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Effect of highly concentrated salt on retention of organic solutes by nanofiltration polymeric membranes

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\begin{abstract}
During desalination of feed with highly concentrated salt by nanofiltration (NF), predictive modeling was difficult due to the effect of salt on retention of organic solutes. Consequently, a better understanding of salt effect on membrane and organic solutes was required. In this study, four well-known commercially available NF polymeric membranes, NF270, NF-, Desal-5 DL and Nanomax50, were analyzed by a model based on an extended Nernst–Planck equation, using highly concentrated glucose and sodium chloride (NaCl) solutions. The results showed that with increasing salt concentration, the solute-to-pore size ratio ($\lambda_s$) decreased while the ratio of effective membrane thickness to porosity ($\Delta x/\varepsilon$) increased, indicating that the effect of salt may include decreasing solutes size, increasing membrane pore size, and increasing effective membrane thickness. Moreover, such salt effect appeared to be independent of membrane and solute types, and the correction model could well predict the retention of charged solutes at high salt concentration because electrostatic repulsion effect between charged solutes and membranes was completely screened by the salt ions. Meanwhile, several hypotheses such as membrane swelling, hydration layer thinning and particle collision were provided to explain the change of model parameters by highly concentrated salt.
\end{abstract}

\section{Introduction}

Organic synthesis and food processes frequently produce crude feeds or waste streams containing highly concentrated salt (up to 20\%, w/v) \cite{1–7}. These mixtures can be produced by salt-adding preparation or by acid- or alkali-catalyzing reactions followed by neutralization. A mass of salt in these industrial fluids induces many problems in their post-treatment, and thus the salt should be removed partly. Nanofiltration (NF) can be a good candidate as it can simultaneously achieve concentration of organic solutes and removal of monovalent salts, already applied successfully to dye and dairy industries \cite{8,9}. However, for a concentrated saline solution, salt concentration changes greatly during NF-desalination process, producing a distinct influence on rejection of low molecular weight solutes (e.g., glucose, amino acid) in mixtures, thus leading to a deviation when modeling such process.

Significant research on the effect of inorganic salt on the transfer of organic solutes through NF membranes demonstrated that solutes rejection decreased in the presence of salts \cite{2,10–14}. Three mechanisms were often proposed to explain such a change, including charge screening, solute dehydration and membrane swelling. Firstly, charge screening could weaken the electrostatic repulsion between charged solutes and membrane, facilitating solute passing through the membrane\cite{2}. This explanation had been verified by many studies \cite{15,16} and well accepted by researchers. Secondly, a partial dehydration of solute due to “salting-out” effect (also called Hofmeister effect\cite{17}) would cause a decrease of solute hydrodynamic radius, thus inducing a solute retention drop\cite{12}. As for membrane swelling by salt, it is generally believed that solute retention decreases due to membrane swelling by salt, while the mechanism is still controversial. Bouchoux et al.\cite{12} and Bargeman et al.\cite{18} proposed that membrane swelling (i.e., an increase of average pore size) occurred due to the stronger repulsive interaction between ions with same charge inside the pores when salt was added, implying that electrostatic effect was enhanced by increasing salt concentration. However, such explanation contradicted charge screening by salt. Nilsson et al.\cite{14} argued that membrane swelling due to a salting-in effect (also called Lyotrophic effect\cite{19}) was more suitable to explain their experimental results. As an alternative explanation Bargeman et al.\cite{18} proposed that, due to the pore size distribution, addition of salt with relatively low retention reduced the flux of small pores to a higher extent than larger pores, and more organic solutes would pass through larger pores, thus leading a decrease in solute retention. A change in molecu-

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lar polarity of neutral solutes, could, in some specific cases, be an alternative interpretation [13].

Some recent works on physical characterization and modeling calculation were made to identify above hypotheses, especially the membrane swelling and solute dehydration. A successful attempt of physically measuring membrane expansion and corresponding loss of flux in salt solution was reported by Freger [20], but membrane pore swelling was not found. Bargeman et al. [18] declared that using Maxwell–Stefan model, both of the calculated mean pore size and effective membrane thickness for NF membranes increased with increase of salt concentration. Based on the extended Nernst–Planck equation, Bouranene et al. [21] developed a model to evaluate the salt effect on neutral solutes for NF process. To eliminate the possibility of pore swelling, a rigid ceramic membrane was used, and the fitting results showed that effective size of neutral solutes decreased with increasing salt concentration. For a NF polymeric membrane, recent research by Escoda et al. [22] showed that the decrease of neutral solutes retention by salt could be imputed to a combination of increase of membrane pore size and decrease of the solutes radius. Therefore, these effects should be carefully considered in modeling the NF-desalination process when feed solutions contained high salt concentration. However, most studies were related to diluted solutions with low salt concentration and could not meet the requirements of prediction for real industrial effluents.

