Influence of ion size on the prediction of nanofiltration membrane systems

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Abstract

The major ion partitioning effect may be due to steric, Donnan and dielectric exclusion which are collectively described by the Donnan steric pore model and dielectric exclusion (DSPM-DE). The effect of various ion size on charged solute rejection was studied using the DSPM-DE model. Sodium chloride, sodium sulphate and magnesium chloride were used as model solute. Born solvation energy was used to investigate dielectric exclusion. The effect of variation of physical properties such as viscosity and dielectric constant inside the nanopore was evaluated using the various ionic sizes. Stokes-Einstein, Born’s effective, cavity and Pauling radii were used as ionic size throughout the simulation. It was found that these radii predict the physical properties differently and hence have profound effect on the model predictions. There is a significant variation in the prediction of charge density present in the surface of the membrane using the various ionic radii. The effect of pore size distribution of each ion was studied using log-normal probability density function for both positive and negative charge density, which also showed variation in the prediction. The increase of upper limit of truncated pore size distribution ($r_{\text{max}}$) has significant influence on decreasing the solute rejection.

Keywords: Nanofiltration; Stokes-Einstein radius; Born’s effective radius; Pauling radius; Pore size distribution

1. Introduction

The use of nanofiltration (NF) membrane technology has increased rapidly in the chemical, biological and desalination industries, since it overcomes several operational problems associated with conventional techniques. NF comes in between reverse osmosis (RO) and ultrafiltration (UF). The major separation in RO and UF is due to solution diffusion and sieving effect. NF takes into account both solution diffusion, as well as sieving effect, Donnan, dielectric exclusion and...
in addition, electromigration, which makes it useful to separate both charged solute and organic solutes.

The era of NF technology started in 1970s when membrane processes are changing the energy intensive process. Energy consumption in RO was more due to high operating pressure and the permeate flux was very low. An alternate membrane process was searched which can produce high permeate flux with operation in lower pressure. Initially, such membranes were called low pressure reverse osmosis. Due to the advent of sophisticated instrument such as Atomic Force Microscope (AFM) revealed that these membranes possess pores in the scale of nano which renamed as NF [1]. Successful implementation of NF technology as pretreatment to seawater has gained considerable importance in this decade. Usually the product recovery in convention seawater reverse osmosis (SWRO) is 28% and operating pressure is around 65 bar. When NF membranes were used in the pretreatment section of conventional RO, the product recovery increased to 36.4% with reduction in operating pressure to 54 bar which resulted in enormous amount of energy reduction. The top brine temperature in conventional multi stage flash (MSF) can be increased above 120°C, when NF was used as pretreatment which reduces the scaling propensity of calcium and magnesium salts [2].

Besides desalination industry, the application of NF technology today includes disinfection by removal of virus [3], arsenic removal [4] and recovery of high value organometallic catalysts from reaction mixtures allowing the catalyst to be reused [5]. Pharmaceutical applications includes isolation of industrially important antiviral drug precursor N-acetyl-D-neuraminic acid [6], clindamycin from fermentation waste water [7] and sodium cefuroxime from cephalosporin-C [8].

Models for NF are usually based either on a mechanism-independent approach, such as irreversible thermodynamics (IT) or structural mechanism dependence. The models based on IT treat the membrane as a black box ignoring the structure of the membrane or any transport mechanism. These models are utilized at high rejection of solutes and fail to predict at lower rejection. Mechanistic models assume a membrane structure and the model equations account for the effects of physical and chemical characteristics of both the membrane and electrolyte solution. Most mechanistic models fall in two categories: those based on the space-charge (SC) model and Teorrell-Meyer-Sievers (TMS) model. The SC model is mathematically complicated and computationally expensive when compared with TMS model. Donnan steric pore model (DSPM) is an extension of TMS model with additional modifications.

Dielectric exclusion arises due to the difference in polarization charges which results in difference in dielectric constant between the bulk and nanocavity. Bandini et al. [10] investigated the phenomena in rigorous manner. Szymczyk et al. [11] investigated the transport properties of NF membranes by means of improved transport model which includes dielectric exclusion in terms of both Born dielectric effect and image force contribution. It was clearly shown that dielectric exclusion cannot be neglected in the analysis of the filtration properties of NF membrane. The charge density was determined approximately by streaming potential measurements and pore dielectric constant was used as an fitting parameter in their study. Freger et al. [12] concluded that the average charge of the skin that determines the selectivity towards ions of different charge can be quite low and, on average, the membrane skin layer behaves as a dielectric medium. Sophisticated experimental techniques namely nuclear magnetic resonance (NMR) and Fourier transform infrared spectra (FT-IR) show weak signals at the surface of the membrane. The surface charge is generated due to the unreacted species at the surface during interfacial polymerization.
The DSPM (Donnan Steric Pore Model) is known to be predictive for monovalent ions rejection [9]. However, the prediction of the model depends on a complex fitting procedure for membrane characterization. Moreover, the choice of the ion size presents additional difficulties. In fact, the ion radius affects the entire fabric of the model, e.g. pore size distribution, diffusion properties, electromigration, etc., which may put the prediction of the model under high uncertainty.

