Investigation of Dehydration and Pore Swelling Effects on the Transfer of PEG Through NF Membranes

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ABSTRACT

In order to investigate the significance of "salting-out" and "pore swelling" effects on the nanofiltration of neutral solutes, rejection properties of two NF ceramic and organic membranes were studied with single polyethylene glycol (PEG) solution and mixed PEG/inorganic electrolyte solutions. For both membranes, the rejection rate of PEG was found to decrease significantly in the presence of ions. In the case of the ceramic membrane (rigid pores), this phenomenon was imputed to the sole partial dehydration of PEG molecules induced by the surrounding ions. This assumption was confirmed by the lowering of the PEG rejection rates which followed the Hofmeister series. Experimental data were used to compute the resulting decrease in the Stokes radius of PEG molecules in the presence of the various salts. Concerning the organic membrane, the decrease in the rejection rate was found to be systematically higher than for the ceramic membrane. The additional decrease was then ascribed to the swelling of the pores. The experimental data of rejection rates were then used to compute the variation in the mean pore radius in the presence of the various salts. The pore swelling phenomenon due to accumulation of counterions inside pores was supported by electrokinetic charge density measurements.

1. INTRODUCTION

Nanofiltration (NF) has attracted increasing attention over the recent years due to its real application potential for the separation or purification of complex liquid mixtures. However, its development is hindered because of the difficulty to predict its performances when the fluid composition varies. This difficulty could be overcome providing a better understanding of the mechanisms that rule the transfer of the solutes through NF membranes. Some recent studies have shown that the transfer of an organic solute increases in the presence of a salt (Bouchoux 2005, Bargeman 2005, Bouranene 2007, Mandale 2008, Luo 2011) and that this increase also depends on the salt nature and its concentration. Organic solutes such as saccharides (glucose, sucrose, raffinose...), glycerol, benzyl alcohol, sodium benzoate, glutamic acid, iminodiacetic acid, caffeine...in the presence of inorganic salts such as NaCl, CaCl\(_2\),
were filtrated. Several hypotheses have been suggested to explain the decrease in the solute rejection in the presence of salts. These ones are:
- The partial dehydration of the molecules by the surrounding ions (Bouchoux 2005, Bouranene 2007) leading to a decrease in their effective size. This phenomenon is referred as the “salting-out” effect or “Hofmeister” effect from the author’s name who firstly observed the effect of salt nature on the precipitation of hen-egg-white protein (Kunz 2004).
- The increase in the mean pore size (phenomenon referred as “pore swelling”) due to the increase of the membrane charge by adding salt (this increased charge would lead to an increase of the number of counterions inside pores and thus, to a stronger repulsive interactions) (Bouchoux 2005, Bargeman 2005).
- The increase in the mean pore size due to the thinning of the hydration layer at the pore surface resulting from the salting-out effect (Luo 2011).
- The stronger reduction of the flux through small pores as compared with larger pores leading to more organic solutes passing through larger pores, which would determine the rejection (Bargeman 2005).
- The opening of the membrane pores due to the compression of the electrical double layer formed at the membrane surface (Mandale 2008).
- The increase of the effective membrane thickness due to collisions between ions and neutral solutes, which would lengthen the moving path of solutes. However, it should be noted that this assumption cannot explain the decrease of the limiting rejection rate of neutral solutes since the limiting rejection does not depend on the effective membrane thickness (Luo 2011).
- The change in molecular polarity of solutes (Mandale 2008).

The aim of this work was to evaluate the significance of pore swelling and/or salting-out effects in the case of NF ceramic and organic membranes and a model system: a mixture of polyethyleneglycol (PEG) and salt.

2. THEORY

2.1. Rejection rate of neutral solutes

The model used to describe the solute transport through NF membranes has been presented in detail in many papers (Bouranene 2007). That is why only a brief description of the model will be made in this section. For the mathematical derivation of the model, the following assumptions have been considered:
- The membrane consists of a bundle of identical cylindrical pores of radius \( r_p \) and length \( \Delta x \) with \( \Delta x >> r_p \) so that both solute and volume fluxes can be considered one-dimensional.
- The size of solutes is expressed as a Stokes radius \( r_{i,s} \) and is calculated from the diffusion coefficient \( (D_{i,x}) \), with the Stokes-Einstein equation (Eq. (7) in Table 1).
- The solute and volume fluxes are defined in terms of radially averaged quantities.
- The volume flux is fully developed inside the pore and has a parabolic profile of the Hagen-Poiseuille type.
Table 1. Summary of Equations used in the model (all symbols are defined in the nomenclature section).

