EVALUATION OF PORE STRUCTURE AND ELECTRICAL PROPERTIES OF NANOFILTRATION MEMBRANES

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Structural parameters and electrical properties of nanofiltration membranes (Desal-5, NF-40, NTR7450 and G-20) were determined with permeation experiments of aqueous solutions of neutral solutes (alcohols and saccharides having different molecular weights) and sodium chloride. The pore radii of these nanofiltration membranes were estimated to range from 0.4 to 0.8 nm based on the steric-hindrance pore model. Neither the constant surface charge density nor the constant surface electrical potential were suitable for interpreting NaCl concentration dependency of reflection coefficients. The fixed charge density of these membranes was evaluated on the basis of the Teorell- Meyer- Sievers model; a simple empirical equation was proposed to represent the dependency of the fixed charge density on NaCl concentration.

Introduction

Recently, much attention has been paid to nanofiltration (NF) membranes4,12,13,21. They were originally applied to reject electrolytes and obtain ultra-pure water with high volume flux at low operating pressure, because most membranes have either positive or negative charge due to their composition. Meanwhile, since NF membranes possess molecular weight cut-off (MWCO) of about a few hundreds to a few thousands, which is intermediate between reverse osmosis (RO) membranes and ultrafiltration (UF) membranes, they have also been used to separate or concentrate organic solutes. Therefore, it is possible to assume that NF membranes have a pore structure similar to those of UF membranes. One can assume that NF membranes consist of a bundle of cylindrical capillaries with structural parameters (pore radius \( r_p \), the ratio of membrane porosity to membrane thickness \( A_p / \Delta x \)) and electrical properties, such as the surface charge density \( q_c \). Although NF membranes are finding increased applicability in various fields, their transport mechanism is not yet well understood because of their unknown structure. In order to predict the transport performances of neutral solutes and electrolytes through a NF membrane, it is important to determine its structural parameters and electrical properties.

To estimate the structural parameters of a membrane, a pore model was developed and applied by Nakao and Kimura10 and Nakao9 to the separation systems of aqueous solutions of a single organic solute and UF membranes. By considering both the steric-hindrance effect of solute and the interaction between solute and membrane wall, the membrane parameters (reflection coefficient \( \sigma \) and solute permeability \( P \)) were interpreted with the structural parameters. Nakao and Kimura10 successfully applied the steric-hindrance pore (SHP) model to estimate \( r_p \) and \( A_p / \Delta x \) of UF membranes in terms of the membrane parameters obtained from permeation experiments of different neutral solutes.

The electrical properties of membranes can be described by the Teorell- Meyer- Sievers (TMS) model3,8,24 and the Space Charge (SC) model2,11,14,15,23. The TMS model, which assumes uniform distribution of fixed charges in a membrane, was used to investigate the membrane potential9, the effective fixed charge density24 and salt rejection3 of charged membranes. In our previous papers, the TMS model has been successfully applied to predict electrolyte rejection by charged UF membranes in aqueous solutions of both single electrolyte and mixtures by combining with the extended Nemst-Planck equation19,22. The pore radii of charged UF membranes were also estimated from the SHP model to be a few nanometers5,6,18, which seems to be larger than those of NF membranes. On the other hand, the SC model takes into account the radial distributions of electrical potential and ion concentration, therefore it seems that the SC model is more realistic than the TMS model in describing various transport phenomena of electrolytes through charged capillaries, especially for membranes with large pore radii. In our preceding paper23, the SC model has been applied to predict transport performance of aqueous solutions of single electrolyte through NF membranes. Comparison of the SC model with its simplified models and the TMS model has been also carried out. For the case of a dimensionless electrical potential gradient on pore surface less than 1.0, the TMS model coincides with the SC model.

So far, the structural parameters and electrical prop-

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erties of NF membranes have not been investigated. In the present study, the structural parameters \( r_p \) and \( A / \Delta x \) of four kinds of NF membranes (NF-40, NTR7450, Desal-5 and G-20) were estimated from permeation experiments of different neutral solutes on the basis of the SHP model; the electrical properties were investigated from the dependency of rejection of sodium chloride with different concentrations on volume flux across the membranes based on the TMS model.

