Relationship between volumetric properties and mass transfer through NF membrane for saccharide/electrolyte systems

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ABSTRACT

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Recent studies have shown that unexpected performances can be obtained with NF membranes, when applied to the treatment of solutions containing significant amount of electrolyte. This study deals with the investigation of the mechanisms governing the mass transfer of neutral species through NF membranes with a focus on the role of ions. More precisely, it consists to determine the apparent molar volume of saccharides, which characterizes the hydration state of solutes in presence of electrolyte, and to assess the relationship between these parameters and those characterizing the mass transfer. The transfer of saccharides of increasing molecular weights (xylose, glucose and sucrose) through a NF membrane is studied in a diffusion regime. Different electrolytes ($NaCl$, Na_2SO_4, $CaCl_2$, $MgCl_2$) are chosen with respect to their hydration level. A specific procedure was developed to dissociate the flux variation due to the modifications of the solute properties and of the membrane material induced by the electrolyte. The results show that the mass transfer modification is mainly due to the influence of the electrolyte on the solute properties. Then, the mass transfer parameters are put in parallel with the apparent molar volume of saccharides measured in solutions of different ionic compositions.

For a given electrolyte, Na_2SO_4, a good quantitative relationship is obtained regardless of saccharide nature, concerning the influence of the electrolyte concentration. This result confirms that the saccharide transfer increase can be due to its dehydration in presence of electrolyte. However, from these results, it is not possible to establish a clear relationship regardless of the electrolyte nature.

1. Introduction

The application field of membrane processes, such as nanofiltration (NF), is growing to fluids of increasing complexity, containing both mineral and organic compounds sometimes at high concentrations. This is specially the case in the food industry for organic acids, dairy products, saccharides, etc., as well as for environmental applications concerning the treatment of brines, lixiviates, concentrates, etc.

However, it was recently pointed out that the presence of electrolyte can change significantly the process performances because of the resulting modification of the neutral solutes transfer [1–5]. In any case, it was observed that increasing the electrolyte concentration results in a higher transfer and that this increase depends on the nature of the electrolyte [3–6]. It was also reported, in the case of glucose/electrolyte solutions, that the lowest the salt retention the most the influence on the glucose retention [2]. Moreover, the glucose retention was found to remain constant when adding a completely retained anion [5].

The transfer of a neutral solute is governed by size exclusion which is fixed by the solute to the pore size ratio. Then, the mass transfer increase can be ascribed to an increase of the pore radius, to a decrease of the solute radius or more probably to a combination of both.

Several assumptions have been suggested to explain the influence of electrolytes on the transfer of neutral solutes [1–3,6].

Firstly, the addition of electrolyte can lead to an increase of the membrane charge density and to a higher concentration of counterions in the electrical double layer at the pore surface. Wang et al. [1] assumed that these electrostatic interactions result in a lower hydration shell at the pore surface, whereas Bargeman et al. [2] proposed that "pore swelling" can appear because of stronger repulsion forces between the pore walls.

Secondly, the impact of the pore size distribution has been also proposed [2]. Indeed, in the presence of ions in the pores, the flux

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through the small pores is expected to be reduced to a higher extend than in larger ones. Consequently, the retention of neutral solute, determined by the larger pores, can increase.

More recently, Mandale and Jones [7] proposed that the unexpected weak negative retention of neutral solute in presence of phosphate ions can be due to the polarisability of the molecules leading to interactions with the negatively charged membrane.

Finally, the influence of electrolyte on the overall transfer of neutral solutes can be explained by a change in the solute properties, more particularly by a modification of the solute hydration, since it is expected to vary with the ionic composition. Indeed, in mixed neutral solute/electrolyte solutions, water can preferentially solvate the ions to the detriment of the neutral solute ("salting out" phenomenon). Then, the solutes less hydrated, may have a lower apparent size than in the absence of electrolyte and an increased transfer through the membrane can be obtained.

This latter explanation has been firstly proposed by Bouchoux et al. [3], who established a qualitative correlation between the hydration scale of ions and the increase of the transfer of organic solutes through NF membranes. These results were found to be in agreement with the dehydration of neutral solutes in presence of electrolyte since more hydrated electrolytes or higher concentrations inducing a higher dehydration, tend to increase the solute transfer.

As explained previously, the influence of the ionic composition on the transfer of neutral solute through NF membrane could be explained by a modification of the membrane properties, due to electrostatic effects, and/or by a solute dehydration induced by the electrolyte. Recently, Escoda et al. have proposed a procedure to dissociate these two contributions [6]. On one hand, the ability of pore swelling of an organic NF membrane was evaluated. The Stokes radii of PEG in electrolyte solutions were determined from the retentions obtained with PEG/electrolyte solutions and a ceramic membrane, which is not expected to swell [4]. Then the average pore radius of the organic membrane was computed from the retentions of PEG in the same electrolyte solutions. In this manner, different apparent pore sizes were obtained depending on the electrolyte. For increasing electrolyte concentrations, increasing pore sizes were also obtained, suggesting that the membrane can swell. Moreover, it was shown that this "pore swelling" assumption can be supported by electrokinetics charge density data, determined by tangential streaming potential measurements. Indeed, it was pointed out that increasing membrane surface charges were linked to increasing values of the computed average pore radius. However, to our knowledge, the relationship between the mass transfer and the solute properties, i.e. dehydration, in presence of electrolytes, has never been investigated.

In this context, the aim of this study is to investigate the mechanisms governing the transfer of neutral species through NF membranes with a focus on the role of ions on the solute properties. Relevant physicochemical parameters will be determined to characterize the hydration state of solutes. Then, the relationship between these parameters and those characterizing the mass transfer will be investigated.

Different thermodynamic methods can be used to quantify the hydration state of a solute. The measurement of the density can provide the apparent molar volumes (AMV) of solutes in solutions. The AMV values are usually interpreted in terms of the structural hydration model developed by Gurney [8] to investigate saccharide/electrolyte or amino-acid/electrolyte interactions [9–11]. Zhuo et al. have thus studied the interactions between saccharides (xylose, arabinose, glucose, galactose) and NaCl at various ionic compositions [9]. It was pointed out that the AMV of saccharides increase for increasing NaCl concentrations. According to the hydration model, increasing AMV reveals a dehydration of saccharide in presence of NaCl in solution.

In the present work, the apparent molar volume of various saccharides (xylose, glucose and sucrose) in presence of electrolytes of various hydrations ($NaCl$, Na_2SO_4, $CaCl_2$, $MgCl_2$) will be thus determined to characterize the hydration state of saccharides. Then, the transfer of these saccharides through a NF membrane, in presence of electrolytes, will be studied in a diffusion regime. A specific procedure will be developed to dissociate the change of the diffusion flux, due to the modifications of the solute properties and of the membrane material, induced by the electrolyte. Then, the mass transfer parameter, which characterizes the impact of the electrolyte on the solute properties, is put in parallel with the apparent molar volume of saccharides to evaluate to what extend a relationship can be drawn between the hydration state of the solute, and its transfer through a membrane.