The objective of the present study was to investigate the effect of various ion radii such as Stokes-Einstein, Born’s effective, cavity and Pauling radii in the prediction of Donnan steric pore model with dielectric exclusion (DSPM-DE). The effect of the radii on the hindrance factors and physical properties was also considered. Various solutes that are considered in the present study are sodium chloride, sodium sulphate and magnesium chloride. Pore size distribution of each ion for each radii were also considered using truncated log normal density function.

2. Formulation of Donnan steric pore model and dielectric exclusion

A one-dimensional Donnan steric pore model with dielectric exclusion was developed for transport of electrolytes through nanofiltration membranes [9]. A schematic diagram of the coordinate system used is shown in Fig. 1. The following simplifying assumptions are used in the derivation of the model equations [9]:

1. The solution is assumed to behave ideal.
2. Transport inside the pore is due to convection, diffusion and electromigration.
3. Transport effects with convection and diffusion are corrected with hindrance factors.
4. Nanofiltration (NF) membrane has porous structure; Hagen-Poiseuille type relationship was used for solvent velocity.
5. The flow inside the pore is assumed laminar.
6. Chemical potential of solute depends on operating pressure.
7. The solvent within the pores is consisting of one layer of oriented water molecules.
8. Variation of solvent viscosity and dielectric constant inside the pore are considered.
9. Concentration polarization across the surface of the membrane is neglected.
10. Partial molar volume and diffusion coefficient inside pore are independent of concentration.
11. The separation at the pore interface is due to steric, Donnan effect and dielectric exclusion.
12. Electroviscous term is neglected for velocity of ions in the solvent.

![Coordinate system for the DSPM-DE.](image)
13. The concentration and potential gradient is varied axially and radial variation is neglected.

14. Lateral solute concentration distribution at the pore entrances is ignored.

The molar flux of ion $i$ is given by the Extended Nernst-Planck (ENP) equation as follows:

$$j_i = K_i c_i u + \left( -\frac{c_i D_{w, i} d\mu}{RT} d\lambda \right)$$  \hspace{1cm} (1)

where $u$ is the solvent velocity and $K_i$ is a hindrance factor accounting for the effects of pores walls on the species motion and is given by

$$K_i = (2 - \phi_i)(1.0 + 0.054\lambda_i + 0.988\lambda_i^2 + 0.441\lambda_i^3)$$  \hspace{1cm} (2)

$\phi_i$ is the dimensionless steric partition coefficient of ion $i$ and may be given by

$$\phi_i = (1 - \lambda_i)^2$$  \hspace{1cm} (3)

where $\lambda_i$ is the dimensionless ratio of ion or solute radius $i$ ($r_i$) to effective pore radius ($r_p$) and given as follows

$$\lambda_i = \frac{r_i}{r_p}$$  \hspace{1cm} (4)

and $D_{wp}$ is the pore diffusion coefficient of ion $i$ and may be given by

$$D_{wp} = K_{id} D_{w, i} \frac{\eta_0}{\eta}$$  \hspace{1cm} (5)

where $K_{id}$ is ionic hindrance factor for diffusion accounting for the effect of pore to reduce the solute-solvent diffusion coefficient below its value in the free bulk solution (water), $D_{w, i}$, i.e. the diffusivity of species $i$ in water at infinite dilution. $K_{id}$ may be written as

$$K_{id} = 1.0 - 2.30\lambda_i + 1.154\lambda_i^2 + 0.224\lambda_i^3$$  \hspace{1cm} (6)

As shown in Eq. (5), the pore diffusion coefficient of ion $i$ ($D_{wp}$) is affected by the change of the viscosity inside the pore ($\eta$). It has been shown by many investigators that the viscosity inside the pore increases by the decrease in pore radius [13]. The viscosity ratio is given by

$$\frac{\eta}{\eta_0} = 1.0 + 18\left( \frac{d}{r_p} \right) - 9\left( \frac{d}{r_p} \right)^2$$  \hspace{1cm} (7)

where $\eta_0$ is the bulk solvent viscosity.

The electrochemical potential ($\mu_i$) is given by

$$\mu_i = RT \ln a_i + V_i P + z_i F \psi_i + \text{constant}$$  \hspace{1cm} (8)

The ion activity of species $i$ ($a_i$) as a function of concentration ($c_i$) may be given by

$$a_i = \gamma_i c_i$$  \hspace{1cm} (9)

where $\gamma_i$ is the activity coefficient of species $i$.