The present work was based on the research of Bouranene et al. [21] and Escoda et al. [22], and for practical application, glucose, iminodiacetic acid (IDA) [6] and glutamic acid (Glu) [5] were used as relevant organic solutes with high concentration. The aim of this study was to evaluate the influence of highly concentrated salt (NaCl) on the performance of NF polymeric membranes, and to establish mathematical models for predicting the rejection of organic solutes at different salt concentrations.

2. Theory

2.1. Model description [21,22]

The extended Nernst–Planck equation describes uncharged solutes transport through a membrane as follows:

\[ j_i = -K_{id}D_{∞,i,c} \frac{dc_i}{dx} + K_{ie}c_i V \]  

where \( j_i \) is the molar flux of solute, \( K_{id} \) and \( K_{ie} \) are correctly hydrodynamic coefficients for diffusion and convection, respectively, \( D_{∞,i,c} \) is the diffusion coefficient of solute at infinite dilution, \( c_i \) is the solute concentration in the pore and \( V \) is the solvent velocity inside the pores.

Hydrodynamic coefficients \( K_{ie} \) and \( K_{id} \) depend on the solute to pore size ratio, \( \lambda_i \), defined as:

\[ \lambda_i = \frac{r_s}{r_p} \]  

where \( r_s \) is the Stokes radius of solutes and \( r_p \) is the mean effective pore size of the membrane.

Using the model based on extended Nernst–Planck equation, Bouranene et al. [21] investigated the influence of salt on the retention of polyethylene glycol (PEG) with a ceramic membrane, and found that calculated \( r_s \) values of PEG decreased with increasing salt concentration. Escoda et al. [22] found that, for a polymeric membrane, the decrease of \( r_s \) values could not solely explained the retention variation. Moreover, the salt effect on PEG retention did not follow the Hofmeister series, so they concluded that \( r_s \) values were also affected by salt ions. In the present study, polymeric membranes were used and \( r_p \) would increase due to membrane swelling by salt [18,22], and thus \( \lambda_i (r_s/r_p) \) would decrease with increasing salt concentration (\( r_s \) and \( r_p \)).

For calculation convenience, the molar flux of solutes could be described as follows:

\[ j_i = \frac{f_v C_{i,p}}{ε} \]  

where \( f_v \) is the volumetric flux per unit area of membrane, \( C_{i,p} \) is the solute concentration in permeate and \( ε \) is the membrane porosity.

Substituting Eq. (3) into Eq. (1) and then integrating with the boundary condition of \( C = C_{i,m} \) at \( x = 0 \) and \( C = C_{i,p} \) at \( x = Δx \) yields the expression of intrinsic rejection:

\[ R_i = 1 - \frac{C_{i,p}}{C_{i,m}} = 1 - \frac{\Phi_i K_{ie} \epsilon}{(1 - \Phi_i K_{ie} \epsilon \exp(-Pe))} \]  

where \( C_{i,m} \) is the solute concentration at membrane surface, \( \Phi_i \) is the steric partitioning coefficient, holding a relation of \( \Phi_i = (1 - \lambda_i)^2 \) for cylindrical pore, and \( Pe \) denotes the Peclet number inside the membrane defined as:

\[ Pe = \frac{K_{id}j_v Δx}{K_{ad}D_{∞,i,c}ε} \]  

where \( Δx \) is the effective membrane thickness.

As shown in Eqs. (4) and (5), the intrinsic rejection of uncharged solutes not only depends on the solute to pore size ratio (\( \lambda_i \)) but also relies on the ratio of effective membrane thickness to porosity (\( Δx/ε \)). By fitting the data of solutes retention, values of \( λ_i \) and \( Δx/ε \) at different salt concentrations can be obtained.