2. Materials and methods

2.1. Chemicals

The neutral solutes used in the experiments were saccharides of increasing molecular weights, xylose ($150.13\,g\,mol^{-1}$), glucose ($180.16\,g\,mol^{-1}$) and sucrose ($342.29\,g\,mol^{-1}$) from Acros Organics. Electrolytes of various hydrations were used, $NaCl$, Na_2SO_4, $CaCl_2$ and $MgCl_2$ (Acros Organics). The corresponding ion hydration scale is given as follows [12,13]:

$$\text{anions}: \quad Cl^- < SO_4^{2-} \qquad \text{cations}: \quad Na^+ < Ca^{2+} \approx Mg^{2+}$$
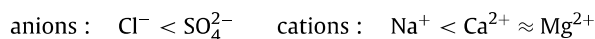
Ultra-pure water (Milli-Q RG, Millipore) was used to prepare the solutions. The pH of the various solutions is about (6 ± 0.5) without any adjustment.

2.2. Analytical methods

For any set of experiments, the saccharide concentration was obtained by HPLC with a Dionex system, using a CarboPac PA1 column with an electrochemical ED40 detector. The mobile phase was a 150 mM NaOH solution and the flow rate was $1\,mL\,min^{-1}$. The column temperature was set as 30 °C. The injection volume was 25 μL.

2.3. Volumetric properties

The AMV of saccharides were obtained from density measurements, using the following equations for saccharide/water and saccharide/electrolyte solutions, respectively [9,14]:

$$V_{\Phi S}(m_S) = \frac{M_S}{d_S} - \frac{1000(d_S - d_0)}{m_S d_S d_0} \tag{1}$$

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

where M_E and M_S are the molecular weights of electrolyte and saccharide, m_E and m_S the molalities of electrolyte and saccharide (in mol per kg 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. The errors in molality were within ±0.01% for saccharides and ±0.04% for electrolyte. The scale of molality for both solutes was from 0 to 2 mol kg^{-1}.

Solution densities were measured with a vibrating tube digital density meter (Model DMA 5000, Anton Paar, Austria) at 25 °C ± 0.001 °C. The error in density was estimated to be ±5.10^{-6} g cm^{-3}.

2.4. Membrane and diffusion experimental set-up

Diffusion experiments were carried out with a Dow Filmtec NF membrane. It is a thin film composite membrane negatively charged at pH higher than 5.1 [15,16]. For any set of operating conditions, the membrane was negatively charged since the pH of the solutions was about (6 ± 0.5).

The main characteristics are an average molecular weight cut-off of 150–200 g mol^{-1} [17,18] and a hydraulic permeability of 7.1 L h^{-1} m^{-2} bar^{-1} [19].

The total membrane area in the diffusion cell was 120 cm^2. The thickness of the feed and eluate compartment was 0.1 cm. The compartments were co-currently fed by two pumps at a fixed flow rate of 4 L h^{-1}. The feed tank was fed with 0.5 L of an electrolyte solution (or pure water) containing a saccharide at a fixed concentration. The eluate tank was fed with 0.5 L of a solution at the same ionic composition (electrolyte or water) but without saccharide. The electrolyte concentration during the diffusion experiment at both sides of the membrane was the same to avoid the impact of the electrolyte transfer on the saccharide one.

Due to the difference of saccharide concentration across the membrane, a saccharide flux takes place from the feed to the eluate compartment. This solute flux can be accompanied by an osmotic flux, but for any set of conditions it was found to be negligible since no variation of the volume in either compartment was observed.

Diffusion experiments were carried out in a batch mode during 4 h, with initial saccharide and electrolyte concentrations fixed at 1 mol L^{-1} and 1 equiv. L^{-1}, respectively. The temperature was fixed at 25 °C.

The diffusion fluxes were deduced from the variation of the solute mass transferred versus time, for all the experiments, these variations were linear (deviation less than 10%) so that one can consider that the transfer was carried out at a constant concentration gradient.

2.5. Experimental procedure

A specific experimental procedure was developed to dissociate the impact on the diffusion flux due to the modifications of the solute properties and of the membrane material induced by the electrolyte.

As previously mentioned, the electrolyte can increase the average pore size due to an increase of the membrane charge density. In aqueous solution, the polymeric membrane charge is mainly fixed by acido-basic dissociation and adsorption of anions on hydrophobic sites [20–24]. Thus, for a negatively charged membrane, the impact of the electrolyte on the membrane properties depends on the type of anion, which fixes the membrane charge, as well as on the nature of the cation, the counter ion of the membrane.

The membrane was soaked in the given electrolytic solution at 1 equiv. L^{-1} for at least 12 h and rinsed with ultra-pure water for about 10 min.

Then, diffusion experiments were carried out with saccharide/water and saccharide/electrolyte solutions, respectively. This procedure was repeated for each electrolyte studied in this work.

For saccharide/water systems, the variation of the conductivity in the feed compartment was lower than 5 μS cm^{-1}. Consequently one can assume that the electrolyte do not diffuse out of the soaked membrane during experiments.

The impact of the electrolyte on the membrane properties was estimated from the saccharide flux measured in water, J_S^W. Then, the overall effect of the electrolyte on the saccharide transfer was characterized by the saccharide flux in electrolyte solutions, J_S^E. Finally, the impact of the electrolyte on the solute properties was obtained from the difference between the saccharide flux obtained in
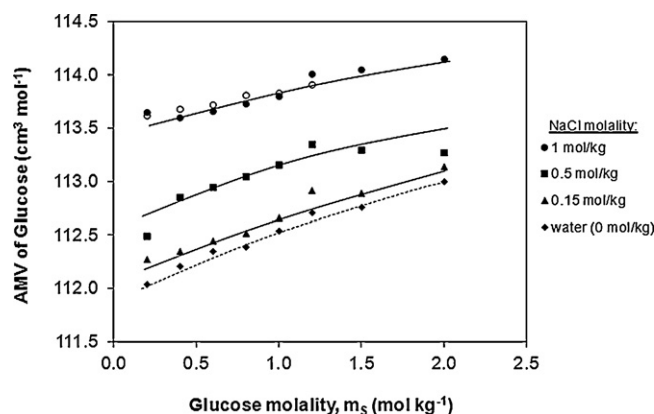

Fig. 1. AMV of glucose versus its molality for the glucose/NaCl solutions: influence of the NaCl molality (full symbols) at 25 °C. Comparison with published values [9] (empty symbols).

saccharide/electrolyte systems and that measured in saccharide/water systems, $\Delta J = J_S^E - J_S^W$ (further called additional flux).