Differentiating Eq. (8) and substituting in Eq. (1) yields

$$j_i = K_i c_i u - D_{wp} c_i(x) \frac{\partial}{\partial x} \ln \gamma_i - D_{wp} \frac{\partial}{\partial x} c_i(x)$$

$$- \frac{1}{RT} V_i D_{wp} c_i(x) \frac{\partial}{\partial x} P - \frac{F}{RT} z_i D_{wp} c_i(x) \frac{\partial}{\partial x} \psi_i$$  \hspace{1cm} (10)

Since the concentration inside the pore is very small, the activity coefficient term in Eq. (10) is neglected according to the Debye-Huckel theory [9]. The Hagen-Poiseuille equation for laminar flow is used to give constant pressure gradient along the pore as follows:

$$\frac{\partial^2 P}{\partial x^2} = \frac{8\eta \mu}{r_p^2}$$  \hspace{1cm} (11)
where $\Delta P_e$ is the effective pressure and is given by

$$\Delta P_e = \Delta P - \Delta \pi$$  \hspace{1cm} (12)

$\Delta P$ and $\Delta \pi$ are the applied and osmotic pressure difference across the pore respectively.

Substituting Eq. (11) in Eq. (10) yields

$$j_i = \left[ K_{ic} - \left( \frac{8\eta}{RT r_p^2} \right) D_{ip} V_i \right] c_i u - D_{ip} \frac{dc_i}{dx}$$

$$- \frac{F}{RT z_i D_{ip}} \frac{d\psi}{dx}$$

Eq. (13) contains three transport terms namely convection, ionic diffusion and electromigration. The molar flux ($j_i$) is also linked by the filtration condition

$$j_i = C_i(\delta^+) u$$  \hspace{1cm} (14)

Substituting Eq. (14) into (13) yields

$$\frac{dc_i}{dx} = \left[ K_{ic} - \left( \frac{8\eta}{RT r_p^2} \right) D_{ip} V_i \right] c_i - C_i(\delta^+)$$

$$\frac{u}{D_{ip}} - \frac{F}{RT z_i D_{ip}} \frac{d\psi}{dx}$$

Multiplication of Eq. (15) by $z_i$ and summation over all ions may give

$$\sum_{i=1}^{n} z_i \frac{dc_i}{dx} =$$

$$\sum_{i=1}^{n} \left[ K_{ic} - \left( \frac{8\eta}{RT r_p^2} \right) D_{ip} V_i \right] c_i - C_i(\delta^+)$$

$$- \frac{F}{RT} \sum_{i=1}^{n} z_i^2 c_i$$

The ion concentrations are bounded by electroneutrality conditions as follows:

* external solution

$$\sum_{i=1}^{n} z_i C_i(0^-) = 0, \quad \sum_{i=1}^{n} z_i C_i(\delta^+) = 0$$  \hspace{1cm} (17)

* internal solution

$$\sum_{i=1}^{n} z_i c_i(x) = \chi_d$$

where ($\chi_d$) is the membrane volumetric charge density.

Differentiation of Eq. (18) and substituting in Eq. (16) yields

$$\frac{d\psi}{dx} =$$

$$\sum_{i=1}^{n} \left[ K_{ic} - \left( \frac{8\eta}{RT r_p^2} \right) D_{ip} V_i \right] c_i - C_i(\delta^+) \frac{z_i u}{D_{ip}}$$

$$- \frac{F}{RT} \sum_{i=1}^{n} z_i^2 c_i$$

The assumption of quasi-equilibrium at the feed and permeate-membrane interfaces allows the ionic concentration within the pore to be related to feed and permeate concentrations through partition coefficients. The ionic partition coefficient of ion $i$ accounts for different physico-chemical interactions between the ions in solution and between the ions in the pores and the membrane matrix and may be written as:

$$k_i = [\text{steric}] \times [\text{electrostatic (Donnan)}] \times [\text{solvation (Born)}] \times [\text{dielectric}] \times ...$$

(20)

Eqs. (15) and (19) form a boundary value problem with the following boundary conditions:
where the Donnan potential ($\Psi_D$) for the feed and permeate side is given by

\[\Delta \Psi_p(0) = \psi(0^+) - \psi(0^-) \quad \text{(feed)}\]
\[\Delta \Psi_p(\delta) = \psi(\delta^-) - \psi(\delta^+) \quad \text{(permeate)}\] (23)

and $\Delta W_i$ is the solvation energy barrier. The solvation energy barrier is estimated from the Born model [9] as follows:

\[\Delta W_i = \frac{z^2 e^2}{8\pi\varepsilon_\infty r_i} \left[ \frac{1}{\varepsilon_p} - \frac{1}{\varepsilon_b} \right]\] (24)

