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Role of the triple solute/ion/water interactions on the saccharide hydration: A volumetric approach

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A B S T R A C T

The aim of this study is to further the understanding of the mechanisms that govern the hydration behavior of neutral solutes, with respect to the ions' properties that are present in a solution. For that, a systematic volumetric study of saccharides (xylose, glucose and sucrose), in the presence of various electrolytes (LiCl, NaCl, KCl, Na₂SO₄, K₂SO₄, CaCl₂, MgCl₂, MgSO₄) has been carried out with density measurements at 298.15 K. From this data, the standard transfer molar volume of the saccharide $\Delta V_{\phi,S}^0$, which characterizes the hydration state of the solute, has been determined.

Positive and increasing values of $\Delta V_{\phi,S}^0$ with increasing electrolyte concentrations were obtained. This indicated the dehydration of the saccharide in the presence of the electrolyte, due to the predominance of saccharide/cation interactions.

Concerning the influence of the cation, it was shown that saccharides are more dehydrated in the presence of divalent cations than in the presence of monovalent ones. This is because the interactions are stronger between saccharides and divalent cations, in comparison to those with monovalent cations. For a specific cation valence and molality, regardless of the anion, saccharide dehydration increases according to the following sequences: $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ and $\text{Mg}^{2+} < \text{Ca}^{2+}$. These saccharide dehydration sequences have been explained by the Gibbs free energy of hydration of the cations, reflecting the cation/water interactions. For a specific cation valence, it was concluded that decreasing cation/water interactions induce the increase of saccharide dehydration.

Concerning the influence of the anion, it was also observed that saccharides are more dehydrated in the presence of divalent anions than in the presence of monovalent ones. It was stated that saccharide/cation interactions are modulated by the nature of the anion. The anion impact was again attributed to its capacity to interact with water molecules. It was pointed out that anions with increasing values of Gibbs free energy of hydration cause an increase in saccharide/cation interactions or a decrease in saccharide/anion interactions. Therefore, saccharide dehydration increases.

Keywords:

Saccharides

Electrolyte

Hydration

Standard transfer partial molar volumes

Interactions

1. Introduction

In the fields of the environment, chemistry, biochemistry, biophysics and food, the characterization and the understanding of the interactions between electrolytes and saccharides, have gained great interest over the past 20 years [1–7]. Properties of aqueous solutions of saccharides are influenced by the ions. These can perturb interactions between saccharides and water molecules. For instance, in the food industry, organoleptic properties of various substances can be tuned by using salts that control water-solute

interactions [1,8]. Studying saccharide interactions with electrolytes, in aqueous media, contributes to the increase in scientific knowledge about mechanisms that govern saccharide biologic activity. Basic research in chemistry and biology treats this property. As an example, the cryoprotectant action of saccharides on biological molecules can be modulated by using salts, modulations that can be attributed to changes in saccharide hydration [9,10]. In fact, the structural organization of water molecules can increase or decrease in the presence of electrolytes, and can result in changes in the saccharide hydration layer [1].

The development of thermodynamic methods to determine properties of saccharides in electrolytic aqueous solutions are gaining interest. Indeed, thermodynamic properties can provide valuable characteristics for comprehending the changes in the

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hydration behavior of saccharides in the presence of ions [11–14]. For instance, compressibility measurements enable the evaluation of changes in the first two layers of solvents around a molecule [1,7,8,15]. Viscosity and conductivity measurements are also adapted for the study of interactions between solutes and ions [6,7,11,16–20]. Volumetric properties (apparent molar volume) for saccharide/electrolyte/water systems can provide information on the structural interactions in solutions and a number of studies deals with these properties [3–5,21–24].

More recently in the field of membrane separation, volumetric properties have been used to understand the increase of the mass transfer of neutral species, such as saccharides, through nanofiltration membranes in the presence of electrolytes [25]. From the apparent molar volume of saccharides, which characterizes the saccharide hydration, a relationship has been established between the increase in mass transfer and the dehydration of the neutral solutes, depending on the ionic composition.

Some papers treat a systematic study of interactions of various saccharides with only one electrolyte. For instance, Zhuo et al. have investigated the interactions between saccharides (xylose, arabinose, glucose, and galactose) and NaCl at various concentrations [5]. Other authors reported the dependence of the saccharides hydration on their stereochemistry (mono-saccharide, disaccharide, tri-saccharide) in one electrolyte [26,27]. Few studies treat the impact of the nature of ions (cation or anion, valence, size), on the saccharide-electrolyte interactions.

A number of studies are available on the interactions of saccharides with monovalent cations [28,29]. For instance, in order to investigate the influence of the ion size, Zhuo and al. reported volumetric properties of CsCl and NaCl with monosaccharides (D-galactose, D-xylose and D-arabinose) [22,30]. This authors explained the greater impact of CsCl, compared to NaCl on the saccharides' hydration, by the larger volume of Cs⁺ in comparison to Na⁺. However, it remains difficult to explain the mechanisms and interactions that are involved in such system.

There is little information in the literature concerning interactions of various saccharides with different divalent cations. Still, thermodynamic properties that characterize the interactions between Ca²⁺ and some saccharide isomers have been determined by Morel et al. [31]. Banipal et al. also reported the apparent molar volumes, for various monosaccharides in aqueous solutions of magnesium chloride (MgCl₂) [26]. The results showed that divalent cations have stronger interactions with saccharides than monovalent ones [26,32,33].

The influence of the anion (different size and charge) of the electrolyte on the volumetric properties of saccharides has also been scarcely studied. In the case of halide solutions, it was suggested that the impact of the anion on the saccharide volumetric properties may be attributed to its ability to “structure” or to “break” the water [34]. Different behavior of saccharides in the presence of Na₂SO₄ and NaOOCCH₃ have also been reported by Banipal and al [35]. It was shown that the saccharides are more dehydrated in the presence of 1:2 electrolytes than in the presence of 1:1 electrolytes. These differences have been attributed to the stronger ability of SO₄²⁻ ions to stabilize the water structure, in comparison to CH₃COO⁻. Boy et al. [25] also pointed out the influence of the anion on the volumetric properties of saccharide/NaCl and Na₂SO₄ systems, which has been attributed to the anion hydration properties. However, conclusions concerning the impact of the anion are not so clear and still remain difficult to generalize to other systems.

These latter works have shown that the volumetric properties of saccharides are pertinent for the investigation of the saccharide/electrolyte interactions and the saccharide hydration state. However, the lack of systematic experimental data makes it difficult to

understand the relationship between these properties and the ions characteristics (cation/anion, charge, size, and hydration).

In this context, the objective of the present study is to deepen the understanding of the mechanisms that govern the saccharide/electrolyte interactions, and more specifically the saccharide hydration state, depending on the ions' properties. Therefore, this work proposes a systematic volumetric study of saccharides of increasing molecular weights (xylose, glucose and sucrose) in the presence of various electrolytes (LiCl, NaCl, KCl, Na₂SO₄, K₂SO₄, CaCl₂, MgCl₂, MgSO₄). The investigation of a large number of systems means that more information is available about the volumetric properties of saccharides in the presence of electrolytes that contain various monovalent and divalent ions. In addition, the investigation will establish the relationship between the ions' properties and the saccharide/electrolyte interactions (cation/anion, charge, size, and hydration).

