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Influence of the ionic composition on the diffusion mass transfer of saccharides through a cation-exchange membrane

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A B S T R A C T

Recent studies have pointed out that the presence of salts can change significantly the membrane process performances because of the resulting modification of the neutral solutes transfer through the membrane. The influence of the ionic composition on the transfer of neutral solutes through membranes could be explained by a modification of the membrane properties, due to electrostatic effects, by a modification of the solute radius, likely due to its dehydration induced by the electrolyte, or more probably by a combination of both.

This study deals with the investigation of the mechanisms governing the mass transfer of neutral species through an ion-exchange membrane used in electrodialysis, CMX, with a focus on the role of ions. The mass transfer of various saccharides (xylose, glucose and sucrose) as well as the solvent transfer in different electrolytic solutions (NaCl, NH₄Cl, CaCl₂ and MgCl₂) was studied in a diffusion regime. A specific procedure has been used to dissociate the solvent or solute fluxes variations due to the modifications of the solute properties and of the membrane material induced by the electrolyte.

The results showed that the transfer modification is mainly due to the influence of the electrolyte on the membrane properties, which is fixed by the membrane soaking. A quantitative correlation has been established between the solvent and solute transfer and the hydration number of the membrane counter-ion. In presence of electrolyte, the saccharide mass transfer increased but the impact of the presence of electrolyte is much less than the one of membrane soaking. However, in this case, a relationship has been also established between the increase of the saccharide mass transfer and the cation hydration state.

Keywords:

Saccharide
Electrolyte
Hydration
Mass transfer
Cation-exchange membrane

1. Introduction

In the context of process intensification, efficient processes, like membrane operations, and especially nanofiltration and electrodialysis, are required for the treatment of complex fluids containing variable quantities of organic and mineral species, to fit with environmental regulations as well as product quality constraints. This is specially the case in the food industry (production of organic acids, sugar industry, milk products, etc.) as well as for environmental concerns (treatment of waste waters, lixivates or brines, 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 [1–8]. In any case, it was observed that, an increasing electrolyte

concentration results in a higher transfer and that this increase depends on the nature of the added electrolyte. This was mainly observed in the case of nanofiltration while studies relating these phenomena with ion-exchange membranes used in electrodialysis are rather scarce. Nevertheless, in the case of the demineralization of a synthetic liquid waste, containing acetic acid and different kinds of salts, it was reported that the diffusion of acetic acid through the ion-exchange membranes changed according to the salt composition. It was more important in presence of sodium sulfate or calcium chloride than with sodium chloride [7,8].

The transfer of a neutral solute through a membrane 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].

On one hand, the addition of electrolyte can lead to an increase of the membrane charge density and to a higher concentration of counter-ions in the electrical double layer at the pore surface. Wang et al. [1] assumed that these electrostatic interactions result

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Nomenclature

J_S	saccharide density flux ($\text{g m}^{-2} \text{s}^{-1}$)
$J_{v os}$	solvent density flux ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$)
L_p	membrane permeability ($\text{m s}^{-1} \text{Pa}^{-1}$)
P_S	solute permeability ($\text{g m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$)

Greek letters

$\Delta\Pi$	osmotic pressure (Pa)
μ	dynamic viscosity (Pa s)
σ	reflection coefficient

Subscripts

E	electrolyte
S	saccharide
W	water

Abbreviations

Glu	glucose
Suc	sucrose
Xyl	xylose

in a lower hydration shell at the pore surface, whereas Bargeman et al. [2] proposed that the stronger repulsion forces between the pore walls are likely to lead to an increase of the pore radius, commonly called “pore swelling”, assuming a certain elasticity of the membrane. For polymeric ion-exchange membranes, like those used in electrodialysis, the electrolyte composition can change the membrane characteristics because of membrane/solute interactions [9]. These membranes are particularly sensitive to the swelling, like ion-exchange resins. The swelling is characterized by the contact of the materials and the solution due to attractive or repulsive forces. It can be described as a variation of the free volume inside the material. It depends on the crosslinking, the rigidity of the material, exchange capacity or the hydration of the fixed site as well as on the solution properties such as concentration and nature of the solvent and counter-ion. The influence of the electrolyte on the swelling of an ion-exchange membrane may be complex and can be characterized by various experimental methods such as the determination of water content.

On the other hand, 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 [10]. Indeed, in mixed neutral solute/electrolyte solutions, the hydration shells of two neighbor solutes can overlap, displacing some water molecules from the hydration shell into the bulk. 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 link between the hydration 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 or ion-exchange membranes could be explained by a modification of the membrane properties, and/or by a solute dehydration induced by the electrolyte. The contributions of those two coupled phenomena can change with respect to the electrolyte composition and to the structural properties of the membranes. However, very few studies were devoted to the link between the mass transfer and the ionic composition to check these assumptions. Moreover, most of them concern NF membranes [6,11].

In this context, the aim of this paper is to investigate the mechanisms governing the transfer of neutral species through a cation-membrane with a focus on the influence of the ion composition. More precisely, the mass transfer of various saccharides (xylose, glucose and sucrose) as well as the solvent transfer in presence of electrolytes of various hydrations (NH_4Cl , NaCl , CaCl_2 , MgCl_2)

will be determined in a diffusion regime. A specific procedure will be used to dissociate the influence of the solute properties and of the membrane material, induced by the electrolyte, on the solvent and solute transfer. Then, the contribution due to the modification of membrane properties as well as solute ones, due to the electrolyte, will be evaluated.

2. Materials and methods

2.1. Chemicals

The neutral solutes used in the experiments were saccharides of increasing molecular weights, xylose ($150.13 \text{ g mol}^{-1}$), glucose ($180.16 \text{ g mol}^{-1}$) and sucrose ($342.29 \text{ g mol}^{-1}$) from Acros Organics. Electrolytes containing chloride ions and cations of various hydrations were used, NH_4Cl , NaCl , CaCl_2 and MgCl_2 (Acros Organics). The corresponding hydration numbers of the cations are given in Table 1 [12,13].

Ultra-pure water (Milli-Q RG, Millipore) was used to prepare the solutions. The pH of the various solutions was about (6 ± 0.5) without any adjustment.

2.2. Analytical methods

For any set of experiments, the saccharide concentration was analyzed by HPLC with a Dionex ICS 3000 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 is set as $30 \text{ }^\circ\text{C}$. The injection volume is $25 \text{ } \mu\text{L}$.

2.3. Membrane and diffusion set-up

Diffusion experiments were carried out with an electrodialysis stack (EUR-2B-10), supplied by Eurodia Industries, equipped with a cation exchange membrane, CMX (Neosepta, Tokuyama corp., Japan), a thin film membrane made of polystyrene divinyl benzene with sulfonic acid groups. CMX commercial ion-exchange membrane has been selected since it is widely used for many applications of electrodialysis processes (sea water treatment, cheese whey demineralization, food and sugar desalination, etc.). Moreover, this membrane has been used in the only study which pointed out that the presence of electrolyte can change the neutral solute transfer [7,8]. The main average characteristics, provided by

Table 1
Cation hydration numbers at $25 \text{ }^\circ\text{C}$.

Cation	NH_4^+	Na^+	Ca^{2+}	Mg^{2+}
Hydration number	4.6	6.5	10.4	11.7

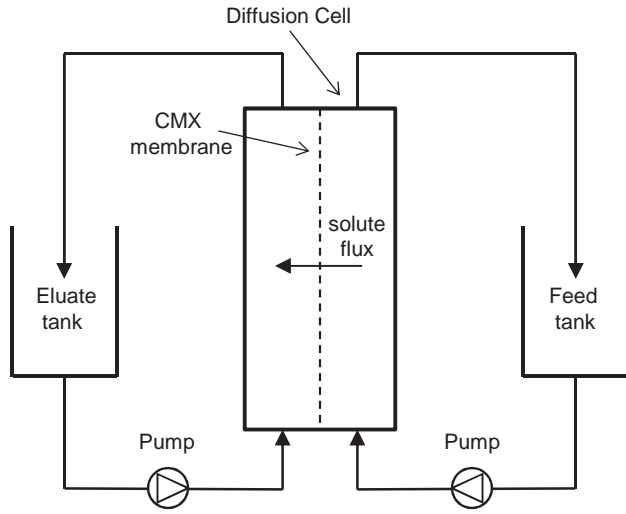


Fig. 1. Diffusion set-up diagram.

the supplier, are the exchange capacity ($1.4\text{--}1.7 \text{ meq g}^{-1}$), the specific electrical resistance ($2.0\text{--}3.5 \Omega \text{ cm}^{-1}$) and the thickness ($0.16\text{--}0.18 \text{ mm}$).

The diffusion set-up is depicted in Fig. 1. The total membrane area in the diffusion cell was 0.2 m^2 (10 membranes 0.02 m^2 each). 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 90 L h^{-1} . The feed tank was fed with 2 L of an electrolyte solution (or pure water) which contained saccharide at a fixed concentration. The eluate tank was fed with 2 L of a solution at the same ionic composition (electrolyte or water) but without saccharide.

Due to the difference of saccharide concentration on either side of the membrane, a diffusion saccharide flux takes place from the feed to the eluate compartment. Meanwhile, an osmotic flux, can also take place in the opposite direction.

Experiments are carried out in a batch mode during 2 h , with initial saccharide and electrolyte concentrations fixed at 1 mol L^{-1} and 1 eq L^{-1} , respectively. A heat exchanger is used to keep the temperature of the fluids at $25 \text{ }^\circ\text{C}$.

The diffusion and osmotic fluxes were respectively deduced from the variations of the solvent volume and solute mass transferred versus time. For all the experiments, these variations were linear (deviation less than 15%) so that one can consider that the transfer was carried out at a constant concentration gradient.

2.4. Experimental procedure and data treatment

A specific experimental procedure was developed to dissociate the influence of the modifications of the membrane characteristics from that of the solute properties, induced by the electrolyte, on the solvent and solute transfer variation.

As previously mentioned, the electrolyte has an influence on the mass transfer since it fixes the free volume, i.e. the volume accessible to the diffusing species, inside the material. More precisely, it has been shown that the free-volume of ion exchange membranes changes with the nature of the membrane counter-ion. Thus, for a cation-exchange membrane, the membrane properties depend on the nature of the cation.

Therefore, the membranes were previously equilibrated with the corresponding electrolyte. They were soaked in 4 L of the electrolytic solution at 1 eq L^{-1} for 4 h . Since the ions amount in the soaking solution (4 eq) was 50 times higher than the total ion-exchange capacity of the CMX membrane in the diffusion cell (lesser

than 70 meq), this procedure ensured that the counter-ion of the membrane was completely exchanged against that of the electrolyte. Then, the membranes were rinsed with ultra-pure water for about ten minutes, in order to remove the remaining electrolyte solution inside the membrane. This was checked by measuring the conductivity during experiments with saccharide/water systems. The variation was found to be lower than $15 \mu\text{S cm}^{-1}$ showing that the electrolyte does not diffuse out of the soaked membrane during experiments.

Diffusion experiments were carried out with such conditioned membranes using saccharide/water and saccharide/electrolyte solutions, respectively. This procedure was repeated for each electrolyte studied in this work.

The influence of the membrane soaking, i.e. the impact of the electrolyte on the membrane properties, was estimated from the solvent flux density, $J_{v,os}^W$, and the saccharide flux density, J_S^W , measured with saccharide/water systems. Then, the overall effect of the electrolyte was characterized by the solvent flux density, $J_{v,os}^E$, and the saccharide flux density, J_S^E , determined with saccharide/electrolyte solutions.

In a diffusion regime, the solvent and solute transfer through a permeable membrane separating two well-mixed compartments can be expressed from the equations, derived from irreversible thermodynamics, proposed by Kedem and Katchalsky [14]. These equations express the osmotic solvent flux density, $J_{v,os}$, and the solute flux density, J_S , by the following expressions, respectively:

$$J_{v,os} = L_p \sigma \Delta \Pi \quad (1)$$

$$J_S = P_S \Delta \Pi \quad (2)$$

where L_p is the membrane permeability to the solvent; $\Delta \Pi$ is the osmotic pressure gradient across the membrane; s and v refer to the solute and the solvent, respectively. P_S is the solute permeability coefficient, which is specific for each component and σ is the reflection coefficient, which represents the relative restriction of the membrane to the solvent or the solute fluxes. It varies from 0 for a freely permeable molecule to 1 for a non-permeating one.

Finally, the contributions due to the membranes soaking on one hand, and to the presence of electrolyte in solution on the other hand, on the transfer of the saccharides, were determined using the following expressions:

– contribution due to the membrane soaking :

$$\Gamma = \frac{P_S^W \mu^W}{P_S^E \mu^E} \times 100 \quad (3)$$

– contribution due to the addition of electrolyte :

$$100 - \Gamma = \left[1 - \frac{P_S^W \mu^W}{P_S^E \mu^E} \right] \times 100 \quad (4)$$

where μ^W and μ^E are the water and electrolyte solution viscosities.

The viscosities of water and electrolyte are included in these expressions in order to take into account the influence of the solvent viscosity on the diffusion of the saccharide through the membrane. Indeed, it was explained that the soaking solution inside the membrane is replaced by water during the membrane rinsing at the end of the soaking procedure.

The values of the viscosities of the electrolytic solutions used in this work are reported in Table 2 [15].

Table 2

Dynamic viscosities of the electrolytic solutions at $25 \text{ }^\circ\text{C}$ and $[\text{electrolyte}] = 1 \text{ eq L}^{-1}$.

Solution	Water	NH_4Cl	NaCl	CaCl_2	MgCl_2
Viscosity ($\times 10^{-3} \text{ Pa s}$)	0.890	0.872	0.975	1.095	1.084

3. Results and discussion

Firstly, diffusion experiments were carried out with saccharide/water systems for a membrane soaked in a given electrolyte in order to highlight the impact of the electrolyte on the membrane properties. The solvent and saccharide fluxes were discussed in terms of the product of the membrane permeability by the reflection coefficient, $L_p\sigma$, further called apparent membrane permeability, and of the solute permeability, P_s .

Then, the overall impact (membrane and solute properties modifications) of the electrolyte on the solvent and saccharide transfer was measured with saccharide/electrolyte systems.

Finally, the contributions due to the membrane soaking on one hand, and to the presence of electrolyte in solution on the other hand, on the transfer of the saccharides, were determined.

3.1. Influence of the membrane soaking

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

The variations of the solvent volume and of the mass of sucrose transferred versus time through the membranes soaked in NH_4Cl , are plotted in Figs. 2 and 3, respectively. The same tendencies are obtained for the other saccharides and membrane soakings (results not shown). Since these variations are linear (deviation from linearity < 15%), one can obtain the solvent and solute flux densities from the slope of the corresponding straight and the total membrane area. The corresponding values of the flux densities, J_v^W and J_s^W , for various membrane soakings and saccharides, are reported in Tables 3 and 4, respectively.

The apparent membrane permeability, $(L_p\sigma)^W$, and the solute permeability, P_s^W , are then determined knowing the osmotic pressure gradient (using Eqs. (1) and (2)). For a saccharide concentration fixed at 1 mol L^{-1} , the osmotic pressure of xylose, glucose and sucrose are 28, 29 and 35 ($\times 10^5$) Pa, respectively [16,17]. The corresponding values of the apparent membrane permeability and solute permeability, obtained for the different membrane soakings, are given in Tables 3 and 4, respectively.

Considering that the transfer of saccharide is governed by steric effects, the transfer is expected to decrease for an increasing saccharide size. This is confirmed by the values of J_s^W and P_s^W given in Table 4.

Moreover, one can observe that, for a given membrane soaking, the apparent membrane permeability increases with the saccharide size: $(L_p\sigma)_{\text{Xyl}}^W < (L_p\sigma)_{\text{Glu}}^W < (L_p\sigma)_{\text{Suc}}^W$.

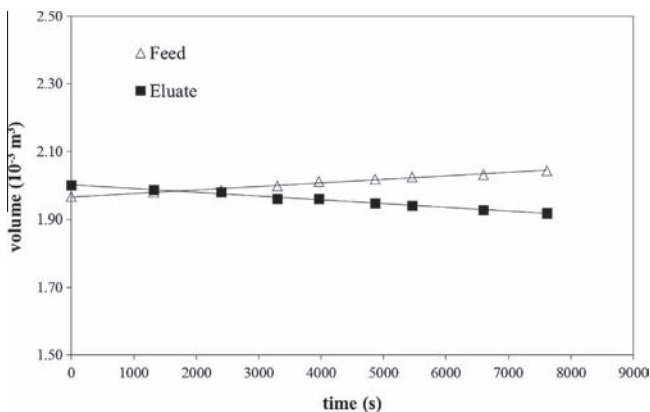


Fig. 2. Variation of volume in the feed and eluate compartments versus time for sucrose/water solutions and for a membrane soaked in NH_4Cl at 25°C ; $[\text{Sucrose}] = 1 \text{ mol L}^{-1}$.

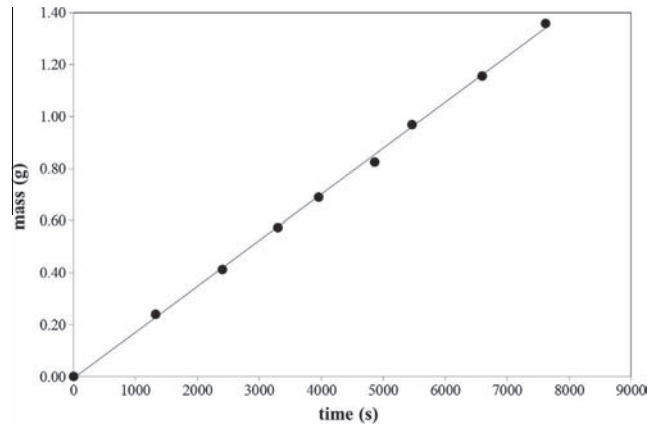


Fig. 3. Variation of the mass of sucrose transferred in the eluate compartment versus time for sucrose/water solutions and for a membrane soaked in NH_4Cl at 25°C ; $[\text{Sucrose}] = 1 \text{ mol L}^{-1}$.

This result is in agreement with the expected variation of the reflection coefficient, σ , which measures the restriction to the solute transfer. Indeed, this parameter, ranged between 0, for a freely permeable solute, and 1, for a completely retained molecule, is expected to increase with the size of a neutral solute.

Concerning the influence of the membrane soaking, these results show that, for a given saccharide, the apparent membrane permeability, as well as the solute permeability, vary according to the following sequence: $\text{NH}_4\text{Cl} > \text{NaCl} > \text{CaCl}_2 > \text{MgCl}_2$.

The ratio between the highest solvent membrane permeability, i.e. for NH_4Cl soaking, and the lowest one, i.e. for MgCl_2 , ranges between 2.2 and 2.8 according to the saccharide. While for the solute permeability, this ratio ranges between 4 and 5. Thus, the solute transfer is more affected than the solvent one by the modification of the membrane soaking.

These results can also be correlated to the hydration scale of the membrane counter-ion: $\text{NH}_4^+ < \text{Na}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$. The variation of the membrane permeability, $(L_p\sigma)^W$, and solute permeability, P_s^W , versus the cation hydration number, given in Table 1, are represented in Figs. 4 and 5, respectively. One can observe that the membrane permeability as well as the solute permeability decrease with the hydration number of the cation, i.e. the counter ion. Moreover, for both solvent and solute transfer, a linear relation is obtained depending on the saccharide nature, even if the values obtained with xylose and glucose in NaCl soaking are systematically lower than those expected from the linear variation.

These solvent and solute transfer variations reflect changes in the membrane properties associated with the hydration of the counter-ion coming from swelling mechanisms at a microscopic scale. These effects were particularly studied in the case of ion-exchange resins [18,19] and Nafion membranes [20]. In presence of solvent, the ion exchanger usually expands or swells due to the combination of different phenomena such as the solvation of the fixed and mobile ions, the osmotic pressure difference between the solutions inside and outside the ion-exchanger and the electrostatic repulsion between the fixed ionic groups [18]. Ion exchangers swell in solvent only to a limited degree since swelling equilibrium is reached when the expanded forces balance the contractive force of the elastic matrix. As previously mentioned, the influence of the nature of the counter-ion on the swelling of an ion exchanger may be very complex. Indeed, for moderately and highly cross-linked ion-exchangers, swelling increases with the counter-ion hydration whereas this order may be partially or completely reversed in very highly cross-linked ion-exchangers due to incomplete solvation.

Table 3

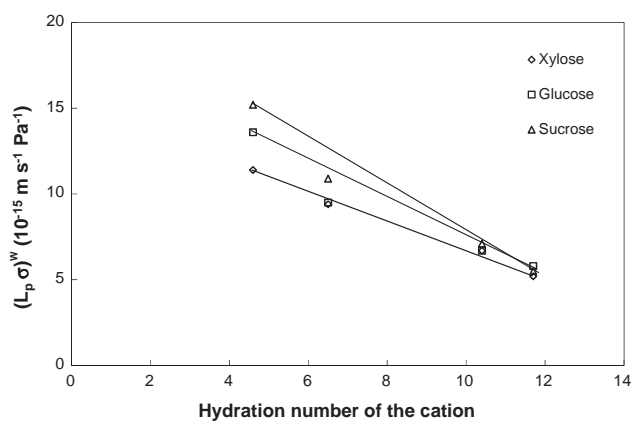
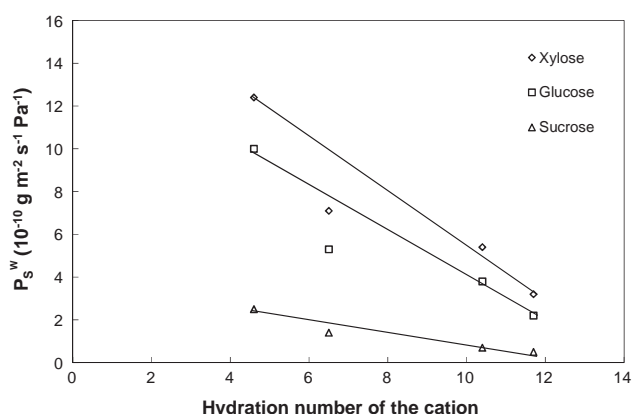
Solvent density fluxes and apparent membrane permeabilities for saccharide/water and saccharide/electrolyte systems at 25 °C.

Electrolyte	Saccharide/water						Saccharide/electrolyte					
	$J_{ws}^W (\times 10^{-8} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1})$			$(L_p\sigma)^W (\times 10^{-15} \text{ m s}^{-1} \text{ Pa}^{-1})$			$J_{eos}^E (\times 10^{-8} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1})$			$(L_p\sigma)^E (\times 10^{-15} \text{ m s}^{-1} \text{ Pa}^{-1})$		
	Xyl	Glu	Suc	Xyl	Glu	Suc	Xyl	Glu	Suc	Xyl	Glu	Suc
NH ₄ Cl	3.2	3.9	5.3	11.4	13.6	15.2	3.1	3.9	5.4	11.2	13.3	15.5
NaCl	2.7	2.8	3.8	9.4	9.5	10.9	2.3	2.9	4.2	8.1	9.8	11.9
CaCl ₂	1.9	1.9	2.5	6.7	6.7	7.1	2.0	2.1	2.9	7.2	7.1	8.4
MgCl ₂	1.5	1.7	1.9	5.2	5.8	5.5	1.5	1.7	2.4	5.4	5.7	6.9

Table 4

Saccharides density fluxes and solute permeabilities for saccharide/water and saccharide/electrolyte systems at 25 °C.

Electrolyte	Saccharide/water						Saccharide/electrolyte					
	$J_S^W (\times 10^{-3} \text{ g m}^{-2} \text{ s}^{-1})$			$P_S^W (\times 10^{-10} \text{ g m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1})$			$J_S^E (\times 10^{-3} \text{ g m}^{-2} \text{ s}^{-1})$			$P_S^E (\times 10^{-10} \text{ g m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1})$		
	Xyl	Glu	Suc	Xyl	Glu	Suc	Xyl	Glu	Suc	Xyl	Glu	Suc
NH ₄ Cl	3.5	3.0	0.9	12.4	10.0	2.5	3.8	3.4	1.0	13.6	11.7	2.8
NaCl	2.0	1.6	0.5	7.1	5.3	1.4	2.2	1.7	0.5	7.8	5.9	1.4
CaCl ₂	1.5	1.1	0.3	5.4	3.8	0.7	1.6	1.1	0.3	5.7	3.9	1.0
MgCl ₂	0.9	0.7	0.2	3.2	2.2	0.5	1.0	0.7	0.2	3.5	2.5	0.5

**Fig. 4.** Variation of the apparent membrane permeability in saccharide/water systems versus the hydration number of the cation.**Fig. 5.** Variation of the solute permeability in saccharide/water systems versus the hydration number of the cation.

Various experimental methods were proposed and used to characterize ion-exchange membrane swelling such as the determination of the water content which is considered to be a key parameter in the transport behavior [21,22]. Indeed, the water

content can be used to characterize the hydration state of the membrane and to give an image of possible structural modifications of it. The influence of the nature of the counter-ion on the water content has been mainly investigated with Nafion cation-exchange membranes for which the water content values range between 4 and 30% according to the nature of the counter-ion. It was reported that the water content increases for decreasing atomic number or size of the cation and that the water content rises for increasing hydration number of the counter-ion [22–25]. In the case of alkali ions, the water content increases according to the following sequence: $\text{Cs}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$. It was also observed that the water content increases with the cation valence: monovalent < divalent < trivalent [23,25]. As an example, when the water content in alkali ion-form ranges between 7.5% and 10.2%, values of 14.7%, 16.7% and 18.9% are obtained with Ca^{2+} , Mg^{2+} and Al^{3+} counter ions, respectively [25].

The water content of the CMX membrane considered in this work is about 25–30% [26–28]. Few studies have been devoted to investigate the influence of the nature of the counter-ion on this type of membrane. Tuan et al. have investigated the properties of CMS and CMV cation-exchange membranes which are also made of polystyrene divinyl benzene with sulfonic acid groups [9,29]. They have shown that the water content in the H^+ -form is 27–29%, and is slightly lower in Na^+ -form, 20–24%, Na^+ being less hydrated than H^+ . These results are in agreement with those obtained with Nafion membranes.

But an important distinction has to be made between the “bound solvent” content (solvent in the solvation shells) and the “free solvent” content (not in the solvation form), this last being the more relevant property to interpret the transfer of neutral solutes through ion-exchange membranes. Indeed, it is well known that swelling and water content of the alkali ion-forms of strong cation-exchangers increase with the hydration of the counter-ion whereas the free-water content decreases [18,30].

The determination of the membrane electrical conductivity, based on impedance spectroscopy methods, has been also used to characterize ion-exchange membranes in various electrolytes. The experimental results are usually interpreted using the micro-heterogeneous model [31], which represents an ion-exchange membrane as a two phases system, containing a gel and an inter-gel phases. The gel phase includes the polymer matrix, the fixed and mobile ions and water. The inter-gel phase represents

the inner parts of the meso- and macropores, which can be considered as a free volume inside the material. It is supposed to have the same properties as the outer solution.

Several works showed that the influence of the counter-ion on the inter-gel phase fraction depends on the nature of the membrane material. For instance, high values of the inter-gel phase fraction (more than 30%) were obtained for heterogeneous ion-exchange membranes have because of the macro porous cavities separating the inert material and the ion-exchange particles [32]. But no tendency can be drawn concerning the influence of the counter ion since the values do not change significantly enough [33,34]. On the contrary, with homogeneous ion-exchange membranes that are less macro porous, several works showed that the inert-gel volume fraction depends on the nature of the electrolyte. For instance, in the case of a CMX membrane, it has been observed that for a given anion (Cl^-) the inter-gel fraction decreases from 32% to 11% when the cation, NH_4^+ , is replaced by Na^+ , which is more hydrated [26,35]. Similarly, but to a lesser extent, it was reported that the inter-gel fraction of a CM2 membrane is higher in Na^+ -form (7%) than in Li^+ -form (5%) which is more hydrated [36]. On the contrary, for CMS and CMV cation exchange membranes, it was observed that for a given anion (SO_4^{2-}) the inter-gel fraction decreases from 29% and 19% down to 13% and 10%, respectively, when the cation, H^+ , is replaced by Na^+ , which is less hydrated [9,29]. The highest values observed for H^+ -form can be due to its specific hydration, as it has been previously suggested to explain the current-voltage curve of CMX membrane in contact with HCl solution [37].

The influence of the counter-ion has been also observed with anion-exchange membranes. For monovalent anions, no clear tendency can be drawn since the values do not change significantly. However, the influence of the anion valence was pointed out with various anion-exchange membranes (AFN, AMX, ACS and ACM) by Elattar et al. [38] and Pismenkaya et al. [39]. It was observed that the inter-gel phase fraction decreases for increasing anion valence, i.e. hydration number. For instance in the case of AMX membranes, inter-gel fraction of 25%, 15% and 5% were obtained for mono- (Cl^- , F^- , NO_3^-), di- (SO_4^{2-}) and trivalent (PO_4^{3-}) anions respectively.

The "free volume" in ion-exchange membranes can be also estimated from Positron Annihilation Lifetime Spectroscopy (PALS). PALS has been developed as a powerful tool for the microscopic structure characterization of a variety of polymer such as poly(ethylene oxide) films [40,41], Nafion membranes [42,43] or thin film composite polyamide nanofiltration membranes [44,45]. This method correlated the lifetime and relative intensity of positrons (anti-electrons) annihilating in the free volume of the membrane with the free volume element size and the fraction of free volume. It is recognized that the free volume values obtained by PALS correlates well with transport properties in polymeric material as diverse as gas separation membranes and hydrated polymer hydrogels [46]. However, few works have been devoted to the investigation of the influence of the nature of the counter-ion on the free volume of ion-exchange membranes. Nevertheless, in the case of Nafion membrane, it has been shown that the free volume increases as the size of monovalent cations increases, i.e. as the cation hydration decreases, according to the following sequence: $\text{H}^+ \approx \text{Li}^+ < \text{Na}^+ < \text{K}^+ \approx \text{Rb}^+ < \text{Cs}^+$ [42]. Moreover, this work also pointed out a lower free volume for a Nafion membrane soaked with divalent cations which are more hydrated than monovalent ones.

The solvent and solute transfer variations reflect changes in the membrane properties at microscopic scale such as the free volume. A previously discussed, water content, membrane electrical conductivity and PALS measurements can be used to investigate the influence of the counter-ion on the ion-exchange membrane properties. From these results, one can conclude that the free volume of ion-exchange membranes decreases with the hydration of the

counter-ion. Therefore, the presence of a more hydrated counter-ion is expected to reduce the free volume in the material, and thus decreasing the solvent and solute transfer. This is in agreement with the experimental results reported in this work.

3.2. Influence of the presence of electrolyte

A previously mentioned, experiments were carried out with saccharide/electrolyte systems to evaluate the overall impact (membrane and solute properties modifications) of the electrolyte on the solvent and saccharide transfer.

In any case, as observed for saccharide/water systems, the variations of the volume and mass of saccharide transferred versus time are linear (deviation from linearity < 15%; results not shown). The flux densities, $J_{v,os}^E$ and J_S^E , for the various saccharide/electrolyte systems, are reported in Tables 3 and 4, respectively. The corresponding apparent membrane permeability, $(L_p\sigma)^E$, and solute permeability, P_S^E , are also reported.

Concerning the solvent transfer, the values of $J_{v,os}^E$ and $(L_p\sigma)^E$ obtained in presence of various electrolytes are close to those measured in water. Concerning the saccharide transfer parameter, P_S^E , one can observe that the values are systematically higher in presence of electrolyte compared to those obtained in water. These results are in agreement with previous ones obtained during electrodialysis [7,8] as well as nanofiltration experiments [1-6], showing that the transfer of a neutral solute is increased by the addition of an electrolyte.

Then, in order to evaluate the influence of the electrolyte nature, the contributions due to the membranes soaking on one hand, and to the presence of electrolyte in solution on the other hand, on the transfer of the saccharides are determined using Eqs. (3) and (4).

The results are plotted in Fig. 6 for the 3 saccharides and the different electrolytes investigated.

One can observe that the contribution due to the presence of electrolyte in solution is lower than that of the membrane soaking. On the other hand, for a given electrolyte, the impact of the presence of electrolyte is of the same order of magnitude regardless the saccharide nature, except for sucrose/ CaCl_2 system for which higher values are obtained.

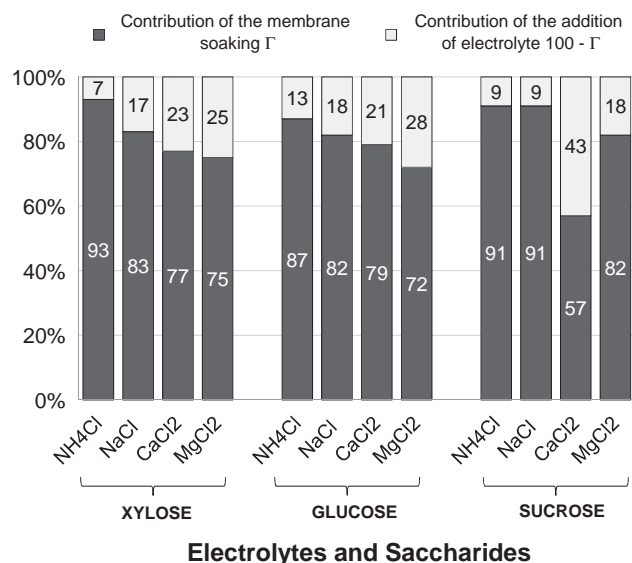


Fig. 6. Contributions of the membranes soaking and the presence of electrolyte on the saccharide transfer: influence of the electrolyte nature.

Finally, the contribution due to the electrolyte addition increases according to the following sequence: $\text{NH}_4\text{Cl} < \text{NaCl} < \text{CaCl}_2 < \text{MgCl}_2$, except for sucrose/ CaCl_2 system.

These results can be correlated to the hydration scale of ions. Indeed, for a given anion, Cl^- , the saccharide transfer is even higher than the cation is hydrated.

These results can be put in parallel with those obtained in a previous study, in which identical saccharide/electrolyte systems were used with a nanofiltration membrane [11].

Firstly, the specific behavior for sucrose/ CaCl_2 system was also pointed out and explained by strong interactions existing between sucrose and calcium ions [47,48].

Secondly, it was also shown that the diffusion flux through the nanofiltration membrane systematically increases in presence of electrolytes compared to water. This increase was found to be more important in presence of more hydrated ions in solution. Finally, it was concluded that the main contribution is due to the influence of the electrolyte on the saccharide properties. On the contrary, with the CMX membrane used in the present study, we have shown that the impact of the membrane soaking is preponderant. However, common figures can be drawn with the two types of membrane regarding the influence of the electrolyte on the solute properties and its consequences on the solute transfer. Indeed, it is observed that, for a same anion, Cl^- , the impact due to the presence of the electrolyte increases with the hydration of the cation: $\text{Na}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$.

Meanwhile, the hydration state of saccharides in various electrolyte solutions was also investigated, under the same conditions as those used in the present work. A physicochemical parameter, the apparent molar volume obtained from density measurements, was chosen to characterize the solute hydration [11]. It was shown that the saccharides are less hydrated in presence of more hydrated ions and for increasing electrolyte concentrations. It was thus concluded that the increase of the saccharide transfer as observed in nanofiltration in presence of electrolyte is due to the resulting dehydration.

Accordingly, the variation of the contribution due to the presence of the electrolyte on the saccharide flux through a cation exchange membrane is in agreement with the assumption of the dehydration of neutral solutes in presence of electrolyte since more hydrated ions induce a higher dehydration.

4. Conclusion

The aim of this work was to investigate the transfer of neutral species such as saccharides through a cation-exchange membrane with a focus on the role of ions. Indeed, previous studies had demonstrated that the transfer of neutral solutes depends on the nature of the added electrolyte. Different assumptions have been proposed to explain such phenomenon, like the modification of the membrane properties, and/or the solute dehydration induced by the electrolyte.

The methodology proposed in this study was based on the experimental determination of the solvent and solute transfer in various electrolyte solutions in a diffusion regime. A procedure has been used to dissociate the impact of the electrolyte due to the modifications of the solute properties from that coming from the possible change of the membrane properties.

It was shown that the solvent and solute transfer systematically decreased with the increase of the counter-ion hydration. Moreover, a quantitative correlation was drawn between the solvent and solute transfer and the hydration number of the membrane counter-ion. These modifications were related to the influence of the electrolyte nature on the membrane swelling, as previously observed with ion-exchange membranes. Indeed, the presence of

more hydrated counter-ion in the membrane leads to a decrease of the free-water content or the free volume and therefore to a decrease of the solvent and solute transfer.

In presence of electrolyte, the saccharide mass transfer increased compared to that in water but the impact of the presence of electrolyte was much less than the one of the membrane soaking. Nevertheless, a relationship has been established between the increase of the saccharide transfer and the cation hydration state. Indeed, it has been pointed out that this increase is more important in presence of more hydrated cations. These results were put in parallel with the hydration state of saccharides in presence of electrolyte determined in a previous study. In this manner the contribution due to the presence of the electrolyte on the saccharide flux through a cation exchange membrane was found to be in agreement with the assumption of the partial dehydration of neutral solutes in presence of electrolyte since more hydrated electrolytes induce less hydrated solutes.

Further work will be devoted to investigate the membrane/electrolyte interactions to evaluate the influence of the counter-ion nature on the membrane swelling for the systems (membrane and electrolyte) used in this study on one hand, and to study the impact of these phenomena during the demineralization of salted fluids containing a neutral organic solute by electro dialysis, on the other hand.

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