line ($\alpha = 1$) for high fluidities (high T_g/T) but diffusion decouples from viscosity ($\alpha < 1$) at low fluidities (high T_g/T). The value of the decoupling constant in this region is similar to that observed for ionic solutes ($\alpha = 0.61 \pm 0.05$). As mentioned in relation to Figure 4, the modified Walden plot for the diffusion of water in sucrose and trehalose is similar to that of the ionic salts, while the results for the diffusion of the disaccharides, not shown in Figure 5, are close to the ideal line.

The measured values of the decoupling constant, α , for the mobility of NaCl in polyol–water glass-forming mixtures is 0.63 ± 0.01 in disaccharides (sucrose and trehalose), 0.78 in glucose (monosaccharide), and 0.91 in glycerol, indicating that the decoupling in these binary systems decrease as the size of the polyol molecule becomes closer to that of water. Probably there is a correlation between the decoupling and the capacity of the solute to induce structural heterogeneities around it (preferential solvation). On the other hand, for the self-diffusion of bulky single-component glass-forming liquids in the supercooled regime $\alpha = 0.77–0.80$,^{26,27} which is attributed to spatially heterogeneous dynamics.^{26–28}

Certainly, the decoupling in the binary aqueous glass-forming mixtures studied in this work could be determined in the supercooled regime by a combination of structural and dynamics heterogeneities, but the relative contribution of each of these effects is difficult to estimate.

The Walden plots of ionic solutes in supercooled disaccharide solutions resemble to those reported by Mizuno et al.⁵³ for superionic water-free protonic conductors, such as trimethylammonium dihydrogen phosphate, indicating that the decoupling of the ion mobility from the disaccharide matrix is similar to that observed for protons in glass formers. As far as we know, the mobility behavior of ferrocene methanol in supercooled disaccharide solutions is the first report where the transition from a decoupled to an ideal behavior is observed on the superionic side of the Walden plot. This is also the case of fluorescein, not shown in Figure 5 due to the high dispersion in the experimental data. The opposite behavior was reported by McLin and Angell,⁵⁴ when analyzing the conductance of LiClO_4 and sodium triflate solutions in poly(propylene oxide). They observed that the salt mobility approaches the ideal line at low fluidities, while a reduction in the mobility was observed at high fluidities due to an increment in ionic pairing.

Conclusions

The molar conductivity of CsCl, KCl, Bu_4NBr , and Bu_4NI was studied in stable and supercooled sucrose and trehalose aqueous solutions over a wide viscosity range, explored by changing the disaccharide concentration and the temperature of the solutions.

The decoupling index, α , defined by the modified Walden rule, eq 4, was obtained from the experimental results and compared to values already available in the literature. It was observed that the decoupling for the different salts is similar in both disaccharides, with values of α between 0.61 and 0.74, increasing slightly with the size and charge of the constituent ions.

The conductivity of Bu_4NI in trehalose (39.13 wt%) aqueous solutions was performed on a wide range of temperatures (268–293 K) as a function of salt concentration in the region

where Onsager's equation is valid. This allowed us to carry out a detailed analysis of the salt mobility using the local viscosity, in order to obtain local or effective dielectric constant values. At a temperature around 280 K, the effective dielectric constant seems to switch between the value of the bulk solution above this temperature, and the value of pure water below it.

We probed, using a classical model, that the dielectric friction between the ionic solutes and the water-sugar solvent is small enough to account for the breakdown of the Walden rule observed for ionic solutes in the liquid and supercooled regimes.

Finally, the decoupling of the ionic solutes studied in this work was compared to that observed for other ionic and nonionic solutes measured in the same disaccharide solutions. The Walden plots seems to indicate that the mobility of ionic solutes decouples from the solution viscosity all over the range of reduced temperatures studied, following the behavior of water in the same stable and supercooled systems. Bulky neutral solutes, as ferrocenemethanol, obey the classical hydrodynamic model (SE relation) over a wide range of T_g/T but decoupling is observed when the temperature decreases. The magnitude of this decoupling, determined by α , is extremely similar to that observed for ionic solutes.

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