2. Materials and methods

Chemicals used in the experiments, from Acros organics, were saccharides of increasing molecular weights: xylose (150.13 g mol⁻¹), glucose (180.16 g mol⁻¹) and sucrose (342.29 g mol⁻¹). Salts had a purity >99.9%: LiCl, NaCl, KCl, MgCl₂•6H₂O, CaCl₂•2H₂O, Na₂SO₄, K₂SO₄ and MgSO₄•7H₂O. They were used as such, without further purification.

Saccharides and anhydride salts were dried under vacuum at 333 K to a constant weight.

Hygroscopic salts were also dried in a vacuum desiccator, at a temperature corresponding to the loss of adsorbed water on the crystal surface: MgCl₂•6H₂O (40 °C); CaCl₂•2H₂O (50 °C); MgSO₄•7H₂O (55 °C). Protocols used for MgCl₂, CaCl₂ and MgSO₄ are reported in Refs. [36] [37], and [38] respectively. After this treatment, the characterization of salts was performed with thermogravimetric analyses, to control the amount of water in the salt.

Saccharides and salts were then stored on top of a silica gel in desiccators.

All solutions were freshly prepared with ultra-pure water (Milli-Q RG, Millipore) with a resistivity of 18.2 mΩ cm⁻¹. The pH of the various solutions was about (6 ± 0.5) without any adjustment. Solutions were weighed on a Mettler balance (AE 240) to the nearest of ±0.1 mg.

Density measurements were carried out on a vibrating tube digital density meter (Model DMA 5000, Anton Paar, Austria). The temperature was kept constant at 25 °C with an accuracy of temperature control of ±0.001 °C. The density of each sample was measured at least three times, after temperature equilibrium had been reached. The uncertainty in density was estimated to be ±15 · 10⁻⁶ g cm⁻³. At the beginning and at the end of each working day, an air check was performed. If necessary, the density meter was calibrated using both air and ultra-pure fresh water at atmospheric pressure.

3. Results and discussions

Densities of various saccharides in water and in electrolytes measured at 298.15 K enable the calculation of the apparent molar volumes of saccharides. From this data, the standard transfer molar volume of the saccharide can be determined in order to obtain information about the saccharide hydration, depending on the ions' properties.

3.1. Standard partial molar volumes

Apparent molar volumes of saccharides, $V_{\phi,S}$ (in cm³ mol⁻¹), were calculated from density measurements, using the respective

equations for saccharide/water and saccharide/electrolyte solutions [5,25,39]:

$$V_{\phi,S}(m_S) = \frac{M_S}{d_S} - \frac{1000(d_S - d_0)}{m_S d_S d_0} \quad (1)$$

$$V_{\phi,S}(m_S, m_E) = \frac{M_S}{d} - \frac{(1000 + m_E M_E)(d - d_E)}{m_S d d_E} \quad (2)$$

where M_E and M_S are the molecular mass of the electrolyte and the saccharide (in $\text{g}\cdot\text{mol}^{-1}$), m_E and m_S are the molalities of the electrolyte and the saccharide (in $\text{mol}\cdot\text{kg}^{-1}$ of pure water), and d , d_S , d_E and d_0 , the densities of saccharide/electrolyte, saccharide/water, electrolyte/water, and pure water solutions, respectively (in $\text{g}\cdot\text{cm}^{-3}$ of solution). The molality uncertainty is approximately $\pm 0.01\%$ for saccharides and $\pm 0.04\%$ for electrolytes. For both solutes, the scale of molality was from 0 to 2 $\text{mol}\cdot\text{kg}^{-1}$. Standard deviation in $V_{\phi,S}$ values was approximately $0.02\text{ cm}^3\cdot\text{mol}^{-1}$.

The apparent molar volume at infinite dilutions ($V_{\phi,S}^0$), which is equal to the standard partial molar volume, can be obtained from Masson's equation [40], by least-square fitting of the experimental data, $V_{\phi,S}$ versus m_S :

$$V_{\phi,S} = V_{\phi,S}^0 + S_S^* m_S \quad (3)$$

where S_S^* is the experimental slope (in $\text{cm}^3\cdot\text{kg}\cdot\text{mol}^{-2}$). The standard partial molar volume of the saccharide, $V_{\phi,S}^0$, characterizes the solute-solvent interactions since solute-solute interactions are negligible at infinite dilutions [41].

The slope S_S^* is known as the volumetric virial coefficient and characterizes the solute-solute interactions [19,42]. Positive S_S^* values characterize attractive saccharide-saccharide interactions. These interactions take place through the overlap of the solvated region of the saccharides. As the concentration of the solute increases, both hydrated regions of adjacent saccharides can overlap. Thus, the average number of water molecules engaged in hydration reduces and a quantity of water is released into the bulk [42].

Concerning the experimental measurements, the densities of the solutions containing saccharides in water and in electrolytes are given as supplementary data in Table S1. The corresponding apparent molar volumes of the saccharide $V_{\phi,S}$ are also given in Table S1, as a function of the electrolyte molality. Fig. 1 shows the variation of the apparent molar volume of glucose, versus its molality, for increasing NaCl (Fig. 1-a) and CaCl_2 molalities (Fig. 1-b). The variation of the apparent molar volume for sucrose versus its molality, at different NaCl and CaCl_2 molalities, are presented in Fig. 2 (a) and Fig. 2 (b) respectively. The difference between the experimental values obtained in this work and the ones previously reported [30] for the glucose/NaCl system does not exceed 0.3% (Fig. 1-a). Similar variations are obtained for the other saccharide/electrolyte systems investigated in this work (results not shown). Figs. 1 and 2 show that the apparent molar volume of saccharide is always higher in electrolyte solutions compared to water. For a given saccharide molality, it can be noted that the apparent molar volume of the saccharide increases with the electrolyte concentration. Moreover, the apparent molar volume $V_{\phi,S}$ increases linearly with increasing saccharide molality (m_S).

Values of S_S^* and of $V_{\phi,S}^0$, obtained for the saccharide/electrolyte systems investigated, are reported in Tables 1–3. These results can be compared with previous experimental studies reported in the literature. For instance, the standard partial molar volume of glucose in an NaCl aqueous solution of $0.5\text{ mol}\cdot\text{kg}^{-1}$ is found to be $112.73\text{ cm}^3\cdot\text{mol}^{-1}$ in this study, which is close to the value of