2.2. Description of concentration polarization

Intrinsic rejection can be calculated by solutes concentration in permeate (\( C_{i,p} \)) and at membrane surface (\( C_{i,m} \)). \( C_{i,p} \) can be obtained easily by analyzing permeate samples, while \( C_{i,m} \) must be calculated by a mathematical model. According to film theory described in the literature [23], \( C_{i,m} \) can be calculated by following equation:

\[ j_v = k \ln \left( \frac{C_{i,m} - C_{i,f}}{C_{i,f} - C_{i,p}} \right) \]  

where \( C_{i,f} \) is the solute concentration in feed, \( k \) is the mass transfer coefficient, which can be calculated from an empirical relationship [24]:

\[ \frac{kr}{D_{∞,i,c}} = \Psi \left( \frac{ω^2}{ν} \right)^{0.567} \left( \frac{ν}{D_{∞,i,c}} \right)^{0.33} \]  

where \( r \) is the radius of the stirred cell, \( ω \) is the angular velocity, \( ν \) is the kinematic viscosity, \( ψ \) is a constant which depends on the module geometry and can be experimentally determined as described in previous work [25,26]. Here, the value is 0.335 for the stirred cell used in the present work.

3. Materials and methods

3.1. Membranes and chemicals

Four commercial NF polymeric membranes (NF270, NF-, Desal-5 Dl, Nanomax50) were used in the present work. NF270 (DOW-Filmtec) is a thin-film polyamide NF membrane with polysulfone support. NF-(DOW-Filmtec) is a three-layer polysulfone based membrane with a polyimidezane top layer. Desal-5 DL (GE-Osmonics) is also a three-layer polysulfone based membrane but with a proprietary polyamide top layer. Like NF270, Nanomax50 (Millipore) is a NF membrane also with a polyamide top layer on polysulfone support. Based on the manufacturers’ data sheet and literature [27–31], the properties of these NF membranes are summarized in Table 1.
The neutral solute used for modeling was glucose of analytic grade (Amresco, USA). The salt used was NaCl and amphoteric solutes such as iminodiacetic acid (IDA) and glutamic acid (Glu) were also employed for verifying the model. NaCl and IDA were of analytical grade and purchased from Beijing Chemicals Reagent Company, Beijing, China. Glu was of biochemical grade and supplied by Shanghai Kangda Amino-Acid Factory, Shanghai, China. The relevant characteristics of these organic solutes are listed in Table 2 [6,12,32–34]. Deionized water was used as solvent and all solutions were filtered through 0.22 μm microporous filters (MERBRA, Germany) before use.

3.2. Analytical methods

The glucose concentration was determined using the 3,5-dinitrosalicylic acid (DNS) method [35]. The pH value and NaCl concentration of the solutions were measured using an ion meter equipped with pH and Cl− electrodes (PXSJ-216, Precision & Scientific Instrument, China). IDA concentration was measured with a spectrophotometer (UV757CRT, Precision & Scientific Instrument, China) at 235 nm after nitrosation [6] and Glu concentration was measured using the ninhydrin method [36]. The standard curves of glucose, IDA and Glu were established at different salt concentrations to eliminate the effect of salt on test results. The dynamic viscosity of solutions was determined by a rheometer (DV-III Ultra, Brookfield, USA), and the calculated values of kinematic viscosity are given in Table 3.

3.3. Experimental procedure

Fig. 1 illustrates the schematic diagram of the set-up for NF experiments. The dead-end filtration experiments were conducted in a laboratory-constructed magnetically stirred cell in diafiltration mode. The suspended bar impeller (length: 2 cm, diameter: 0.6 cm) inside the cell was magnetically driven by a magnetic agitator (85-2, Shanghai Sile Instrument, China). The stirring speed was monitored using a digital optical tachometer (RM-1000, Prova Instruments Inc., China). The gap between the impeller and the membrane was about 1.2 mm. The working volume of the cell was 12.8 mL. This device could be fitted with a membrane disc hav-

Table 1

Membranes properties.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>NF270</th>
<th>NF-</th>
<th>Desal-5 DL</th>
<th>Nanomax50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacture</td>
<td>DOW-Filmtec</td>
<td>DOW-Filmtec</td>
<td>GE-Osmotics</td>
<td>Millipore</td>
</tr>
<tr>
<td>Surface material</td>
<td>Polyamide</td>
<td>Polypiperazine amide</td>
<td>Proprietary polyamide</td>
<td>Polyamide</td>
</tr>
<tr>
<td>Molecular weight cut-off (Da)</td>
<td>150–200 [27]</td>
<td>200 [28]</td>
<td>150–300 [27]</td>
<td>400 [29]</td>
</tr>
<tr>
<td>Lp, (L m−2 h−1 bar−1) 25 °C</td>
<td>13–14 [a]</td>
<td>9.5–10 [a]</td>
<td>5.5–6.5 [a]</td>
<td>6.5–7 [a]</td>
</tr>
<tr>
<td>Max. temperature (°C)</td>
<td>45</td>
<td>45</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Max. pressure (MPa)</td>
<td>4.1</td>
<td>4.1</td>
<td>4.0</td>
<td>4.1</td>
</tr>
<tr>
<td>pH Range</td>
<td>3–10</td>
<td>3–10</td>
<td>2–11</td>
<td>4–10</td>
</tr>
<tr>
<td>Isoelectric point (pH)</td>
<td>~5.2 [27]</td>
<td>~5.1 [30]</td>
<td>~4.1 [27]</td>
<td>~4.5 [31]</td>
</tr>
</tbody>
</table>

Lp, pure water permeability.

[a] Measured in this work.

Table 2

Characteristics of the organic solutes used.

<table>
<thead>
<tr>
<th>Items (25 °C)</th>
<th>Glucose</th>
<th>IDA</th>
<th>Glu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g mol−1)</td>
<td>180</td>
<td>133</td>
<td>147</td>
</tr>
<tr>
<td>Diffusivity D∞ (10−10 m2 s−1)</td>
<td>6.9 [12]</td>
<td>8.15 [a]</td>
<td>7.62 [34]</td>
</tr>
<tr>
<td>Stokes radius rs (nm)</td>
<td>0.365 [12]</td>
<td>0.30 [a]</td>
<td>0.32 [34]</td>
</tr>
</tbody>
</table>

[a] Calculated by the model presented in the literature [33].
ing an effective diameter of 24 mm within the module, with an
effective membrane surface area of 4.52 × 10⁻⁴ m². Feed solution
was pumped at constant flow rate into the filtration cell through
a switching valve (V-7, Pharmacia, Sweden) using a high perfor-
manence positive displacement pump (P-500, Pharmacia, Sweden).
When deionized water was used as feed, it was pumped into the cell
directly. When a mixture solution was used as feed, it was diverted
into an injection column (Superloop 50 mL, Pharmacia, Sweden)
through a switching valve, where a given volume of the mixture
solution was pre-filled. The deionized water pumped continuously
into the column would push the mixture solution into the cell. The
transmembrane pressure (TMP) was continuously monitored by a
pressure sensor (MLH0408SB09A, Honeywell, USA) and the data
were collected automatically by a computer.

Taking into account the additional osmotic pressure due to
salt addition, a constant permeate flux mode was adopted in this
work to ensure a constant convective transport of organic solutes
towards the membrane at different salt concentrations. All exper-
iments were performed at a temperature of 25 ± 0.5°C and at a
stirring speed of 1400 ± 10 rpm.

A new membrane was used for each series of experiments. New
membranes were dipped in 50% ethanol solution for about
5 s to remove manufacturing residues from the membrane surface,
then soaked in deionized water for at least 12 h prior to use. Once
installed, each membrane was compacted at a high flux until the
transmembrane pressure (TMP) remained constant (3.5 MPa), and
then pure water permeability (λp) was measured as a function of
flux. About 12.8 mL feed solution was injected into stirred cell, and a
solution with the same salt concentration as permeate was injected
into the cell to ensure that the filtrations were performed in a way
similar to the total recycling operation mode (i.e., circulating the
permeate back to the stirred cell to keep the solution compositions
unchanged). In these cases, the permeate concentration was first
measured again after the filtration experiments to ensure that
membrane fouling was controlled at an acceptable level (less than
10%).

Retention experiments with solutions containing 2 g L⁻¹ glucose
were performed to determine the pore radius (rP) and the ratio
effective membrane thickness to porosity (Δx/e). To investi-
gate the influence of the presence of salt on the organic solutes
for some industrial fluids, experiments were carried out using con-
centrated feeds with 15 g L⁻¹ glucose, 30 g L⁻¹ IDA, and 10 g L⁻¹ Glu,
respectively and the salt concentrations used in these tests were
0.1–3.0 mol L⁻¹ NaCl.

4. Results and discussion

4.1. Characterization of membrane

As shown in Fig. 2, the experimental volumetric flux of glucose
solution as a function of TMP displays the same plots as pure water
flux for each membrane. Similar phenomena were also reported
by Bowen and Welfoot [37] in nanofiltration of NaCl solution. This

![Fig. 2. Experimental volumetric flux, Jv, as a function of TMP for pure water and glucose solution (2 g L⁻¹).](image)

suggested that over the whole range of pressures studied, concen-
tration polarization was not significant and osmotic pressure of
glucose could be negligible for the diluted solution. NF270 had
the highest permeate flux and solute rejection among these mem-
branes, as shown in Figs. 2 and 3. Moreover, glucose retentions
for NF270 and NF- were much higher than those for Desal-5 DL
and Nanomax50, as expected on the basis of the molecular weight
cut-off (MWCO) values presented in the literatures (see Table 1).
Fig. 3 also shows that the error for retention measurements was
the largest for Desal-5 DL, which could be ascribed to its wider
pore size distribution (MWCO of 150–300, Table 1) and a variation
of the mean pore size between the membrane samples used.

![Fig. 3. Intrinsic retention as a function of permeate flux for a single glucose solution (2 g L⁻¹).](image)
The mean pore size ($r_p$) and the ratio of effective membrane thickness to porosity ($\Delta x/\epsilon$) for the four membranes, calculated through fitting of experimental glucose retention using a mathematical model (Section 2.1), are listed in Table 4. NF270 and NF- had the smallest pore size and the calculated values of $r_p$ were 0.43 nm, the same as reported in references [18,38]. While the Desal-5 DL appeared to be a little more open, the $r_p$ value was 0.50 nm, very close to the result reported by Bowen and Mohammad [39]. Barge-man et al. [40] reported that the calculated mean pore radius for Desal-5 DL was equal to 0.45 nm, a little smaller than our result. In their estimation the data was obtained in cross flow mode while our work was carried out in dead-end mode. Tansel et al. [40] found that ions rejections by NF in dead-end mode were always lower than that in cross flow mode because of different shear force, and therefore, glucose retention in dead-end mode might be lower than that in cross flow mode, leading to the bigger pore size calculated in our work. Nanomax50, having a MWCO of 400 Da as reported by Antonucci et al. [29], was the most open membrane ($r_p = 0.73$ nm) used in the present work. Bowen et al. [41] presented a calculated value of $r_p$ (0.55 nm) much less than our result, which could be possibly explained by difference in pre-treatment procedure of membrane. The ratio of effective membrane thickness to porosity ($\Delta x/\epsilon$) for Nanomax50 was much greater than that for the other three membranes, for which the $\Delta x/\epsilon$ values were of the same order of magnitude (see Table 4).

### Table 4

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$r_p$ (nm)</th>
<th>$r_p$ in reference (nm)</th>
<th>$\Delta x/\epsilon$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF270</td>
<td>0.43</td>
<td>0.43 [38]</td>
<td>0.85</td>
</tr>
<tr>
<td>NF-</td>
<td>0.43</td>
<td>0.43 [18]</td>
<td>0.84</td>
</tr>
<tr>
<td>Desal-5 DL</td>
<td>0.50</td>
<td>0.45 [18], ~0.51 [39]</td>
<td>0.73</td>
</tr>
<tr>
<td>Nanomax50</td>
<td>0.73</td>
<td>0.55 [41]</td>
<td>0.50</td>
</tr>
</tbody>
</table>

#### 4.2. Effect of salt on glucose retention and flux

The effect of salt on membrane characteristics for NF270 and Desal-5 DL was determined by measuring glucose retention and flux at different salt concentrations. To provide guidance for practical application, concentrations of glucose and salt used were much higher than those in previous articles. Fig. 4 shows that glucose retention for NF270 decreased with increasing salt concentration, and model prediction was in good agreement with experimental data for single-solute, indicating that interaction between solute molecules could be negligible for the 15 gl$^{-1}$ glucose solution when no salt was added. However, with increasing salt concentration, salt effects (salting-out [17], salting-in [19], pore swelling [22]) on glucose molecules and membrane should be considered seriously, and the deviation between experimental retention and prediction increased significantly. A similar trend for salt effect on glucose retention was found for Desal-5 DL, as displayed in Fig. 5. But the prediction was a little different from the measured data for single-solute, this was possibly caused by a variation of the mean pore size between membrane samples of Desal-5 DL. Bouchoux et al. [12] also found that glucose retention differed distinctly from one membrane to another with three different samples of the Desal-5 DK membrane.

For a solution containing 15 gl$^{-1}$ glucose, concentration polarization and osmotic pressure could be no longer neglected, and the permeate flux was smaller than pure water flux, as shown in Figs. 6 and 7. Moreover, when salt was added, permeate flux decreased for both NF270 and Desal-5 DL. The flux reduction might result from the increasing osmotic pressure by the addition of salt, but this effect was very limited because with increasing salt concentration, salt rejection decreased as expected [18] (data not shown). Two other possible explanations were made: the first was...
that water viscosity in membrane pores was increased by salt ions, as reported by Bowen and Yousef [42]; the second was that bulk fluid viscosity increased with salt concentration (see Table 3), as a result, the back diffusion of glucose decreased, and consequently the concentration polarization of glucose was enhanced [43]. All these could result in a low flux. While for all salt concentrations studied, the relation between TMP and flux showed an excellent linearity, implying that filtration was operated below the “critical flux” [44].

4.3. Effect of salt on model parameters

Using the model in Section 2.1, the ratio of glucose to pore size ($\Delta x_\varepsilon$) and the ratio of effective membrane thickness to porosity ($\Delta x/\varepsilon$) were calculated, and the results are listed in Table 5, showing that with increasing salt concentration, $\lambda_i$ decreased while $\Delta x/\varepsilon$ increased for both NF270 and Desal-5 DL. From Eqs. (4) and (5), we could easily know that an increase of $\Delta x/\varepsilon$ enhanced solutes retention, but finally the retention decreased because the effect of $\lambda_i$ on retention was much more significant (smaller $\lambda_i$ would lower retention), and the positive effect of $\Delta x/\varepsilon$ was counteracted completely. With the help of the model and fitting results, supposing that membrane porosity was constant, salt effects were thought to be divided into three aspects: increasing pore size, decreasing solute size and increasing effective membrane thickness. These salt effects could be explained by different mechanisms. Firstly, membrane pores were supposed to be more open due to membrane swelling by salt, as presented by many researchers [2,14,18,22]. Similarly, membrane thickness would also increase if membrane surface swelled. However, to our knowledge, there has been no direct observation to prove that membrane pores or thickness increased when salt was added. Instead, Freger [20] detected that membrane thickness in 15% (w/v) NaCl solution at pH = 3 and pH = 10 was thinner than that in pure water at pH = 7, suggesting that membrane did swell when the properties of solution changed. Secondly, there was a partial dehydration of glucose molecules in the presence of salt ions because water would preferentially solvate ions, thus leading to thinning of the hydration layer around glucose molecules, decreasing the effective size of the solutes, as reported by Bouranene et al. [21]. Moreover, for a membrane having an inter-connected porous structure, smaller solutes were expected to go through longer paths because they could permeate through the smaller pores of network [21,45], thus enlarging the effective membrane thickness as solutes effective size reduced. These could reasonably explain why the fitted values of $\lambda_i$ decreased but $\Delta x/\varepsilon$ values increased with increasing salt concentration. Thirdly, when the number of salt ions in membrane pores grew, the probability of collision between ions and glucose molecules increased, thus prolonging the moving path of glucose when passing through membrane, therefore leading to greater $\Delta x/\varepsilon$ values.

By analyzing the data listed in Table 5, the relationships between model parameters and salt concentrations were found, as illustrated in Figs. 8 and 9. The increase of $\lambda_i$ showed a negative exponential relationship with an increase in salt concentration. The

![Fig. 7. Experimental volumetric flux for Desal-5 DL as function of TMP for glucose solutions with different salt concentrations (glucose = 15 gL\(^{-1}\)).](image1)

![Fig. 8. Variation of the solute to pore size ratio ($\lambda_i$) as a function of salt concentration. $\Delta \lambda = \lambda_0 - \lambda_i$, $\lambda_0$ is shown in Table 4.](image2)

![Fig. 9. Variation of the ratio of effective membrane thickness to porosity ($\Delta x/\varepsilon$) as a function of salt concentration. $A = \Delta x/\varepsilon$, $A_0$ represents $\Delta x/\varepsilon$ without salt, see Table 4.](image3)
The gap of \(\Delta x/e\) increased linearly with \(C_{\text{salt}}\), and the slope was related to its initial value. These relationships might be used to predict the retention of other organic solutes at different salt concentrations using following equations:

\[
\lambda_i = \lambda_0 - 0.10[1 - \exp(-1.10C_{\text{salt}})]
\]

\[
A = 0.74A_0C_{\text{salt}} + A_0
\]

where \(\lambda_0\) and \(A_0\) represent the ratio of solute to pore size and the ratio of effective membrane thickness to porosity \((\Delta x/e)\) in solution without salt, respectively.

### 4.4. Prediction by correction parameters

#### 4.4.1. Prediction for different membranes

Taking into account concentration polarization and salt effect, glucose retentions by NF- and Nanomax50 were predicted using the correction model, and the simulation results agree well with experimental data, as shown in Figs. 10 and 11. The effect of salt on glucose retention for NF- was obvious but, for Nanomax50, when salt concentration was more than 1 mol L\(^{-1}\), the variation of glucose retention by salt was negligible. This could be explained by significant increase of \(\Delta x/e\) with increasing salt concentration for Nanomax50 since high \(\Delta x/e\) would enhance the solutes retention according to Eqs. (4) and (5). From Eq. (9), it was found that the variation of \(\Delta x/e\) was proportion to the initial value of \(\Delta x/e\) \((A_0)\), and Nanomax50 had the biggest \(A_0\) in this study (see Table 4), leading to a different trend as compared with other membranes.

In many literatures [12,18,22], membrane swelling mechanism by salt was supposed to be caused by electrostatic repulsion between ions in electrical double layer at pore walls or salting-in effect [14]. Thus, swelling degree might be somewhat different for membranes with different physical and chemical properties. However, the good agreement between prediction and experimental data indicated that, for the four polymeric membranes with different surface materials and electric charges (see Table 1), salt effect on membranes was almost the same. This was contradictory to the explanation of membrane swelling. Thus a purely swelling explanation was not valid for our experimental findings. Another interpretation was proposed for increase of pore size by salt. It was well known that there were some water molecules adsorbed on the membrane pore walls [46,47], and the layer of adsorbed water would become thinner at high temperature, resulting in lower retention of solutes, as reported by Tsuru et al. [48]. Similarly, when a large number of salt ions existed in membrane pores, the layer of adsorbed water on pore walls would be thinner due to “salting-out” effect, and thus the effective pore size increased. Such interaction occurred between ions and water molecules, being scarcely affected by membrane characteristics.

#### 4.4.2. Prediction for different solutes

Bruni and Bandini [16] found that, at salt concentration higher than 0.005 mol L\(^{-1}\) NaCl, the proper membrane charge due to the acid/base dissociation was completely screened by the salt ions. Thus, for the highly concentrated salt in the present study, electrostatic repulsion effects between charged solutes and membranes could be negligible and the model could also be used to predict retentions of IDA and Glu at high salt concentration. The pH of solutions was all adjusted to 5.2 ± 0.1 according to practical feeds. The Stokes radius of IDA and Glu in Table 2 could not be used for modeling at pH = 5.2 because these data were obtained at pH of their isoelectric point, while the hydration radius around amphoteric solutes correlated well with charge density [49].

The values of \(\lambda_0\) and \(A_0\) for amphoteric solutes could be calculated using experimental data. By fitting retention data at a salt concentration for NF270, \(\lambda_i\) and \(A_i\) were obtained, and then using Eqs. (8) and (9), \(\lambda_0\) and \(A_0\) were calculated (for IDA, \(A_0 = 0.87, A_0 = 0.26\ \mu m\); for Glu, \(A_0 = 0.85, A_0 = 0.91\ \mu m\)). The results showed that IDA size was greater than Glu size, and effective membrane thickness of IDA was smaller than that of Glu, which were not consistent with the \(r_s\) data listed in Table 2. The reason was that the isoelectric points of IDA and Glu were 2.1 and 3.22, respectively (see Table 2), and at pH = 5.2, the charge density of IDA was more than that of Glu, inducing thicker hydration layer around IDA [49].

With the calculated \(\lambda_0\) and \(A_0\), retentions of IDA and Glu at different salt concentrations were predicted by Eqs. (4), (8) and (9), and simulation results agreed well with experimental data, as displayed in Figs. 12 and 13. As compared with retention plots of Glu, IDA showed lower retention at low flux though its effective size was bigger. This could be attributed to a higher diffusion coefficient for IDA (see Table 2), and diffusive transport was dominant at low flux. This model could well predict retention of charged solutes at high salt concentration, but it could not be used for solution without salt because electrostatic repulsion was not considered in this model. As highly concentrated salt are commonly encountered in practical solutions, the proposed models would be very convenient for practical applications.
Influence of highly concentrated salt on retention of organic solutes by nanofiltration (NF) polymeric membranes was investigated, and an obvious decrease of solutes rejection in the presence of salt was found. Based on the extended Nernst–Planck equation, a model was developed to estimate the salt effect on membrane and solutes, and the results showed that, with increasing salt concentration, the solute to pore size ratio ($\lambda_i$) decreased while the ratio of effective membrane thickness to porosity ($\Delta x/\varepsilon$) increased. Therefore, the salt effect may include decreasing solutes size, increasing membrane pore size, and increasing effective membrane thickness. Moreover, for different membranes examined (NF270, NF-, Desal-5 DI, Nanomax50), the salt effect was almost the same for glucose retention. Using the correction model, retentions of iminodiacetic acid (IDA) and glutamic acid (Glu) at different salt concentrations were predicted, and simulation results agreed well with the experimental data because at high salt concentrations, electrostatic repulsion effect between charged solutes and membranes was completely offset by salt ions.

Several hypotheses were provided to explain the change of model parameters by highly concentrated salt. Firstly, with increasing salt concentration, pore size could increase since the hydration layer on pore walls became thinner due to salting-out effect. Secondly, a partial dehydration of glucose molecules in the presence of salt ions (Hofmeister effect) could result in a decrease of solutes effective size (e.g., Stokes radius). Thirdly, the points that smaller solutes were expected to flow through longer paths in the porous network of membrane, and that collision by salt ions prolonged the moving path of organic solutes, could lead to an increase of effective membrane thickness. As a supplementary for membrane swelling hypothesis, these could well explain the decrease of organic solutes retention by salt and provide valuable guidance for future modeling.

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### List of symbols

- **$A_0$** the ratio of effective membrane thickness to porosity without salt
- **$A_i$** the ratio of effective membrane thickness to porosity
- **$c_1$** solute concentration in the pores (g L$^{-1}$, mol L$^{-1}$)
- **$C_{i,f}$** solute concentrations in feed (g L$^{-1}$, mol L$^{-1}$)
- **$C_{i,p}$** solute concentration in permeate (g L$^{-1}$, mol L$^{-1}$)
- **$C_{i,m}$** solute concentration at membrane surface (g L$^{-1}$, mol L$^{-1}$)
- **$C_{salt}$** salt concentration in feed (mol L$^{-1}$)
- **$D_{L,\infty}$** diffusion coefficient of solute at infinite dilution (m$^2$ s$^{-1}$)
- **$J_i$** molar flux of solute (mol m$^{-2}$ s$^{-1}$)
- **$J_V$** volumetric flux per unit area of membrane (m$^3$ m$^{-2}$ h$^{-1}$)
- **$k$** mass transfer coefficient (m$^{-1}$ s$^{-1}$)
- **$K_{i,c}$** correctly hydrodynamic coefficient for diffusion
- **$K_{i,d}$** correctly hydrodynamic coefficient for convection
- **$P_e$** Peclot number
- **$r$** radius of the stirred cell (m)
- **$r_p$** effective pore radius (m)
- **$r_s$** effective solute radius (m)
- **$R_{int}$** intrinsic rejection of solute
- **$V$** solvent velocity inside the pores (m s$^{-1}$)
- **$\Delta x$** effective membrane thickness (m)

### Greek symbols

- **$\varepsilon$** membrane porosity
- **$\lambda_0$** ratio of solute to pore size without salt
- **$\lambda_i$** ratio of solute to pore size
- **$\psi$** kinematic viscosity (m$^2$ s$^{-1}$)
- **$\Omega$** steric partitioning coefficient
- **$\psi$** geometry coefficient of stirred cell
- **$\omega$** angular velocity (rad s$^{-1}$)

### References