where $\varepsilon_p$ and $\varepsilon_b$ are dimensionless pore and bulk dielectric constants, respectively. The average pore dielectric constant $\varepsilon_p$ can be obtained on the assumption that the wall of the pore is covered with one layer of oriented water molecules of thickness $(d)$ and dielectric constant $\varepsilon^*$ and the inner part of the pore has the bulk dielectric constant ($\varepsilon_b$). The $\varepsilon_p$ may be given as follows:

\[-\frac{d r_p - d}{r_p^2} \int_0^{r_p} 2\pi r \varepsilon_p' dr + \frac{1}{r_p^2} \int_{r_p}^{r} 2\pi r \varepsilon^* dr\]

\[\varepsilon_p = \frac{\int_0^{r_p} 2\pi r \varepsilon_p' dr + \int_{r_p}^{r} 2\pi r \varepsilon^* dr}{\pi r^2}\]

\[= \varepsilon_b - 2(\varepsilon_b - \varepsilon^*) \left( d \frac{1}{r_p} + (\varepsilon_b - \varepsilon^*) \left( d \frac{1}{r_p} \right)^2 \right)\] (25)

The solute radius in Eqs. (4) and (24) has been a subject of contradiction among the researchers for a decade.

The pore wise rejection of solute $i$ is given by

\[R_i = 1 - \frac{C_i(\delta^+)}{C_i(0^-)}\] (26)

For uncharged solutes, $\frac{dc_i}{dx} = 0$ and Eq. (15) thus become

\[\frac{dc_i}{dx} = \left[ K_{ic} - \left( \frac{8\pi}{RT r_p^2} \right) D_p V_i \right] c_i - C_i(\delta^+) \frac{u}{D_p}\]

with the following boundary conditions:

at $x = 0$

\[k_i\bigg|_0 = \frac{c_i(x)_{x=0^-}}{C_i(0^-)} = \phi_i\] (28)

at $x = \delta$

\[k_i\bigg|_\delta = \frac{c_i(x)_{x=\delta^-}}{C_i(\delta^+)} = \phi_i\] (29)

Eq. (27) can be integrated with the boundary conditions to give an analytical relationship for the uncharged solute rejection as follows:
\[ R_i = 1 - \frac{(K_{sc} - \beta_i) \phi_i}{1 - \left[ 1 - (K_{sc} - \beta_i) \phi_i \right] \exp(-P_{e_i})} \]  

(30)

where \( \beta_i \) is dimensionless quantity given by

\[ \beta_i = \frac{8\eta}{RT r_{p}^2} D_{\theta} V_i \]  

(31)

and \( P_{e_i} \) is the dimensionless modified Peclet number given by

\[ P_{e_i} = \frac{(K_{sc} - \beta_i)r_{p}^2 \Delta P_{e}}{8\eta D_{\theta}} \]  

(32)

For evaluating pore size distribution, lognormal probability density distribution function was used, which is a function of distribution mean (\( r^* \)) and standard deviation (\( \sigma^* \)). A summary of pore size distribution is given here and more details can be found elsewhere [14]:

\[ f_R(r) = \frac{1}{r \sqrt{2 \pi b}} \exp \left[ - \frac{\log \left( \frac{r}{r^*} \right) + \frac{b}{2}}{2 \log \left( 1.0 + \frac{\sigma^*}{r^*} \right)^2} \right] \]  

(33)

where

\[ b = \log \left( 1.0 + \frac{\sigma^*}{r^*} \right)^2 \]

Renormalizing the distribution by using truncation yields

\[ \frac{f'_R(r)}{f_R(r)} \bigg|_{r_{max}}^{r_{min}} = \int_{r_{min}}^{r_{max}} f_R(r) dr \]  

(34)

Overall rejection of solute \( i \) (\( R_i \)) can be related to porewise rejection of solute \( i \) (\( R_i(r) \)) as follows:

\[ R_i = \frac{\int_{0}^{r_{max}} \left( f_R'(r) - r^4 \right) R_i(r) dr}{\int_{0}^{r_{max}} \left( f_R'(r) - r^4 \right) dr} \]  

(35)

By using the truncated pore size distribution, a finite pore radius and the upper limit of distribution \( r_{max} \) (\( 0 < r < r_{max} \)) is introduced in the calculation. The pore size distribution data for NF membrane are not available and it is difficult to have a specific value for \( r_{max} \). For the present study it was set to \( r_{max} \leq 2r^* \). Significant advantage of truncation is that the range of integration is greatly reduced, removing the requirement for time consuming integration from \( 0 < r < \infty \). Truncation gives pores in nano size range and discards the electroviscous effects.