1. Theoretical

Transport phenomena of UF, NF and RO membranes in pressure-driven processes can be described by irreversible thermodynamics. The volume flux \( (J_v) \) and the solute flux \( (J_s) \) through a membrane were originally introduced by Kedem and Katchalsky\(^7\) as follows:

\[
\begin{align*}
J_v &= L_p (\Delta P - \sigma \cdot \Delta x) \\
J_s &= P \cdot (c_m - c_p) + (1 - \sigma) \cdot J_v c
\end{align*}
\]

(1)

where \( \sigma \), \( P \) and \( L_p \) are the membrane parameters reflection coefficient, solute permeability and pure water permeability, respectively. When high concentration difference between the retentate and the permeate exists, Spiegler and Kedem\(^9\) expressed Eq. (1) in a differential form as follows,

\[
J_s = -P' \frac{dc}{dx} + (1 - \sigma) J_v c
\]

(2)

\( P' \) is local solute permeability defined as \( P' = P \cdot \Delta x \).

Integrating Eq. (2) across the membrane thickness yields

\[
R = 1 - \frac{c_p}{c_m} = \frac{\sigma (1 - F)}{(1 - \sigma F)}
\]

where

\[
F = \exp \left[ - \frac{1 - \sigma}{P'} J_v \right].
\]

(3)

Equation (3) is the well-known Spiegler-Kedem equation. From Eq. (3), one can see that \( \sigma \) corresponds to maximum rejection at infinite volume flux. \( \sigma \) and \( P \) can be determined from experimental data of \( R \) as a function of \( J_v \) by a best-fit method. However, this model assumes that the membrane is a black box and no information about the transport mechanism can be obtained from it. Therefore, several transport models have been proposed to interpret \( \sigma \) and \( P \) by means of the membrane structure and the electrical properties.

For a system of single neutral solute and a NF membrane, \( \sigma \) and \( P \) can be calculated based on the SHP model\(^9,10\):

\[
\begin{align*}
\sigma_s &= 1 - H_F S_F \\
P_s &= H_D S_D D_3 (A_k / \Delta x)
\end{align*}
\]

(4)

\( H_F \) and \( H_D \) are the steric parameters related to the wall correction factors of the solute in convection and diffusion conditions, respectively, and expressed by the following equations.

\[
\begin{align*}
H_F &= 1 + 16 / 9 \cdot \eta^2 \\
H_D &= 1
\end{align*}
\]

(6)

where \( \eta = r_s / r_p \)

\( \eta \) is defined as the ratio of solute radius \( (r_s) \) to pore radius \( (r_p) \). \( S_F \) and \( S_D \) are the averaged distribution coefficients determined only by the steric effect of the solute in convection and diffusion conditions, respectively, and are expressed as follows.

\[
\begin{align*}
S_F &= (1 - \eta)^2 [2 - (1 - \eta)^2] \\
S_D &= (1 - \eta)^2
\end{align*}
\]

(7)

To a system of a 1-1 type electrolyte and the NF membrane with negative charge polarity, \( \sigma \) and \( P \) can be expressed on the basis of the TMS model\(^3,23\) with the following equations:

\[
\sigma_s = 1 - \frac{2}{(2\alpha - 1)\xi + (\xi^2 + 4)^{1/2}}
\]

(8)

\[
P_s = D_3 (1 - \sigma) (A_k / \Delta x)
\]

(9)

where \( \xi = X / c \)

\( \xi \) is defined as the ratio of fixed charge density \( (X) \) of membrane to electrolyte concentration \( (c) \) at the membrane surface\(^3,23\).

In the research field of interface and colloid chemistry, the electrical properties of a charged membrane are usually related to the assumption of constant surface charge density \( (q_u) \) or constant surface electrical potential \( (\Psi_{ew}) \)\(^1\). By assuming a NF membrane with pore radius \( (r_p) \) and constant surface charge density \( (q_u) \), \( X \) can be expressed as follows.

\[
X = \frac{2\pi r_p q_u}{\alpha r_p^2} = \frac{2 \sqrt{\psi_{ew}}}{r_p F}
\]

(11)

\( q_u \) in the above Eq. (11) can be expressed with the surface electrical potential \( (\Psi_{ew}) \), based on the Gouy-Chapman electrical double layer theory\(^1\) in the following equation.

\[
q_u = \sqrt{2RT \varepsilon_0 \varepsilon_r \cdot \alpha \sinh \left( - \frac{\varepsilon_r F \Psi_{ew}}{2RT} \right)}
\]

(12)

For this case, \( q_u \) is directly proportional to the square root of electrolyte concentration.

