MATHEMATICAL MODELING TO PREDICT SURFACE CHARGE DENSITY OF NANOFILTRATION MEMBRANES

ABSTRACT

Two commercial nanofiltration (NF) membranes viz., Desal-HL and NF 700 MWCO were investigated experimentally using neutral and charged solutes viz., glucose, sodium chloride and magnesium chloride. Effect of pH was studied for sodium chloride rejection and isoelectric point of the membrane was deduced. Experimental results were analyzed using Donnan steric pore and dielectric exclusion models. Dielectric exclusion arises due to the difference in dielectric constant between the bulk and the nano pore. Stokes-Einstein, Born effective and Pauling radii were used for theoretical simulation, which accurately predicted the different charge densities. Empirical correlations were proposed between charge density, concentration and pH for each radius. Charge density decreased drastically when dielectric exclusion term was included in the theoretical model, which showed the real physical characteristics of the membranes employed. Charge density was found to be an important surface parameter in understanding the fouling and separation effects in NF membranes.

Results of this chapter are submitted to Journal of Membrane Science (2007)
VIII.A.1. INTRODUCTION

In recent years, the use of nanofiltration (NF) membranes has increased rapidly in chemical, petrochemical, biological and desalination industries, since the NF technology overcomes the operational problems that are associated with the conventional techniques. The separation in RO and UF occurs due to solution-diffusion and sieving effects. However, NF takes into account both solution-diffusion as well as the sieving effect, Donnan, dielectric exclusion and electro-migration, which makes it useful to separate both charged as well as uncharged organic solutes. Since, the energy consumption in RO is high due to high operating pressure and low permeate flux, an alternate membrane process was sought, which could produce high permeate flux at lower pressures. Such membranes were initially called low-pressure RO membranes. However, atomic force microscopy (AFM) could reveal that these membranes possess pores in the scale of nano, thereby the process is called [1] as NF. Successful implementation of NF technology as a pretreatment to seawater has gained considerable importance in recent years. Usually, the product recovery in convention seawater reverse osmosis (SWRO) is 28% at an operating pressure of around 65 bar. When NF membranes were used in the pretreatment section of conventional RO, the product recovery has increased to 36.4% with a reduction in operating pressure up to 54 bar, thus resulting in a large amount of energy reduction [2].

Besides desalination industry, the application of NF technology today includes disinfection by removal of organics,[3] arsenic removal [4] and recovery of high value organometallic catalysts from reaction mixtures allowing the catalyst to be reused [5]. NF also can be used to separate inorganic salts with much smaller size than the pore size according to electrostatic repulsions. Pharmaceutical applications include the isolation of industrially important antiviral drug precursor, N-acetyl-D-neuraminic
Membrane Based Separation Processes for Effluent Treatment

acid, [6] clindamycin from fermentation wastewater, [7] sodium cefuroxime [8] from cephalosporin-C and cephalexin [9, 10]. Removal of dye from textiles [11] and distillery [12] wastewater were other frontier applications of NF. The presently used NF membranes are mostly negatively charged or neutral. In order to fully realize the application potential of NF and to properly predict the membrane performance, it is important to propose a mathematical transport model. The ionic transport and selectivity of NF membranes mainly depend upon three effects: charge repulsion, steric/hydrodynamic and dielectric effects. The first effect is caused by the charged nature of the membrane and electrolytes, while the second effect is caused by the relative size of ions to the membrane pores; third effect is caused by the differences in dielectric constant between bulk and membrane pore. Additional phenomena can affect the membrane performance viz., ion-membrane affinity, specific adsorption and hydration.

Models for NF are usually based either on a mechanism-independent approach, such as irreversible thermodynamics or structural mechanism dependence. Models based on irreversible thermodynamics 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, but fail to predict at lower rejection. Mechanistic models assume the membrane structure and model equations account for effects of physical and chemical characteristics of both the membrane and electrolyte solution. Most mechanistic models fall into two categories: those based on space-charge (SC) model and Teorrel-Meyer-Sievers (TMS) model. The SC model is mathematically complicated, but computationally expensive compared to the 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 the difference of dielectric constant between the bulk and nanocavity. Bandini et al. [13] investigated the phenomena quite rigorously. Role of the difference existing between dielectric constant of the aqueous solution in the pores and dielectric constant of the membrane material is assumed to be dominant in determining the rejection mechanism related to dielectric effects. Szymczyk et al. [14, 15] investigated the transport properties of NF membranes using an improved transport model, which includes the 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 filtration properties of NF membrane. The charge density was thus determined approximately by streaming potential measurements and pore dielectric constant was used as a fitting parameter in their study. Freger et al. [16] concluded that the average charge of the skin that determines the selectivity towards ions of different charges can be quite low and on an average, the membrane skin layer behaves as a dielectric medium. Experimental techniques such as nuclear magnetic resonance (NMR) and Fourier transform infrared spectra (FT-IR) show week signals at the surface of the membrane; however, the surface charge is generated due to the unreacted species at the surface during interfacial polymerization.

The influence of ionic radii via Stokes-Einstein, Born and Pauling equations has a profound effect to predict the charge density at the surface of the membrane. DSPM was investigated for various solutes like sodium chloride, sodium sulfate, magnesium chloride and magnesium sulfate [17]. DSPM-dielectric exclusion (DSPM-DE) model was also investigated for various radii. Differences in the predictions were observed when the membrane is positively or negatively charged. The effect of pore size distribution was also investigated, which gave a different prediction for
various radii [18, 19]. The principal objective of the present study is to investigate the influence of ionic radii viz., Stokes-Einstein, Born and Pauling to predict the radii of DSPM and DSPM-DE model for two commercial membranes viz., Desal-HL (from GE Osmonic USA) and NF 700 MWCO (from Permionics, India). Sodium chloride and magnesium chloride were used as model solutes. The effect of pH on the rejection rates was studied to determine the NF isoelectric point of the membrane. The effect of radii on the hindrance factor was also investigated. Physical properties of the membrane like radius of pore and charge densities were deduced from the theoretical models.

\[
\begin{align*}
C_i(0^-) & \quad & C_i(\delta^+) \\
\text{Feed} & & \text{Permeate Phase} \\
\text{(Retentate Phase)} & & \\
\end{align*}
\]

\[
\begin{align*}
\Delta \psi_D(0) & \quad & \Delta \psi_D(\delta) \\
\Delta W(0) & \quad & \Delta W(\delta) \\
\end{align*}
\]