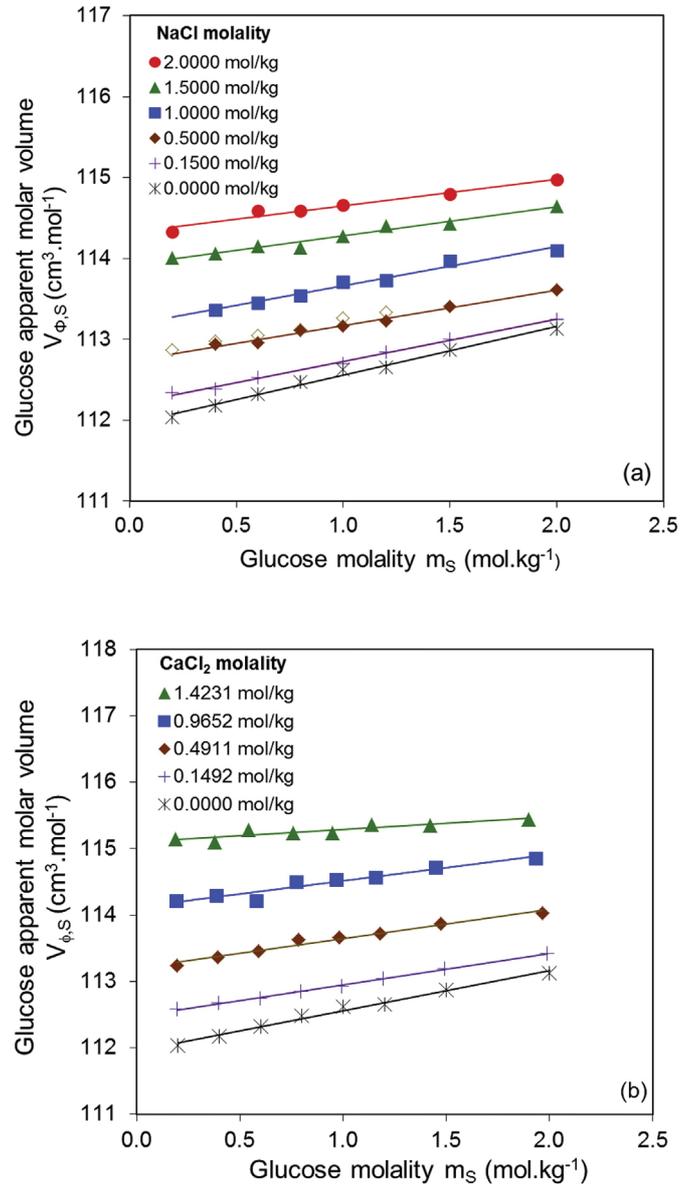


Fig. 1. Apparent molar volume of glucose versus its molality for glucose/NaCl solutions (a) and glucose/ CaCl_2 solutions (b) at 298.15 K: influence of the electrolyte molality. Comparison with published values (empty symbols) [30].

$112.77\text{ cm}^3\cdot\text{mol}^{-1}$ reported in comparable conditions [30]. For xylose in an NaCl aqueous solution of $0.5\text{ mol}\cdot\text{kg}^{-1}$, the standard partial molar volume reported in this work, $96.11\text{ cm}^3\cdot\text{mol}^{-1}$, is also correlates well to the $96.09\text{ cm}^3\cdot\text{mol}^{-1}$ reported elsewhere.

The S_S^* values ($\pm 0.03\text{ cm}^3\cdot\text{kg}\cdot\text{mol}^{-2}$) are positive in each case. The positive values of S_S^* show that saccharide-saccharide interactions are attractive and, that, as the saccharide concentration increases, saccharide-saccharide interactions become stronger. Moreover, the S_S^* values tend to decrease when the electrolyte molality m_E increases. Thus, the saccharide-saccharide interactions are greater in water than in electrolyte solutions and become weaker as the electrolyte concentration increases.

Results also show that the standard partial molar volumes of the saccharide in electrolytes are higher than those in water and increase when electrolyte molality increases (discussed later).

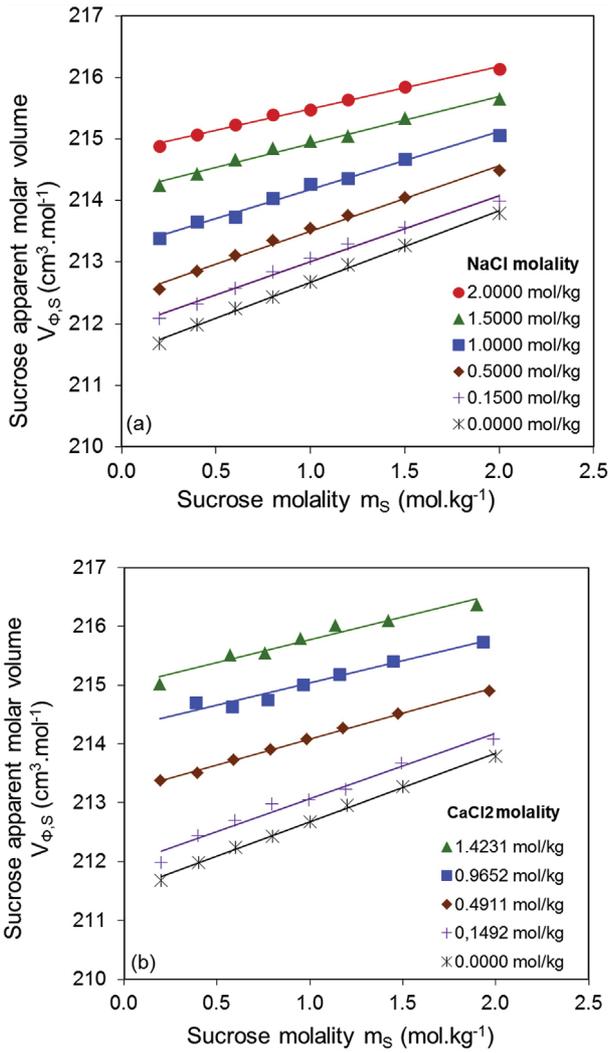


Fig. 2. Apparent molar volume of sucrose versus its molality for sucrose/NaCl solutions (a) and sucrose/CaCl₂ solutions (b) at 298.15 K: influence of the electrolyte molality.

3.2. Standard transfer partial molar volumes

The standard transfer partial volume $\Delta V_{\phi,S}^0$ of a saccharide, at infinite dilution, from water, $V_{\phi,S}^0(\text{water})$, to an electrolyte solution at molality m_E , $V_{\phi,S}^0(m_E)$ is defined by equation (4) [16,26]:

$$\Delta V_{\phi,S}^0 = V_{\phi,S}^0(m_E) - V_{\phi,S}^0(\text{water}) \quad (4)$$

The results concerning the standard transfer partial volume of a solute, $\Delta V_{\phi,S}^0$, can be interpreted from the structural hydration model [43] based on the co-sphere concept developed by Gurney [44]. According to this model, the overall influence of the solute on the structure of water is represented by a shell of water surrounding the solute, which is the solute hydration shell. As the solute concentration increases, the hydration shells of two neighbor solutes can overlap, displacing water molecules from the hydration shell into the bulk, thus modifying the thermodynamic properties of the solution.