3. Computational procedure

Eqs. (15) and (19) for each pore are solved by the shooting method based on the Runge-Kutta Gear method and Newton-Raphson technique using FORTRAN subroutines namely DGEAR and ZSPOW. Double precision was used in all simulations. The numerical procedure is shown in Fig. 2. The integration of Eq. (35) for pore size distribution was performed numerically with trapezoidal rule.

4. Results and discussion

In this study we considered various ionic radii such as Stokes-Einstein, Born’s effective, cavity and Pauling. To familiarize the reader with these radii their definitions are given as follows:

The Stokes-Einstein radius is derived from Stokes-Einstein relation [15]:
The Stokes-Einstein radii at 298.15 K are shown in Table 1. The dynamic viscosity of water ($\eta_0$) at 25°C is taken as $0.89 \times 10^{-3}$ Pa.s.

The Born’s effective radius is derived from Born theory. Fig. 3 illustrates the structure of solutes, which consists of a bare ion radius interacting with the solvent. As it can be seen that a cation is surrounded by water molecules with oxygen atoms approaching them, while an anion is surrounded by water molecules with hydrogen atoms approaching them. $R_{\text{ion}}$ is the ionic radius and is purely a property of the ion. $R_{\text{max}}$ is defined as the position of the first peak in the ion-solvent radial distribution function; it depend on both ion and molecular nature of solvent.

The Born model has been successfully used to treat the solvation free energy of an ion. However, the use of ionic radius ($R_{\text{ion}}$) overestimates the magnitude of the solvation energy. Babu and Lim [16] have shown by using molecular dynamics simulation of ions of varying charges, that the Born’s effective radius is given by

$$r_i = \frac{(R_{\text{ion}} + R_{g\text{max}})}{2.0}$$  \hspace{1cm} (37)

The Born’s effective radius for hydrated ions are shown in Table 1. Cavity radius is the radius of sphere that have negligible charge density. It is obtained by increasing the radii by 7% for ionic radii of anions and covalent radii of cations. Pauling radius is defined as the bare ion crystal radius. Recent rejection measurements for ion mixtures using artificial nanofilters have shown that Pauling radius is the best choice [15]. The Pauling radii for hydrated ions (Na+, Mg²⁺, Cl⁻, SO₄²⁻) are shown in Table 1.

Experimental data for reassessing the dielectric constant inside the pore were taken from literature [9]. When the membrane is uncharged, there will be no Donnan effect. The separation will be due to steric and dielectric exclusion. This can be achieved by variation of pH. The point at which the membrane is uncharged can be called as amphoteric, isoelectric point and point of zero charge. The variation of permeate flux with pressure drop and pore radius was also taken from the literature [9].
Fig. 3. Schematic diagram of the orientation of water dipoles around (a) cations and (b) anions [16].

Table 1
Parameters used in the simulation [15–20]

<table>
<thead>
<tr>
<th>Ion</th>
<th>$D_\text{ion}$, $10^{-9}$ m$^2$ s$^{-1}$</th>
<th>$V_\text{r}$, cm$^3$ mol$^{-1}$</th>
<th>$r_\text{r}$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>1.33</td>
<td>1.20</td>
<td>0.184</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>2.03</td>
<td>17.82</td>
<td>0.121</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.72</td>
<td>21.57</td>
<td>0.341</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>1.06</td>
<td>14.18</td>
<td>0.231</td>
</tr>
</tbody>
</table>

Fig. 4 illustrates the determination of the dielectric constant $\varepsilon'$ of the oriented water layer inside the nanopore. The following least square equation is implemented for determination of

$$\theta = \left( \sum_{j}^{n} \left( R_{\exp} - R_{j} \right)^2 \right) / jn - 1$$

(38)

where $j$ and $n$ are number of data points and number of solutes respectively.

Table 2 gives the values of dielectric constant for various radii. These values are in consistent with the molecular dynamic simulation conducted with water molecule in an confined nanocavity using the soft sticky dipole (SSD) and simple point charge/extended (SSDE) model [21]. Born’s effective and cavity radii gave similar values, since the radius of both the solute are more or less same as shown in Table 1.

4.1. Membrane performance with uniform pore size

The effect of dielectric exclusion is included in the simulation for sodium chloride with the
Fig. 4. Rejection versus pressure drop for reassessed dielectric constant using different radii.

Fig. 5. Sodium chloride rejection for various radii (Stokes-Einstein, Born’s effective, Pauling) at $\zeta = 0.50$, $r_p = 0.5$ nm.

Fig. 6. Sodium chloride rejection for various radii (Stokes-Einstein, Born’s effective, Pauling) at $\zeta = -0.50$, $r_p = 0.5$ nm.
reassessed dielectric constant for the corresponding radii as shown in Figs. 5 and 6. Positive and negative charged membranes were compared. Positive charged membrane predicted higher rejection for the Stokes-Einstein radius when compared to other radii. When the membrane is negatively charged, Pauling radius predicted higher rejection. For both cases, Born’s effective radii predicted lower rejection.