**Figure VIII.A.1.** Coordinate system for the DSPM-DE.

**VIII.A. 2. MATHEMATICAL MODELING**

In this work, one-dimensional Donnan steric pore model with dielectric exclusion is developed for studying the transport of electrolytes through NF membranes [18]. A schematic diagram of the coordinate system used is shown in Figure VIII.A.1. Several simplifying assumptions were used in the derivation of the model equations:[18] (1) the solution is assumed to behave ideal and transport inside the pore is considered to be due to convection, diffusion and electromigration; (2) transport effects with
convection and diffusion are corrected with hindrance factors and the NF membrane was considered to have a porous structure such that Hagen-Poiseuille type relationship was used for solvent velocity the flow inside the pore was assumed laminar (3) chemical potential of the solute depends on the operating pressure and solvent within the pores consist of one layer of oriented water molecules; (4) variations of solvent viscosity and dielectric constant inside the pore are considered, but concentration polarization across the surface of the membrane is neglected; (5) partial molar volume and diffusion coefficient inside pore are independent of concentration; the separation at pore interface is considered to be due to steric Donnan effect and dielectric exclusion; (6) Electroviscous term were neglected for velocity of ions in the solvent while the concentration and potential gradient was varied axially and radial variation was neglected; the lateral solute concentration distribution at the pore entrances was ignored.

Molar flux of the ion, $i$ is given by the Extended Nernst-Planck (ENP) equation:

$$ j_i = K_{ic} c_i u + \left( \frac{c_i D_i d\mu_i}{RT} \right) $$

(VIII.A.1)

where $u$ is solvent velocity and $K_{ic}$ is a hindrance factor accounting for the effects of pore walls on the motion of solute, which is given by:

$$ K_{ic} = (2 - \phi_i)(1.0 + 0.054\lambda_i - 0.988\lambda_i^2 + 0.441\lambda_i^3) $$

(VIII. A.2)

where $\phi_i$ is dimensionless steric partition coefficient of ion, $i$ and defined by:

$$ \phi_i = (1 - \lambda_i)^2 $$

(VIII. A.3)

where $\lambda_i$ is the dimensionless ratio of ion or solute radius $i$ ($r_i$) to effective pore radius ($r_p$) given as follows:
The pore diffusion coefficient, $D_\phi$, of ion, $i$ is given by as:

$$D_\phi = K_{id} D_m \frac{\eta_w}{\eta} \quad \text{(VIII. A.5)}$$

Here $K_{id}$ is ionic the hindrance factor for diffusion accounting for effect of pore to reduce solute-solvent diffusion coefficient below its value in the free bulk solution (water); $D_m$ is diffusivity of species, $i$ in water at infinite dilution; $K_{id}$ is given by:

$$K_{id} = 1.0 - 2.30 \lambda_i + 1.154 \lambda_i^2 + 0.224 \lambda_i^3 \quad \text{(VIII. A.6)}$$

As per eq. (VIII.A.5), the pore diffusion coefficient ($D_\phi$) of ion $i$ is affected by the change in viscosity ($\eta$) inside the pore. The viscosity inside the pore increases by a decrease in pore radius [18] such that viscosity ratio is given by:

$$\frac{\eta}{\eta_0} = 1.0 + 18 \left( \frac{d}{r_p} \right) - 9 \left( \frac{d}{r_p} \right)^2 \quad \text{(VIII. A.7)}$$

where $\eta_0$ is bulk solvent viscosity. The electrochemical potential ($\mu_i$) is given by:

$$\mu_i = RT \ln a_i + V_i P + z_i F \psi + \text{constant} \quad \text{(VIII.A.8)}$$

The ion activity ($a_i$) of species, $i$ as a function of concentration ($c_i$) is given by:

$$a_i = \gamma_i c_i \quad \text{(VIII.A.9)}$$

where $\gamma_i$ is activity coefficient of species $i$. Differentiating eq. (VIII.A.8) and substituting in eq. (VIII.A.1) we get:

$$j_i = K_{id} c_i (x) a_i - D_\phi c_i (x) \partial_i \ln \gamma_i - D_\phi \partial_i c_i (x) - \frac{1}{RT} V_i D_\phi c_i (x) \partial_i P - \frac{F}{RT} z_i D_\phi c_i (x) \partial_i \psi \quad \text{(VIII.A.10)}$$

Since the concentration inside the pore is very small, the activity coefficient term in eq. (VIII.A.10) is neglected according to Debye-Huckel theory.
Membrane Based Separation Processes for Effluent Treatment

[20]. Hagen-Poiseuille equation for laminar flow can be used to give a constant pressure gradient along the pore as follows:

\[
\frac{\partial P}{\partial x} = \frac{8\eta u}{r_p^2} \quad (VIII.A.11)
\]

where \( \Delta P_e \) is the effective pressure given by:

\[
\Delta P_e = \Delta P - \Delta \pi \quad (VIII.A.12)
\]

Here, \( \Delta P \), and \( \Delta \pi \) are the applied and osmotic pressure difference across the pore, respectively. Substituting eq. (VIII.A.11) into eq. (VIII.A.10) yields:

\[
j_i = \left[K_e \left(\frac{8\eta}{RT r_p^2}\right)D_i V_i\right] c_i u - D_i \frac{dc_i}{dx} - \frac{F}{RT} z_i c_i \frac{dy}{dx} \quad (VIII.A.13)
\]

Eq. (VIII.B.13) contains three transport parameters viz., convection, ionic diffusion and electromigration. The molar flux \( (j_i) \) values are also linked by the filtration condition such that:

\[
j_i = C_i(\delta^*) u \quad (VIII.A.14)
\]

Substituting eq. (VIII.A.14) into eq. (VIII.A.13) yields:

\[
\frac{dc_i}{dx} = \left[K_e \left(\frac{8\eta}{RT r_p^2}\right)D_i V_i\right] c_i - C_i(\delta^*) - \frac{u}{D_i} - \frac{F}{RT} z_i c_i \frac{dy}{dx} \quad (VIII.A.15)
\]

Multiplication of eq. (VIII.A.15) by \( z_i \) and summation over all the ions gives the following equation:

\[
\sum_{i=1}^{n} \frac{dz_i}{dx} = \sum_{i=1}^{n} \left[K_e \left(\frac{8\eta}{RT r_p^2}\right)D_i V_i\right] c_i - C_i(\delta^*) - \frac{z_i u}{D_i} - \frac{F}{RT} \left(\sum_{i=1}^{n} z_i^2 c_i\right) \frac{dy}{dx} \quad (VIII.A.16)
\]