3. Results and discussion

Firstly, the AMV of saccharide in saccharide/water and saccharide/electrolyte solutions were determined from density measurements to evaluate the influence of the electrolyte nature and concentration on the saccharide hydration state.

Then, diffusion experiments were carried out in order to highlight the influence of the electrolyte on the transfer of saccharides and to determine the additional flux (ΔJ), which characterizes the impact on the flux due to the modifications of the solute properties induced by the electrolyte.

Finally, the additional flux, (ΔJ), was put in parallel with the apparent molar volume of saccharides, to evaluate if a relationship can be drawn between the mass transfer increase and the dehydration of neutral solutes in presence of electrolytes, as revealed by the AMV variations.

3.1. Determination of apparent molar volumes

The AMV of some saccharides were previously determined for different molalities of NaCl [9,10]. However, the values for the other electrolytes considered in the present study are not accessible.

Our experimental measurements were first evaluated by comparison with literature data for saccharide/NaCl systems. Then, the AMV were determined for the other saccharide/electrolyte systems.

Fig. 1 shows the variation of the AMV of glucose versus its molality, for increasing NaCl molalities. Previous results are also reported on the same graph for comparison [9].

One can state that there is a very good agreement. The difference between the experimental values obtained in this work and the ones previously reported for the saccharide/NaCl systems (molalities ranging between 0 and 2 mol kg^{-1}) does not exceed 0.5%.

Then, the variations of the AMV of glucose versus its molality at different Na$_2$SO$_4$ molalities are presented in Fig. 2.

Figs. 1 and 2 show that the AMV of glucose is always higher in an electrolyte solution compared to water. Moreover, for a given molality of glucose, the AMV increases with the electrolyte concentration.

The variation of the AMV of the saccharides in electrolyte solutions can be interpreted from the structural hydration model [25], based on the co-sphere concept developed by Gurney [8]. According to this model, the overall influence of the solute on the structure
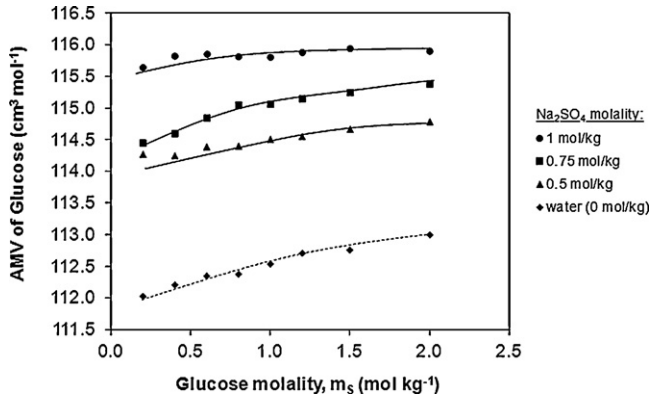
Fig. 2. AMV of glucose versus its molality for the glucose/Na$_2$SO$_4$ solutions at 25 °C: influence of the Na$_2$SO$_4$ molality.

Fig. 4. AMV of glucose versus its molality for the glucose/electrolyte solutions at 25 °C: influence of the electrolyte nature (m_{cation} = 1 mol kg^{-1}).

of water is represented by a spherical shell of water surroundings the solute, which is the solute hydration shell. As the solute concentration increases, the hydration shells of two neighbor solutes can overlap, displacing some water molecules from the hydration shell into the bulk, thus modifying the thermodynamic properties. These modifications can be explained according to different kinds of solute/co-solute interactions [25]. For saccharide/electrolyte systems, the possible interactions are: (i) hydrophilic–ionic interactions, between the hydrophilic (−OH) sites of the saccharide molecules and the ions, and (ii) hydrophobic-ion interactions between the hydrophobic groups of the saccharide molecules and the ions [9,10]. Depending on the kind of interaction, one can expect different variations of the AMV. Indeed, the attractive (−OH)/cation interaction results in an enhancement of the overall structural order of water in the bulk so that the AMV is increased compared to that in water. Conversely, the repulsive (−OH)/anion and hydrophobic/ionic interactions lead to decreasing values of the AMV in presence of electrolyte.

The variation of the AMV, ΔV, is expressed as the difference between the AMV of the saccharide in an electrolyte solution, $V_{\phi S}(m_S, m_E)$, and that in water, $V_{\phi S}(m_S)$. Typical variations of ΔV versus Na$_2$SO$_4$ molality are plotted in Fig. 3 for the three saccharides at a given molality of 1 mol kg^{-1}. Similar variations are obtained for the other electrolytes (results not shown). One can observe that the ΔV values obtained for any saccharide are positive and that they increase with the electrolyte molality. Therefore, according to the structural hydration model, it means that, in our conditions, the (−OH)/cation interactions are predominant and that the saccharide dehydration increases with the electrolyte molality [9,10,26,27].
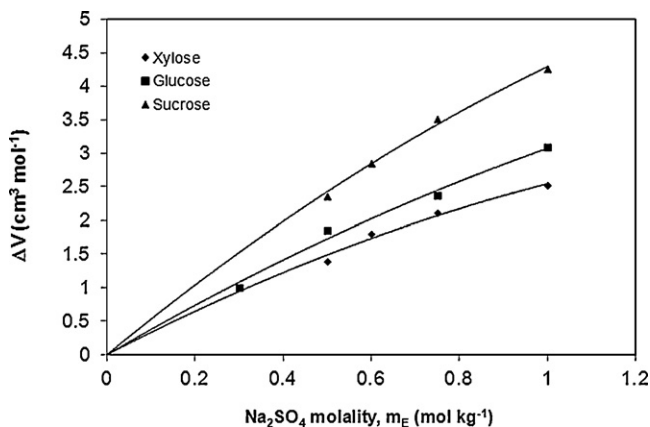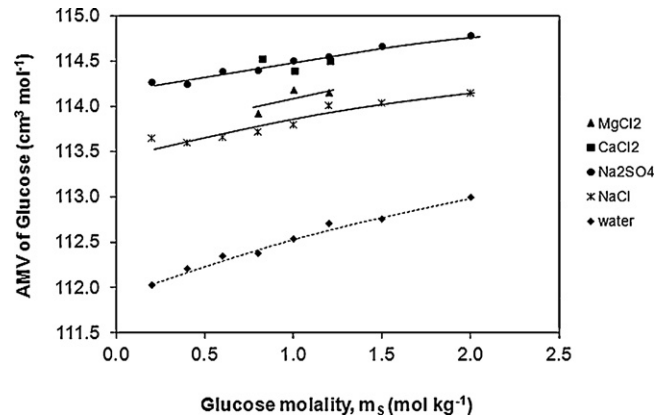
The influence of the electrolyte nature on the AMV of saccharides can be evaluated from the values determined at a fixed cation molality since the positive ΔV values are due to the predominance of the (−OH)/cation interactions. Thus, the variation the AMV of glucose and sucrose versus their molality, in various electrolyte at a given cation molality of 1 mol kg^{-1}, is presented in Figs. 4 and 5, respectively. Whatever the electrolyte, one can observe that the AMV of the saccharide in an electrolyte is higher than that one in water. The influence of the electrolyte nature on the variation of the AMV of the saccharides, ΔV, is then represented in Fig. 6 for saccharide and cation molalities fixed at 1 mol kg^{-1}.