These modifications can be explained according to different kinds of solute/co-solute interactions. In the ternary water/saccharide/salt system, the four possible interactions between the solute (the saccharide) and the co-solute (anion or cation of the electrolyte) are:

Table 1

Standard partial molar volumes $V_{\phi,S}^0$ ($\text{cm}^3 \cdot \text{mol}^{-1}$) of the saccharides in chloride solutions, with monovalent cations. Electrolyte molality m_E ($\text{mol} \cdot \text{kg}^{-1}$) and slopes S_S^* in brackets ($\text{cm}^3 \cdot \text{kg} \cdot \text{mol}^{-2}$) of Eq. (3) at 298.15 K.

	m_E	Xylose	Glucose	Sucrose	
Water	0.0000	95.53 (0.38)	111.95 (0.60)	211.51 (1.16)	
LiCl	0.1500	95.65 (0.36)	112.21 (0.49)	211.86 (1.06)	
	0.5000	95.79 (0.37)	112.44 (0.50)	212.11 (1.10)	
	1.0000	96.07 (0.33)	112.85 (0.41)	212.69 (1.01)	
	2.0000	96.78 (0.17)	113.49 (0.41)	213.82 (0.71)	
NaCl	0.1500	95.68 (0.37)	112.20 (0.52)	211.93 (1.07)	
	0.5000	96.11 (0.32)	112.73 (0.44)	212.44 (1.06)	
	1.0000	96.57 (0.26)	113.13 (0.54)	213.25 (0.94)	
	1.5000	97.00 (0.27)	113.92 (0.36)	214.16 (0.77)	
	2.0000	97.37 (0.23)	114.32 (0.33)	214.80 (0.69)	
	KCl	0.1500	95.66 (0.39)	112.15 (0.57)	211.88 (1.05)
		0.5000	96.08 (0.34)	112.71 (0.48)	212.67 (0.91)
		1.0000	96.58 (0.26)	113.44 (0.34)	213.68 (0.67)
2.0000			114.38 (0.28)	214.88 (0.53)	

Table 2

Standard partial molar volumes $V_{\phi,S}^0$ ($\text{cm}^3 \cdot \text{mol}^{-1}$) of the saccharides in chloride solutions, with divalent cations. Electrolyte molality m_E ($\text{mol} \cdot \text{kg}^{-1}$) and slopes S_S^* in brackets ($\text{cm}^3 \cdot \text{kg} \cdot \text{mol}^{-2}$) of Eq. (3) at 298.15 K.

	m_E	Xylose	Glucose	Sucrose
MgCl ₂	0.1500	95.76 (0.36)	112.37 (0.50)	212.07 (1.03)
	0.4744	96.17 (0.34)	112.92 (0.49)	212.84 (0.97)
	0.9024	96.66 (0.34)	113.56 (0.41)	213.73 (0.79)
	1.2907	97.04 (0.30)	114.35 (0.21)	214.46 (0.72)
CaCl ₂	0.1492	95.91 (0.32)	112.48 (0.47)	211.95 (1.11)
	0.4911	96.38 (0.33)	113.20 (0.44)	213.21 (0.88)
	0.9652	97.23 (0.31)	114.12 (0.39)	214.28 (0.76)
	1.4231	97.68 (0.29)	115.10 (0.19)	215.00 (0.77)

- (1) hydrophilic - cation interactions between the hydrophilic groups (-OH, -C=O, -O-) of saccharide and the cation of the electrolyte
- (2) hydrophilic - anion interactions between the hydrophilic groups (-OH, -C=O, -O-) of saccharide and the anion of the electrolyte
- (3) hydrophobic - cation interactions between the hydrophobic groups (-CH, -CH₂, -CH₃) of saccharide and the cation of the electrolyte
- (4) hydrophobic - anion interactions between the hydrophobic groups (-CH, -CH₂, -CH₃) of saccharide and the anion of the electrolyte

According to the model, only the overlap of the co-sphere of

Table 3

Standard partial molar volumes $V_{\phi,S}^0$ ($\text{cm}^3 \cdot \text{mol}^{-1}$) of the saccharides in sulfate solutions, with monovalent and divalent cations. Electrolyte molality m_E ($\text{mol} \cdot \text{kg}^{-1}$) and slopes S_S^* in brackets ($\text{cm}^3 \cdot \text{kg} \cdot \text{mol}^{-2}$) of Eq. (3) at 298.15 K.

	m_E	Xylose	Glucose	Sucrose
Na_2SO_4	0.1500	96.15 (0.30)	112.82 (0.45)	212.34 (1.12)
	0.5000	96.97 (0.42)	114.05 (0.38)	214.40 (0.76)
	0.7500	97.64 (0.34)	114.90 (0.26)	215.64 (0.53)
	1.0000	98.18 (0.25)	115.49 (0.19)	216.39 (0.53)
K_2SO_4	0.1500		112.68 (0.49)	212.73 (0.93)
	0.3000		113.41 (0.42)	213.58 (0.83)
	0.5000	97.35 (0.23)	114.23 (0.27)	214.60 (0.67)
MgSO_4	0.1472	95.86 (0.42)	112.45 (0.54)	212.40 (1.00)
	0.4703	96.73 (0.29)	113.57 (0.41)	213.90 (0.72)
	0.8880	97.61 (0.23)	114.63 (0.25)	215.38 (0.54)
	1.2614		115.43 (0.23)	216.36 (0.43)

hydrophilic sites of the saccharide and of the cation (saccharide/cation interactions, type 1) confers a positive value to the transfer volume. Interactions 2, 3 and 4 provide negative values to the transfer volume.

Typical variations of $\Delta V_{\phi,S}^0$ versus NaCl molality are plotted in Fig. 3 for the three saccharides. One can observe that the $\Delta V_{\phi,S}^0$ values of all saccharides are positive and increase with the electrolyte molality. The same variations are observed for other saccharide/electrolyte systems (results not shown). Therefore, positive values of the standard transfer partial volume signify that saccharide/cation interactions (hydrophilic groups of the saccharide and the cation) are predominant in saccharide/electrolyte systems. Similar variations have been observed by other authors for saccharides in electrolyte solutions [26,32,34].

A commonly used model for the apparent molar volume at an infinite dilution enables the understanding of the $\Delta V_{\phi,S}^0$ values and

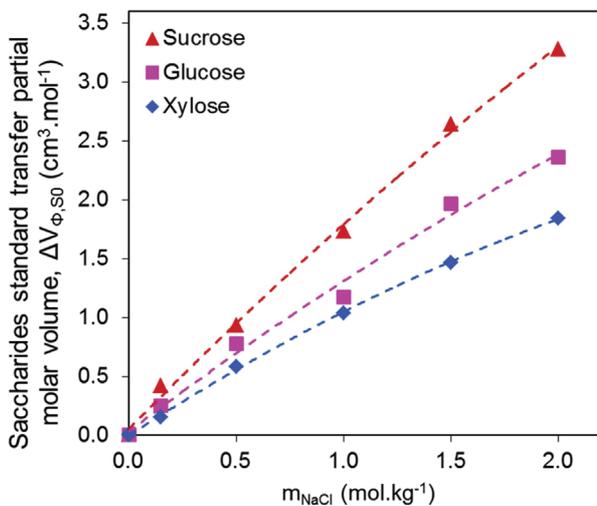


Fig. 3. Standard transfer partial molar volumes in aqueous solution of NaCl for the three saccharides at 298.15 K: influence of the saccharide size.

variations. At an infinite dilution, when the apparent molar volume of the saccharide is equal to the standard partial molar volume, the standard partial molar volume can be expressed by the Shahidi equation [45]:

$$V_{\phi,S}^0 = V_{V,W} + V_{\text{void}} - V_{\text{shrinkage}} \quad (5)$$

where $V_{V,W}$ is the van der Waals volume, V_{void} is the empty volume, and $V_{\text{shrinkage}}$ is the shrinkage volume due to the interaction of the solute with water. The shrinkage in volume is caused by hydrogen-bonding of water molecules to the hydroxyl groups of the saccharides. $V_{V,W}$ and V_{void} are meant to have the same magnitudes in water and in aqueous electrolyte solutions. Hence, positive values of $\Delta V_{\phi,S}^0$ arise from the decrease of $V_{\text{shrinkage}}$, due to the reduced electrostriction of water. Because of the predominance of the attractive saccharide/cation interactions, saccharide-water hydrogen bonds are weaker; water molecules are thus released from the hydration layer to the bulk. Released water has a higher volume contribution than that comprised in the hydration layer, and, as a consequence, the $V_{\phi,S}^0$ values increase. In other words, positive values of $\Delta V_{\phi,S}^0$ characterize the saccharide dehydration [42].