**ENP equation:**

\[
J_i = -K_{i,t}D_i = \frac{dc_i}{dx} + K_{i,t}c_i \frac{J_i}{A_k} \tag{1}
\]

**Steric hindrance factors:**

\[
K_{i,t} = \frac{6\pi}{K_{i,t}} \tag{2}
\]

\[
K_{i,t} = \frac{(2 - \phi_i)K_{i,s}}{2K_{i,t}} \tag{3}
\]

**Hydrodynamic drag coefficients:**

\[
K_{i,t} = \frac{9}{4}\pi^2 \sqrt{2} (1 - \lambda_i)^{\frac{3}{2}} \left[ 1 + \sum_{n=1}^{\infty} a_n (1 - \lambda_i)^n \right] + \sum_{n=0}^{4} a_{n+1} \lambda^n \tag{4}
\]

\[
K_{i,t} = \frac{9}{4}\pi^2 \sqrt{2} (1 - \lambda_i)^{\frac{3}{2}} \left[ 1 + \sum_{n=1}^{\infty} b_n (1 - \lambda_i)^n \right] + \sum_{n=0}^{4} b_{n+1} \lambda^n \tag{5}
\]

with \(a_1 = -73/60, a_2 = 77.293/50.400, a_3 = -22.5083, a_4 = -5.6117, a_5 = -1.216, a_7 = 1.647, b_1 = 7/60, b_2 = -2.227/50.400, b_3 = 4.0180, b_4 = -3.9788, b_5 = -1.9215, b_6 = 4.392, b_7 = 5.006.

**Steric partitioning coefficient:**

\[
c_i(0^+)^{\phi_i} c_i(\Delta x^-)^{\phi_i} = \phi_i = \left(1 - \frac{r_{i,s}}{r_p}\right)^2 \tag{6}
\]

\[
\text{with } r_{i,s} = \frac{k_i T}{6\pi\eta D_{i,p}} \tag{7}
\]

**Filtration condition:**

\[
j_i = \frac{J_i}{c_{i,p} / A_k} \tag{8}
\]

**Intrinsic and observed rejection rates:**

\[
R_{\text{obs}} = 1 - \frac{c_{i,p}}{c_{i,m}} = 1 - \frac{\phi_i K_{i,c}}{1 - \left[ \exp\left( -\frac{K_{i,t}J_i\Delta x}{K_{i,t}D_{i,p}A_k} \right) \right] (1 - \phi_i K_{i,c})} \tag{9}
\]

\[
R_{\text{lim, in}} = 1 - \phi_i K_{i,c} \tag{10}
\]

\[
R_{\text{obs}} = 1 - \frac{c_{i,p}}{c_{i,t}} \tag{11}
\]

\[
R_{\text{obs}} = \frac{R_{\text{obs}} \exp(J_i / k)}{1 - R_{\text{obs}} (1 - \exp(J_i / k))} \tag{12}
\]

\[
\text{with } k = \frac{D_{i,p}}{\delta} \tag{13}
\]

**Sherwood correlation:**

\[
Sh = k_d \sigma / D_{i,p} = \alpha_i \Re \sigma \Sc \alpha_i \tag{14}
\]
The main equations used for the model are summarised in Table 1. The model is based on the application of the extended Nernst-Planck equation to describe the transport of solutes through the membrane (Eq. (1)). The terms on the RHS of this equation represent transport due to diffusion and convection, respectively. $K_{i,d}$ and $K_{i,c}$ are the hindrance factors for the diffusion and convection, accounting for the effect of finite solute and pore sizes on the diffusive and convective components of solute transport. For purely steric exclusion mechanism between solute and cylindrical pores, the solute partitioning coefficient at both membrane/solution interfaces is given by Eq. (6). Integrating Eq. (1) across the membrane thickness (i.e. from $x = 0$ to $x = \Delta x$) while considering the filtration condition (Eq. 8) gives the expression for the intrinsic rejection rate (Eq. (9)). The intrinsic rejection rate is independent of the concentration polarization phenomenon (Zydney 1997) and thus characterizes the real performance of the membrane. As shown by Eq. (9), the intrinsic rejection rate of neutral solutes, at a given filtration flux $J_v$, is a function of two parameters, $\lambda_i$ and $\Delta x/A_k$. It increases with $J_v$ and reaches a limiting value of $1-\phi_i K_{i,c}$ at infinite $J_v$ (Eq. (10)), which only depends on $\lambda_i$.