For any saccharide, one can observe that, for a given cation Na$^+$, ΔV is higher with Na$_2$SO$_4$ than with NaCl. Again, according to the structural hydration model, this means that the saccharides are less hydrated in Na$_2$SO$_4$ solutions than in NaCl ones. Thus, it seems that the predominance of the (−OH)/cation (Na$^+$) interactions depends on the nature of the anion (Cl$^-$ and SO$_4^{2-}$) present in the solution. This observation could be due to the different properties of these anions such as size, charge and hydration level [12]. Indeed, although the sulfate ion charge is higher than that of chloride, its higher size can lead to lower repulsion interactions.

Fig. 6 also shows that, for a given anion, Cl$^-$, ΔV varies according to the following sequence:

$$\Delta V(\text{NaCl}) < \Delta V(\text{MgCl}_2) < \Delta V(\text{CaCl}_2) \quad \text{for glucose and xylose}$$
$$\text{and} \quad \Delta V(\text{NaCl}) < \Delta V(\text{CaCl}_2) < \Delta V(\text{MgCl}_2) \quad \text{for sucrose.}$$

These results show that saccharides have stronger interactions and are less hydrated with divalent cations (Mg^{2+}, Ca^{2+}) than with a monovalent one (Na$^+$). There are in accordance with those recently

Fig. 3. Variation of the AMV of saccharides, ΔV, versus Na$_2$SO$_4$ molality at 25 °C (m_S = 1 mol kg^{-1}).
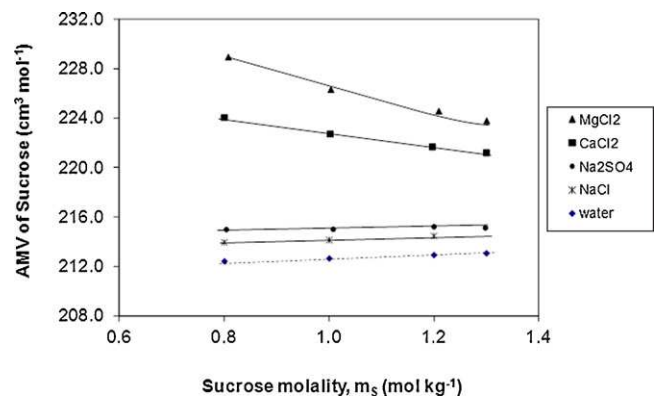

Fig. 5. AMV of sucrose versus its molality for the sucrose/electrolyte solutions: influence of the electrolyte nature at 25 °C (m_{cation} = 1 mol kg^{-1}).
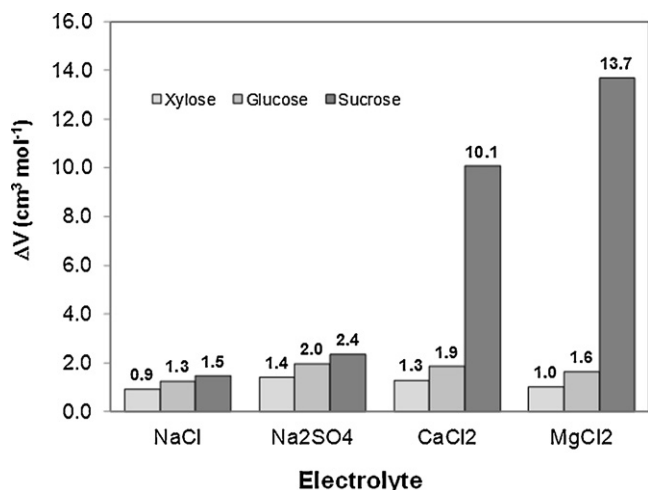
Fig. 6. Variation of the AMV of saccharides, ΔV, in electrolytes of various nature at 25 °C ($m_S = m_{cation} = 1\,mol\,kg^{-1}$).
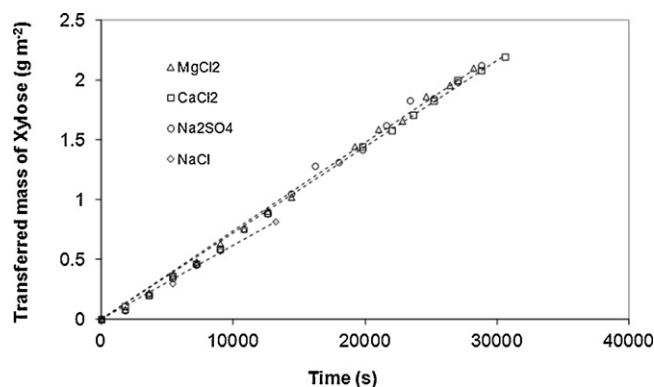

Fig. 7. Variation of the mass of xylose transferred per unit area of membrane versus time for xylose/water solutions and for a membrane soaked in various electrolyte at 25 °C; [Xylose] = 1 mol L^{-1}.

obtained by Banipal et al. [28] showing that a 2:1 electrolyte (MgCl$_2$) has a greater influence on the values of the standard partial molar volumes at infinite dilution compared to a 1:1 electrolyte (NaCl).

The higher ΔV values obtained with divalent cations may be explained by their specificity (Na$^+$, Ca^{2+}, Mg^{2+}). Indeed, these results are in accordance with the ion hydration scale: Na$^+$ < Ca^{2+} $\approx$ Mg^{2+} [12]. Then, the more pronounced saccharide dehydration in presence of Ca^{2+} and Mg^{2+} compared to Na$^+$ can be linked to the higher hydration of the divalent cations (Ca^{2+}, Mg^{2+}) compared to monovalent ones (Na$^+$).