2. Experimental

The structural parameters and the electrical properties of NF membranes can be evaluated in the following procedures.

First, permeation experiments of two types of aqueous solutions were carried out: a) aqueous solutions of neutral solutes with different Stokes radii and b) aqueous solutions of sodium chloride of different concentrations. The observed rejection at a certain volume flux is corrected
Table 1. Diffusivities and Stokes radii of neutral solutes

<table>
<thead>
<tr>
<th>solute</th>
<th>molecular weight [g mol⁻¹]</th>
<th>$D_ν$ [$10^{-6}$ m² s⁻¹]</th>
<th>$r_ν$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyl alcohol</td>
<td>46</td>
<td>1.24</td>
<td>0.198</td>
</tr>
<tr>
<td>isopropyl alcohol</td>
<td>60</td>
<td>1.02</td>
<td>0.241</td>
</tr>
<tr>
<td>n-butyl alcohol</td>
<td>74</td>
<td>0.95</td>
<td>0.258</td>
</tr>
<tr>
<td>t-butyl alcohol</td>
<td>74</td>
<td>0.88</td>
<td>0.279</td>
</tr>
<tr>
<td>glucose</td>
<td>180</td>
<td>0.67</td>
<td>0.365</td>
</tr>
<tr>
<td>saccharose</td>
<td>342</td>
<td>0.52</td>
<td>0.471</td>
</tr>
<tr>
<td>raffinose</td>
<td>504</td>
<td>0.42</td>
<td>0.584</td>
</tr>
<tr>
<td>α-cyclodextrin</td>
<td>972</td>
<td>0.35</td>
<td>0.701</td>
</tr>
</tbody>
</table>

Table 2. Pure water permeabilities of NF membranes and observed rejections of glucose and NaCl

<table>
<thead>
<tr>
<th>membranes</th>
<th>Desal-5</th>
<th>NF-40</th>
<th>NTR7450</th>
<th>G-20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_p$ [$10^{-9}$ m³ s⁻¹ MPa⁻¹]</td>
<td>1.00</td>
<td>0.80</td>
<td>2.00</td>
<td>1.50</td>
</tr>
<tr>
<td>$A_p/Δx$ [10⁻³ m³]</td>
<td>4.45</td>
<td>2.80</td>
<td>2.90</td>
<td>1.67</td>
</tr>
<tr>
<td>$R_{on}$ of glucose [-]</td>
<td>0.03</td>
<td>0.88</td>
<td>0.13</td>
<td>0.10</td>
</tr>
<tr>
<td>$R_{on}$ of NaCl [-]</td>
<td>0.49</td>
<td>0.35</td>
<td>0.35</td>
<td>0.13</td>
</tr>
</tbody>
</table>

All experiments were carried out at applied pressure of 0.5 MPa; observed rejections of glucose and sodium chloride were measured with feed concentrations of 100 ppm and 30 mol m⁻³, respectively. $A_p/Δx$ were calculated from $L_p$ by using Eq. (13).

to obtain the real rejection based on the concentration polarization model(9).

Secondly, the dependency of real rejection on volume flux is studied to obtain the membrane parameters (reflection coefficient $σ$ and solute permeability $P$) by a best-fit method using the Spiegler-Kedem Eq. (3)(16).

Finally, by comparison of the membrane parameters obtained from several experiments with those from the corresponding models mentioned in the section of Theoretical, the membrane structural parameters ($r_p$ and $A_p/Δx$) are estimated by the SHP model using Eqs. (4) to (7) and the fixed charge densities ($X$) are evaluated by the TMS model using Eqs. (8) to (12).

2.1 Membranes and solutes

Four kinds of NF membranes, NF-40 (Film Tec.), NTR7450 (Nitto Denko), Desal-5 and G-20 (Desalination System Inc.), were employed. They are flat-sheet type and thin film composite membranes, made by interfacial polymerization on a polysulfone base. One can consider that these commercial NF membranes are negatively charged membranes because their barrier layers are made of polyamide (NF-40) or sulfonated polysulfone (NTR7450, G-20 and Desal-5)(12).