Figs. 7–9 compare the rejection of uncharged, positively and negatively charged membrane for sodium sulphate. It can be seen that the Pauling radius predicted higher rejection than Stokes-Einstein and Born’s effective radii for uncharged and negative charged membrane. Stokes-Einstein radius predicted higher rejection for positive charged membrane. Born’s effective and Pauling radii predicted similar rejection. As clearly shown that all the radii predicted higher rejection of above 90%.

Figs. 10–12 compare the theoretical rejection of an uncharged, positive and negative charged membrane with all the corresponding radii for magnesium chloride. In all the cases, Pauling radius predicted higher rejection. For positive charged membrane, all the radii predicted similar rejection.

Fig. 7. Sodium sulphate rejection for various radii (Stokes-Einstein, Born’s effective, Pauling) at $\zeta = 0, r_p = 0.5$ nm.

Fig. 8. Sodium sulphate rejection for various radii (Stokes-Einstein, Born’s effective, Pauling) at $\zeta = 0.2, r_p = 0.5$ nm.

Fig. 9. Sodium sulphate rejection for various radii (Stokes-Einstein, Born’s effective, Pauling) at $\zeta = -0.001, r_p = 0.5$ nm.
Fig. 10. Magnesium chloride rejection for various radii (Stokes-Einstein, Born’s effective, Pauling) at $\zeta = 0$, $r_p = 0.5$ nm.

Fig. 11. Magnesium chloride rejection for various radii (Stokes-Einstein, Born’s effective, Pauling) at $\zeta = 0.05$, $r_p = 0.5$ nm.

Fig. 12. Magnesium chloride rejection for various radii (Stokes-Einstein, Born’s effective, Pauling) at $\zeta = -0.1$, $r_p = 0.5$ nm.

rejection. Stokes-Einstein radius predicted higher rejection than Born’s effective radius for uncharged and got reversed for negative charged membrane.

The present study illustrates the difference of prediction of charge density for different radii. The choice of the solute radii has an important effect on the prediction of charge density. To our knowledge, hydrated radii of uncharged solute were not available. If its available, there will be a change in the prediction of radius of pore and correspondingly the dielectric constant inside nano pore and results in different charge density. The charge density can be obtained experimentally by membrane potential and Donnan potential measurements. There is wide hiatus in the prediction of experiment and theory, since the membrane carry a small charge. At present, by sophisticated theoretical prediction only, the charge density can be obtained. Most of the NF membranes are negatively charged due to the sulfonyl group present at the surface of the membrane. The charge density depends on the nature of the solute membrane interactions as well as pH of the system.
4.2. Membrane performance with pore size distribution

A detailed analysis of solute transport and membrane properties were quantified to determine the pore radius dependence of NF separation. It enhances the predictive capability of nanofiltration modeling and will be more close to the physical phenomena arising at the surface of the membrane.

Fig. 13 compares the individual truncations for the positive charge membrane for sodium chloride. As shown that at \( r_{\text{max}} \) of 0.6 nm, Stokes-Einstein radius predicted higher rejection. For \( r_{\text{max}} \) of 1.0 nm, Pauling radii predicted higher rejection. In all the simulations, Born’s effective radii prediction was low in comparison with other radii. It is clearly shown that the increase of \( r_{\text{max}} \) decreases the rejection for all radii. The prediction of uniform pores and reduced \( r_{\text{max}} \) of 0.6 nm were similar as shown in Figs. 5 and 13. As the value of \( r_{\text{max}} \) is increased to 1.0 nm, the rejection decreases eventually leads to more solute permeation as shown in Fig. 13.

Fig. 14 shows individual truncation behaviour for all corresponding radii for an negatively charged membrane for sodium chloride. At reduced \( r_{\text{max}} = 0.6 \) nm and increased \( r_{\text{max}} = 1.0 \) nm, the Pauling radius predicted the highest rejection. One of the interesting aspects is that the prediction of Born’s effective and Stokes-Einstein radii are similar. It can be seen that the increase of \( r_{\text{max}} \) has a profound effect on the rejection of solute. At increased \( r_{\text{max}} \) there is a difference in prediction between positively charged membrane and negatively charged membranes. There is a significant difference in rejection for positively charged between Stokes-Einstein and Born’s effective radii and this is not observed for negatively charged, where both radii predicted a similar rejection as shown in Fig. 14.

The Pauling radii prediction at reduced \( r_{\text{max}} = 0.6 \) nm and uniform pores was similar and is shown in Figs. 6 and 14. For other radii, slight variation was seen, but the trend was similar. As the value of \( r_{\text{max}} \) was increased to 1 nm, the rejection decreases more steeply as shown in Fig. 14.