One can also observe that the ΔV values obtained with sucrose in presence of MgCl$_2$ and CaCl$_2$ are much higher than those obtained for xylose and glucose. This is interesting to put in parallel with the number of (−OH) sites of the saccharide molecules, which are involved in sugar/electrolyte interactions. Indeed, xylose and glucose contains (4 −OH and 1 −O−) and (5 −OH and 1 −O−) sites, respectively, whereas sucrose is composed by (8 −OH and 3 −O−). Moreover, sucrose is made from a glucose molecule covalently bonds to a fructose one by a glycosidic linkage and it is known that the fructose molecule can form complexes with calcium ions, which is not the case of glucose. Then, one can expect higher solute/electrolyte interactions with sucrose than with the other two saccharides. This behavior is used in the field of saccharides separation with cation exchange resins in calcium form [29,30].

3.2. Diffusion flux density

3.2.1. Saccharide/water systems

As previously mentioned, the impact of the electrolyte on the membrane material properties is evaluated from the diffusion fluxes obtained with saccharide/water systems and a membrane previously soaked in the electrolyte.

The variations of the mass of xylose transferred per unit area of membrane are plotted versus time in Fig. 7, for the membrane soaked in the different electrolyte solutions. Since these variations are linear (deviation from linearity < 10%), one can obtain the flux density from the slope of the corresponding straight. The same tendencies are obtained for glucose and sucrose (results not shown). The corresponding values of the flux density, J_S^W, are reported in Table 1 for the various saccharides.

Considering that the transfer of saccharide is governed by a steric effect, one expects a decreasing flux density for increasing saccharide size. This is confirmed by the values of J_S^W given in Table 1, except for sucrose when the membrane is soaked in an electrolyte solution containing divalent cations (MgCl$_2$ and CaCl$_2$). Indeed, while the size of the sucrose is higher than that of glucose and xylose, highest values are obtained for the flux. Such results probably come from strong interactions between sucrose and the membrane soaked with Ca^{2+} or Mg^{2+}. These interactions have also been pointed out in former section concerning the determination of the apparent molar volume (see Section 3.1, Fig. 6). Therefore, the transfer of sucrose through the membrane soaked with Ca^{2+} or Mg^{2+}, is not governed by a single steric effect.

The influence of the electrolyte nature is evaluated using a normalized flux value, which is the ratio of the flux measured for a given membrane soaking to that obtained with the membrane soaked in Na$_2$SO$_4$, J_S^W(Electrolyte)/J_S^W(Na$_2$SO$_4$).

Fig. 8 shows that, in any condition, the normalized flux is close to one except, again, for sucrose when the membrane is soaked with divalent cations (Mg^{2+} and Ca^{2+}).

Finally, one can conclude that, in saccharide/water systems, the solute flux is weakly influenced by the nature of the electrolyte used for the membrane soaking. Therefore, the impact of the modification of the membrane charge on the solute flux is negligible, except when there are strong interactions such as those observed between sucrose and divalent cations.

3.2.2. Saccharide/electrolyte systems

From the fluxes obtained with saccharide/electrolyte systems, J_S^E, it is possible to evaluate the overall impact (membrane and solute properties modifications) of the electrolyte on the saccharide transfer.

Table 1
Sugars fluxes for saccharide/water and saccharide/electrolyte systems at 25 °C: influence of the electrolyte nature. [Saccharide] = 1 mol L^{-1}; [Electrolyte] = 1 equiv. L^{-1}.

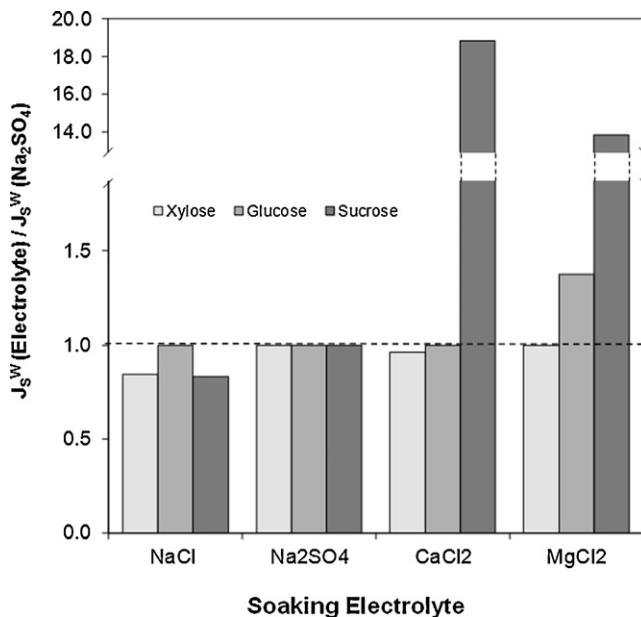| Saccharide	Electrolyte	Saccharide/Water J_S^W ($\times 10^{-7}$ mol m^{-2} s^{-1})	Saccharide/Electrolyte J_S^E ($\times 10^{-7}$ mol m^{-2} s^{-1})
Xylose	NaCl	4.3	7.5
	Na$_2$SO$_4$	5.1	15.3
	CaCl$_2$	4.9	11.6
	MgCl$_2$	5.1	13.2
Glucose	NaCl	1.6	4.6
	Na$_2$SO$_4$	1.6	12.1
	CaCl$_2$	1.6	12.1
	MgCl$_2$	2.2	14.4
Sucrose	NaCl	0.5	0.7
	Na$_2$SO$_4$	0.6	6.3
	CaCl$_2$	11.3	22.8
	MgCl$_2$	8.3	18.3

Fig. 8. Normalized flux J_S^W(Electrolyte)$/J_S^W$(Na$_2$SO$_4$) for saccharide/water systems: influence of the electrolyte used for the membrane soaking; [Saccharide] = 1 mol L^{-1}.

The variations of the mass of glucose transferred per unit area of membrane versus time are represented in Fig. 9 for different glucose/electrolyte solutions. The results obtained with glucose/water solutions are also plotted for comparison. The same tendencies are obtained for xylose and sucrose (results not shown). The flux densities, J_S^E, determined from the slope, are given in Table 1.

As observed for saccharide/water system, the flux density decreases for increasing saccharide size except for glucose and to a higher extend for sucrose, in presence of CaCl$_2$ and MgCl$_2$.

Moreover it is shown that the transfer of saccharides increases in presence of electrolyte compared to water and that it depends on the electrolyte nature. As an example, the average flux density for the xylose/water system is 4.9×10^{-7} mol m^{-2} s^{-1} whereas the flux determined for the xylose/electrolyte system, ranges between 7.5×10^{-7} and 13.2×10^{-7} mol m^{-2} s^{-1} for different electrolytes.