For a neutral solute solution, the intrinsic rejection rate is related to the observed rejection rate by Eq. (12) (Table 1). The observed rejection rate, which depends on the concentration polarization phenomenon, corresponds to an experimentally measured value unlike the intrinsic rejection rate which can be only computed.

The mass-transfer coefficient $k$ in Eq. (13) can be assessed from a Sherwood correlation (Eq (14)).

2.2. Electrokinetic charge density

The zeta-potential is a parameter directly related to the electrokinetic charge density. Streaming potential is the most commonly used tool for determining the zeta-potential of membranes. Measurements of streaming potential can be performed in a transversal or tangential mode. In the case of NF membranes, it is advisable to use the second mode (Labbez 2001, Yaroshchuk 2002). The tangential streaming potential (TSP) technique consists in applying a pressure difference across a thin channel formed by two identical membrane samples facing one another and separated by a spacer. Cell electric conductance measurements allow taking into account the possible contribution of the membrane porous body to the conduction phenomenon during the streaming potential process. The zeta-potential can then be determined using the following relation:

$$
\zeta = \frac{\Delta \phi_s}{\Delta P} G_t \frac{\eta}{\varepsilon_0 \varepsilon_r} \left( \frac{l}{2h L_c} \right)
$$

where $\Delta \phi_s$ is the streaming potential, $\Delta P$ the pressure difference between the ends of the channel, $G_t$ the total conductance of the membrane/channel/membrane sandwich, $\varepsilon_0$ the vacuum permittivity, $\varepsilon_r$ the relative dielectric constant of the solvent, $\eta$ its dynamic viscosity, $2h$ the channel height, $L_c$ its width and $l$ its length.

The zeta-potential is related to the electrokinetic charge density into electrokinetic charge density $\sigma_{ek}$ (expressed in C m$^{-2}$) as follows (Hunter 1881):
\[ \sigma_{ek} = -\text{sign}(\zeta) \sqrt{\left[ 2 \varepsilon_r \varepsilon_0 RT \sum_i c_{i,f} \left[ \exp \left( \frac{-z_i F \xi}{RT} \right) - 1 \right] \right]} \]  

where \( c_{i,f} \) is the concentration of ion \( i \) in the feed solution.

Here, we assume that the charge density inside pores is the same as the external charge density estimated from TSP measurements and Eq. (16).

3. EXPERIMENTAL

3.1. Membranes

Filtration experiments were performed with two commercial NF membranes: a polyamide thin film composite membrane (labeled Desal GH and produced by GE Osmonics) and a TiO\(_2\) tubular membrane (labeled Filtanium and produced by TAMI-Industries).

3.2. Chemicals

Polyethylene glycol (PEG) with a molar mass of 600 g mol\(^{-1}\) (Fluka) and KCl, LiCl, MgCl\(_2\) and K\(_2\)SO\(_4\) salts of pure analytical grade (Prolabo) were used for experiments. Single-PEG and mixed PEG/salt solutions at a PEG concentration of 2 g L\(^{-1}\) were prepared with milli-Q quality water (conductivity < 1 µS cm\(^{-1}\)). The salt concentration in mixed-solute solutions was in the range 0.05-1 mol L\(^{-1}\) for rejection experiments and 0.0005-0.005 mol L\(^{-1}\) for electrokinetic measurements. The pH of solutions was 6.0 ± 0.2. The concentration of PEG in both feed and permeate solutions was determined from COD measurements and the salt concentration by conductivity measurements.

3.3. Filtration experiments

They were conducted under cross-flow conditions with the TAMILAB\(^R\) filtration unit for the ceramic membrane and the Osmonics Sepa CFII cell for the organic membrane. The filtration area was 220 and 140 cm\(^2\) for the ceramic and organic membranes, respectively. The feed concentration was maintained constant by totally recycling the retentate and permeate. Rejection rates were measured as a function of the permeate volume flux by varying the transmembrane pressure. The working hydrodynamic conditions are given in Table 2.