Fig. 15 shows the individual contribution of lower value \( r_{\text{max}} = 0.6 \) nm and higher value of \( r_{\text{max}} = 1.0 \) nm for an uncharged membrane for sodium sulphate. In all the simulations, Born’s effective radius predicted lower rejection and Pauling radius predicted higher rejection. As the value of \( r_{\text{max}} = 1.0 \) nm is increased, the rejection started to decrease, although there was steric effect due to size of solute, it kept the rejection more when compared to sodium chloride as shown in Fig. 15. Reduced \( r_{\text{max}} = 0.6 \) nm and uniform pores predicted similar rejection as shown in Figs. 7 and 15.

Individual comparisons of \( r_{\text{max}} \) for magnesium chloride are shown in Fig. 16. In all the simulations, the prediction of Pauling radius rejection was high with Born’s effective and Stokes-Einstein radii predictions were almost similar. As

![Graph showing variation of pore size distribution for sodium chloride using various radii with \( r_{\text{max}} = 1.2 r^* \) and \( r_{\text{max}} = 2r^* \) for truncated pore size distribution \( (r^* = 0.5 \text{ nm}, \sigma^* = 0.25 \text{ nm}, \zeta = 0.50) \).]
Fig. 14. Variation of pore size distribution for sodium chloride using various radii with $r_{\text{max}} = 1.2 r^*$ and $r_{\text{max}} = 2 r^*$ for truncated pore size distribution ($r^* = 0.5 \text{ nm, } \sigma^* = 0.25 \text{ nm, } \zeta = -0.50$).

Fig. 15. Variation of pore size distribution using various radii for sodium sulphate with $r_{\text{max}} = 1.2 r^*$ and $r_{\text{max}} = 2 r^*$ for truncated pore size distribution ($r^* = 0.5 \text{ nm, } \sigma^* = 0.25 \text{ nm, } \zeta = 0$).

The value of $r_{\text{max}}$ was increased to 1 nm, the rejection decreased for both Stokes-Einstein radii and Born’s effective, but Pauling radii rejection was the same as shown in Fig. 16. Although, the solute size of Pauling radii was small, but the effect of solvation free energy kept the rejection high. The uniform pores and reduced ($r_{\text{max}} = 0.6 \text{ nm}$) yielded similar profiles as shown in Figs. 10 and 16. It is evident that at increased $r_{\text{max}}$ resulted in significant decrease in rejection as shown in Fig. 16.

5. Conclusions

A rigorous Donnan steric pore model and dielectric exclusion (DSPM-DE) is implemented to investigate the effect of ion size and pore size distribution on the performance of nanofiltration membrane systems. Born’s solvation energy expression was used for dielectric exclusion. Various radii such as Stokes-Einstein, Born’s effective and Pauling radii were used in the DSPM-DE model for comparative purpose. The pore viscosity and dielectric constant inside the
nanopore were considered. The dielectric constant was determined by fitting the model with the experimental data where the membrane was operated at amphoteric condition with zero charge. The obtained values of dielectric constant were in consistent with molecular dynamic simulation performed for a nanocavity. For sodium chloride, Born’s effective radius predicted lower rejection for both positive and negatively charged membrane. Similar observation was obtained for sodium sulphate. In the case of magnesium chloride, Born’s effective radius predicted lower rejection for uncharged membrane and Stokes-Einstein radius predicted lower rejection for negatively charged membrane. Log-normal probability density function was used to quantify the pore size distribution. The density function is suitably scaled for truncation. In this simulation, solvent velocity, pore viscosity and rejection are all function of pore radius. As the value of \( r_{\text{max}} \) was increased, Pauling radius predicted higher rejection for all the solute. For sodium chloride when the membrane is negatively charged, the prediction of Born’s effective and Stokes-Einstein radii were similar. Born’s effective radius predicted lower rejection for sodium sulphate. The increase of \( r_{\text{max}} \) has negative effect on the rejection.

From this study, it is concluded that charge density has an important dependence on the selection of the radius of solute. Experimental comparison of the present results is underway.