The influence of the electrolyte concentration on the saccharide transfer is also evaluated in presence of sodium sulfate. Fig. 10 shows the variation of the mass of xylose transferred per unit area of membrane versus time for different Na$_2$SO$_4$ concentrations. The same behavior is obtained for glucose and sucrose (results not
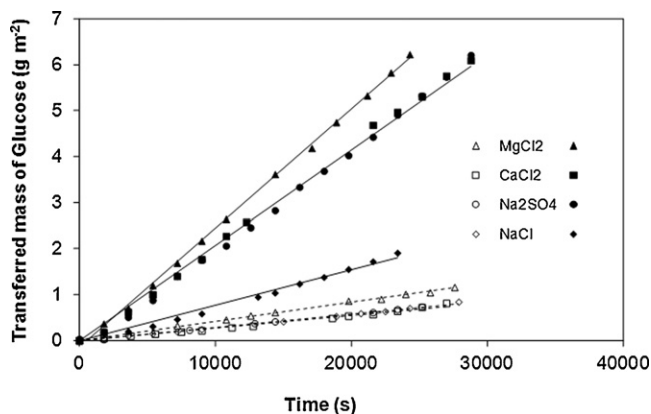

Fig. 9. Variation of the mass of glucose transferred per unit area of membrane versus time for glucose/electrolyte for different electrolytes (full symbols) at 25 °C. Comparison with glucose/water solutions (empty symbols); [Glucose] = 1 mol L^{-1}; [Electrolyte] = 1 equiv. L^{-1}.
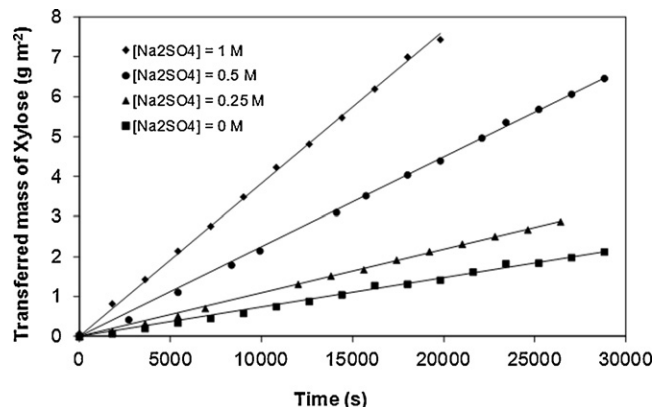

Fig. 10. Variation of the mass of xylose transferred per unit area of membrane versus time for xylose/Na$_2$SO$_4$ solutions for different Na$_2$SO$_4$ concentrations (full symbols) at 25 °C. Comparison with xylose/water solution (cross symbols); [Xylose] = 1 mol L^{-1}; [Na$_2$SO$_4$] = 0–0.25–0.5–1 mol L^{-1}.

shown). The corresponding flux densities for saccharide/Na$_2$SO$_4$ systems are given in Table 2. The values measured in water for a membrane soaked in Na$_2$SO$_4$ are also reported.

In any case, the flux density increases for increasing Na$_2$SO$_4$ concentrations. For instance, the glucose flux increases by a factor 2.4 when Na$_2$SO$_4$ concentration increases from 0.25 to 0.5 M.

Then, the contribution due to the presence of electrolyte in the solution on the saccharide transfer is determined from the ratio $\Delta J/J_S^E$, where J_S^E represents the overall impact (membrane and solute properties modifications) of the electrolyte on the saccharide transfer while the additional flux, $\Delta J = J_S^E - J_S^W$ characterizes the impact due to the modifications of the solute properties induced by the electrolyte.

The results are plotted in Fig. 11 for the different saccharide/electrolyte systems investigated.

On can observe that, for a given electrolyte, the impact of the presence of electrolyte increases with the solute size and the number of (−OH) sites, since it is more important with glucose than with xylose. For sucrose, it is more difficult to conclude, because of the previously mentioned interactions existing with the membrane soaked with electrolyte containing divalent cations (see former section).

In any case, for a given cation, Na$^+$, the impact of NaCl in the solution is significantly lower than that of Na$_2$SO$_4$. Moreover, for a common anion, the contribution of the electrolyte increases according to the following sequence: Na$^+$ < Ca^{2+} ≈ Mg^{2+}.

The results obtained with different Na$_2$SO$_4$ concentrations are plotted in Fig. 12, showing that the contribution due to the addition of electrolyte increases with the Na$_2$SO$_4$ concentration. On the other hand, for a given Na$_2$SO$_4$ concentration, this contribution

Table 2
Sugars fluxes for saccharide/Na$_2$SO$_4$ solutions at 25 °C: influence of the Na$_2$SO$_4$ concentration. [Saccharide] = 1 mol L^{-1}.

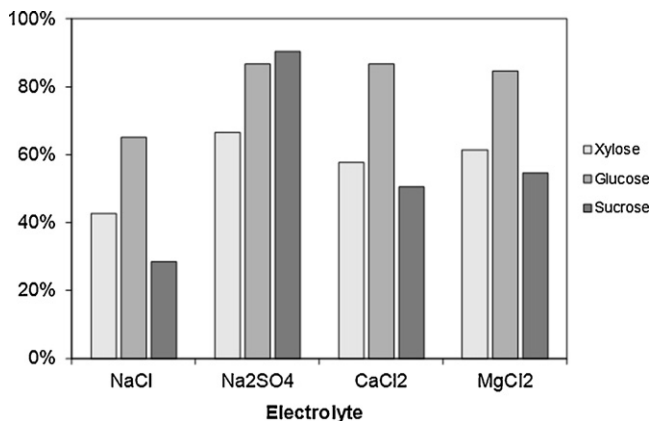| Saccharide	[Na$_2$SO$_4$] (mol L^{-1})	J_S^E ($\times 10^{-7}$ mol m^{-2} s^{-1})
Xylose	0	5.1
	0.25	7.5
	0.5	15.3
	1.0	25.0
Glucose	0	1.6
	0.25	5.0
	0.5	12.1
Sucrose	0	0.6
	0.25	2.6
	0.5	6.3

Fig. 11. Contributions of the presence of electrolyte on the saccharide flux: influence of the electrolyte nature.

increases with the saccharide size and the number of the (−OH) sites: Xylose < Glucose < Sucrose.

These results can be correlated to the hydration scale of ions. Indeed, for a given anion, Cl⁻, the saccharide transfer is all the more increased as the cation is hydrated. Similarly, for a fixed cation, Na⁺, the saccharide transfer is all the more increased as the anion is hydrated.

All together, these results are in agreement with the assumption of the partial dehydration of neutral solutes in presence of electrolyte since more hydrated electrolytes or higher concentrations induce a higher dehydration.

Moreover, the contribution due to the addition of electrolyte varies in accordance with the number of (−OH) sites of the saccharide molecules, i.e. Xylose < Glucose < Sucrose, except for sucrose in presence of divalent cations. Indeed, as previously explained (see Section 3.1), the variation of the saccharide hydration is expected to result from the change of the attractive interactions between the hydrophilic (−OH) sites of the solute and the cation of the electrolyte. Finally, while such interactions are predominant with respect to the solute hydration, it was observed that the solute hydration, and then its transfer through the membrane, is modified according to the anion present in the electrolyte solution.

3.3. Solute flux versus volumetric properties

The investigation of the influence of the ionic composition on the saccharide transfer highlights that the additional flux,
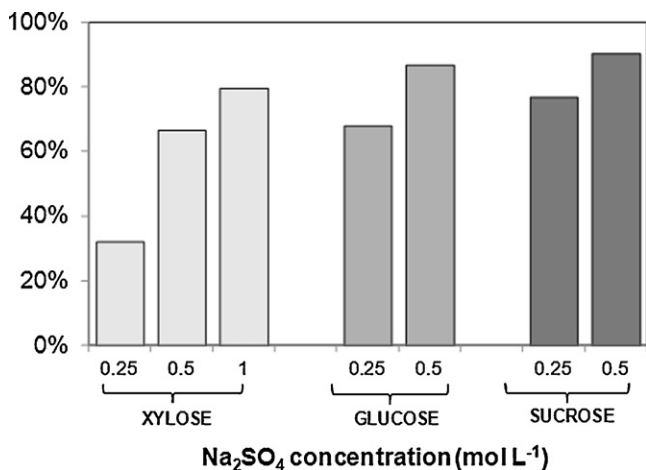

Fig. 12. Contributions of the presence of electrolyte on the saccharide flux: influence of Na_2SO_4 concentration.
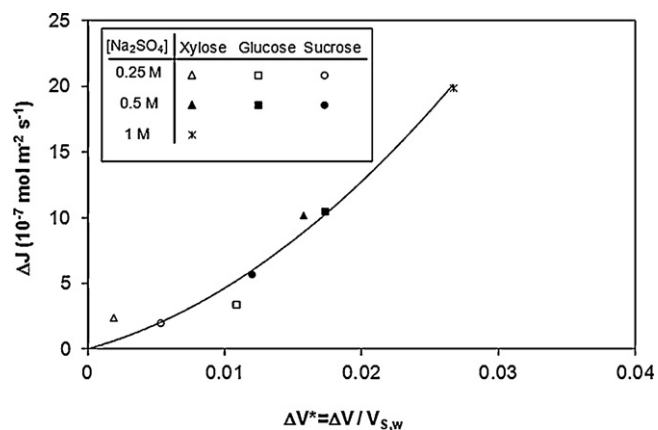

Fig. 13. Additional flux, ΔJ, versus the normalized variation of the AMV of saccharides, ΔV^*, for different Na_2SO_4 concentrations at 25 °C; [Saccharide] = 1 mol L⁻¹; [Na_2SO_4] = 0–0.25–0.5–1 mol L⁻¹.

ΔJ, which characterizes the impact of the electrolyte on the solute properties, is in agreement with the assumption of its dehydration.

On the other hand, the influence of the ionic composition on the hydration of saccharides has been quantified by the variation of the apparent molar volume, ΔV, which is the difference between the AMV of the saccharide in electrolyte solution, $V_{\phi S}(m_S, m_E)$, and that one in water, $V_{\phi S}(m_S)$. As explained, positive and increasing values of ΔV reveal decreasing hydration of the solute.

Then, the objective in this part is to put in parallel the additional flux, ΔJ, with the variation of the AMV, in order to evaluate if a relationship can be drawn between the dehydration of the neutral solutes in presence of electrolytes and the mass transfer increase, expected to be the consequence of the solute dehydration.

In order to compare the various saccharides, their hydration state is here characterized using a normalized variation of the AMV, ΔV^*, defined as the ratio of the variation of the AMV, ΔV, to the AMV in water, $V_{\phi S}(m_S)$:

$$\Delta V^*(m_S, m_E) = \frac{V_{\phi S}(m_S, m_E) - V_{\phi S}(m_S)}{V_{\phi S}(m_S)} = \frac{\Delta V(m_S)}{V_{\phi S}(m_S)} \tag{3}$$

The additional flux and the corresponding AMV, ΔV and ΔV^* values are reported in Tables 3 and 4.

The additional flux, ΔJ, is also plotted in Fig. 13 versus the normalized variation of the AMV, ΔV^*, for a given electrolyte, Na_2SO_4, at various concentrations.

It is observed that the additional flux continuously increases with ΔV^*, which characterizes the dehydration of the saccharide. Moreover, for a given electrolyte (Na_2SO_4), the values obtained with the different solutes are located on the same curve. This confirms that the increase of the transfer of neutral solutes can be attributed to its dehydration in presence of electrolyte.

The values of ΔJ are plotted versus ΔV^* in Fig. 14 for the different electrolytes and saccharides investigated. Previous results obtained for different Na_2SO_4 concentrations are also plotted on the same graph. One can state that it is much more difficult to draw a tendency regardless of the nature of the electrolyte. Nevertheless, values obtained with a fixed cation (Na⁺) in saccharide/NaCl or saccharide/Na_2SO_4 systems are very close. As already mentioned, the deviation observed with divalent cations (Ca²⁺, Mg²⁺) is probably due to stronger interactions between these ions and the saccharides.

Table 3
Additional flux, ΔJ, and the corresponding volumetric properties: $V_{\phi S}$, ΔV and ΔV^*, at 25 °C: influence of the Na_2SO_4 concentration. [Saccharide] = 1 mol L^{-1}.

Saccharide	[Na$_2$SO$_4$] (mol L^{-1})	ΔJ ($\times 10^{-7}$ mol m^{-2} s^{-1})	$V_{\phi S}$ (cm^3 mol^{-1})	ΔV (cm^3 mol^{-1})	$\Delta V^* = \Delta V/V_{\phi S}$ ($\times 10^{-3}$)
Xylose	0	–	95.92	–	–
	0.25	2.4	96.10	0.18	1.9
	0.5	10.2	97.43	1.51	15.7
	1.0	19.9	98.48	2.56	26.7
Glucose	0	–	112.60	–	–
	0.25	3.4	113.82	1.22	10.8
	0.5	10.5	114.55	1.95	17.3
Sucrose	0	–	213.03	–	–
	0.25	2.0	214.16	1.13	5.3
	0.5	5.7	215.58	2.55	12.0

Table 4
Additional flux, ΔJ, and the corresponding volumetric properties: $V_{\phi S}$, ΔV and ΔV^*, at 25 °C: influence of the electrolyte nature. [Saccharide] = 1 mol L^{-1}; [Electrolyte] = 1 equiv. L^{-1}.

Saccharide	Solution	ΔJ ($\times 10^{-7}$ mol m^{-2} s^{-1})	$V_{\phi S}$ (cm^3 mol^{-1})	ΔV (cm^3 mol^{-1})	$\Delta V^* = \Delta V/V_{\phi S}$ ($\times 10^{-3}$)
Xylose	Water	–	95.92	–	–
	NaCl	3.2	97.01	1.09	11.4
	Na$_2$SO$_4$	10.2	97.43	1.51	15.7
	CaCl$_2$	6.7	96.67	0.75	7.8
	MgCl$_2$	8.1	96.96	1.04	10.9
Glucose	Water	–	112.60	–	–
	NaCl	3.0	114.01	1.41	12.5
	Na$_2$SO$_4$	10.5	114.55	1.95	17.3
	CaCl$_2$	10.5	113.63	1.03	9.1
	MgCl$_2$	12.2	113.52	0.92	8.2
Sucrose	Water	–	213.03	–	–
	NaCl	0.2	214.71	1.68	7.9
	Na$_2$SO$_4$	5.2	215.58	2.55	12.0
	CaCl$_2$	11.5	218.07	5.04	23.6
	MgCl$_2$	10 0	219 70	6 67	31 3
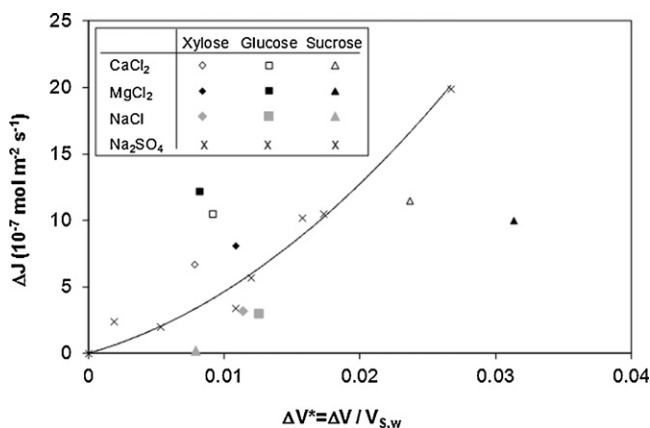
Fig. 14. Additional flux, ΔJ, versus the normalized variation of the AMV of saccharides, ΔV^*, for various ionic compositions at 25 °C; [Saccharide] = 1 mol L^{-1}; [Electrolyte] = 1 equiv. L^{-1}; [Na$_2$SO$_4$]: see Fig. 13.

4. Conclusion

The aim of this work was to investigate the mechanisms governing the mass transfer of neutral species such as saccharides through nanofiltration membranes with a focus on the role of ions. Indeed, it was demonstrated in previous studies that the addition of electrolyte increases the transfer of solutes like saccharides and that this increase depends on the nature and concentration of the electrolyte. Different assumptions were proposed to explain such observations, like a modification of the membrane properties, and/or a solute dehydration induced by the electrolyte.

The methodology proposed in this study was based on the coupling between the characterization of the solute hydration state from the determination of the apparent molar volume, AMV, and the measurement of the solute transfer parameters in electrolyte solutions. A procedure has been developed to dissociate the impact of the electrolyte due to the modifications of the solute properties from that coming from the change of the membrane properties.

From the AMV values in combination with a model of the solute/electrolyte interactions and their influence on the hydration shell, it was shown that the saccharide is less hydrated in presence of any electrolyte compared to water. More hydrated ions and increasing electrolyte concentrations were found to increase this dehydration, which was quantified through the variation of the AMV, since it is expected to reflect the release of water from the solute hydration shell.

The influence of the electrolyte on the saccharide transfer (xylose, glucose and sucrose) in various electrolyte solutions (NaCl, Na$_2$SO$_4$, CaCl$_2$ and MgCl$_2$) was also investigated. It was shown that the diffusion flux systematically increases in presence of electrolyte compared to water and for increasing electrolyte concentrations. Moreover, it was pointed out that this variation is more important with more hydrated ions. Finally, it was concluded that, for any conditions investigated in this study, the influence of the electrolyte is mainly due to the resulting change of the saccharide properties, since only weak influence was observed on the membrane properties, as characterized with saccharide/water systems. From a qualitative point out view, these results were in accordance with those obtained from the investigation of AMV of saccharides.

Finally, the additional fluxes, ΔJ, characterizing the impact of the electrolyte on the solute properties, were put in parallel with the normalized variation of the AMV, ΔV^*, in order to evaluate if a

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Nomenclature

d	density of sacharide/electrolyte solutions ($\mathrm{g\,cm^{-3}}$)
d_E	density of electrolyte/water solutions ($\mathrm{g\,cm^{-3}}$)
d_S	density of saccharide/water solutions ($\mathrm{g\,cm^{-3}}$)
d_0	density of pure water ($\mathrm{g\,cm^{-3}}$)
J_S^E	saccharide flux in saccharide/electrolyte solution for a soaked membrane with an electrolyte ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
J_S^W	saccharide flux in saccharide/water solution for a soaked membrane with an electrolyte ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
ΔJ	additional flux, defined as $\Delta J = J_S^E - J_S^W$ ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
m	molality ($\mathrm{mol\,kg\ of\ pure\ water^{-1}}$)
M	molecular weight ($\mathrm{g\,mol^{-1}}$)
$V_{\phi S}(m_S)$	apparent molar volume of saccharide for saccharide/water solution ($\mathrm{cm^3\,mol^{-1}}$)
$V_{\phi S}(m_S, m_E)$	apparent molar volume of saccharide for saccharide/electrolyte solution ($\mathrm{cm^3\,mol^{-1}}$)
ΔV	variation of the apparent molar volume, defined as $\Delta V = V_{\phi S}(m_S, m_E) - V_{\phi S}(m_S)$ ($\mathrm{cm^3\,mol^{-1}}$)
ΔV^*	normalized variation of the apparent molar volume, defined as $\Delta V^* = \frac{V_{\phi S}(m_S, m_E) - V_{\phi S}(m_S)}{V_{\phi S}(m_S)}$

Subscripts

E	electrolyte
S	saccharide
W	water

relationship can be established between the mass transfer increase and the dehydration of the neutral solutes in presence of electrolytes.

A good relationship was obtained for a given electrolyte, Na_2SO_4, at different concentrations regardless of the saccharide nature. From this result it is possible to conclude that the increase of the saccharide transfer in presence of electrolyte is due to the resulting dehydration.

Finally, no tendency was drawn from the results obtained with different electrolytes, especially with those containing divalent cations. This is probably due to the existence of other solute/electrolyte interactions, which become predominant in such systems compared to the (—OH)/cation ones.

Further work will be devoted to improve the understanding of these mass transfer mechanisms by investigating other electrolytes at various concentrations and using other thermodynamic parameters characterizing the hydration state, such as for instance the water activity.

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