<p>| Table 2. Hydrodynamic conditions for filtration experiments performed with ceramic and organic membranes. |
|---------------------------------|-------------------------------|-----------------------------|</p>
<table>
<thead>
<tr>
<th>Transmembrane pressure ( \Delta P ) (bars)</th>
<th>Ceramic membrane</th>
<th>Organic membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic diameter ( d_h ) (mm)</td>
<td>3.6 (</td>
<td>) 0.51</td>
</tr>
<tr>
<td>Reynolds number ( Re )</td>
<td>12000-40000 (</td>
<td>) 100-150</td>
</tr>
<tr>
<td>Schmidt number ( Sc )</td>
<td>1600-2200 (</td>
<td>) 1600-2200</td>
</tr>
<tr>
<td>Sherwood correlation</td>
<td>( Re = 0.0096 Re^{0.91} Sc^{0.35} )</td>
<td>( Re = 0.2 Re^{0.57} Sc^{0.4} )</td>
</tr>
</tbody>
</table>
3.4. Electrokinetic and electric measurements

TSP and conductance measurements were performed with a ZETACAD (CAD Inst., France) zeta-meter and a Solartron impedance spectrometer (1286 electrochemical interface and 1255 frequency response analyzer), respectively. The entire set-up and the exact measuring procedure can be found elsewhere (Fievet 2003). These measurements were only applied to the organic membrane. Samples of 50 x 30 mm, corresponding to the measuring cell, were cut in the sheet membrane. Experiments were conducted using a single channel height (2h), which was estimated from the channel hydraulic permeability by using Hagen-Poiseuille formula for slit channels (Szymczyk 2007).

4. RESULTS AND DISCUSSION

4.1. Determination of pore radius and thickness-to-porosity ratio using PEG

Fig. 1 shows an example of the intrinsic rejection rates of PEG 600 vs. permeate volume flux ($J_v$) for the ceramic and organic membranes. As expected, the rejection increases with $J_v$ before leveling off at about 68% for the ceramic membrane and 90% for the organic one. As shown by the full lines, the data are well fitted by Eq. (9). Single-solute solutions of PEGs with different molar masses (400 and 1000 g mol$^{-1}$) were also filtrated through the ceramic membrane (results not shown). The effective pore radius and the ratio of the effective membrane thickness-to-porosity inferred from the fitting procedure are collected in Table 3.

![Fig. 1. Intrinsic rejection rate of PEG 600 vs. permeate volume flux for the ceramic and organic membranes. PEG feed concentration: 2 g L$^{-1}$; Symbols: experimental data; Full lines: intrinsic rejection rates computed from Eq. (9). $D_{PEG,\infty} = 3.14 \times 10^{-10}$ m$^2$ s$^{-1}$.](image)

<table>
<thead>
<tr>
<th></th>
<th>Ceramic membrane</th>
<th>Organic membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_p$ (nm)</td>
<td>1.18 ± 0.04</td>
<td>0.875 ± 0.015</td>
</tr>
<tr>
<td>$\Delta x/A_k$ (µm)</td>
<td>3.92 ± 3.08</td>
<td>3.96 ± 0.74</td>
</tr>
</tbody>
</table>

Table 3. Effective pore radius ($r_p$) and thickness-to-porosity ratio ($\Delta x/A_k$) of ceramic and organic membranes determined from rejection data of PEG 600 (for a single-solute solution) and from a fitting procedure (Eq. (9)).
It appears that the ratio $\Delta x/A_k$ is almost identical for the two membranes and that the ceramic membrane ($r_p = 1.18$ nm) is a little more open than the organic one ($r_p = 0.875$ nm) by a factor 1.35.

4.2. Salt effects on PEG rejection in mixed-solute solutions

For both membranes, it was observed that rejection of PEG 600 is significantly lower in mixed-solute solutions (i.e. when a salt is present) than in single-solute solutions and that the decrease in the rejection rate increases with the salt concentration. Examples of the influence of the salt concentration on the PEG rejection by the ceramic and organic membranes are shown in Figs 2a and b, respectively. It should be noted that the rejection rate drop with increasing salt concentration, which was observed for all salts, cannot be ascribed to concentration polarization effects since rejection rates are compared at identical permeate volume fluxes $J_v$ (indeed, at different $J_v$, the concentration polarization would be different and then also the osmotic pressure would be different).

Fig. 2. Intrinsic rejection rate of PEG 600 vs. permeate volume flux for single-solute and mixed-solute solutions. PEG feed concentration: 2 g L$^{-1}$; Symbols: experimental data; Full lines: intrinsic rejection rates computed from Eq. (9); (a): ceramic membrane; (b): organic membrane.
As illustrated by Figs 3a-c, the rejection rate of PEG also depends on the salt nature. For the ceramic membrane, it is found that the decrease of the PEG rejection rates follows the Hofmeister series, i.e. $\text{Mg}^{2+} > \text{Li}^+ > \text{K}^+ > \text{SO}_4^{2-} > \text{Cl}^-$ at all concentrations whereas these sequences are not observed with the organic membrane (the drop in the rejection rate follows the sequence: $\text{Li}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{SO}_4^{2-} > \text{Cl}^-$ at 0.5 eq L$^{-1}$). Since pores of the ceramic membrane are rigid, the hypothesis of pore swelling can be eliminated with this membrane. The rejection rate drop is then ascribed to the partial dehydration of PEG molecules induced by surrounding ions. In order to investigate the influence of the salt nature on the dehydration effect, the mean $r_p$ and $\Delta x/A_k$ values estimated from single-solute solutions were used to fit the rejection data of PEG in mixed-solute solutions, the Stokes radius of PEG 600 ($r_{\text{PEG},s}$) being the single adjustable parameter.
Fig. 3. Intrinsic rejection rate of PEG 600 vs. permeate volume flux for single-solute and mixed-solute solutions. PEG feed concentration: 2 g L\(^{-1}\); Symbols: experimental data; Full lines: intrinsic rejection rates computed from Eq. (9); (a) ceramic membrane and salt concentration: 1 mol L\(^{-1}\); (b) ceramic membrane and salt concentration: 0.1 mol L\(^{-1}\); (c) organic membrane and salt concentration: 0.5 eq L\(^{-1}\).

Fig. 4 shows the relative variation of the effective size of the PEG 600 with the salt concentration of the various mixed-solute solutions. The Stokes radius of PEG 600 in single-solute solution was taken as 0.61 nm according to Afonso (2001). As can be seen, the salt effect varies from one salt to another. Regarding the effect of cations, the largest decrease in the effective size of PEG is obtained in the presence of MgCl\(_2\) (~26% at 1 mol L\(^{-1}\)) and this reduction is larger for LiCl (~22% at 1 mol L\(^{-1}\)) than for KCl (~9% at 1 mol L\(^{-1}\)). As to the effect of anions, the effective size of PEG is found to decrease by ~6% and ~11% in the presence of KCl and K\(_2\)SO\(_4\) at 0.1 mol L\(^{-1}\), respectively. These findings are justified by the fact that the more ions are charged the more ions are hydrated, and the more ions are small (in terms of ionic radius) the more ions attract water molecules (due to a stronger electric field at the surface) and then, the number of water molecules that interact with the PEG 600 decreases. As expected, the salting-out effect depends on the ion concentration and also on both ion charge and ion size according to Hofmeister series.

Fig. 4. Relative variation of the Stokes radius of PEG 600 vs. salt concentration in the various mixed-solute solutions. PEG feed concentration: 2 g L\(^{-1}\); Ceramic membrane.

Unlike the ceramic membrane, the salting-out effect cannot be solely invoked with the organic membrane since the results obtained with this membrane are not in accordance with the Hofmeister series for cations and anions. Moreover, as shown in Fig. 5, the decrease in the limiting rejection rate is systematically higher for the organic membrane than for the ceramic membrane regardless of the salt and concentration.
Fig. 5. Decrease of the limiting rejection rate of PEG 600 (expressed in %) in the presence of various salts at different concentrations for ceramic and organic membranes by comparison with the limiting rejection rate of PEG 600 in a single-solute solution. $R_{SS}$: limiting rejection rate of PEG 600 in a single-solute solution; $R_{MS}$: limiting rejection rate of PEG 600 in a mixed-solute solution.

Since the salting-out phenomenon is independent of the membrane, the additional decrease observed with the organic membrane was then ascribed to the swelling of the pores. In order to evaluate the significance of the pore swelling phenomenon, the experimental data of rejection rates obtained with the organic membrane were used to compute the variation in the mean pore radius (and the membrane thickness-to-porosity ratio) in the presence of the various salts (the Stokes radii of PEG molecules in the presence of the various salts having been determined previously from rejection rates obtained with the ceramic membrane). Results show that the effective pore size depends on the salt nature and increases with salt concentration (Fig. 6). A variation from 7 to 31%, 19 to 50%, 16 to 59% and 14 to 51% is observed for MgCl$_2$, KCl, LiCl and K$_2$SO$_4$, respectively, when concentration increases from 0.1 to 1 eq L$^{-1}$ for the first three salts and from 0.1 to 0.5 eq L$^{-1}$ for the last salt. No conclusion can be drawn at the lowest concentration. At 0.5 and 1 eq L$^{-1}$, the increase in the effective pore size is found to follow the order: K$_2$SO$_4$ > LiCl > KCl > MgCl$_2$ (K$_2$SO$_4$ could not be studied at the highest concentration). A number of studies have reported that the surface charge density depends on the salt nature and its concentration (Afonso 2001, Bruni 2008). The increase in the membrane charge density with the increasing salt concentration is believed to be caused by adsorption of ions from the solution onto the membrane surface. Thus, the addition of a salt in a solution could lead to an increase in the surface charge density resulting in a greater counterions concentration inside pores in order to compensate the surface charge. This effect could lead to pore swelling due to stronger electrostatic repulsions between counterions. The lowest increase in the effective pore size obtained with MgCl$_2$ and the greatest one observed with K$_2$SO$_4$ seem to support this assumption. Indeed, magnesium and sulfate ions, which are known to specifically adsorb onto the membrane surface (Afonso 2001, Schaep 2001) could lead to lower membrane charge density with MgCl$_2$ and to higher one with K$_2$SO$_4$. 
As for the influence of salt nature on the relative variation of the ratio $\Delta x/A_k$, no tendency could be observed due to overlapping of the experimental data for the various salts (results not shown).

![Graph showing relative variation of the effective pore radius of the organic membrane as a function of salt concentration of mixed-solute solutions. PEG feed concentration: 2 g L$^{-1}$.](image)

**Fig. 6.** Relative variation of the effective pore radius of the organic membrane as a function of salt concentration of mixed-solute solutions. PEG feed concentration: 2 g L$^{-1}$.

*Notes:* some symbols are shifted from 0.1 eq L$^{-1}$ for more clarity.

4.3. Electrokinetic charge density of membranes

The salt effect on the membrane charge density was investigated by implementing coupled streaming potential coefficient ($\Delta \phi_s/\Delta P$) and electric conductance ($G_t$) measurements. Zeta-potentials ($\zeta$) were determined from Eq. (14) and then converted into electrokinetic charge density ($\sigma_{ek}$) according to Eq. (15). It should be noted that electrokinetic measurements have been carried out in salt solutions less concentrated than mixed-solute solutions so as to obtain a sufficiently high streaming potential. As shown in Fig. 7, the membrane is negatively charged regardless of the salt and the charge density increases (in absolute value) with salt concentration, probably due to an increasing adsorption of ions from the solution onto the membrane surface. Concerning the effect of the salt nature, the surface charge density (in absolute value) follows the sequence: $K_2SO_4 > LiCl > KCl > MgCl_2$ at 0.001 and 0.01 eq L$^{-1}$ (except for KCl and MgCl$_2$ which cannot be ranked at 0.001 eq L$^{-1}$). This charge density order is in accordance with that reported by Afonso (2001) with the same membrane and similar salts, i.e. $Na_2SO_4 > NaCl > MgCl_2$ (provided that $Na^+$ ions have the same influence on the membrane charging process as $K^+$ ions). It should be pointed out that the charge density order is strictly identical to the pore swelling order. If the salt effect on the membrane charge density is considered to be qualitatively the same at higher concentrations, it can then be concluded that the decrease of the PEG rejection in the presence of a salt is partly due to a pore swelling caused by an increase of the surface charge density.
4.4. Contribution of dehydration and pore swelling to the decrease in PEG rejection

The salting-out and pore swelling effects on the transfer of PEG through the organic membrane could be decoupled by calculating the limiting rejection rate due to only salting-out effect. To this end, the effective pore radius of the organic membrane in the absence of a salt (i.e., $r_p = 0.875$ nm) and the Stokes radii of PEG 600 in the presence of salts (assessed from rejection data measured with the ceramic membrane) were used in Eq. (10). Fig. 8 shows the contribution of the two phenomena – salting-out and pore swelling – to the decrease in the limiting intrinsic rejection rate of PEG. Results reveal that the contribution of the salting-out effect follows the Hofmeister series for all salt concentrations, and varies between ~25 and ~50% depending on salt and concentration.

The dehydration of PEG molecules by ions is then also demonstrated in the case of the organic membrane. Both phenomena – dehydration and pore swelling – contribute
similarly to the rejection rate drop in the presence of \( \text{K}_2\text{SO}_4 \) or \( \text{MgCl}_2 \) salts whereas the pore swelling becomes dominant in the presence of \( \text{KCl} \) or \( \text{LiCl} \).

4.5. Impact of PEG on salt rejection

As illustrated by Fig. 9, the presence of PEG did not affect significantly the rejection of ions, for both ceramic and organic membranes, which is mainly controlled by electrostatic effects (Donnan exclusion and/or dielectric exclusion due to production of image forces). This finding is in accordance with result reported by Bouchoux (2001) with a polyamide NF membrane.

![Graph showing rejection rate vs. permeate volume flux](image)

*Fig. 9. Observed rejection rate of \( \text{MgCl}_2 \) (ceramic membrane) and \( \text{KCl} \) (organic membrane) as a function of permeate volume flux for single salt solutions and mixed-solute solutions (i.e. in the presence of PEG 600 at 2 g L\(^{-1}\)).*

**CONCLUSION**

The salting-out phenomenon was highlighted for PEG molecules in the presence of various salts and its impact on PEG rejection by NF membranes was studied for both ceramic and organic membranes. For the organic membrane, it was found that the salting-out effect cannot solely explain the rejection lowering of a neutral solute in the presence of salt. An additional phenomenon – the pore swelling – was then considered. The contribution of both phenomena to the ion-induced decrease in the neutral solute rejection could be quantified. It was found that the contribution of the salting-out effect follows the Hofmeister series. The pore swelling phenomenon due to accumulation of counterions inside pores resulting from an increase in the membrane charge was supported by electrokinetic charge density measurements. The identification of the mechanisms involved in relationship with the transfer should allow to improve the prediction of the membrane processes performances and thus their implementation for different applications.
NOMENCLATURE

$A_k$  porosity of the membrane top layer
$c$   salt concentration
$c_i$  concentration of solute $i$ in the membrane
$c_{i,f}$  concentration of solute $i$ in the feed solution
$c_{i,m}$  concentration of solute $i$ at the membrane surface (at the membrane/feed solution interface)
$c_{i,p}$  concentration of solute $i$ in the permeate
$c_i(0^+)$  concentration of solute $i$ just inside the membrane pores (at the membrane/feed solution interface)
$c_i(\Delta x^-)$  concentration of solute $i$ just inside the membrane pores (at the membrane/permeate interface)
$D_{i,\infty}$  bulk diffusion coefficient of solute $i$ at infinite dilution
$d_h$  hydraulic diameter
$F$  Faraday constant
$G_t$  total conductance
$h$  channel half-height
$j_i$  molar flux density of solute $i$
$J_v$  permeate volume flux
$K_{i,c}$  hydrodynamic coefficient accounting for the effect of pore walls on convective transport
$K_{i,d}$  hydrodynamic coefficient for hindered diffusion inside pores
$K_{i,s}$  hydrodynamics function
$k_B$  Boltzmann constant
$k$  mass-transfer coefficient $k$
$l$  channel length
$L_c$  channel width
$L_p$  pure water permeability
$r_p$  effective pore radius
$r_{i,s}$  Stokes radius of solute $i$
$R$  ideal gas constant
$Re$  Reynolds number
$R_{int}$  intrinsic rejection rate
$R_{lim,int}$  limiting intrinsic rejection rate
$R_{obs}$  observed rejection rate
$Sh$:  Sherwood number
$Sc$:  Schmidt number
$T$  temperature
$x$  coordinate
$z_i$  charge number of ion $i$
Greek symbols

δ          thickness of the polarization layer
Δφs        streaming potential
ΔP         hydrostatic pressure difference
Δx         effective thickness of the top layer
ε0         vacuum permittivity
εr         effective dielectric constant inside pores
φi         steric partitioning coefficient for solute i
λi         ratio of the solute size to pore size (λi = ri/s r)
η           dynamic viscosity of the fluid
σek         electrokinetic charge density
ζ           zeta potential

REFERENCES