Fig. 3 also shows the systematic increase of $\Delta V_{\phi,S}^0$ with the electrolyte concentration, which indicates the strengthening of the saccharide/cation interactions in the range of the studied concentrations. Thus, one can conclude that saccharide dehydration increases with electrolyte concentration.

For a given electrolyte, $\Delta V_{\phi,S}^0$ values increase with the saccharide size (mono- to di-saccharides) in the following order: $\Delta V_{\phi,S}^0$ (xylose) < $\Delta V_{\phi,S}^0$ (glucose) < $\Delta V_{\phi,S}^0$ (sucrose) (Fig. 3). Similar trends for the standard transfer partial volume have been reported in the literature for some mono- and di-saccharides in aqueous solutions of KCl [32].

The $\Delta V_{\phi,S}^0$ values reflect that sucrose interacts more strongly with electrolytes than xylose does. The variation of the saccharide hydration in the presence of electrolytes is higher in the case of sucrose than in the case of xylose. As explained in a previous investigation [25], this observation supports the hypothesis that there is a direct link between the number of hydrophilic sites of the saccharide molecules involved in saccharide/electrolyte interactions, and the standard transfer partial molar volume.

Indeed, xylose and glucose contain (4 -OH and 1 -O-) and (5 -OH and 1 -O-) sites, respectively, whereas sucrose is composed of (8 -OH and 3 -O-). Therefore, one can expect higher solute/electrolyte interactions with sucrose than with the other two saccharides.

Xylose (a pentose) and glucose (a hexose) have dominant conformations in water, which are respectively 1e2e3e4e and 1e2e3e4e6e (e for equatorial). Based on the conclusions of Galema and al. [12], hydration of carbohydrate is mostly dependent on the position of the OH (4). D-Xylose and D-glucose, with their equatorial OH (4) fit well into the structure of water. Then, given that glucose has one OH group more than xylose, glucose is more hydrated than xylose, in water.

Dehydration of the OH groups in position 1 to 4 of the xylose and glucose, should lead to approximately the same positive value contribution on the standard transfer partial molar volume. The higher standard transfer molar volume values of glucose, compared to xylose, arises from the additional OH group possessed by glucose, in position 6. Then, for a given electrolyte, glucose releases more water and is more dehydrated than xylose.

Sucrose is made of two hexoses: a glucose molecule covalently bonds to a fructose molecule (1e2e3e4e5a) by a glycosidic linkage. As are xylose and glucose, this molecule is compatible with the water structure.

The hydration of sucrose in water is much higher than that of xylose, almost twice the hydration of xylose if one refers to Galema's study [12]. As a consequence, there are more interactions between sucrose and the electrolyte than with xylose and the transfer molar volume of sucrose is almost twice that of xylose, for a given electrolyte molality. Thus, for a given electrolyte, sucrose releases twice more water molecules than xylose. This behavior can be attributed to the difference in hydration properties in water.

4. Influence of the electrolyte on the saccharide hydration state

4.1. Saccharide/electrolyte interactions

The influence of the nature of the electrolyte on the saccharide can be evaluated from the standard transfer partial molar volumes of the saccharide in different electrolytes. For example, $\Delta V_{\phi,S}^0$ variations of sucrose versus the electrolyte molality are represented in Fig. 4. One can observe that $\Delta V_{\phi,S}^0$ depends on the electrolyte (cation and anion) and varies according to the following order:

$$\Delta V_{\phi,S}^0 (\text{LiCl}) < \Delta V_{\phi,S}^0 (\text{NaCl}) < \Delta V_{\phi,S}^0 (\text{KCl}) < \Delta V_{\phi,S}^0 (\text{MgCl}_2) < \Delta V_{\phi,S}^0 (\text{CaCl}_2) < \Delta V_{\phi,S}^0 (\text{MgSO}_4) < \Delta V_{\phi,S}^0 (\text{Na}_2\text{SO}_4) < \Delta V_{\phi,S}^0 (\text{K}_2\text{SO}_4)$$

Similar features are also observed for xylose and glucose (results not shown). For a given saccharide, it is shown that the saccharide interacts more strongly with K_2SO_4 than with LiCl. In other words, as indicated from the $\Delta V_{\phi,S}^0$ values, the saccharides are more dehydrated in the presence of K_2SO_4 compared to LiCl.

4.2. Saccharide/cation interactions

The influence of the cation of the electrolyte on the saccharide hydration state is evaluated from the standard transfer partial molar volumes of the saccharides. For instance, $\Delta V_{\phi,S}^0$ of sucrose is plotted in Fig. 5 versus the cation molality, for a given anion Cl^- . It is observed that the saccharide standard transfer partial molar volume increases according to the following sequence:

$$\Delta V_{\phi,S}^0 (\text{LiCl}) < \Delta V_{\phi,S}^0 (\text{NaCl}) < \Delta V_{\phi,S}^0 (\text{KCl}) < \Delta V_{\phi,S}^0 (\text{MgCl}_2) < \Delta V_{\phi,S}^0 (\text{CaCl}_2)$$

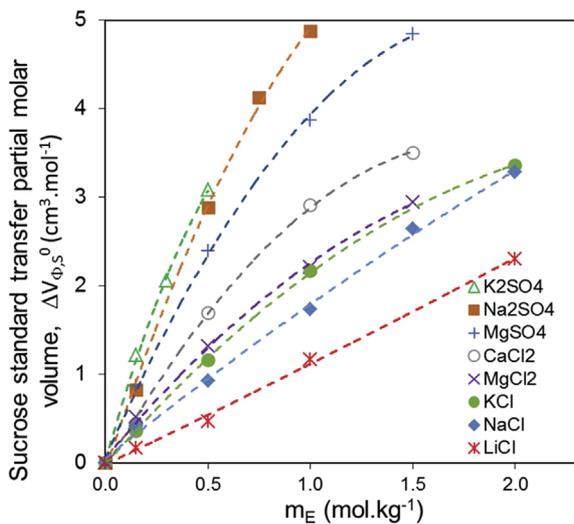


Fig. 4. Standard transfer partial molar volumes of sucrose versus the electrolyte molality m_E at 298.15 K: influence of the electrolyte.

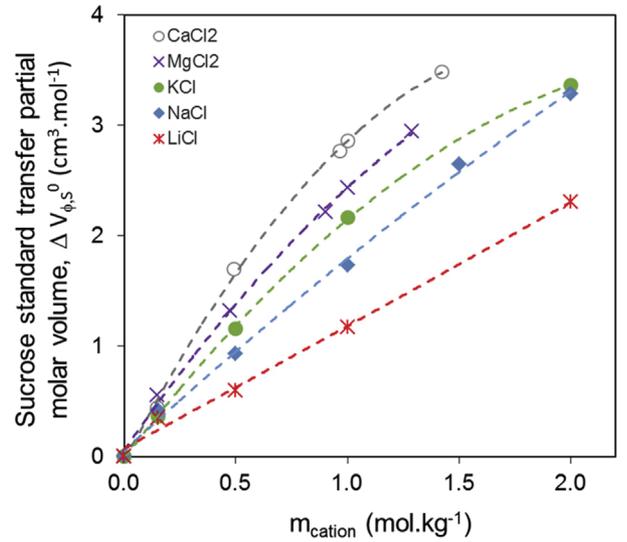


Fig. 5. Standard transfer partial molar volumes of sucrose, for a given anion Cl^- , versus the cation molality m_{cation} , at 298.15 K: influence of the cation of the electrolyte.

The same results are obtained for xylose and glucose (not shown). It is observed that the $\Delta V_{\phi,S}^0$ values obtained for divalent cations, Mg^{2+} and Ca^{2+} , are higher than those for monovalent ones, Li^+ , Na^+ , K^+ , which correlates well with previous investigations [25,26].

For a 1:1 electrolyte, one can observe the following sequence:

$$\Delta V_{\phi,S}^0 (\text{LiCl}) < \Delta V_{\phi,S}^0 (\text{NaCl}) < \Delta V_{\phi,S}^0 (\text{KCl})$$

The standard transfer partial molar volumes of the saccharide are larger in the presence of KCl than in the presence of LiCl. In KCl solutions, dehydration of saccharides occurs more than in the presence of LiCl and NaCl. Banipal and al. also reported larger transfer volumes of saccharides in solutions of KCl than NaCl [32,33].

The $\Delta V_{\phi,S}^0$ values of saccharides in 2:1 electrolyte follow the order:

$$\Delta V_{\phi,S}^0 (\text{MgCl}_2) < \Delta V_{\phi,S}^0 (\text{CaCl}_2)$$

The $\Delta V_{\phi,S}^0$ values are higher in the presence of solutions of CaCl_2 than MgCl_2 which reveals that the dehydration effect of Ca^{2+} ions on the saccharides is more pronounced than that of Mg^{2+} ions.

The $\Delta V_{\phi,S}^0$ values for sucrose in the presence of SO_4^{2-} versus the cation molality are reported in Fig. 6. The same tendencies are obtained for xylose and glucose (results not shown). For a given cation molality, it is also observed that the interactions between the cation and the (-OH,-O-) sites of the saccharides, vary with the cation and increase according to the following order:

$$\Delta V_{\phi,S}^0 (\text{Na}_2\text{SO}_4) < \Delta V_{\phi,S}^0 (\text{K}_2\text{SO}_4) < \Delta V_{\phi,S}^0 (\text{MgSO}_4)$$

This sequence is the same as that observed with Cl^- .

Thus, for a given cation molality, the $\Delta V_{\phi,S}^0$ sequence does not depend on the anion of the electrolyte, i.e. $\Delta V_{\phi,S}^0 (\text{Na}^+) < \Delta V_{\phi,S}^0 (\text{K}^+) < \Delta V_{\phi,S}^0 (\text{Mg}^{2+})$.

In the presence of SO_4^{2-} or Cl^- , divalent cations have a greater impact on the $\Delta V_{\phi,S}^0$ than monovalent ones. K^+ has a greater influence on the $\Delta V_{\phi,S}^0$ values compared to Na^+ .

From the investigations of the impact of the cation on the saccharide/electrolyte interactions, i.e. saccharide dehydration in

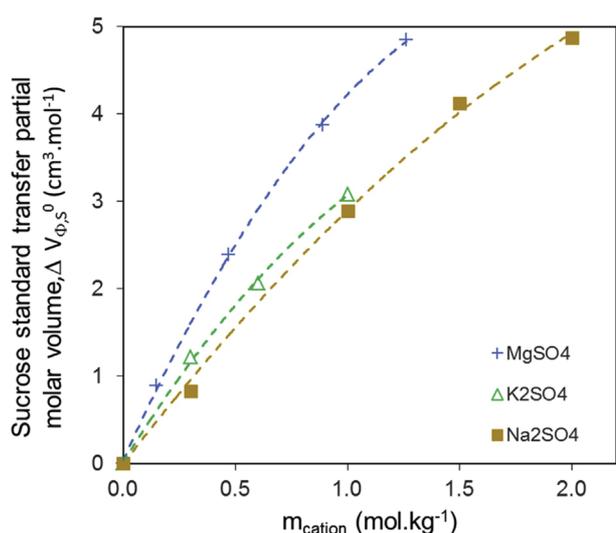
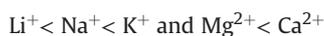


Fig. 6. Standard transfer partial molar volumes of sucrose, for a given anion SO_4^{2-} , versus the cation molality m_{cation} , at 298.15 K: influence of the cation of the electrolyte.

the presence of electrolyte, one can conclude that:

- monovalent cations have less influence than divalent ones;
- for a given valence, the saccharide dehydration increases according to the following sequences:



- anions have no influence on the cation-dependence order

Therefore, one can conclude that saccharides are more dehydrated in the presence of divalent cations than in the presence of monovalent ones. This is due to stronger interactions between saccharides and divalent cations in comparison to monovalent cations (saccharide/cation interactions).

This result can be explained according to the charge of the cations. Indeed, due to their higher charge, divalent cations interact more strongly than monovalent cations with the hydrophilic groups of the saccharides (-OH, -O- sites), and lead to more pronounced saccharide dehydration.

For a specific cation valence, the saccharide dehydration is expected to increase with a decreasing ion size (higher charge density) due to stronger saccharide/cation interactions. For instance, Li^+ (or Mg^{2+}) may have more interactions with the saccharide hydrophilic groups than Na^+ or K^+ (or Ca^{2+}). This trend contradicts the sequence of the saccharide standard transfer partial molar volume as observed in this work. It is therefore necessary to put forward other phenomena to explain the impact of the cation on the saccharide hydration.

As previously underlined in the introduction, the influence of ions on the standard transfer partial molar volumes can be attributed to their ability to structure or to break the water network.

Gibbs free energy of hydration of an ion can express both the hydration radius, the charge to size ratio, and the charge [46] and reflects the interactions between the ion and the water molecules in the hydration shell (ion/water interactions).

Then, in order to evaluate the role of the cations on the saccharides hydration, Gibbs free energies of hydration of ions (Table 4) are compared with the volumetric properties of the three

Table 4

Gibbs free energy of hydration of some cations at 298.15 K, $|\Delta G_{\text{hyd}}|$ (absolute value) [47] and cations molar mass.

Ion	Molar mass (g.mol^{-1})	$ \Delta G_{\text{hyd}} \text{ (kJ.mol}^{-1}\text{)}$
Li^+	6.94	475
Na^+	22.99	365
K^+	39.10	295
Cs^+	132.91	250
Mg^{2+}	24.30	1830
Ca^{2+}	40.08	1505

saccharides.

Gibbs free energy of hydration for divalent cations varies between 1505 and 1830 kJ mol^{-1} , and for monovalent cations between 295 and 475 kJ mol^{-1} . Moreover, for a given valence, the Gibbs free energy of hydration of the cations decreases as the molar mass of the cations increases.

Fig. 7 shows the variation of the saccharides standard transfer partial molar volumes versus the absolute value of Gibbs free energy of hydration of monovalent cations, for a given cation molality (1 mol kg^{-1}). The same trends are obtained for other molalities (results not shown). One can observe that in the presence of Cl^- , the $\Delta V_{\phi,S}^0$ values increase (i.e. saccharide dehydration increases) for a decrease in Gibbs free energy of hydration of the cations (absolute values).

The relationship between the Gibbs free energy of hydration of the cations and the standard transfer partial molar volumes of saccharide in the presence of the electrolyte is confirmed from the volumetric properties of saccharides in the presence of CsCl . Indeed, Jiang and al [22], observed that $\Delta V_{\phi,S}^0(\text{CsCl}) > \Delta V_{\phi,S}^0(\text{NaCl})$. These results can be related to the lower Gibbs free energy of hydration of Cs^+ in comparison to Na^+ : $|\Delta G_{\text{hyd}}|(\text{Cs}^+) < |\Delta G_{\text{hyd}}|(\text{Na}^+)$.

Fig. 7 also shows, for a 1:2 electrolyte (in the presence of SO_4^{2-}), that the $\Delta V_{\phi,S}^0$ values increase (i.e. saccharide dehydration increases) for a decrease in Gibbs free energy of hydration of the cations.

The variation of the saccharides standard transfer partial molar volumes, for divalent cations at a molality of 1 mol kg^{-1} , versus the

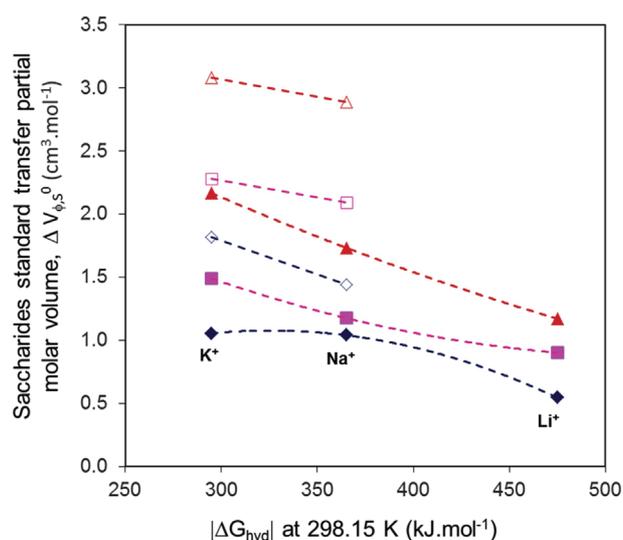


Fig. 7. Relationship between the standard transfer molar volume of sucrose \blacktriangle , glucose \blacksquare and xylose \diamond and the Gibbs free energy of hydration of the cations (absolute value) for a cation molality $m_{\text{cation}} = 1 \text{ mol kg}^{-1}$ (monovalent cations): influence of the Gibbs free energy of hydration of the cations. Sulfate salts: empty symbols; Chloride salts: full symbols.

Gibbs free energy of hydration of the cations is plotted in Fig. 8. The same tendencies are obtained for other molalities (results not shown). As for monovalent cations, it is observed that the saccharides are more dehydrated with decreasing in Gibbs free energy of hydration of the divalent cations.

As previously mentioned, the saccharide dehydration is mainly fixed by the saccharide/cation interactions. However, for a given cation valence, the saccharide dehydration is affected by the cation/water interactions. More specifically, an increase in Gibbs free energy of hydration of cations is indicative of an increase of cation/water interactions. Higher cation/water interactions induce lower saccharide dehydration. The triple interaction saccharide/cation/water must be considered in order to improve the understanding of the saccharide dehydration in the presence of various cations.

4.3. Saccharide/anion interactions

It is previously shown that, regardless of the electrolyte, the $\Delta V_{\phi,S}^0$ values are positive, due to the predominance of the saccharide/cation interactions, and that the anions have no influence on the cation-dependence order. However, it is observed that the $\Delta V_{\phi,S}^0$ values depend on the anion (Fig. 4).

The variation of the standard transfer molar volume of sucrose versus cation molality, in the presence of sulfate and chloride, is represented in Fig. 9. Similar results are obtained for xylose and sucrose (results not shown).

For a given cation molality, one can observe the following sequences:

$$\Delta V_{\phi,S}^0(\text{NaCl}) < \Delta V_{\phi,S}^0(\text{Na}_2\text{SO}_4),$$

$$\Delta V_{\phi,S}^0(\text{KCl}) < \Delta V_{\phi,S}^0(\text{K}_2\text{SO}_4),$$

$$\text{And } \Delta V_{\phi,S}^0(\text{MgCl}_2) < \Delta V_{\phi,S}^0(\text{MgSO}_4).$$

For a given cation molality and regardless of the saccharide, $\Delta V_{\phi,S}^0$ values are higher in the presence of SO_4^{2-} than in the presence of Cl^- . This means that saccharides are more dehydrated in sulfate

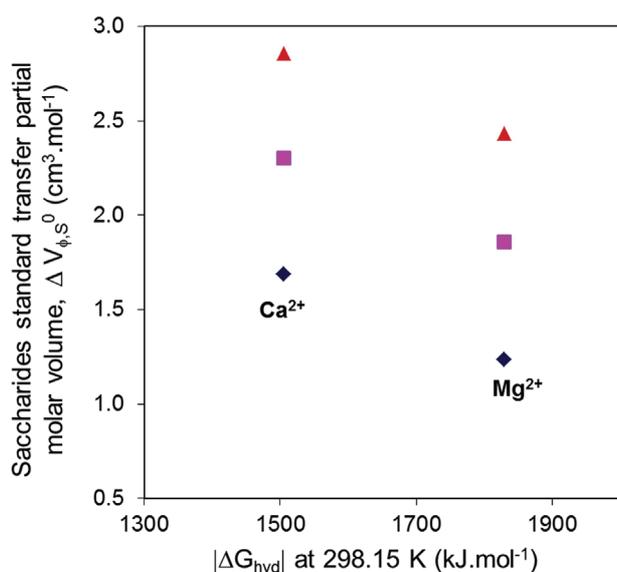


Fig. 8 : Relationship between the standard transfer partial molar volumes of sucrose ▲, glucose ■ and xylose ◆ and the Gibbs free energy of hydration of the cations (absolute value), for a cation molality $m_{\text{cation}} = 1 \text{ mol kg}^{-1}$ in chloride salts: influence of the Gibbs free energy of hydration of the cations.

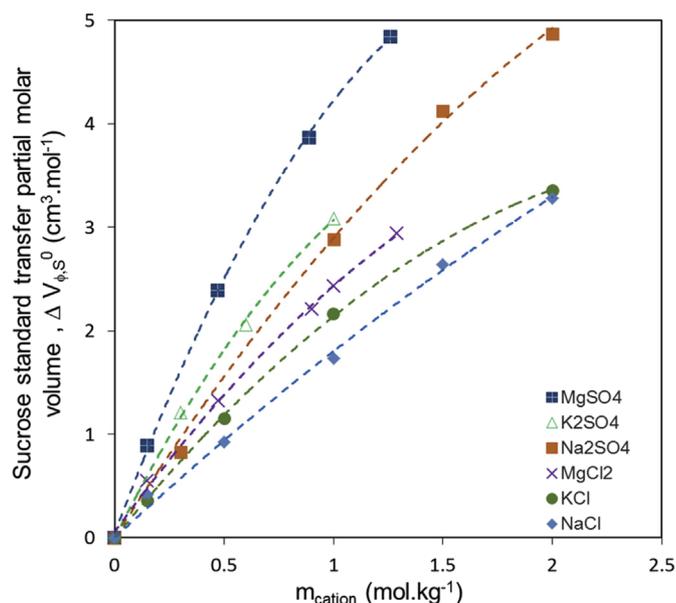


Fig. 9. Standard transfer partial molar volumes for the sucrose/electrolyte solutions versus the cation molality at 298.15 K: influence of the anion of the electrolyte.

solutions than in chloride ones.

These results are consistent with previous ones, in which a more pronounced increase in the solubility of amino acids, i. e. lower dehydration, in the presence of MgCl_2 compared to mixtures containing MgSO_4 [48], has been reported.

From the positive $\Delta V_{\phi,S}^0$ values, it can be concluded that the strength of predominant saccharide/cation interactions is modulated by the nature of the anion. According to the structural hydration model, two different reasons can be considered to explain the increasing saccharide dehydration in the presence of sulfate ions, in comparison to chloride ones. The first reason is that the presence of sulfate ions cause decreasing saccharide/anion interactions, making less negative contribution to $\Delta V_{\phi,S}^0$. The second reason is that SO_4^{2-} provokes increasing saccharide/cation interactions (higher positive contribution to $\Delta V_{\phi,S}^0$).

As previously performed for the investigation of the impact of the cation on the saccharide hydration state, the Gibbs free energy of hydration of the anions, which characterizes the strength of ion/water interactions, enhances the understanding of the influence of the anion on the saccharide hydration.

The values of Gibbs free energy of anions, given in Table 5, show that the SO_4^{2-} /water interactions are stronger than those of Cl^- /water.

Considering the saccharide/anions interactions, which contribute negatively to the $\Delta V_{\phi,S}^0$ values, one can state that saccharide/ SO_4^{2-} interactions are lower than saccharide/ Cl^- ones, due to higher SO_4^{2-} /water interactions. As a consequence, the $\Delta V_{\phi,S}^0$ values are higher in the presence of SO_4^{2-} than in the presence of Cl^- .

Another explanation can be considered according to the

Table 5

Gibbs free energy of hydration of some anions at 298.15 K, $|\Delta G_{\text{hyd}}|$ (absolute value) and ions molar mass.

Ion	Molar mass (g.mol ⁻¹)	$ \Delta G_{\text{hyd}} $ (kJ.mol ⁻¹)
Cl^-	35.45	340 [47]
CH_3COO^-	59.04	373 [49]
SO_4^{2-}	96.06	1080 [47]

influence of the anion on the saccharide/cations interactions. Indeed, due to the higher SO_4^{2-} /water interactions compared to Cl^- , SO_4^{2-} is expected to have less interactions with the cation. Consequently, the higher $\Delta V_{\phi,S}^0$ values obtained in the presence of SO_4^{2-} compared to Cl^- can be due to the stronger saccharide/cation interactions.

These tendencies are consistent with results reported by Banipal and al. Indeed, these authors have shown that the saccharide transfer values were higher in the presence of Na_2SO_4 than in the presence of NaOOCCH_3 [35]. This observation correlates with the explanation proposed in this study, since Gibbs free energy of hydration of CH_3COO^- is lower than that of SO_4^{2-} (Table 5).

Thus, considering the anion impact, one can conclude that the contribution of saccharide/cation interactions are modulated by the anion/water ones. The anion impact can again be attributed to its capacity to interact with water molecules. Anions with increasing Gibbs free energy of hydration cause either increasing saccharide/cation interactions, or decreasing saccharide/anion interactions. Therefore, saccharide dehydration increases. Again, triple interactions saccharide/anion/water must be taken into account to understand the saccharide solvation behavior in the presence of different anions.

5. Conclusion

The aim of this work was to study the mechanisms that govern the interactions in solutions containing different saccharides (xylose, glucose, sucrose) and electrolytes (LiCl , NaCl , KCl , CaCl_2 , MgCl_2 , Na_2SO_4 , K_2SO_4 , MgSO_4). Investigations on a large number of systems provide to focus on the role of the cation and of the anion on the saccharides hydration and then link the properties of ions (valence, size, charge, hydration) with the saccharide/electrolyte interactions (i.e. the saccharide dehydration). The volumetric properties of the saccharide were determined. Indeed, previous studies showed that these properties are very effective to estimate the hydration behavior of neutral solutes.

Densities of various saccharides in water and in electrolytes were measured at 298.15 K. From the density measurements, the apparent molar volumes of saccharides were calculated and then used to determine the saccharide standard partial molar volume. The standard transfer partial molar volume of the saccharides was then used to obtain information about the saccharide hydration. The saccharide dehydration is linked to saccharide/electrolyte interactions.

It was shown that the values of the standard transfer partial molar volumes of the saccharides are positive and increase with the electrolyte concentration. It was thus concluded that the saccharide dehydration in the presence of an electrolyte is due to the predominance of the saccharide/cation interactions. The impact of the cation and the anion on the saccharide/electrolyte interactions has enabled a better understanding of the mechanisms that govern the saccharide dehydration in the presence of electrolytes. Thanks to the investigations of a large number of systems, it became possible to link the ions' properties with the saccharide dehydration.

Firstly, it was shown that the saccharides are more dehydrated in the presence of divalent cations than in the presence of monovalent ones. This is due to stronger interactions between saccharides and divalent cations, in comparison to monovalent cations (saccharide/cation interactions).

Regarding the impact of the cation on the saccharide/electrolyte interactions, it was observed that the standard transfer partial molar volumes increase according to the following sequences: $\Delta V_{\phi,S}^0(\text{Li}^+) < \Delta V_{\phi,S}^0(\text{Na}^+) < \Delta V_{\phi,S}^0(\text{K}^+)$ and $\Delta V_{\phi,S}^0(\text{Mg}^{2+}) < \Delta V_{\phi,S}^0(\text{Ca}^{2+})$. The anions (Cl^- or SO_4^{2-}) have no influence on the cation-dependence order.

Gibbs free energy of hydration of ions, which characterizes ion/water interactions, correlates well with the standard transfer partial molar volumes of the saccharides. This correlation explains the influence of the anions and the cations, for a given valence.

For a given cation valence, it was shown that the saccharide dehydration depends on the strength of cation/water interactions. It was concluded that cations with increasing Gibbs free energy of hydration induce lower saccharide dehydration. Concerning the anion impact, it was found that the contribution of the saccharide/cation interactions are also modulated by the anion/water interactions. Furthermore, anions with increasing Gibbs free energy of hydration cause either increasing saccharide/cation interactions, or decreasing saccharide/anion interactions. Therefore, the saccharide dehydration increases.

The influence of the electrolyte on the saccharide hydration state, characterized by the volumetric properties, results from multiple interactions taking place at the nanoscale (saccharide/ions; ions/water). Therefore, further work will be devoted to characterize these interactions at the molecular level using quantum mechanics.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.carres.2017.06.006>.

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