Alcohols (ethyl alcohol, isopropyl alcohol, n-butyl alcohol and t-butyl alcohol) and saccharides (glucose, saccharose, raffinose and α-cyclodextrin) were chosen as neutral solutes as listed in Table 1. They were from Wako Pure Chemical Industries and Sigma, and employed without further purification. The Stokes radii in Table 1 were calculated with the Stokes-Einstein equation ($r_p = kT/6πμD_ν$) from literature diffusivities in dilute aqueous solution. Their concentrations were measured with a total organic carbon analyzer (TOC5000, Shimazu). Sodium chloride was used to estimate the charge density of these NF membranes. NaCl concentration was measured with an electrical conductivity meter.

2.2 Permeation experiments

The experimental apparatus was essentially the same as shown in our previous paper(9). The test cell for permeation experiments was made by Nitto Denko Corporation. The area of the membrane used was 35.3 cm². Both the retentate and the permeate were recycled to the feed tank to keep the feed concentration constant and the temperature was controlled at 25 °C. The feed concentration of neutral solutes was kept at 100 ppm to prevent flux change caused by osmotic pressure; the NaCl concentration was varied from 10 to 500 mol m⁻³. The feed flow rate was held at 6.0 × 10⁻³ m³ min⁻¹ and the real rejection was calculated from the observed rejection based on the concentration polarization model(9). The applied pressure across the membrane ranged from 0.3 to 0.8 MPa for G-20 and NTR7450 membranes and from 0.5 to 1.6 MPa for Desal-5 and NF-40 membranes according to the magnitude of their pure water permeabilities ($L_p$). The pure water used for all experiments was purified by passing through reverse osmosis and ion-exchange modules (Milli-RX12, Millipore Corp.).

3. Results and Discussion

3.1 Determination of structural parameters

The pure water permeabilities ($L_p$) of the four kinds of NF membranes ranged from 0.8 to 2.0 × 10⁻⁵ m s⁻¹ MPa⁻¹ as shown in Table 2. The permeation experimental results of different neutral solutes at the applied pressure of 0.5 MPa indicated that observed rejections depend on the molecular weights of solutes and the approximate MWCOSs of these NF membranes are estimated to range from 200 to 2,000 g mol⁻¹ as shown in Fig. 1.

Figure 2 shows the dependency of the real rejection of NTR7450 membrane on volume flux. The larger the molecular weight of the solute, the higher the real rejection. From these data, the membrane structural parameters ($r_p$ and $A_p/Δx$) were evaluated as follows. First, based on the
**Fig. 2** Reaction of NTR7450 membrane as a function of volume flux at the feed concentration of 100 ppm with different solutes: ○... glucose, △... saccharose, ◇... raffinose, and ▽... α-cyclodextrin.

The curves were fitted by the Spiegler-Kedem equation

**Table 3.** $\sigma$ and $P$ of neutral solutes and $r_p$ and $A_k/\Delta x$ of NF membranes determined from the SHP model

<table>
<thead>
<tr>
<th>membrane</th>
<th>solute</th>
<th>$\sigma$ [L]</th>
<th>$P$ [10$^6$ m$^{-1}$ s$^{-1}$]</th>
<th>$r_p$ [nm]</th>
<th>$A_k/\Delta x$ [10$^6$ m$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyl alcohol</td>
<td>0.33</td>
<td>156</td>
<td>0.42</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>isopropyl alcohol</td>
<td>0.60</td>
<td>81.2</td>
<td>0.38</td>
<td>0.500</td>
<td></td>
</tr>
<tr>
<td>Desal-5</td>
<td>n-butyl alcohol</td>
<td>0.49</td>
<td>61.0</td>
<td>0.45</td>
<td>0.510</td>
</tr>
<tr>
<td></td>
<td>$t$-butyl alcohol</td>
<td>0.87</td>
<td>26.3</td>
<td>0.34</td>
<td>0.330</td>
</tr>
<tr>
<td></td>
<td>glucose</td>
<td>0.98</td>
<td>3.86</td>
<td>0.39</td>
<td>0.750*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.40 (av.)</td>
<td>0.460 (av.)</td>
</tr>
<tr>
<td>NF-40</td>
<td>ethyl alcohol</td>
<td>0.24</td>
<td>74.5</td>
<td>0.50</td>
<td>0.190</td>
</tr>
<tr>
<td></td>
<td>isopropyl alcohol</td>
<td>0.43</td>
<td>46.0</td>
<td>0.45</td>
<td>0.210</td>
</tr>
<tr>
<td></td>
<td>$n$-butyl alcohol</td>
<td>0.38</td>
<td>40.6</td>
<td>0.50</td>
<td>0.235</td>
</tr>
<tr>
<td></td>
<td>$t$-butyl alcohol</td>
<td>0.80</td>
<td>21.3</td>
<td>0.35</td>
<td>0.170</td>
</tr>
<tr>
<td></td>
<td>glucose</td>
<td>0.95</td>
<td>4.34</td>
<td>0.41</td>
<td>0.180*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.45 (av.)</td>
<td>0.200 (av.)</td>
</tr>
<tr>
<td></td>
<td>saccharose</td>
<td>0.65</td>
<td>86.8</td>
<td>0.69</td>
<td>1.550</td>
</tr>
<tr>
<td></td>
<td>raffinose</td>
<td>0.90</td>
<td>39.3</td>
<td>0.68</td>
<td>3.400*</td>
</tr>
<tr>
<td>NTR-7450</td>
<td>α-cyclodextrin</td>
<td>0.99</td>
<td>17.6</td>
<td>0.70</td>
<td>1.350 (av.)</td>
</tr>
<tr>
<td></td>
<td>glucose</td>
<td>0.31</td>
<td>72.7</td>
<td>0.80</td>
<td>0.370</td>
</tr>
<tr>
<td></td>
<td>saccharose</td>
<td>0.50</td>
<td>45.4</td>
<td>0.80</td>
<td>0.520</td>
</tr>
<tr>
<td>G-20</td>
<td>raffinose</td>
<td>0.73</td>
<td>23.3</td>
<td>0.80</td>
<td>0.760</td>
</tr>
<tr>
<td></td>
<td>α-cyclodextrin</td>
<td>0.83</td>
<td>7.28</td>
<td>0.84</td>
<td>1.350*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.80 (av.)</td>
<td>0.550 (av.)</td>
</tr>
</tbody>
</table>

* These data were excepted for calculation of average $A_k/\Delta x$.

dependency of real rejection on volume flux, the membrane parameters ($\sigma$ and $P$) were determined by a best-fit method using the Spiegler-Kedem Eq. (3) and the results were listed in Table 3 together with those of other NF membranes employed. Then, the most suitable pore radius, to each solute was calculated in reverse from its membrane parameters ($\sigma$ and $P$) based on the SHP model$^{10}$ by Eqs. (4), (6) and (7). The average pore radii of Desal-5, NF-40, NTR7450 and G-20 membranes were estimated to be 0.40, 0.45, 0.70 and 0.80 nm, respectively, as shown in Table 3.

As shown in Fig. 3, the experimental values of reflec-

**Fig. 3** Reflection coefficient as a function of ratio of Stokes radius to pore radius for four kinds of NF membranes. The curve was calculated from the SHP model by Eqs. (4) to (7).

**Fig. 4** shows that the real rejection of NaCl

**3.2 Determination of electrical properties**

At an applied pressure of 0.5 MPa, the observed rejections of sodium chloride of 30.0 mol m$^{-3}$ by the four kinds of NF membranes ranged from 0.13 to 0.49 as shown in Table 2.
by the NF-40 membrane as a function of volume flux was dependent upon NaCl concentration. As was mentioned in our previous paper\(^3\), the higher the NaCl concentration was, the lower the real rejection was. The real rejection approached zero when NaCl concentration was more than about 1,000 mol-m\(^{-3}\), whereby the steric hindrance effect of NaCl became negligible. By a best-fit method using the Spiegler-Kedem Eq. (3), the membrane parameters were obtained from the dependency of NaCl real rejection on volume flux.

The reflection coefficients (\(\sigma\)) of NF-40 membrane were plotted against NaCl concentrations in Fig. 5. Based on the TMS model from Eqs. (8) and (10), the fixed charge densities (\(X\)) of the four kinds of NF membranes was determined from the NaCl concentration dependency of \(\sigma\) as shown in Fig. 6. Figure 6 indicates that \(X\) is dependent on NaCl concentration. As has been confirmed by many researchers\(^8, 17, 18, 24\), with various experiments such as measurements of membrane potential and distribution coefficients of ions, \(X\) of charged membranes varies with concentrations and kinds of electrolytes. The reason is not yet clear.

On the other hand, the reflection coefficients (\(\sigma\)) can be calculated from the TMS model with Eqs. (8) and (10) under the assumptions of constant surface charge density represented by Eq. (11) and constant surface electrical potential represented by Eq. (12). NaCl concentration dependency of \(\sigma\) for the cases of constant surface charge density a) \((q_a = 0.012 \; C \cdot m^{-2})\) and b) \((q_a = 0.030 \; C \cdot m^{-2})\), and the cases of constant surface electrical potential, c) \((\psi_a = 0.0257 \; V)\) and d) \((\psi_a = 0.0514 \; V)\), were plotted in Fig. 5. The comparison of theoretical curves with experimental values of \(\sigma\) indicates that neither the constant surface charge density, nor the constant surface electrical potential is suitable for understanding the salt concentration dependency of \(\sigma\). However, one can see that the theoretical curve of case b) \((q_a = 0.030 \; C \cdot m^{-2})\) was a good approximation to experimental values if NaCl concentration was high, while the theoretical curve of case d) \((\psi_a = 0.0514 \; V)\) was a good approximation if NaCl concentration was low. The assumptions of constant surface charge density and constant surface electrical potential were found to be applicable locally for the range of high and low concentrations, respectively, for all NF membranes employed. Therefore, introducing effective fixed charge density (\(\phi X\)) into Eq. (10) instead of \(X\) enables interpretation of its dependency on concentration (\(c\)) of NaCl. The relation between \(\phi X\) and \(c\) of NaCl can be estimated by the following empirical equation.

\[
\phi X = \frac{Ac^{0.5}}{1 + Bc^{0.5}}
\]  

(14)

At low salt concentration (\(c << 1/B^2\)), \(\phi X\) is approximately proportional to the square root of concentration, which can be interpreted by the assumption of constant surface electrical potential from Eq. (12). The surface electrical potential can be approximately estimated from parameter A by using Eqs. (11), (12) and (14). At very high salt concentration (\(c >> 1/B^2\)), \(\phi X\) approaches a maximum
value \( A/B \) that corresponds to fixed charge density. Table 4 shows the empirical parameters \( A \) and \( B \) obtained from the salt concentration dependency of \( \phi X \) by the least squares method. As shown in Fig. 6, the fitted curves of Eq. (14) express the salt concentration dependency of \( \phi X \) of the four kinds of NF membranes employed very well.

The effective fixed charge density \( (\phi X) \) of the four kinds of NF membranes are shown as a function of NaCl concentration in Fig. 6. At the same salt concentration, the order of \( \phi X \) from low to high was given as: G-20 < NTR7450 < NF-40 < Desal-5, while the order of pore radii from small to large was presented in reverse as follows: Desal-5 < NF-40 < NTR7450 < G-20. It indicated that the membrane with smaller \( r_p \) have higher \( \phi X \). As can be explained by Eq. (11), the four kinds of NF membranes have similar values of surface charge density at the same salt concentration. For the experimental range of NaCl concentration, combining \( \phi X \) with \( r_p \) for four kinds of NF membranes indicates that the dimensionless electrical potential gradient on pore surface is less than 1.0. Therefore the simplified calculation based on the TMS model instead of the SC model is sufficient for the case of NF membranes on the basis of the conclusions of our preceding paper.

Conclusions

The pore radii and fixed charge density of practical NF membranes (Desal-5, NF-40, NTR7450 and G-20) were evaluated from permeation experiments of different neutral solutes of sodium chloride. The membrane parameters were obtained by a best-fit method using the Spiegler-Kedem equation from the above experiments. The pore radii of these NF membranes were estimated to range from 0.4 to 0.8 \( \text{nm} \), based on the SHP model from reflection coefficients of different neutral solutes. Neither the constant surface charge density nor the constant surface electrical potential was suitable for explaining the dependency of reflection coefficients of NaCl on its concentration. The fixed charge density of these NF membranes was estimated on the basis of the TMS model and a simple empirical equation was proposed to represent the dependency of effective fixed charge density on NaCl concentration.

Nomenclature

\( A, B \) = empirical parameters in Eq. (14)
\( A_1 \) = membrane porosity [-]
\( c \) = concentration \( \text{[mol-m}^{-3}\text{]} \)
\( D_i \) = diffusivity of \( i \)-th ion \( \text{[m}^2\text{-s}^{-1}\text{]} \)
\( D_S \) = solute diffusivity for neutral molecule or generalized diffusivity for 1-1 type of electrolyte defined as \( D_S = 2D_iD_j/(D_i+D_j) \) \( \text{[m}^2\text{-s}^{-1}\text{]} \)
\( F \) = Faraday constant \( \text{[C-mol}^{-1}\text{-s}^{-1}\text{-Pa}^{-1}\text{-m}^{-1}\text{-K}^{-1}\text{-s}^{-1}\text{-mm}^{-1}\text{-V}^{-1}\text{-m}^{-1}\text{-s}^{-1} \)
\( H_D \) = steric parameter related to wall correction factors in diffusion condition [-]
\( H_F \) = steric parameter related to wall correction factors in convection condition [-]
\( J_i \) = solute or ion flux \( \text{[mol-m}^{-2}\text{-s}^{-1}\text{]} \)
\( J_v \) = volume flux \( \text{[mol-m}^{-2}\text{-s}^{-1}\text{]} \)
\( J_p \) = pure water permeability \( \text{[mol-m}^{-2}\text{-s}^{-1}\text{-Pa}^{-1}\text{-m}^{-1}\text{-s}^{-1}\text{-mm}^{-1}\text{-V}^{-1}\text{-m}^{-1}\text{-s}^{-1} \)
\( P \) = applied pressure or solute permeability \( \text{[Pa]} \)
\( q_e \) = surface charge density \( \text{[C-m}^{-2}\text{]} \)
\( r_p \) = pore radius \( \text{[m]} \)
\( r_s \) = Stokes radius of neutral solute \( \text{[m]} \)
\( R \) = real rejection or gas constant \( \text{[8.314]} \)
\( R_{obs} \) = observed rejection [-]
\( S_D \) = distribution coefficient of solute in diffusion condition [-]
\( S_F \) = distribution coefficient of solute in convection condition [-]
\( T \) = temperature \( \text{[K]} \)
\( X \) = fixed charge density \( \text{[mol-m}^{-2}\text{]} \)
\( \Delta x \) = membrane thickness \( \text{[m]} \)
\( \varepsilon_i \) = electrochemical valence of \( i \)-th ion [-]
\( \alpha \) = transport number of cation in free solution defined as \( \alpha = D_i/(D_i+D_j) \) [-]
\( \varepsilon_0 \) = dielectric constant of vacuum \( (8.8542 \times 10^{-12}) \) \( \text{[C}^2\text{-J}^{-1}\text{-m}^{-1}\text{-s}^{-1}\text{-mm}^{-1}\text{-V}^{-1}\text{-m}^{-1}\text{-s}^{-1} \)
\( \varepsilon_r \) = relative dielectric constant of water \( (78.303) \) [-]
\( \eta \) = ratio of solute radius to pore radius [-]
\( \mu \) = viscosity of solution \( \text{[Pa-s]} \)
\( v_e \) = stoichiometric coefficient of electrolyte [-]
\( \Delta \pi \) = osmotic pressure difference defined as \( \Delta \pi = RTv_i(\gamma_+-\gamma_-)(c_+-c_-) \) \( \text{[Pa]} \)
\( \sigma \) = reflection coefficient [-]
\( \phi X \) = effective fixed charge density \( \text{[mol-m}^{-2}\text{]} \)
\( \psi \) = surface electrical potential \( \text{[V]} \)
\( \zeta \) = ratio of fixed charge density to salt concentration [-]

Literature Cited

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