6. Symbols

- \( a_i \) — Activity of ion \( i \), mol m\(^{-3}\)
- \( b \) — Parameter defined by Eq. (31)
- \( C_f(0^+) \) — Solute feed solution concentration, mol m\(^{-3}\)
- \( C_f(\delta^-) \) — Solute permeate concentration, mol m\(^{-3}\)
- \( c_i(x) \) — Concentration of ion \( i \) within pore, mol m\(^{-3}\)
- \( d \) — Thickness of the oriented solvent layer, 0.28 nm
- \( D_{ip} \) — Pore diffusion coefficient of ion \( i \), m\(^2\) s\(^{-1}\)
- \( D_{iO} \) — Ion bulk diffusion coefficient, m\(^2\) s\(^{-1}\)
- \( e \) — Electronic charge, 1.602177\( \times \)\( 10^{-19} \) C
- \( f_R \) — Theoretical probability density function, m\(^{-1}\)
- \( f'_R \) — Truncated probability density function, m\(^{-1}\)
- \( F \) — Faraday constant, 96487 C mol\(^{-1}\)
- \( j \) — Number of data points per solute in fitting, dimensionless
- \( j_i \) — Flux of ion \( i \), mol m\(^{-2}\) s\(^{-1}\)
- \( k \) — Boltzmann constant, 1.38066\( \times \)\( 10^{-23} \) JK\(^{-1}\)
- \( k_i \) — Ionic partition coefficient of ion \( i \)
- \( K_{ic} \) — Hindrance factor for convection of ion \( i \), dimensionless
- \( K_{id} \) — Hindrance factor for diffusion of ion \( i \), dimensionless
- \( n \) — Number of solutes in fitting, dimensionless
- \( P_{ei} \) — Modified Peclet number of ion \( i \), dimensionless
- \( r \) — Pore radius, m
- \( r_{\text{max}} \) — Upper limit of truncated pore size distribution, m
- \( r_i \) — Radius of ion \( i \), m
- \( r'_p \) — Effective pore radius, m
- \( r' \) — Mean pore radius, m
- \( R_i \) — Overall rejection of solute \( i \), calculated through Eq. (26), dimensionless
- \( R'_i \) — Overall rejection of solute \( i \), calculated through Eq. (35), dimensionless
- \( R_{\text{exp}} \) — Rejection measured through experiment, dimensionless
- \( R \) — Universal gas constant, 8.314 J mol\(^{-1}\) K

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$T$</td>
<td>Absolute temperature, K</td>
</tr>
<tr>
<td>$u$</td>
<td>Solvent velocity, m s$^{-1}$</td>
</tr>
<tr>
<td>$V_i$</td>
<td>Partial molar volume of ion $i$, m$^3$ mol$^{-1}$</td>
</tr>
<tr>
<td>$x$</td>
<td>Axial position within the pore, m</td>
</tr>
<tr>
<td>$z_i$</td>
<td>Valence of ion $i$, dimensionless</td>
</tr>
<tr>
<td>$\lambda_d$</td>
<td>Effective charge density, mol m$^{-3}$</td>
</tr>
<tr>
<td>$\sigma^*$</td>
<td>Distribution standard deviation, m</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Ratio of effective charge density to bulk feed concentration, dimensionless</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Potential within the pore, V</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Sum of square objective function in fitting, dimensionless</td>
</tr>
</tbody>
</table>

Greek Symbols:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>$\beta_i$</td>
<td>Ion function, dimensionless</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Membrane thickness, m</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>Applied pressure, N m$^{-2}$</td>
</tr>
<tr>
<td>$\Delta P_e$</td>
<td>Effective pressure driving force, N m$^{-2}$</td>
</tr>
<tr>
<td>$\Delta\pi$</td>
<td>Osmotic pressure, N m$^{-2}$</td>
</tr>
<tr>
<td>$\Delta\Psi_d(0)$</td>
<td>Donnan potential at the feed membrane interface, V</td>
</tr>
<tr>
<td>$\Delta\Psi_d(\delta)$</td>
<td>Donnan potential at the permeate membrane interface, V</td>
</tr>
<tr>
<td>$\Delta W(0)$</td>
<td>Born solvation energy barrier at the feed membrane interface, J</td>
</tr>
<tr>
<td>$\Delta W(\delta)$</td>
<td>Born solvation energy barrier at the permeate membrane interface, J</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Bulk dielectric constant, dimensionless ($\varepsilon_0 = 80$)</td>
</tr>
<tr>
<td>$\varepsilon_p$</td>
<td>Pore dielectric constant, dimensionless</td>
</tr>
<tr>
<td>$\varepsilon^*$</td>
<td>Dielectric constant of oriented water layer</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of free space, 8.85419 × 10$^{-12}$ J C$^{-1}$ m$^{-1}$</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Solvent viscosity within pores, N s m$^{-2}$</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>Bulk solvent viscosity, N s m$^{-2}$</td>
</tr>
<tr>
<td>$\gamma_i$</td>
<td>Activity coefficient of ion $i$ within pore, dimensionless</td>
</tr>
<tr>
<td>$\lambda_i$</td>
<td>Ratio of ion radius to pore radius, dimensionless</td>
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<tr>
<td>$\mu_i$</td>
<td>Electrochemical potential of ion $i$, J mol$^{-1}$</td>
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<tr>
<td>$\phi_i$</td>
<td>Steric partition coefficient of ion $i$, dimensionless</td>
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</tbody>
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References: