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HOW DO IONS ENHANCE THE TRANSFER DURING NANOFILTRATION OF SACCHARIDES? EXPERIMENTAL ASSESSMENT OF THE DEHYDRATION ASSUMPTION

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The aim of the work was to improve the understanding of the role of ion hydration on the transfer during nanofiltration of saccharides. More precisely, it consisted in evaluating the physical relevance of the dehydration assumption to explain the increased transfer of saccharides in presence of electrolytes. Experiments were carried out using saccharides (xylose, glucose) and electrolytes containing ions of different hydration levels (NaCl, Na₂SO₄). The Filmtec NF membrane (previously referred to as NF45) was used. Unlike saccharide/NaCl solutions, Na₂SO₄ had a weak influence on the saccharide transfer. This means that the impact of the electrolyte on the transfer of saccharide was strongly affected by the ions retention. Indeed, SO₄²⁻ ions were much more often retained than Cl⁻. Thus, an enhanced saccharide transfer was expected as the electrolyte concentration in the permeate was high. The physical relevance of the assumed dehydration was evaluated. The decrease of the saccharide radius was determined from the mass transfer modelling. It was shown that the decrease was physically relevant with the dehydration phenomenon since this decrease corresponded to a fraction of the water molecule (2–3 %). Next, the increased transfer was compared with the variation of the apparent molar volume, characterizing the hydration state of solutes, to better understand the mechanisms involved. For a given electrolyte, the transfer increased continuously with saccharide dehydration. This result could confirm that the increase of the transfer could be attributed to the saccharide dehydration caused by the electrolyte.

Keywords: nanofiltration, mass transfer modelling, hydration, saccharide, electrolyte

INTRODUCTION

Membrane processes, and more particularly nanofiltration (NF), are moving towards increasingly complex fluids which sometimes may contain high concentrations of mineral and organic components. This is the case, for example, in the food industry and in the environmental field.

Several investigations showed that the addition of salts can modify the process efficiency owing to the changes of the transfer of the neutral solutes.^[1–7] It was reported that when the concentration of the electrolyte increases the transfer is enhanced. This enhancement depends on the type of the electrolyte.

It was further shown that the enhanced transfer of the neutral solute results from two contributions. Firstly, the structural properties of the material can be modified depending on the type and of the concentration of the electrolyte (swelling phenomenon).^[1,2,6] Secondly, it was reported that the apparent size of the solute can vary as it is less hydrated when the electrolyte is added in solution.^[3,8]

The transfer of neutral solutes, like saccharides or PEG (polyethylene glycol), through NF membranes was investigated for various electrolyte solutions.^[3,4,6] It was seen that the transfer is more significant for increasing electrolyte concentrations and with more hydrated ions.

The effects of electrolytes on NF membranes were summarized in a critical review.^[9] Based on the data published, mechanisms involved were reported to better the understanding of this issue.

However, contradictory results can be found in the literature regarding the influence of the nature or concentration of the ions as well as that of the membrane materials or operating conditions. Bargeman et al. have studied the transfer of glucose through two

different NF membranes with three electrolytes having a common anion, Cl⁻.^[2] A higher transfer of glucose was found with K⁺ and Na⁺ in relation to Ca²⁺ which is more hydrated. Then, the increase of the neutral solute flux is less pronounced with more hydrated cations. A similar tendency has also been reported by Umpuch et al. who studied the addition of Cl⁻ and SO₄²⁻ on the glucose transfer for a common cation, Na⁺.^[7] They have shown that the increased transfer of glucose is smaller with more hydrated anions (SO₄²⁻).

More recently, the effect of the type and the concentration of the electrolyte on the transfer of saccharides through a NF membrane has been studied in a diffusion regime.^[8] It was found that the variation of the mass transfer is more important with more hydrated ions. It was also seen that the transfer change according to the electrolyte is mainly attributable to its effect on the solute properties, i.e. dehydration, since only a weak effect was seen on the membrane properties. Moreover, for an electrolyte at different concentrations, a good quantitative relationship was found, irrespective of the type of the saccharide, between the saccharide transfer increase and a physicochemical parameter, the apparent molar volume, which characterizes the change of solute hydration in the presence of electrolyte.

Ion	Na ⁺	Cl ⁻	SO ₄ ²⁻
Hydration number	6.5	3.9	5.3

From the process point of view, the diffusion regime is not viable since productivity is very low. Consequently, it is necessary to better perceive the action of ions on the solute transfer through NF membrane in filtration regime (convection/diffusion). To our knowledge, the evaluation of the dehydration assumption to explain the effect of the electrolyte on the neutral solutes transfer in filtration regime is rather scarce in the literature.^[4,6] The goal of this research work is to better appreciate the role of ions on the transfer in a filtration mode using the approach previously developed in the diffusion regime.^[8] More precisely, this work is focused on the relationship between the transfer of saccharides and the hydration of the ions present in solutions since contradictory results have been highlighted in the literature. In the present study, the effects of salts (NaCl and Na₂SO₄) on the transfer of saccharides (xylose and glucose) will be studied in saccharide/electrolyte systems during NF. The physical relevance of the dehydration effect will be evaluated by computing the variation of the saccharide radius from experimental data in both diffusion and filtration regimes. The results obtained for both regimes of transfer (diffusion and filtration) will be compared. Then, the mass transfer parameters will be linked to the apparent molar volume values to establish a relationship between the solute hydration and the saccharide transfer through NF membrane.

MATERIALS AND METHODS

Chemical

Saccharides of different molecular weights were used, xylose (150 g · mol⁻¹) and glucose (180 g · mol⁻¹), supplied from Acros Organics, Illkirch, France. Electrolytes containing sodium ions and anions of different hydrations were used, NaCl and Na₂SO₄ (Acros Organics, Illkirch, France). Another anion of higher valency was not studied since it would have been completely retained by the NF membrane.^[1] Table 1 gives the corresponding hydration numbers of ions.^[10,11] Solutions were prepared using ultra-pure water (Milli-Q RG, Millipore, Darmstadt, Germany). Table 2 presents the compositions of studied solutions. For any system, the saccharide concentration was equal to 0.1 mol · L⁻¹. The pH was about (6 ± 0.5) in the absence of any adjustment.

Analytical Methods

A refractometer was used to determine the saccharide concentration for saccharide/water systems (Atago RX-5000 refractometer, Tokyo, Japan).

A HPLC with a Dionex system, equipped with a CarboPac PA1 column and an electrochemical ED40 detector, was used to determine the saccharide concentration for saccharide/electrolyte systems. A 150 mmol · L⁻¹ NaOH solution was used as mobile phase.

The ion concentration was also analyzed for electrolyte/water and saccharide/electrolyte systems by the same device, using an IonPac AS11 column with a conductivity detector CD20 equipped with a suppressor ASRS. A 5 mmol · L⁻¹ NaOH solution and a mixture of NaOH solution at 5 mmol · L⁻¹ (10 %) and

Solutions	Xylose	Glucose	NaCl	Na ₂ SO ₄
Saccharide/water	0.1	0.1	–	–
Electrolyte/water	–	–	0.1–1	0.05–0.5
Saccharide/electrolyte	0.1	–	0.25–1	–
	–	0.1	–	–
	–	0.1	–	0.125

100 mmol · L⁻¹ (90 %) was used as mobile phase for chloride and sulphate ions analysis, respectively.

For any set of experiments, the column temperature was adjusted to 30 °C and the flow rate was equal to 1 mL · min⁻¹.

Membrane and Nanofiltration Setup

A Filmtec NF membrane (previously referred to as NF45) supplied by Dow Chemicals was used. The membrane was a composite membrane and it was negatively charged above a pH of 5.1.^[12,13]

The pH of the solutions was about (6 ± 0.5); this indicates that the membrane was negatively charged for all the experiments.

The characteristics of the membrane were as follows: molecular weight cut-off of 150–200 g · mol⁻¹^[14,15] and hydraulic permeability of 5.5 × 10⁻² L · h⁻¹ · m⁻² · kPa⁻¹.^[2]

The experiments were carried out using a cross-flow filtration system described in previous papers (Figure 1).^[3,7] The total membrane area in the filtration cell was 137 cm². A feed vessel of 5 L equipped with a temperature control system fixed at 25 ± 0.5 °C and connected to a pump was used to feed the membrane cell. A pressure valve mounted on the retentate outlet was used to adjust the transmembrane pressure. The filtration system was used in total recycle mode.

Experiments were carried out at a fixed cross-flow rate of 400 L · h⁻¹, corresponding to 1.33 m · s⁻¹ of cross-flow velocity (Re ≈ 1400) calculated with a channel height of 1.2 mm, for a transmembrane pressure range of 200–2000 kPa. For each pressure, 5 mL of permeate samples were taken and clocked to determine the permeation flux.

Experimental Procedure

Prior to each experiment, the membrane suffered a pre-treatment and a cleaning procedure.

In this study, the membrane was compacted by circulating ultra-pure water at 200 kPa (20 bar) until the permeate flux (J_v) stays constant. This procedure lasted about 30–45 min.

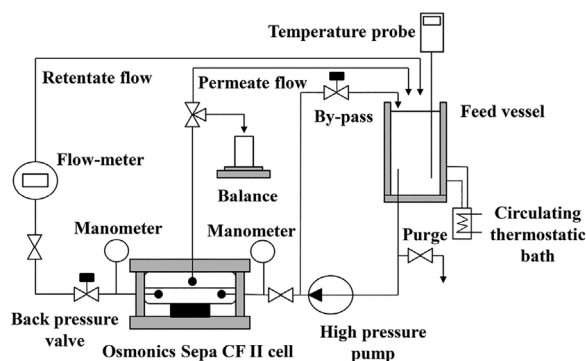


Figure 1. Schematic diagram of the nanofiltration equipment.^[3,7]

After use, the membrane was rinsed by filtering first reverse osmosis water then ultra-pure water until the conductivity of $5 \mu\text{S} \cdot \text{cm}^{-1}$ was reached. The operating conditions of the rinsing procedure were: $T = 25 \text{ }^\circ\text{C}$, 1000 kPa , and $275 \text{ L} \cdot \text{h}^{-1}$.

The hydraulic permeability, L_p , was determined before each experiment. The value of L_p was determined from the linear variation of J_v versus ΔP (maximum standard deviation of $\pm 5 \%$). The membrane tested had an average hydraulic permeability of $9.9 \times 10^{-2} \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{kPa}^{-1}$. The value of L_p determined in the literature is lower. This difference is certainly related to the membrane pre-treatment procedure which has been carried out at a different pressure (4000 kPa against 2000 kPa in this study).

To get a stable state of the membrane for a given electrolyte, it was first equilibrated with the corresponding electrolyte. It was immersed in the electrolytic solution at $1 \text{ eq} \cdot \text{L}^{-1}$ for approximately 12 h and washed with ultra-pure water (10 min) to completely eliminate the residual electrolytic solution of the membrane. The conductivity was followed for saccharide/water experiments to check the washing. In all the cases, the conductivity was lower than $5 \mu\text{S} \cdot \text{cm}^{-1}$, indicating that the electrolyte did not get out of the membrane.

MASS TRANSFER MODELLING

Filtration

The selectivity of a membrane towards a solute, i.e. the capacity to retain the solute, is characterized by a parameter, called retention, to link concentrations on both sides of the membrane. The observed retention, R_{obs} , is the measured value, varying with the concentration polarization, and defined as follows:

$$R_{obs} = 1 - \frac{c_p}{c_0} \quad (1)$$

where c_p and c_0 are the permeate and feed concentrations displayed as $\text{mol} \cdot \text{m}^{-3}$.

The intrinsic retention, R_{int} , is only calculated, is directly related to the concentration at the surface of the membrane ($\text{mol} \cdot \text{m}^{-3}$), c_m , and is defined as follows:

$$R_{int} = 1 - \frac{c_p}{c_m} \quad (2)$$

Because the intrinsic retention is not dependent on the concentration polarization, R_{int} represents an appropriate parameter to characterize the solute/membrane system in terms of selectivity.

In addition, the solute transfer through the membrane can be also evaluated by another parameter, the solute flux ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), J_s , which is expressed by the product between the concentration in the permeate ($\text{mol} \cdot \text{m}^{-3}$) and the permeate flux ($\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), J_v :

$$J_s = c_p \times J_v \quad (3)$$

The solute flux, J_s , can be also calculated using the retention (observed or intrinsic), R , and the permeate flux, J_v :

$$J_s = c_0 \times (1 - R) \times J_v \quad (4)$$

Among the various models developed to investigate the mass transfer of neutral solute through NF membranes, we chose a

hydrodynamic approach, since it is able to express the solute transfer versus the solute and membrane characteristics.^[16] The model developed from the extended Nernst-Planck equation is used in the present study.^[17] This model is obtained thanks to the linear concentration gradient on both sides of the membrane. It considers that the solute diffusion coefficient is independent of the concentration inside the stagnant layer thickness and is equivalent to that at infinite dilution.

The assumptions are as follows:

- the active layer is made of a bundle of straight, parallel, and cylindrical pores of radius r_p (m)
- the pore length L (m) is much higher than the radius (i.e. $L \gg r_p$)

The corresponding equations describing the mass transfer of a neutral solute in a filtration mode are summarized in Table 3.

According to these equations (Equations (5–12), see Table 3), one can calculate the solute flux, J_s , or solute intrinsic retention, R_{int} , from (i) the solute and membrane properties through the diffusion coefficient at infinite dilution ($\text{m}^2 \cdot \text{s}^{-1}$), D_∞ , and the hydraulic membrane resistance ($\text{m} \cdot \text{s}^{-1}$), R_m , (ii) the operating conditions (J_v), and (iii) only one fitting parameter (λ) defined as the ratio of the solute radius (m), r_s , to the mean pore radius (m), r_p .

The mass transfer modelling has been firstly used to get the membrane pore size from the solute retention in saccharide/water systems. Then, the modification of the neutral solute radius in the presence of electrolyte has been evaluated from the investigation of the mass transfer in saccharide/electrolyte systems assuming, as concluded from previous work, that the presence of electrolyte has no impact on the membrane properties.^[8]

As already mentioned, the intrinsic retention, R_{int} , is only calculated whereas the observed retention, R_{obs} , is the measured value varying with the concentration polarization.

Then, considering the film theory which provides a description of the concentration polarization phenomena, one can express the intrinsic retention as a function of the observed one from the following expression:^[4]

$$R_{int} = \frac{R_{obs} \exp(J_v/k)}{1 - R_{obs}(1 - \exp(J_v/k))} \quad (13)$$

where k is the mass transfer coefficient in the polarization layer ($\text{m} \cdot \text{s}^{-1}$), defined as follows:

$$k = \frac{D_\infty}{\delta} \quad (14)$$

where δ denotes the thickness of the polarization layer (m).

The Sherwood equation is used to determine the mass transfer coefficient, as follows:

$$Sh = \frac{k \times d_h}{D_\infty} = p \times Re^q \times Sc^r \quad (15)$$

where Sh is the Sherwood number, d_h is the equivalent hydraulic diameter of the feed channel (m), Re is the Reynolds number, Sc is the Schmidt number, and p , q , and r are the empirical coefficients varying according to the hydrodynamics conditions.

Here, the intrinsic retention, R_{int} , was calculated from the experimental values of the observed retention, R_{obs} , according to Equation (13). According to our experimental conditions, the most appropriate correlation was that established by Schock and Miquel.^[19] The Reynolds and Schmidt numbers were between

Table 3. Equations for the mass transfer modelling: normal filtration regime (convection/diffusion) and diffusion regime

Filtration		Diffusion
$R_{int} = \frac{R_{\infty} [1 - \exp(-Pe_p)]}{R_{\infty} - \exp(-Pe_p)}$	(5)	$Pe_p \ll 1$
$J_S = K_c \times \phi \times J_v \times \frac{c_p - c_m \times \exp(-Pe_p)}{1 - \exp(-Pe_p)}$	(6)	$J_S = \frac{\phi \times K_d \times D_{\infty} \times A_k}{L} \times \Delta C$
with $R_{\infty} = 1 - \phi \times K_c$	(7)	
$Pe_p = \frac{K_c \times r_p^2}{8 \times K_d \times D_{\infty}} \times R_m \times J_v$	(8)	
$R_m = \frac{L}{A_k} \times \frac{8}{r_p^2}$	(9)	
$\phi = \left[1 - \frac{r_s}{r_p}\right]^2 = (1 - \lambda)^2$		(10)
$K_c = (2 - \phi) \times (1 + 0.054 \times \lambda - 0.988 \times \lambda^2 + 0.441 \times \lambda^3)$		(11)*
$K_d = 1 - 2.3 \times \lambda + 1.154 \times \lambda^2 + 0.224 \times \lambda^3$		(12)*
Model parameters		Solute properties: D_{∞} ($m^2 \cdot s^{-1}$); r_s (m) Membrane properties: R_m (m^{-1}); r_p (m) Operating conditions: J_v ($m^3 \cdot m^{-2} \cdot s^{-1}$) Fitting parameter: $\lambda = r_s/r_p$ (r_s or r_p)

*From Bowan et al.^[18]

300–1400 and 700–1300, respectively. Then, the empirical coefficients $p = 0.065$, $q = 0.875$, and $r = 0.25$ were chosen to calculate the mass transfer coefficient (Equation (15)).^[19]

Figure 2 shows the observed glucose retention versus the permeation flux for varying flow rates of 100, 200, and 400 $L \cdot h^{-1}$. The intrinsic retention, calculated from Equations (13) and (15), is added on the chart as well to make the comparison. As expected, the retention increases with the flow rate, and tends towards the intrinsic retention values when the flow rate is equal to 400 $L \cdot h^{-1}$. The maximal deviation obtained between R_{int} and R_{obs} was less than 2%. As mentioned previously, filtration experiments were carried out at a fixed flow rate equal to

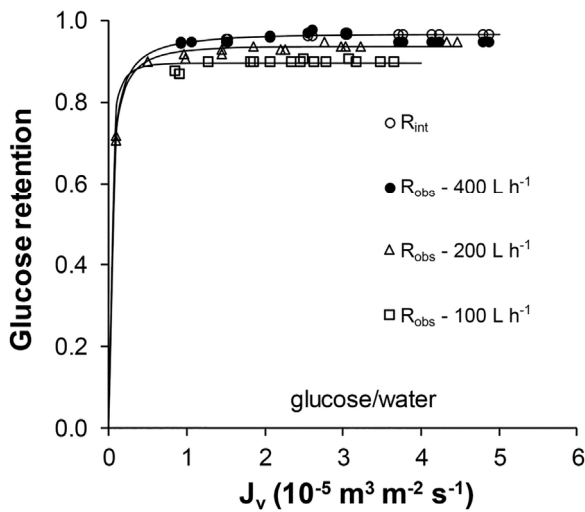


Figure 2. Observed and intrinsic retentions versus permeate flux for single-solute solutions of glucose: influence of the flow rate. [Glucose] = 0.1 $mol \cdot L^{-1}$.

400 $L \cdot h^{-1}$. Indeed, in these operating conditions, the polarization effects are rather weak and the observed retention was further viewed as a good estimation of the intrinsic retention.

Diffusion

The expression of the solute flux in a diffusion regime can be deduced from that in a filtration regime given by Equation (6) according to the following assumptions:

- the diffusion regime is a boundary condition of the filtration one, for which $J_v \rightarrow 0$; hence the Peclet number inside the pore, Pe_p , is much lower than unity and $\exp(-Pe_p) \approx 1 - Pe_p$;
- the transfer in the polarization layer is negligible, the concentration gradient ($mol \cdot m^{-3}$), ΔC , is constant irrespective of the operating conditions, i.e. $\Delta C = c_m - c_p$.

Then, the expression of the solute flux becomes the following:

$$J_S = \frac{\phi \times K_d \times D_{\infty} \times A_k}{L} \times \Delta C \quad (16)$$

where L is the pore length (m), ϕ the partitioning coefficient, K_d the hindrance factor for diffusion, and A_k the membrane porosity.

The main equations of the mass transfer modelling are summarized in Table 3 for the diffusion regime.

RESULTS AND DISCUSSION

Mass Transfer Investigation

Experiments were first achieved with single-solute solutions, i.e. saccharide/water, and then with binary-solute solutions, i.e. saccharide/electrolyte. The effect of the electrolyte on the saccharide transfer was thus investigated by comparing the two series of experiments.

Membrane Characterization

The retention of saccharides versus permeate flux for glucose/water and xylose/water systems is plotted in Figure 3. As can be seen, the retention increases with the permeate flux prior to stabilizing at about 85 % and 90 % for xylose and glucose. As anticipated, for purely steric interactions between the solute and the membrane, the retention goes up with the saccharide size. Another saccharide of higher size, e.g. sucrose ($342 \text{ g} \cdot \text{mol}^{-1}$), was not explored since it would have been completely retained by the NF membrane.^[1] Glucose retention is reasonably in line with the data found in the literature for an identical membrane (deviation less than 10 %).^[1,2,20]

By varying the membrane pore radius (r_p), used in Equations (7–12), the experimental values are fitted properly by Equation (5), as depicted by the full lines. The Stokes radii of xylose and glucose are set at 0.319 nm and 0.363 nm, respectively.^[21] In this manner, the calculated values of r_p are 0.45 nm and 0.50 nm for xylose and glucose. These values are in good agreement with the 0.43 nm previously reported for the same membrane and a glucose solution at $0.01 \text{ mol} \cdot \text{L}^{-1}$.^[2,20]

Moreover, it can be stated that the values of r_p obtained for both solutes are slightly different (0.45 nm for xylose and 0.50 nm for glucose). Such results were also underlined in a previous work during NF of saccharides.^[22] Indeed, pore radii of 0.49, 0.54, and 0.67 nm were obtained respectively for glucose ($180 \text{ g} \cdot \text{mol}^{-1}$), sucrose ($342 \text{ g} \cdot \text{mol}^{-1}$), and raffinose ($504 \text{ g} \cdot \text{mol}^{-1}$). As in the present work, the fitted pore radius was found to increase with the solute size. A possible explanation of these results can be the pore size distribution while the model considers a mean pore radius.^[2] In fact, strongly retained solutes (glucose in this work or raffinose for Mohammad et al.^[22]) are transferred through the larger pores. Consequently, the fitted mean pore radius determined from a strongly retained solute is higher than that obtained from a less retained solute. Moreover, these results can also be explained by the fact that usual models do not take into account the pore constriction.^[23] However, this point is not within the scope of this paper.

The aim of the study is to characterize the variations caused by the electrolyte on the saccharide transfer in terms of the sugar size

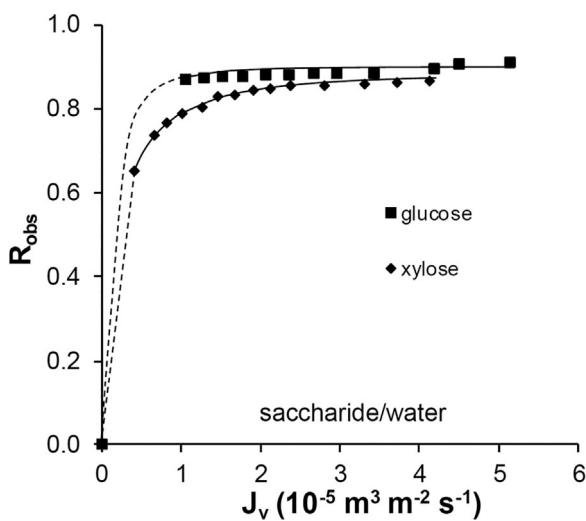


Figure 3. Retention versus permeate flux for single-solute solutions of xylose and glucose. [Saccharide] = $0.1 \text{ mol} \cdot \text{L}^{-1}$. Symbols: experimental data; full lines: best-fit curves obtained from the mass transfer modelling.

modification. From these findings, the use of the pore radius determined for each saccharide rather than an average value was further considered.

Effect of the Ionic Composition on the Transfer of Saccharide

Saccharide/electrolyte systems at various electrolytic compositions were investigated to determine the effect of the electrolyte on the saccharide transfer.

The retention of saccharide is plotted versus the permeate flux in the case of saccharide/NaCl systems for different concentrations of NaCl in Figure 4. In any case, the saccharide retention decreases in the presence of electrolyte and this decrease becomes more significant as the electrolyte concentration increases. The retention variations are weak but they are reproducible (deviation, $\frac{\Delta R}{R} \times 100 = \left(\frac{R_i - R_j}{R_i}\right) \times 100$, less than 5 %) and they are in good agreement with those obtained in previous works.^[1–5]

The corresponding flux of saccharide versus the permeate flux is also plotted in Figure 4. It is seen that, in any case, the saccharide flux increases in a continuous way with the permeate flux. These variations are in accordance with the retention ones. Indeed, as shown by Equation (4), for a constant retention, the flux increases with the permeation flux. The saccharide flux is higher when the electrolyte is added in contrast to that in water, and it increases

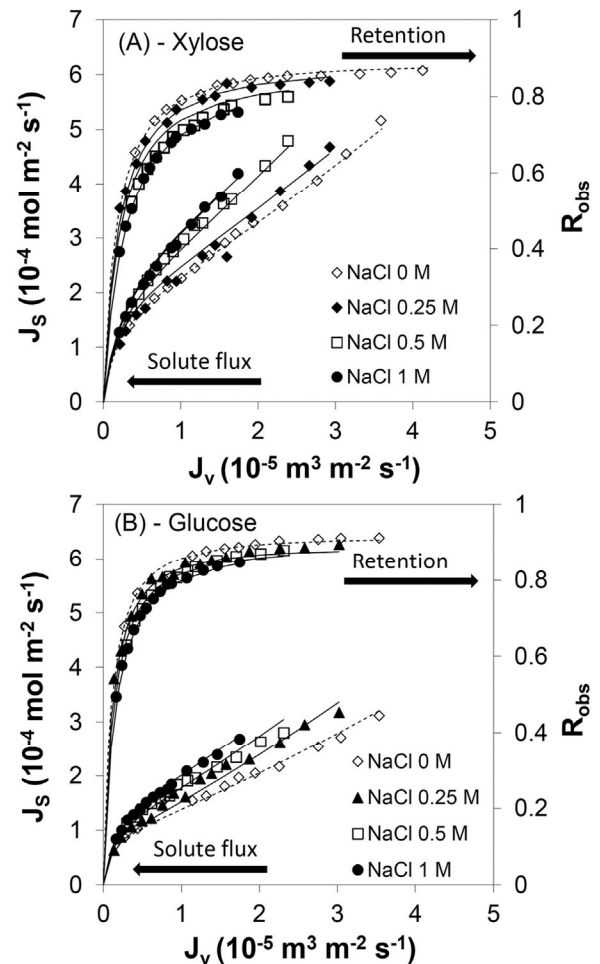


Figure 4. Solute flux and retention versus permeate flux for binary-solute solutions: influence of the NaCl concentration. (A) Xylose and (B) Glucose. [Saccharide] = $0.1 \text{ mol} \cdot \text{L}^{-1}$; [NaCl] = 0–0.25–0.5–1 $\text{mol} \cdot \text{L}^{-1}$. Symbols: experimental data; lines: best-fit curves obtained from the mass transfer modelling.

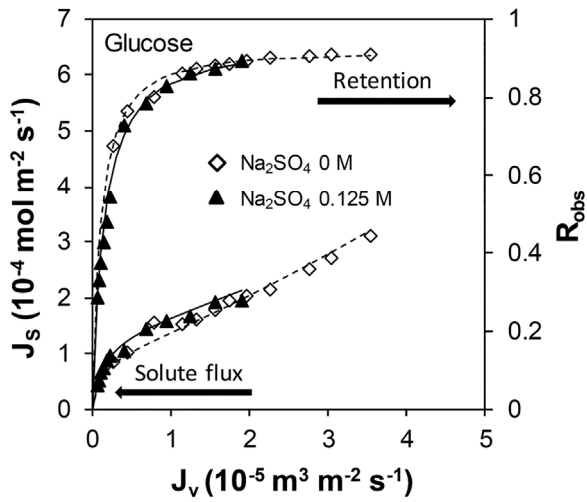


Figure 5. Solute flux and retention versus permeate flux for binary-solute solutions: influence of the Na_2SO_4 concentration. $[\text{Glucose}] = 0.1 \text{ mol} \cdot \text{L}^{-1}$; $[\text{Na}_2\text{SO}_4] = 0\text{--}0.125 \text{ mol} \cdot \text{L}^{-1}$. Symbols: experimental data; lines: best-fit curves obtained from the mass transfer modelling.

with the electrolyte concentration. As expected, the flux of xylose is higher than that of glucose. For a NaCl concentration of $1 \text{ mol} \cdot \text{L}^{-1}$ and a permeate flux of $1 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, the solute flux is 3×10^{-4} for xylose and $2 \times 10^{-4} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ for glucose.

Figure 5 shows the variations of the glucose flux in the presence of Na_2SO_4 at different concentrations. One can see that the glucose flux is slightly higher in the presence of Na_2SO_4 as compared to that in water. This observation is mainly valid for permeate flux, J_v , below $1.5\text{--}2 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. Unlike glucose/NaCl solution (Figure 4b), the concentration of Na_2SO_4 has a weak effect on the flux of glucose and the Na_2SO_4 impact decreases with increasing the permeate flux. This result is in contradiction with a previous study obtained with the same membrane/solute systems but in a diffusion regime where the addition of NaCl had a lower impact than that of Na_2SO_4 on the glucose flux.^[8]

This behaviour can be explained by the difference between the concentrations of the electrolyte on the two sides of the membrane. Indeed, in the diffusion regime, the electrolyte concentration is identical on both sides of the membrane whereas the electrolyte concentration in the permeate relies on the electrolyte retention in the filtration regime. The corresponding retentions of sulphate and chloride ions are plotted in Figure 6.

In contrast to the retentions of chloride, the retentions of sulphate are very high and slightly dependent of the concentration for permeate flux higher than $1 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. The lower impact of Na_2SO_4 on the glucose transfer as compared to that of NaCl can be explained by the much higher retention of sulphate compared to chloride. Indeed, Bargeman et al. established a relationship between the decrease of the glucose retention, i.e. its transfer increase, and the anion concentration in the permeate (Cl^-), for electrolytes containing different cations.^[2] More precisely, they have pointed out that the transfer increase is even more pronounced since the electrolyte concentration in the permeate increases. Equivalent results have been obtained by Umpuch et al. who studied the addition of different electrolytes (NaLac, NaCl, and Na_2SO_4) on the glucose transfer through another NF membrane (Desal 5 DK,

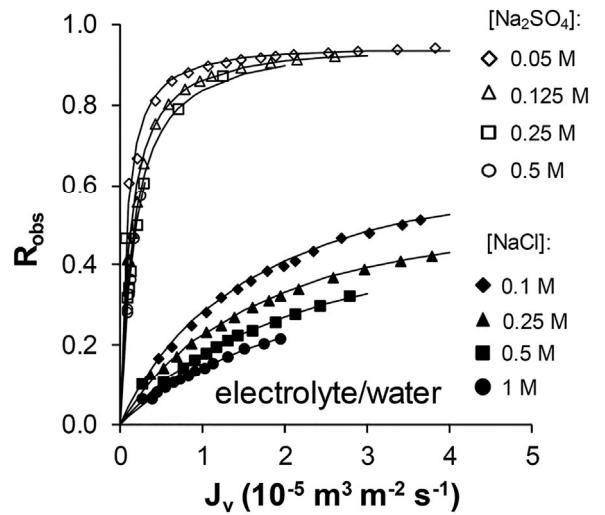


Figure 6. Retention versus permeate flux for single-solute solutions of NaCl and Na_2SO_4 : influence of the electrolyte concentration. $[\text{NaCl}] = 0.1\text{--}0.25\text{--}0.5\text{--}1 \text{ mol} \cdot \text{L}^{-1}$; $[\text{Na}_2\text{SO}_4] = 0.05\text{--}0.125\text{--}0.25\text{--}0.5 \text{ mol} \cdot \text{L}^{-1}$. Symbols: experimental data; full lines: best-fit curves obtained from the mass transfer modelling.

Osmonics).^[7] They have also drawn a link between the increase of the glucose transfer and the anion concentration in the permeate.

To better understand the action of the electrolyte nature as well as to compare the results obtained in different regimes of transfer (diffusion and filtration), we have calculated the additional normalized flux (%), ΔJ^* , which characterizes the role of the electrolyte on the saccharide transfer, according the following equation:

$$\Delta J^* = \left(\frac{\Delta J}{J_{S,El}} \right) \times 100 \quad (17)$$

where ΔJ , which is called the additional flux ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), is defined as the difference between the flux of saccharide in saccharide/electrolyte system, $J_{S,El}$, and that in water, $J_{S,W}$:

$$\Delta J = J_{S,El} - J_{S,W} \quad (18)$$

The saccharide flux determined in water, $J_{S,W}$, and in presence of electrolyte, $J_{S,El}$, for a given pressure are not obtained at the same permeate flux, J_v . Consequently, the calculated fluxes obtained from the mass transfer modelling were used afterwards. It is noted that all the experimental data correspond to permeate fluxes, J_v , higher than $0.2 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. Then, the calculated values of ΔJ^* are plotted versus the permeate flux for varying concentrations of NaCl and Na_2SO_4 in Figure 7. In the presence of NaCl at a given concentration, the additional normalized flux, which represents the impact of the electrolyte on the modification of the neutral solute transfer, increases with the permeate flux. For the highest NaCl concentration ($1 \text{ mol} \cdot \text{L}^{-1}$), the additional normalized flux levels off for a permeate flux higher than $1 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. The variation of ΔJ^* versus the permeate flux can be linked to the influence of the electrolyte concentration in the permeate.^[2,7] In fact, electrolyte concentration in the permeate decreases (retention of the ions increases) as permeate flux increases (for a given NaCl concentration,

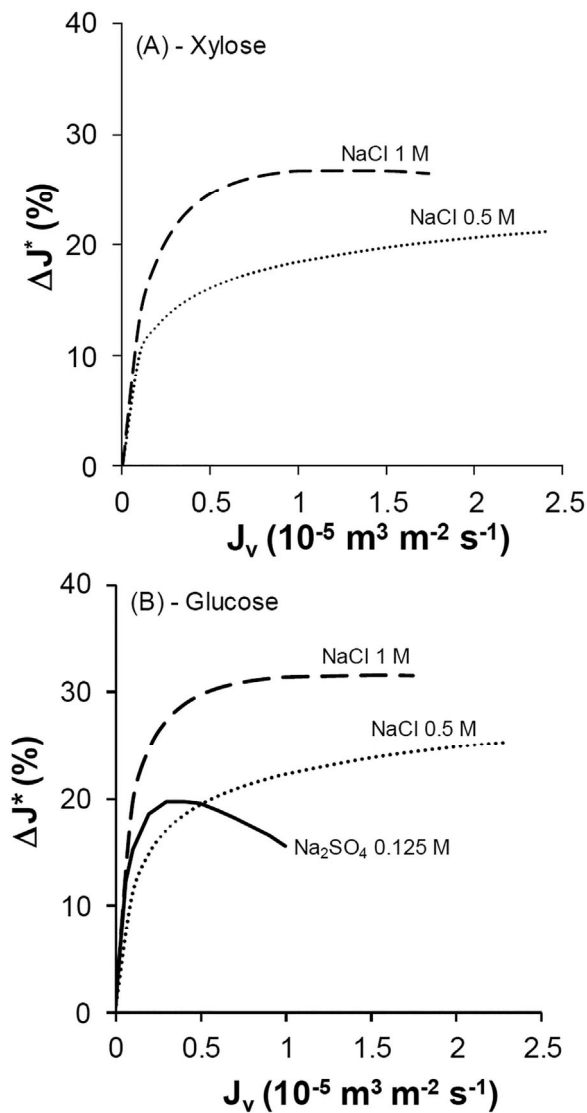


Figure 7. Additional normalized flux versus permeate flux for binary-solute solutions: influence of the ionic composition. (A) Xylose and (B) Glucose. [Saccharide] = $0.1 \text{ mol} \cdot \text{L}^{-1}$; [NaCl] = $0.5\text{--}1 \text{ mol} \cdot \text{L}^{-1}$; [Na_2SO_4] = $0.125 \text{ mol} \cdot \text{L}^{-1}$.

Figure 6). Consequently, a lower impact of the electrolyte on the saccharide transfer is obtained. This observation is also supported by the influence of the electrolyte feed concentration since increasing values of ΔJ^* are obtained for increasing NaCl feed concentrations from 0.5 to $1 \text{ mol} \cdot \text{L}^{-1}$, which gives increasing electrolyte concentration in the permeate. The same tendency is seen for both saccharides in the presence of NaCl (Figure 7a and b).

Figure 7b shows that in the presence of Na_2SO_4 the variation of ΔJ^* is identical to that observed for NaCl for the low permeate fluxes. Then, ΔJ^* goes through a maximum for a flux around $0.25 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. From this value, ΔJ^* decreases sharply and the decline can be related to the high retention of sulphate. As observed in Figure 6, the retention of sulphate is between 30 % and 60 % for a permeate flux below $0.25 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. The concentration of sulphate in the permeate is sufficient to increase the mass transfer of saccharide. However, for higher permeate flux, the retention of sulphate is higher than 80 % at J_v up to $0.25 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, as shown

in Figure 6. The concentration of sulphate in the permeate is too low to achieve any modification of the saccharide transfer.

Then, the results obtained in identical conditions but under different transfer regimes, i.e. diffusion and filtration, are compared. The results concerning the diffusion regime were published in a previous paper.^[8] The effect of the electrolyte on the transfer of saccharide (xylose, glucose, and sucrose) in various electrolytic solutions (NaCl, Na_2SO_4 , CaCl_2 , and MgCl_2) has established that the diffusion flux consistently increases with the electrolyte concentration. Moreover, it was noticed that this increase becomes more pronounced when the ions are more hydrated.

In filtration regime, the role of the electrolyte on the transfer increase, given by the additional normalized flux, ΔJ^* , is 26 % and 30 % for xylose and glucose in presence of NaCl at $1 \text{ mol} \cdot \text{L}^{-1}$, while in a diffusion regime it is 43 % and 65 %, respectively (Table 4). These results highlight that, in our conditions, the effect of the electrolyte has a greater impact on the transfer in diffusion as compared to that in the filtration regime.

As for the effect of the electrolyte concentration, for both regimes, the additional normalized flux, ΔJ^* , increases with the electrolyte concentration. For example at $J_v = 1 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, the ΔJ^* values vary from 18 to 26 % for xylose and from 22 to 30 % for glucose, respectively, as the concentration of NaCl increases from 0.5 to $1 \text{ mol} \cdot \text{L}^{-1}$ (Figure 7). The same tendency is obtained in a diffusion regime in the presence of Na_2SO_4 (Table 4). These results also point out that, for a fixed electrolyte concentration, the contribution of the electrolyte on the saccharide transfer is always higher for glucose than xylose. As previously explained by Boy et al.,^[8] the difference between glucose and xylose can be due to the strength of the saccharide/electrolyte interactions which are mainly fixed by the amount of ($-\text{OH}$) sites of the saccharide molecule. Indeed, xylose contains (4 $-\text{OH}$ and 1 $-\text{O}-$) whereas glucose is composed of (5 $-\text{OH}$ and 1 $-\text{O}-$).

As for the effect of the ions hydration on the modification of the saccharide flux, Figure 7b shows that the impact of SO_4^{2-} is higher than that of Cl^- when the former ion, which is the more hydrated, is not completely retained by the membrane ($\Delta J^* \approx 20$ % with NaCl at $0.5 \text{ mol} \cdot \text{L}^{-1}$ or Na_2SO_4 at $0.125 \text{ mol} \cdot \text{L}^{-1}$). This result is in agreement with those obtained in the diffusion regime since more considerable saccharide transfer increase is observed with more hydrated ions. Thus, these results show good agreement between both regimes of transfer (diffusion and filtration) regardless of the saccharide or electrolyte nature. However, during the filtration, the effect of the electrolyte on the transfer of neutral solute is strongly affected by the retention of the ions. Indeed, the transfer of neutral solute is slightly modified as the electrolyte is completely retained. This observation suggests that ion concentration inside pores controls the phenomenon and that neutral solute/ion interactions inside the membranes should be investigated to get more information about mass transfer.

Solute Flux versus Hydration

As mentioned earlier, two different contributions have been pointed out to explain the variation of the transfer in accordance with the ionic composition: a change in the membrane properties, like an increase of the membrane pore radius (swelling phenomenon), and a decrease of the neutral solute size due to its lower hydration in the presence of electrolytes.

The previous investigation carried out in a diffusion regime,^[8] has shown that the influence of the electrolyte is

Table 4. Additional normalized fluxes, ΔJ^* , sugars fluxes in water, $J_{S,W}$ and in electrolyte, $J_{S,El}$: comparison between the regimes of transfer – Filtration regime: [Saccharide] = $0.1 \text{ mol} \cdot \text{L}^{-1}$, $J_v = 1 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ – Diffusion regime: [Saccharide] = $1 \text{ mol} \cdot \text{L}^{-1}$ (given by Boy et al.^[8] for diffusion only)

Solutions	$J_{S,W}$ ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)	Electrolyte concentration ($\text{mol} \cdot \text{L}^{-1}$)	$J_{S,El}$ ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)	ΔJ^* (%)
<i>Filtration</i>				
xylose/NaCl	2.3×10^{-4}	0.5	2.8×10^{-4}	18
		1	3.1×10^{-4}	26
glucose/NaCl	1.4×10^{-4}	0.5	1.8×10^{-4}	22
		1	2.0×10^{-4}	30
glucose/Na ₂ SO ₄	1.4×10^{-4}	0.125	1.6×10^{-4}	13
<i>Diffusion</i>				
xylose/NaCl	4.3×10^{-7}	1	7.5×10^{-7}	43
xylose/Na ₂ SO ₄	5.1×10^{-7}	0.25	7.5×10^{-7}	32
		0.5	15.3×10^{-7}	67
		1	25.0×10^{-7}	80
glucose/NaCl	1.6×10^{-7}	1	4.6×10^{-7}	65
glucose/Na ₂ SO ₄	1.6×10^{-7}	0.25	5.0×10^{-7}	68
		0.5	12.1×10^{-7}	87

above all ascribable to the resulting saccharide dehydration, as only a slight influence was seen on the membrane properties.

Then, in order to strengthen this explanation, the physical relevance of the assumed dehydration in filtration mode was evaluated. Firstly, the decrease of the solute size likely due to the addition of the electrolyte was determined from the mass transfer modelling. Secondly, as previously done from the diffusion investigation, the additional flux, ΔJ , characterizing the mass transfer increase, was put in parallel with the variation of the apparent molar volume, ΔV , which characterizes the solute hydration state. The objective is to draw a relationship between these two parameters to better understand the mechanisms of transfer involved.

In the filtration regime with saccharide/water systems, the mean pore radius, r_p , can be determined from the mass transfer modelling with the knowledge of the saccharide radius in water, $r_{S,W}$ (see Membrane Characterization section for details). Since the membrane's properties are assumed to be identical whatever the electrolyte composition is, the mean pore radius thus calculated is further assumed to remain constant and independent of the electrolyte composition.

Then, the solute radius in the electrolyte, $\Delta r_s/r_{S,W}$, can be determined from the mass transfer modelling in saccharide/electrolyte systems. The corresponding fitted solute radii are delivered in Table 5.

As anticipated, the solute radius in the electrolyte, $r_{S,El}$, decreases as compared to that in water.

The same procedure has been used by Bouranene et al.^[4] for PEG 600 (polyethylene glycol)/electrolyte (KCl, LiCl, and MgCl₂) systems with a ceramic NF membrane, which was not supposed to swell. The corresponding fitted solute radii are delivered in Table 6 for comparison.^[4] One can observe that the solute radius in the electrolyte, $r_{S,El}$, decreases in the presence of more hydrated ions ($\text{K}^+ < \text{Li}^+ < \text{Mg}^{2+}$).

In diffusion regime, the solute radius in the electrolyte, $r_{S,El}$, is calculated from the saccharide flux in the electrolyte, $J_{S,El}$, using Equation (16) assuming that the mean pore radius, r_p , is constant and independent of the electrolyte composition. The parameters A_k and L in Equation (16) are difficult to assess. Therefore, the solute radius in the electrolyte, $r_{S,El}$, is calculated by considering identical values of A_k and L in the water and in the electrolyte. Thus, the solute radius in the electrolyte is obtained from the comparison between the ratio of the

Table 5. Calculated solute radii, $r_{S,El}$, for saccharide/electrolyte systems: influence of the ionic composition – Filtration regime – Organic NF membrane (Filmtec™)

$$r_p = 0.45 \text{ nm (xylose)} / 0.50 \text{ nm (glucose)} - [\text{Saccharide}] = 0.1 \text{ mol} \cdot \text{L}^{-1}$$

Solute	Electrolyte	$r_{S,El}$ (nm)	$\Delta r_s = r_{S,W} - r_{S,El}$ (nm)	$\Delta r_s/r_{S,W}$ (%)
Xylose $r_{S,W} = 0.319 \text{ nm}$	NaCl (0.5 eq · L ⁻¹)	0.309	0.010	3
	NaCl (1 eq · L ⁻¹)	0.308	0.011	3
Glucose $r_{S,W} = 0.363 \text{ nm}$	NaCl (0.5 eq · L ⁻¹)	0.355	0.008	2
	NaCl (1 eq · L ⁻¹)	0.352	0.011	3
	Na ₂ SO ₄ (0.125 eq · L ⁻¹)	0.356	0.007	2

Table 6. Calculated solute radii, $r_{S,El}$, for PEG/electrolyte systems: influence of the ionic composition – Filtration regime – Inorganic NF membrane (Filtanium[®])

$$r_p = 1.14 \text{ nm} - [\text{PEG 600}] = 2 \text{ g} \cdot \text{L}^{-1} \text{ (given by Bouranene et al.}^{[4]}\text{)}$$

Solute	Electrolyte	$r_{S,El}$ (nm)	$\Delta r_s = r_{S,W} - r_{S,El}$ (nm)	$\Delta r_s/r_{S,W}$ (%)
PEG $r_{S,W} = 0.61 \text{ nm}$	KCl (1 eq · L ⁻¹)	0.55	0.06	10
	LiCl (1 eq · L ⁻¹)	0.47	0.14	23
	MgCl ₂ (2 eq · L ⁻¹)	0.45	0.16	26

experimental values of the flux in electrolyte and in water, $\left(\frac{J_{S,El}}{J_{S,W}}\right)_{exp}$, and calculated ones, $\left(\frac{J_{S,El}}{J_{S,W}}\right)_{cal}$, using a mean square method.

Then, the solute radius in the electrolyte, $r_{S,El}$, calculated from diffusion experiments are reported in Table 7.

The changes of the solute radius in presence of electrolyte (nm), Δr_s , are calculated according to Equation (19) for comparison:

$$\Delta r_s = r_{S,W} - r_{S,El} \quad (19)$$

The normalized variations of the radius, $\Delta r_s/r_{S,W}$, are also determined according to Equation (20) to compare the influence of the electrolyte on the decrease of the solute radius for the different systems (regime of transfer, membrane, solute):

$$\Delta r_s/r_{S,W} = \left(\frac{r_{S,W} - r_{S,El}}{r_{S,W}}\right) \times 100 \quad (20)$$

The corresponding values of Δr_s and $\Delta r_s/r_{S,W}$ are reported in Tables 5, 6, and 7. As for the filtration experiments carried out with PEG/electrolyte systems, one can observe that the saccharide radius decreases with the ions hydration ($\text{Cl}^- < \text{SO}_4^{2-}$).

One can observe that the decrease in the solute radius, Δr_s , ranges between 0.007 and 0.064 nm for the saccharides and 0.06 and 0.16 nm for PEG 600. These values are physically coherent with the dehydration phenomenon since the variation of the solute radius in the presence of electrolyte is mainly one order of magnitude smaller than the water molecule radius (0.15 nm).

For instance, for xylose/NaCl at 1 mol · L⁻¹, the variations of radius are identical, around 3 % for both diffusion and filtration. On the contrary, for glucose/NaCl at 1 mol · L⁻¹, the decline of the radius is close to 3 % in filtration while it is 8 % in diffusion.

In this study, the decrease of the saccharide radius in the filtration regime ranges from 2 to 3 %. Higher variations were previously reported for the filtration of PEG 600, between 10 to 26 % depending on the ionic composition.^[4] Escoda et al. showed similar effects for the same PEG/electrolyte systems

with an organic NF membrane.^[6] They explained these results by a combination of two phenomena (a decline in the size of PEG and an expansion of the mean pore size of the membrane).

The difference between the variations of PEG radius and those of saccharides computed in the present work can be attributed to the various retentions of the ions in the two systems. Indeed, much lower retention of ions was obtained with the membrane used for the filtration of PEG compared to that obtained in our work; retentions were of 20 % for MgCl₂ (0.1 mol · L⁻¹) at $J_v = 2 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ for Bouranene et al.^[4] compared to 90 % and 40 % with Na₂SO₄ (0.05 mol · L⁻¹) and NaCl (0.1 mol · L⁻¹) at the same flux in this study. As previously mentioned, increasing electrolyte concentrations in the permeate are expected to induce higher influence on the neutral solute flux.

Finally, the aim in this part is to draw a parallel between the additional flux, ΔJ , which characterizes the mass transfer increase, and a relevant physicochemical parameter, which characterizes the solute hydration state, to find out if a relationship can be set between the solute dehydration and the enhanced mass transfer, assumed to be the consequence of the solute dehydration.

The characterization of saccharide hydration in different saccharide/electrolyte systems has been the subject of a former work published by Boy et al. on the determination of the variation of the apparent molar volume, ΔV , defined as the difference between the apparent molar volume of a saccharide in the electrolytic solution and that in water.^[8] This parameter is mostly explained by the structural hydration model used to investigate saccharide/electrolyte interactions. According to the hydration model, a positive ΔV value reveals a solute dehydration in the presence of electrolytes, as it is awaited to represent the release of water from the solute hydration shell.^[8]

For the filtration regime, the ΔV values have been calculated with respect to the electrolyte concentration in the permeate since we have shown that the variation of the saccharide transfer depends on the electrolyte concentration in the permeate. It is worth mentioning that the concentration in the permeate

Table 7. Calculated solute radii, $r_{S,El}$, for saccharide/electrolyte systems: influence of the ionic composition – Diffusion regime – Organic NF Membrane (FilmtecTM)

$$r_p = 0.45 \text{ nm (xylose)} / 0.50 \text{ nm (glucose)} - [\text{Saccharide}] = 1 \text{ mol} \cdot \text{L}^{-1} \text{ (given by Boy et al.}^{[8]}\text{)}$$

Solute	Electrolyte	$r_{S,El}$ (nm)	$\Delta r_s = r_{S,W} - r_{S,El}$ (nm)	$\Delta r_s/r_{S,W}$ (%)
Xylose $r_{S,W} = 0.319 \text{ nm}$	NaCl (1 eq · L ⁻¹)	0.309	0.010	3
	Na ₂ SO ₄ (1 eq · L ⁻¹)	0.288	0.031	10
	CaCl ₂ (1 eq · L ⁻¹)	0.296	0.023	7
Glucose $r_{S,W} = 0.363 \text{ nm}$	NaCl (1 eq · L ⁻¹)	0.333	0.030	8
	Na ₂ SO ₄ (1 eq · L ⁻¹)	0.299	0.064	18
	CaCl ₂ (1 eq · L ⁻¹)	0.320	0.043	12

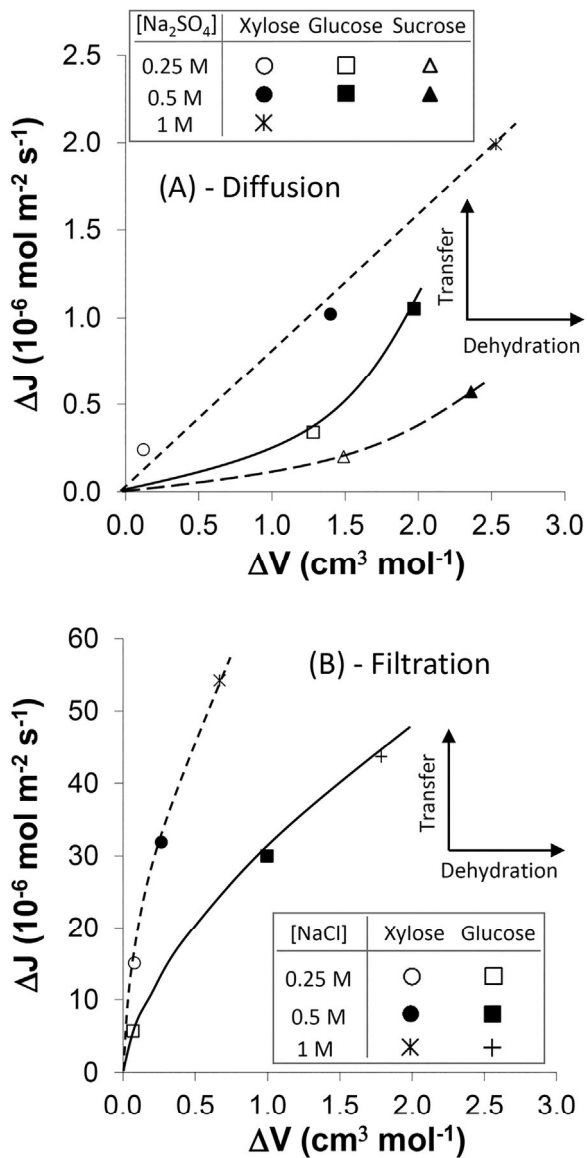


Figure 8. Additional flux, ΔJ , versus the variation of the apparent molar volume of saccharides, ΔV , at 25 °C: influence of the electrolyte concentration. (A) Diffusion regime: [Saccharide] = 1 mol · L⁻¹; [Na₂SO₄] = 0.25–0.5–1 mol · L⁻¹ and (B) Filtration regime ($J_v = 0.5 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$): [Saccharide] = 0.1 mol · L⁻¹; [NaCl] = 0.25–0.5–1 mol · L⁻¹.

depends on the feed concentration. Moreover, the ΔJ values have been determined at a constant permeate flux of $0.5 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$.

The variations of the additional flux, ΔJ , versus the variation of the apparent molar volume, ΔV , are reported in Figure 8 for saccharide/electrolyte systems.

For a given electrolyte, Figure 8 shows that, for both filtration and diffusion regimes, the additional flux continuously increases with ΔV , for a given saccharide and electrolyte. According to the hydration model, a positive ΔV value means that (–OH)/cation interactions are predominant revealing a decreasing hydration of the saccharide. This result could confirm the fact that the enhanced transfer of the neutral solute can be assigned to its dehydration in presence of electrolyte. In addition, it can be noted that for the same ΔV value, the additional flux increases when the saccharide size decreases.

Finally, for both regimes (diffusion and filtration), it can be concluded that the enhancement of the saccharide transfer with electrolyte could be ascribable to the resulting dehydration.

CONCLUSIONS

The objective of this work was to improve the understanding of the role of the ionic composition on the transfer of neutral species through a nanofiltration membrane in filtration regimes (convection/diffusion) and more particularly the relationship with ion hydration.

The effect of the electrolyte on the transfer of saccharide (xylose and glucose) in various electrolytic solutions (NaCl and Na₂SO₄) was investigated. It was shown that the variation of the transfer of saccharide was less pronounced in presence of Na₂SO₄ in comparison with NaCl. This result was in contradiction with previous ones obtained with the same membrane/solute systems but in a diffusion regime. This contradiction has been explained by the influence of the ion retention. Indeed, in the diffusion regime, the ion composition was identical and fixed on the two sides of the membrane whereas the retention of the ions observed during the filtration can reduce the concentration in the permeate side.

Thus, a major difference between the filtration and diffusion regime is that during filtration the retention of the ions is an additional parameter which can modulate the impact of the electrolyte on the solute mass transfer.

The main novelty of this work is that the physical relevance of the dehydration effect has been evaluated from experimental saccharide fluxes in both diffusion and filtration regime. Firstly, it was shown that the variations of the solute radius, obtained from the mass transfer modelling, were physically relevant to the dehydration phenomenon since these values were in the same order of magnitude as a fraction of a water molecule. Secondly, the additional fluxes, ΔJ , characterizing the effect of the electrolyte on the solute flux, were put in parallel with the variation of the apparent molar volume, ΔV , in order to find out if a relationship can be set between the enhanced mass transfer and the dehydration of the neutral solutes. Whatever the regimes of transfer studied, filtration and diffusion, the values assigned to the different saccharides were located on the same line. This result confirms that the enhancement of the transfer of the neutral solute can be due to its dehydration induced by the electrolyte.

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NOMENCLATURE

A_k	porosity of the membrane
c_m	concentration at the membrane surface (mol · m ⁻³)
c_p	concentration in the permeate solution (mol · m ⁻³)
c_0	concentration in the feed solution (mol · m ⁻³)
ΔC	concentration gradient, defined as $\Delta C = c_m - c_p$ (mol · m ⁻³)
d_h	equivalent hydraulic diameter (m)
D_∞	diffusion coefficient at infinite dilution (m ² · s ⁻¹)
J_s	solute flux (mol · m ⁻² · s ⁻¹)
ΔJ	additional flux, defined as $\Delta J = J_{s,EF} - J_{s,W}$ (mol · m ⁻² · s ⁻¹)

ΔJ^*	additional normalized flux, defined as $\Delta J^* = \left(\frac{\Delta J}{J_{S,El}} \right) \times 100 \%$
J_v	permeate flux ($\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)
k	mass transfer coefficient in the polarization layer ($\text{m} \cdot \text{s}^{-1}$)
K_c	hindrance factor for the convection
K_d	hindrance factor for the diffusion
L	length of the pore (m)
L_p	hydraulic membrane permeability ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{kPa}^{-1}$)
p, q, r	empirical coefficients
Pe_p	Peclet number inside the pore
Δp	transmembrane pressure (bar)
r_s	solute radius (m)
Δr_s	variation of the solute radius, defined as $\Delta r_s = r_{S,El} \text{ (m)}$
$\Delta r_s/r_{S,W}$	normalized variation of the solute radius, defined as $\Delta r_s/r_{S,W} = \left(\frac{r_{S,W} - r_{S,El}}{r_{S,W}} \right) \times 100 \%$
r_p	mean pore radius (m)
R	retention
Re	Reynolds number
R_{int}	intrinsic retention
R_m	hydraulic membrane resistance (m^{-1})
R_{obs}	observed retention
R_∞	retention at infinite flux
$\Delta R/R$	variation of retention, defined as $\left(\frac{R_i - R_j}{R_i} \right) \times 100 \%$
Sc	Schmidt number
Sh	Sherwood number
ΔV	variation of the apparent molar volume ($\text{cm}^3 \cdot \text{mol}^{-1}$)

Greek Letters

δ	thickness of the polarization layer (m)
\emptyset	partitioning coefficient
λ	ratio of the solute radius to the mean pore radius

Subscripts

E1	electrolyte
P	pore
S	solute or saccharide
W	water
S,El	saccharide/electrolyte
S,W	saccharide/water

REFERENCES

- [1] X.-L. Wang, C. Zhang, P. Ouyang, *J. Membrane Sci.* **2002**, *204*, 271.
- [2] G. Bargeman, J. M. Vollenbroek, J. Straatsma, C. G. P. H. Schroën, R. M. Boom, *J. Membrane Sci.* **2005**, *247*, 11.
- [3] A. Bouchoux, H. Roux-de Balmann, F. Lutin, *J. Membrane Sci.* **2005**, *258*, 123.
- [4] S. Bouranene, A. Szymczyk, P. Fievet, A. Vidonne, *J. Membrane Sci.* **2007**, *290*, 216.
- [5] S. Mandale, M. Jones, *Desalination* **2008**, *219*, 262.
- [6] A. Escoda, P. Fievet, S. Lakard, A. Szymczyk, S. Déon, *J. Membrane Sci.* **2010**, *347*, 174.
- [7] C. Umpuch, S. Galier, S. Kanchanatawee, H. Roux-de Balmann, *Process Biochem.* **2010**, *45*, 1763.
- [8] V. Boy, H. Roux-de Balmann, S. Galier, *J. Membrane Sci.* **2012**, *390–391*, 254.
- [9] J. Luo, Y. Wan, *J. Membrane Sci.* **2013**, *438*, 18.
- [10] Y. Marcus, *Ion properties*, Marcel Dekker, New York 1997.
- [11] Y. Marcus, *Chem. Rev.* **2009**, *109*, 1346.
- [12] J. Tanninen, M. Mänttari, M. Nyström, *J. Membrane Sci.* **2006**, *283*, 57.
- [13] M. Hesampour, J. Tanninen, S.-P. Reinikainen, S. Platt, M. Nyström, *Chem. Eng. Res. Des.* **2010**, *88*, 1569.
- [14] A. Zhu, F. Long, X. Wang, W. Zhu, J. Ma, *Chemosphere* **2007**, *67*, 1558.
- [15] E. M. Tsui, M. Cheryan, *J. Membrane Sci.* **2004**, *237*, 61.
- [16] W. M. Deen, *AIChE J.* **1987**, *33*, 1409.
- [17] W. R. Bowen, J. S. Welfoot, P. M. Williams, *AIChE J.* **2002**, *48*, 760.
- [18] W. R. Bowen, A. W. Mohammad, N. Hilal, *J. Membrane Sci.* **1997**, *126*, 91.
- [19] G. Schock, A. Miquel, *Desalination* **1987**, *64*, 339.
- [20] J. Luo, Y. Wan, *J. Membrane Sci.* **2011**, *372*, 145.
- [21] N. Mogi, E. Sugai, Y. Fuse, T. Funazukuri, *J. Chem. Eng. Data* **2007**, *52*, 40.
- [22] A. W. Mohammad, R. K. Basha, C. P. Leo, *J. Food Eng.* **2010**, *97*, 510.
- [23] E. Drazevic, K. Kosutic, V. Kolev, V. Freger, *Environ. Sci. Technol.* **2014**, *48*, 11471.