The ion concentrations are bounded by the following electro-neutrality conditions:

\[
\sum_{i=1}^{n} z_i c_i(0^-) = 0, \quad \sum_{i=1}^{n} z_i c_i(\delta^*) = 0 \quad \text{(external solution)} \quad (VIII.A.17)
\]

\[
\sum_{i=1}^{n} z_i c_i(x) = \chi_d \quad \text{(internal solution)} \quad (VIII.A.18)
\]
where \((\chi_0)\) is a membrane volumetric charge density. Differentiation of eq. (VIII.A.18) and substituting into eq. (VIII.A.16) yields:

\[
\frac{d\psi}{dx} = \frac{F}{RT} \sum_{i=1}^{n} z_i^2 c_i
\]

The assumption of quasi-equilibrium at feed and permeate-membrane interfaces allows the ionic concentration within the pore to be related to feed and permeate concentrations through partition coefficients. However, the ionic partition coefficient of ion, \(i\) accounts for different physicochemical interactions between ions in solution and between ions in pores and the membrane matrix:

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

Equations (VIII.A.15) and (VIII.A.19) forms the boundary value problem with the following boundary conditions:

at \(x = 0\)

\[
k_{i0} = \frac{c_i(x)_{\text{feed}}}{C_i(0^-)} = \phi_e \exp\left(-\frac{F z_i}{RT} \Delta \psi_e(0)\right) \exp\left(-\frac{\Delta W(0)}{kT}\right)
\]

\[
\sum_{i=1}^{n} z_i C_i(0^-) \phi_e \exp\left(-\frac{F z_i}{RT} \Delta \psi_e(0)\right) \exp\left(-\frac{\Delta W(0)}{kT}\right) = \chi_d
\]

at \(x = \delta\)

\[
k_{i\delta} = \frac{c_i(x)_{\text{permeate}}}{C_i(\delta^+)} = \phi_p \exp\left(-\frac{F z_i}{RT} \Delta \psi_p(\delta)\right) \exp\left(-\frac{\Delta W(\delta)}{kT}\right)
\]

\[
\sum_{i=1}^{n} z_i C_i(\delta^+) \phi_p \exp\left(-\frac{F z_i}{RT} \Delta \psi_p(\delta)\right) \exp\left(-\frac{\Delta W(\delta)}{kT}\right) = \chi_d
\]

The Donnan potential \((\Delta \psi_D)\) for feed and permeate side is given by:

\[
\Delta \psi_e(0) = \psi(0^+) - \psi(0^-) \text{ (feed) and } \Delta \psi_p(\delta) = \psi(\delta^+) - \psi(\delta^-) \text{ (permeate)}
\]  

The term \(\Delta W\) represents the solvation energy barrier, which can be estimated from the Born model [18] as follows:
\[ \Delta W' = \frac{z^2 e^2}{8 \pi \varepsilon_0 r_f} \left[ \frac{1}{\varepsilon_p} - \frac{1}{\varepsilon_b} \right] \]  \hspace{1cm} \text{(VIII.A.24)}

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

\[ \varepsilon_p = \frac{\int_0^d 2 \pi r \varepsilon' dr + \int_d^\infty 2 \pi r \varepsilon' dr}{\pi r_p^4} = \varepsilon_b - 2(\varepsilon_b - \varepsilon')(\frac{d}{r_p}) + (\varepsilon_b - \varepsilon') \left( \frac{d}{r_p} \right)^2 \]  \hspace{1cm} \text{(VIII.A.25)}

The solute radius in eqs. (VIII.A.4) and (VIII.A.24) has been a subject of contradiction among researchers for decades. However, the rejection of solute \( i \) is given by:

\[ R_i = 1 - \frac{C_i(\delta^+)}{C_i(0^-)} \]  \hspace{1cm} \text{(VIII.A.26)}

For uncharged solutes, \( \frac{dy}{dx} = 0 \) so that eq. (VIII.A.15) becomes:

\[ \frac{dc_i}{dx} = \left[ K_i - \left( \frac{8 \eta}{RT r_p^3} \right) D_p V_i \right] c_i - C_i(\delta^+) \frac{u}{D_p} \]  \hspace{1cm} \text{(VIII.A.27)}

with the following boundary conditions:

we have,

\[ k_i \big|_0 = \frac{c_i(x)^{\text{leq}}}{c_i(0^-)} = \phi_i \]  \hspace{1cm} \text{(VIII.A.28)}

\[ k_i \big|_\delta = \frac{c_i(x)^{\text{leq}}}{c_i(\delta^+)} = \phi_i \]  \hspace{1cm} \text{(VIII.A.29)}
Equation (VIII.A.27) can be integrated with the boundary conditions to give an analytical relationship for the uncharged solute rejection:

\[
R_i = 1 - \frac{(K_e - \beta_i)\phi_i}{1 - [1 - (K_e - \beta_i)\phi_i] \exp(-P_{ei})}
\]  

(VIII.A.30)

where \( \beta_i \) is a dimensionless quantity and \( P_{ei} \) is dimensionless modified Peclet number given by the equations:

\[
\beta_i = \frac{8\eta}{RT r_p^2} D_i V_i
\]  

(VIII.A.31)

\[
P_{ei} = \frac{(K_e - \beta_i)r_p^2\Delta P_e}{8\eta D_i}
\]  

(VIII.A.32)

**VIII.A. 2.1. Description of Different Ion Radii**

Various ionic radii such as Stokes-Einstein, Born effective and Pauling radii were considered. Stokes-Einstein radius was derived from the Stokes-Einstein equation [22]:

\[
r_i = \frac{kT}{6\pi\eta r_D}
\]  

(VIII.A.33)

Stokes-Einstein radius at 298.15 K is given in Table VIII.A.1. The dynamic viscosity of water (\( \eta_w \)) at 25°C is taken as 0.89 \times 10^{-3} \text{ Pa.s}. Born effective radius was derived from the Born theory. Figure VIII.A.2 illustrates the structure of solutes, which consists of bare ion radius interacting with the solvent. It can be seen that the cation is surrounded by water molecules with oxygen atoms approaching them; while anion is surrounded by water molecules with hydrogen atoms approaching them; \( R_{\text{ion}} \) is the ionic radius, which is purely a property of the ion. The \( R_{\text{max}} \) is defined as the position of the first peak in the ion-solvent radial distribution function and it depends on both ion and molecular nature of the 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 [23] have shown, using molecular dynamics simulation of ions of varying charges that the Born effective radius is given by:

$$r_i = (R_{\text{ion}} + R_{\text{g,max}}) / 2.0$$  \hspace{1cm} (VIII.A.34)

The Born effective radii for hydrated ions are given in Table VIII. A.1. The 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 [24]. The Pauling radii for hydrated ions ($\text{Na}^+, \text{Mg}^{2+}, \text{Cl}^-, \text{SO}_4^{2-}$) are given in Table VIII.A.1.

**Figure VIII.A.2.** A schematic diagram of the orientation of water dipoles around (a) cations and (b) anions [23].

**VIII.A.2.2. Computations**

Equations (VIII.A.15) and (VIII.A.19) have been solved by the shooting method based on Runge-Kutta Gear method and Newton-Raphson technique using FORTRAN subroutines namely, DGEAR and ZSPOW. Double precision was used in all the simulations.
Table VIII.A.1. Ion bulk diffusion coefficient, partial molar volumes and various ion radii for different solutes [22-27].

<table>
<thead>
<tr>
<th>solute</th>
<th>$D_{io}$ $10^{-9}$ (m$^2$ s$^{-1}$)</th>
<th>$V_i$ (cm$^3$ mol$^{-1}$)</th>
<th>$r_i$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stokes</td>
<td>Cavity</td>
<td>Born</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.33</td>
<td>-1.20</td>
<td>0.168</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>
<tr>
<td>Glucose</td>
<td>0.69</td>
<td>110</td>
<td>0.368</td>
</tr>
</tbody>
</table>

VIII.A.3. RESULTS AND DISCUSSION

VIII.A.3.1. Determination of Membrane Permeability ($L_p$)

Pure water was subjected to permeation at different operating pressures as shown in Figure VIII.A.3 to obtain the membrane permeability. The plot of volumetric flux against pressure drop yielded a straight line with slope $(L_p = \frac{8\eta \Delta x}{r_p^2} = 22.87 \times 10^{-6} m/s/ Pa)$ as the permeability of the Desal-HL NF membrane. The permeability of NF 700 MWCO was found to be $23.67 \times 10^{-6} m/s/ Pa$ as shown in Figure VIII.A.4. One of the interesting aspects was that both the membranes possess similar permeability values with only a slight difference.

VIII.A.3.2. Determination of Radius of Pore ($r_p$)

The retention of glucose was performed as an uncharged solute to determine the radius of the pore using the uncharged solute model eq. (VIII.A.30). The rejection of glucose increased with pressure drop as shown in Figure VIII.A.5. The uncharged model was fitted with the experimental data using the least squares analysis for the conversion:
\[ \theta = \sqrt{\sum_{j} \sum_{n} (R_{np} - R_{l})} \]  
\text{(VIII.A.35)}

The radius of the pore was found to be 0.48 nm for Desal-HL and 0.78 nm for NF MWCO 700. The model fittings for the two membranes is shown in Figures VIII.A.5 and VIII.A.6, respectively.

**Figure VIII.A.3.** Experimental volumetric flux, \( J_v \), as a function of pressure drop for pure water for Desal-HL NF membrane.

**Figure VIII.A.4.** Experimental volumetric flux, as a function of pressure drop for pure water for NF MWCO 700.
VIII.A.3.3. Validation of Experimental Data with Donnan Steric Pore Model (DSPM)

Figures VIII.A.7 and VIII.A.8 shows the experimental rejection of sodium chloride for Desal HL and NF MWCO700 membranes. Experiments were carried out at normal pH. The negatively charged membrane attracts the positively charged ions, but repels the negatively charged ions as per Donnan effect. At lower concentration, the rejection of sodium chloride was high. As the concentration was increased, the rejection started to decline as shown in Figure VIII.A.7. At higher concentration, the effect of steric hindrance was also negligible due to shielding of charged solutes. When NF membrane was placed in an ionic solution, due to the association and dissociation of functional group at the surface, leads to the formation of charges. The charge generated is usually related to the ionization of functional group existing on the surface of the membrane, which strongly depends on the pH of acid and base dissociation. However, the charge may be due to positive and negative charges prevailing on the functional group, which gives an approximated fixed charge. Chemical and physical interactions exist, resulting in the adsorption of charges. Counter ions usually adsorb on the surface of the membrane, but co-ions adsorb onto the hydrophobic surface of the membrane. Anion adsorption is more favorable due to its lower hydration radii when compared to cations.

It can be inferred that at lower concentration, the adsorption of chloride ions at the surface is negligible but at higher concentration, more of chloride ions will get adsorbed for the negatively charged membrane. Reported data are in good agreement with the interpretation of these results. It is a conventional wisdom that chloride adsorption is prevalent on the membrane with respect to sodium adsorption, since anions show lower hydration radii than cations. NF MWCO 700 has the pore radius larger than the Desal-HL NF membrane and hence, it may
be concluded that the charge effect will play an important role in the retention of sodium chloride, albeit the retention was low as shown in Figure VIII.A.8.

![Figure VIII.A.5. Comparison of the agreement between experimental uncharged solute rejection data and the best curve fit obtained from the uncharged solute model \( r_p = 0.48 \text{nm} \) Desal-HL NF membrane](image1)

![Figure VIII.A.6. Comparison of the agreement between experimental uncharged solute rejection data and best curve fit obtained from the uncharged solute model \( r_p = 0.48 \text{nm} \) for NF MWCO700 membrane](image2)
Experimental data were validated using DSPM. Donnan and steric effects were only taken as partitioning coefficients. All the fundamental radii viz., Stokes-Einstein, Born and Pauling were used in the model equations. The only input to the model used was the dimensionless charge density. Figures VIII.A.7 and VIII.A.8 shows the model fitting of experimental data for Stokes-Einstein radius. At lower concentration, the model fitted the experimental data perfectly, but at higher concentration, certain deviations were observed for Desal-HL NF membrane. Least squares analysis of eq. (VIII.A.35) was employed between the experimental data and model fitting results. Similar procedure was also adopted for Born effective and Pauling radii, respectively. Negative charge densities were fitted to the experimental data. Table VIII.A.2 shows the results of charge density of sodium chloride with concentration for both the membranes. Stokes-Einstein radius predicted higher charge density when compared to Born and Pauling radii. Born radius predicted lower charge density, which can be considered physically realistic, since the NF membrane carry low negative charge at its surface. However, the charge density at the surface is not constant and depends on the variation of concentration. The charge density \( (\chi_u) \) is the product of feed concentration \( (C_f) \) and dimensionless charge density \( (\zeta) \). The charge densities are plotted vs concentration to obtain the linear isotherms. Correlations relating charge density and concentration were obtained for each radii as shown in eqs. (VIII.A.36) and (VIII.A.37) for each membrane. These results are given below.

Figures VIII.A.9 and VIII.A.10 shows the experimental rejection of magnesium chloride. As the concentration of magnesium chloride increased, the rejection was also increased. This was indeed observed by others [32]. As the concentration of magnesium chloride was increased,
more magnesium ions were attracted to the surface to shield the membrane resulting in the positive charge. Charge reversion at the surface can also be expected. The adsorption phenomenon can be regarded as an interfacial precipitation of the metal hydroxide occurring at a pH lower than the bulk value. The adsorption is influenced by the charge and dielectric constant. It was also explained that at higher concentration, pore shrinking is expected [33].

Figure VIII.A.7. Experimental and theoretical rejection as a function of pressure drop for sodium chloride of various bulk concentrations for Stokes-Einstein radius. (DSPM) for Desal-HL NF membrane.

Table VIII.A.2. Comparison of charge densities obtained by DSPM for Desal-HL NF membrane for sodium chloride with various radii.

<table>
<thead>
<tr>
<th>Radii</th>
<th>Desal-HL Charge density ($\chi_d$) (mol/m³)</th>
<th>NF MWCO 700 Charge density ($\chi_d$) (mol/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mol/m³)</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Stokes Einstein</td>
<td>-14.8</td>
<td>-128</td>
</tr>
<tr>
<td>Born’s effective</td>
<td>-5</td>
<td>-43</td>
</tr>
<tr>
<td>Pauling</td>
<td>-10.5</td>
<td>-91</td>
</tr>
</tbody>
</table>
**Figure VIII.A.8.** Experimental and theoretical rejection as a function of pressure drop for sodium chloride of various bulk concentrations for Stokes Einstein radius. (DSPM) for NF MWCO 700 membrane.

**Desal HL NF membrane**

Stokes Einstein radius: \( \chi_d = -5.85C - 37.77 \)
Born’s effective radius: \( \chi_d = -1.98C - 12.61 \)
Pauling radius: \( \chi_d = -3.94C - 28 \)  
(VIII.A.36)

**NF 700 MWCO**

Stokes Einstein radius: \( \chi_d = -1.65C_f - 3.61 \)
Born’s effective radius: \( \chi_d = -0.97C_f - 2.66 \)
Pauling radius: \( \chi_d = -1.465C_f - 3.61 \)  
(VIII.A.37)

DSPM model requires positive charge densities to fit the experimental data for magnesium chloride. Negative charge density gives unrealistic values and does not show physical characteristics at the surface of the membrane. All the fundamental radii namely, Stokes-Einstein, Born and Pauling radii were used in the simulation. The model fittings are shown in **Figures VIII.A.9 and VIII.A.10**, respectively. Least square on eq. (VIII.A.35) was used for experimental and model fitting. Physically, NF membrane carries negative charge, but DSPM predicted positive charge.
This was the anomaly of DSPM in prediction of divalent ions. Due to that researchers were focusing on the utilization of dielectric exclusion. With this influence of ion size, the radius that predicts lower charge density can be regarded as a physical picture of the surface of the membrane.

Table VII.A.3. Comparison of charge densities obtained by DSPM for Desal-HL NF membrane for magnesium chloride with various radii.

<table>
<thead>
<tr>
<th>Radii</th>
<th>Desal-HL Charge density ($\chi_d$) (mol/m$^3$)</th>
<th>NF MWCO 700 Charge density ($\chi_d$) (mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mol/m$^3$)</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Stokes Einstein</td>
<td>0.6</td>
<td>10.4</td>
</tr>
<tr>
<td>Born’s effective</td>
<td>3.85</td>
<td>55</td>
</tr>
<tr>
<td>Pauling</td>
<td>7</td>
<td>102</td>
</tr>
</tbody>
</table>

Figure VII.A.9. Experimental and theoretical rejection as a function of pressure drop for magnesium chloride of various bulk concentrations for Stokes-Einstein radius. (DSPM) for Desal-HL NF membrane.
Figure VIII.A.10. Experimental and theoretical rejection as a function of pressure drop for magnesium chloride of various bulk concentrations for Stokes-Einstein radius. (DSPM) for NF MWCO700 membrane.

Table VIII.A.3 shows the charge densities obtained by theoretical simulation. Pauling radius predicted higher charge density than the other radii. Stokes-Einstein radius predicted the lowest charge densities. It can be concluded that Stokes-Einstein radius can be used for magnesium chloride, since it offers lower charge density and nearer to the surface characteristics of membrane, even though there is a wide hiatus between the obtained results and surface characteristics.

Correlations were obtained relating charge density with concentration as shown in equation (VIII.A.38) and (VIII.A.39):

**Desal-HL**

Stokes Einstein radius: \[ \chi_d = 1.06 C - 0.35 \]

Born's effective radius: \[ \chi_d = 6.03 C - 3.69 \]

Pauling radius: \[ \chi_d = 10.22 C - 1.77 \]  \hspace{1cm} (VIII.A.38)

NF 700 MWCO:

Stokes Einstein radius: \[ \chi_d = 2.67 C_f - 8.33 \]

Born's effective radius: \[ \chi_d = 4.61 C_f - 12.69 \]
Pauling radius: \( \chi_d = 6.67C_f -19.22 \) \hspace{1cm} (VIII.A.39)

VIII.A.3.4. Effect of pH

The rejection of sodium chloride as a function of pressure drop for various pH values displayed in Figures VIII.A.11 and VIII.A.12 shows that rejection of sodium chloride depends strongly upon the operating pH. With increasing feed pH from 3 to 9, sodium chloride rejection shows minima around the pH range of 5-5.5. The point at which minimum rejection occurs is called “isoelectric point,” which is attributed to the fact that electrostatic repulsion between charged membrane surface and solute performed the minimum because surface charges of the membrane increase and decrease with increasing pH.

![Figure VIII.A.11. Variation of experimental 0.01M sodium chloride rejection with pH for Desal-HL NF membrane.](image)

Positive charge of the membrane grows when pH decreases and sodium ions are rejected more and more by amide groups of the membrane. Since the cation and anion cannot act independently, Cl\(^-\) is also rejected to maintain electroneutrality. The charge effect is thus added to steric exclusion and retention increases. At pH higher than the isoelectric point,
an increase in the negative charge will occur at the surface of the membrane due to which more of chloride ions are rejected. The decrease in salt rejection from pH 9.0 to isoelectric point as shown in Figures VIII.A.11 and VIII.A.12 is attributed to a decrease in co-ion charge exclusion. At pH 9.0, when the membrane pore is more negatively charged, the chloride ion experiences an electrostatic repulsion from the membrane pore and will be rejected by the membrane. Because the electroneutrality of permeate solution must be maintained, Na⁺ ions will also be rejected. As the pH decreases, the electrostatic and ion rejection also decreases. At pH 5.0, the rejection reaches a local minimum, since the lack of charge leads not only to no electrostatic repulsion, but also increased pore size and salt passage. Further decrease of pH from the isoelectric point to pH 3 results in an increase of salt rejection dramatically because of the extensive proton passage through the membrane. It is thus clear that pressure has a significant effect on the isoelectric point. It may also be noted that for sodium chloride below and above the isoelectric point, NF membrane behaves as positively and negatively charged surface. By the measurement of zeta potential also the membrane behaved as positively charged surface below pH 5.5 for sodium chloride [34]. At higher acidic pH, the rejection was high; as the pH increased the rejection decrease.

DSPM model was used to the experimental data to study the effect of pH. Desal-HL NF membrane has been studied before [19]. Figures VIII.A.13 and VIII.A.15 show the model fit with the experimental data for Stokes-Einstein radius for NF MWCO 700 membrane for which an excellent fit was obtained. Similar procedures were also followed for Born effective and Pauling radii, respectively. Tables VIII.A.4 and VIII.A.5 show the results obtained from simulation of both positive and negative charge densities. Correlation regarding the charge density with pH was also
obtained as shown eqs. (VIII.A.40), (VIII.A.41), (VIII.A.42) and (VIII.A.43):

**Figure VIII.A.12.** Variation of experimental 0.01M sodium chloride rejection with pH Desal-HL NF membrane

**Figure VIII.A.13.** Experimental and theoretical rejection of sodium chloride of (0.01M concentration) for various pH values for Stokes-Einstein radius (DSPM-positive charge density). NF MWCO 700 membrane
Figure VIII.A.14. Experimental and theoretical rejection of sodium chloride of 0.01M for various pH values for Stokes-Einstein radius (DSPM-negative charge density) for NF MWCO 700 membrane.

Desal HL membrane [19]
Positive charge
Stokes Einstein radius: $\chi_d = -47.91 \, pH + 291.34$
Born effective radius: $\chi_d = -34.06 \, pH + 210.49$
Pauling radius: $\chi_d = -108.68 \, pH + 661.10$ \hspace{1cm} (VIII.A.40)

Negative charge
Stokes-Einstein radius: $\chi_d = -38.44 \, pH + 69.89$
Born effective radius: $\chi_d = -13.36 \, pH + 25.55$
Pauling radius: $\chi_d = -30.14 \, pH + 67.34$ \hspace{1cm} (VIII.A.41)

NF MWCO 700 membrane
Positive charge
Stokes-Einstein radius: $\chi_d = -13.0 \, pH + 77.89$
Born effective radius: $\chi_d = -11.43 \, pH + 68.85$
Pauling radius: $\chi_d = -18.21 \, pH + 112.05$ \hspace{1cm} (VIII.A.42)

Negative charge
Stokes-Einstein radius: $\chi_d = -10 \, pH + 17.5$
Born effective radius: $\chi_d = -6.5 \, pH + 14.5$
Pauling radius: $\chi_d = -8.8 \, pH + 18.5$ \hspace{1cm} (VIII.A.43)
Table VIII.A.4. Comparison of charge density using DSPM for Desal-HL and NF MWCO 700 NF membranes for sodium chloride with various radii (positive charge density).

<table>
<thead>
<tr>
<th>Radii</th>
<th>Desal-HL Charge density ($\chi_d$) (mol/m$^3$)</th>
<th>NF MWCO 700 Charge density ($\chi_d$) (mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.9  4.5  5.0</td>
<td>3.1  4.1  5.0</td>
</tr>
<tr>
<td>Stokes</td>
<td>108  68  56</td>
<td>35  30  10</td>
</tr>
<tr>
<td>Einstein</td>
<td>80   52  43</td>
<td>31   27  9</td>
</tr>
<tr>
<td>Born effective</td>
<td>245  155 127</td>
<td>52   45  17</td>
</tr>
</tbody>
</table>

Table VIII.A.5. Comparison of charge density using DSPM for Desal-HL and NF MWCO 700 membranes for sodium chloride with various radii (negative charge density).

<table>
<thead>
<tr>
<th>Radii</th>
<th>Desal-HL Charge density ($\chi_d$) (mol/m$^3$)</th>
<th>NF MWCO 700 Charge density ($\chi_d$) (mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.0  7.0  8.0  8.8</td>
<td>6.0  7.0  8.0  9.0</td>
</tr>
<tr>
<td>Stokes</td>
<td>-156 -210 -230 -272</td>
<td>-40  -55  -65  -70</td>
</tr>
<tr>
<td>Einstein</td>
<td>-53  -72  -78  -93</td>
<td>-23  -33  -38  -43</td>
</tr>
</tbody>
</table>

VIII.A.3.5. Validation of Experimental Data with Donnan Steric Pore Model- Dielectric Exclusion (DSPM-DE)

Dielectric exclusion arises as a consequence of the difference between the dielectric properties of aqueous solution and the membrane pore. Thus, there will be a decrease in dielectric constant inside the nano pore.
Dielectric exclusion results in the repulsion of ions of whatever charge it carries. However, equilibrium and dynamic properties of a solvent in the confined geometry like pores of NF membranes can differ significantly from those in the bulk (i.e., outside pores) because solvent molecules in such an environment exhibit a greater degree of spatial and orientation order. This ordered structure reduces the ability of solvent molecules to respond to an external electric field and hence, leads to a decrease in solvent dielectric constant. The molecular dynamic simulations have confirmed these results albeit some contradictory results do exist in the literature [35, 36].

Figure VIII.A.15. Rejection versus pressure drop for reassessed dielectric constant using different radii for Desal-HL NF membrane

The excess solvation energy resulting from the difference in dielectric constant between external and internal solutions can be estimated on the basis of Born model. The Born model has the advantage to be easily included in the classical theory without increasing the complexity of calculations. The radius of the ion in the Born model is still an active area.
of research [23, 37]. Since the solvation energy is overestimated as compared to experimental data, radius of the ion has been altered to satisfy the experimental Gibb's free energy and theoretical free energy. For this model to be implemented, rejection data at amphoteric condition are needed for sodium chloride. This can be achieved by varying pH. The point at which rejection of sodium chloride gives minimum rejection is known as isoelectric point or point of zero charge.

![Graph showing rejection versus pressure drop](image)

**Figure VIII.A.16.** Rejection versus pressure drop for reassessed dielectric constant using different radii for NF MWCO 700 membrane.

**VIIIA.3.6. Determination of Pore Dielectric Constant ($\varepsilon^*$)**

Figures VIIIA.15 and VIIIA.16 show the experimental rejection of sodium chloride at isoelectric point for Desal-HL and NF MWCO 700 NF membranes. DSPM-DE model was implemented. Steric and dielectric exclusion parameters were the only partitioning effect. The charge density was kept at zero, while the radius of the pore was determined through the uncharged solute in the model. Stokes-Einstein, Born and Pauling radii were all used. Eq. (VIIIA.35) was used to access the error between the experiment and model fitting. The only fitting parameter in the model was
the pore dielectric constant, which was varied with the experimental data. The model fitting is also shown in Figures VIII.A.13 and VIII.A.14. Each radii predicted different dielectric constants as shown in Table VIII.A.6, but the magnitude of variation was small.

**Table VIII.A.6.** Simulation results for reassessed dielectric constant ($\varepsilon^*$) for various radii.

<table>
<thead>
<tr>
<th>Radii</th>
<th>Reassessed dielectric constant ($\varepsilon^*$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Desal-HL</td>
</tr>
<tr>
<td>700</td>
<td>Stokes-Einstein</td>
</tr>
<tr>
<td></td>
<td>Born effective</td>
</tr>
<tr>
<td></td>
<td>Pauling</td>
</tr>
</tbody>
</table>

For NF MWCO 700, since the pore size is large, the confinement effect is less. Thus, the dielectric constant reduction also small. Confinement effects are predominant for Desal-HL. The confinement can change the dielectric constant of the solvent in a pore or cavity, which in turn, could influence the effective electrostatic field within the liquid and also the dynamic properties. Molecular dynamic (MD) simulations of water confined in smooth hydrophobic pockets, in channels and also in reverse micelles have indicated that water molecules confined in such environments exhibit a great degree of spatial and orientational order than found in the bulk phase with the formation of molecular layers near the cavity surface. Clearly, this ordered structure in the confined systems can affect the ability of water molecules to respond to an external field and hence, can change the dielectric constant [35].

Senapathy and Chandra [35] calculated the dielectric constant of liquid water confined in a spherical nanocavity using MD simulations. The simulations were carried out for two different water models viz., soft sticky dipole (SSD) and simple point charged/extended (SSP/E). Three different
sizes of cavity are considered for each water model. For both the models, dielectric constant of water in the cavity was found to be significantly lower than the bulk value. A nearly 50% decrease in dielectric constant was found when water was confined in a cavity of about 1.2 nm. In the present model, the cavity surface was uncharged and therefore, there was no electrostatic interaction between water molecules and cavity surface. However, the reduction in dielectric constant arises purely due to confinement.

Figure VIII.A.17. Experimental and theoretical rejection as a function of pressure drop for sodium chloride of various bulk concentrations for Stokes-Einstein radius (DSPM-DE) for Desal-HL NF membrane.

In the present investigation, the nano pore carries a charged surface and dielectric constant was around 33 to 35. The effect of electrostatic interaction and confinement decreases the dielectric constant of the solvent from 80 to 35. Recent simulations devoted to the structural and transport properties of potassium chloride solution in nano pore confirmed the effect of external electric field on the orientation of water molecules. In this
investigation, the electric field generated by the fixed charges at the pore walls is expected to produce some additional ordering of solvent dipoles and then a decrease in the effective dielectric constant inside the nano pores [38].

![Stokes Einstein radius](image)

**Figure VIII.A.18.** Experimental and theoretical rejection as a function of pressure drop for sodium chloride of various bulk concentrations for Stokes-Einstein radius (DSPM-DE) for NF MWCO 700 membrane.

DSPM-DE model was implemented to the experimental data of sodium chloride rejection. **Figures VIII.A.17 and VIII.A.18** compare the theoretical model fittings with experimental data for Stokes-Einstein radius. Similar procedure was also adopted for Born effective and Pauling radii. For Desal-HL membrane, at lower concentration of sodium chloride, the model fitted excellent to the experimental data, but at higher concentrations, there was a wide gap. This effect may be due to the significant amount of solute concentration at the pore wall of the membrane. This may be the result of ignoring the concentration dependence by the proposed model for dielectric exclusion, which suggests that
significant ion concentrations within the pore may disrupt the orientation of water molecules and decrease the effect of solvation energy barrier. There is an experimental evidence for it that ion changes water structure in the pore [39]. Table VIII.A.7 shows the results of simulations for both the membranes. Correlation relating charge density with concentration was obtained as shown in eqs. (VIII.A.44) and (VIII.A.45).

Table VIII.A.7. Comparison of charge densities obtained by DSPM-DE for Desal HL and NF MWCO 700 membranes for sodium chloride with various radii

<table>
<thead>
<tr>
<th>Radii</th>
<th>Desal-HL Charge density ($\chi_d$) (mol/m$^3$)</th>
<th>NF MWCO 700 Charge density ($\chi_d$) (mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mol/m$^3$)</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Stokes Einstein</td>
<td>-0.15</td>
<td>-1.2</td>
</tr>
<tr>
<td>Born's effective</td>
<td>-0.09</td>
<td>-0.6</td>
</tr>
<tr>
<td>Pauling</td>
<td>-0.045</td>
<td>-0.25</td>
</tr>
</tbody>
</table>

Desal HL membrane

Stokes Einstein radius: $\chi_d = -0.11C - 0.03$
Born effective radius: $\chi_d = -0.05C - 0.03$
Pauling radius: $\chi_d = -0.02C - 0.02$ (VIII.A.44)

NF MWCO 700 membrane

Stokes Einstein radius: $\chi_d = -0.365C_f - 3.72$
Born effective radius: $\chi_d = -0.065C_f - 3.63$
Pauling radius: $\chi_d = -0.0421C_f - 2.97$ (VIII.A.45)
Figure VIII.A.19. Experimental and theoretical rejection as a function of pressure drop for magnesium chloride of various bulk concentrations for Stokes-Einstein radius. (DSPM-DE) for Desal-HL NF membrane.

Figure VIII.A.20. Experimental and theoretical rejection as a function of Pressure drop for magnesium chloride of various bulk concentrations for Stokes-Einstein radius. (DSPM-DE) for NF MWCO700 membrane.
Figures VIII.A.19 and VIII.A.20 show the experimental rejection of magnesium chloride with operating pressure. Stokes Einstein, Born and Pauling radii were all used in the theoretical simulation along with dielectric constants. The model fittings are shown in Figure VIII.A.19 and VIII.A.20 for Stokes Einstein radius for Desal-HL and NF MWCO 700. The model fitted the experimental data in an excellent manner. Similar procedure was adopted for Born’s and Pauling radii as shown in Figure VIII.A.5. At dilute concentration, Born’s radii did not predict the experimental data and at high concentration, it predicted the experimental data perfectly. Pauling radius could not predict the experimental data, since the rejection was high i.e., more than 99%. This may be due to the sudden decrease in dielectric constant inside the nano pore. Born radius predicted lower charge density at the surface than the Stokes-Einstein radius as shown in Table VIII.A.8. Suitable correlation was obtained relating the charge density with the concentration as given by eq. (VIII.A.46).

Desal-HL
Stokes Einstein radius: \( \chi_d = -0.038C - 0.15 \)
Born’s effective radius: \( \chi_d = -0.005C \) (VIII.A.46)

DSPM-DE predicted negative charge at dilute concentration for NF MWCO 700. As the concentration was increased, it predicted the positive charge. Since the dielectric constant is small and radius of pore is large, there is an accumulation of magnesium ions at the surface, which resulted in a positive charge. One important thing is that the surface charge predicted by DSPM-DE in magnitude is less than that predicted by DSPM. If the image force contribution is included, there can be a change in the prediction.

NF MWCO 700:
Stokes Einstein radius: \( \chi_d = 1.24C_f - 5.15 \)
Born’s effective radius: \( \chi_d = 1.87C_f - 6.19 \)
Pauling radius: \[ \chi_d = 0.77C_f - 3.17 \] (VIII.B.47)

Result of DSPM-DE model shown in Table VIII.A.8 can be compared with DSPM calculation shown in Table VIII.A.3. DSPM needs positive charge density to fit the experimental data. Due to the introduction of reassessed dielectric exclusion, it resulted in lower negative charge. The positive charge obtained from DSPM was altered to slight positive charge by the DSPM-DE.

Table VIII.A.8. Comparison of charge densities obtained by DSPM-DE for Desal-HL NF membrane for magnesium chloride with various radii.

<table>
<thead>
<tr>
<th>Radii</th>
<th>Desal-HL Charge density ((\chi_d)) (mol/m(^3))</th>
<th>NF MWCO 700 Charge density ((\chi_d)) (mol/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mol/m(^3))</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Stokes Einstein</td>
<td>-0.15</td>
<td>-0.4</td>
</tr>
<tr>
<td>Born’s effective effective</td>
<td>-</td>
<td>-0.05</td>
</tr>
<tr>
<td>Pauling</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

From the present analysis, it is realized Desal-HL membrane is slightly negatively charged. Since the radius of the pore as well as dielectric constant is low in a nano pore it resulted in a negative charge. But, NF MWCO 700 membrane is highly negatively charge, even though it has a large pore radius and a high dielectric constant. It may thus be concluded that pore radius and dielectric constant have a great significance in the prediction of charge density. Pauling radius can be used in the simulation of dielectric exclusion, since it offers a less negative charge, but will be close to the real physical properties of the membrane. The high negative charge produced by DSPM was altered to low negative charge by the introduction.
of dielectric exclusion. In the case of magnesium chloride, Desal-HL NF membrane predicted negative charge for magnesium chloride. At lower concentration, the NF MWCO 700 predicted negative charge, but increase in concentration lead to more positive charge at the surface.

**VIII.A.4. CONCLUSIONS**

The present investigation compares two different commercial NF membranes prepared by different procedures. DSPM was applied to the experimental data of sodium chloride rejection. Three different radii viz., Stokes-Einstein, Born and Pauling were used in DSPM model. The radius of the pore was determined by the uncharged solute rejection experiment. Charge density at the surface of the membrane was used as a fitting parameter to experimental data of sodium and magnesium chloride rejection. Each radii predicted different charge densities. Correlations were developed relating charge density with concentration. The effect of pH was studied to identify the isoelectric point of the membrane. DSPM was also applied to the experimental data to study the effect of pH. Positive and negative charges were fitted for below and above the isoelectric point. Correlations were developed relating the charge density with pH. DSPM-DE was also applied to the experimental data of sodium and magnesium chloride rejections. The pore dielectric constant was obtained for different radii. Due to the introduction of dielectric exclusion, the surface charge of the membrane decreased drastically to exhibit the real physical characteristics of NF membrane. The important conclusion of this study is that ionic radii exert a great influence in the prediction of charge density.
Nomenclature and List of Symbols

\[ a_i \] activity of ion \( i \), mol \( m^{-3} \)
\[ C_i(0) \] solute feed solution concentration, mol \( m^{-3} \)
\[ C_i(\delta ) \] 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 \( i \), \( m^2 s^{-1} \)
\[ D_{i00} \] ion bulk diffusion coefficient, \( m^2 s^{-1} \)
\[ e \] electronic charge, \( 1.602177 \times 10^{-19} \) C
\[ F \] 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 \( i \)
\[ K_{li} \] 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
\[ r_i \] radius of ion \( i \), m
\[ r_p \] effective pore radius, m
\[ R_{i} \] overall rejection of solute \( i \), calculated through eq. (VIII.A.26), dimensionless
\[ R_{exp} \] rejection measured through experiment, dimensionless
\[ R \] universal gas constant, 8.314 J mol\(^{-1}\) K
\[ T \] absolute temperature, K
\[ u \] solvent velocity, m s\(^{-1}\)
\[ V_i \] partial molar volume of ion \( i \), m\(^3\) mol\(^{-1}\)
\[ x \] axial position within the pore, m
\[ z_i \] valence of ion \( i \), dimensionless

GREEK SYMBOLS

\[ \beta_i \] ion function, dimensionless
\[ \delta \] membrane thickness, m
\[ \Delta P \] applied pressure, N m\(^{-2}\)
\[ \Delta P_e \] effective pressure driving force, N m\(^{-2}\)
\[ \Delta \pi \] osmotic pressure, N m\(^{-2}\)
\[ \Delta \psi_D (0) \] Donnan potential at the feed membrane interface, V
\[ \Delta \psi_D (\delta) \] Donnan potential at the permeate membrane interface, V
\[ \Delta W (0) \] Born solvation energy barrier at the feed membrane interface, J
$\Delta W$ (s)  Born solvation energy barrier at the permeate membrane interface, $J$

$\varepsilon_b$  bulk dielectric constant, dimensionless ($\varepsilon_b=80$)

$\varepsilon_p$  pore dielectric constant, dimensionless

$\varepsilon^*$  dielectric constant of oriented water layer

$\varepsilon_0$  permittivity of free space, $8.85419 \times 10^{-12}$ J C$^{-2}$ m$^{-1}$

$\eta$  solvent viscosity within pores, N s m$^{-2}$

$\eta_0$  bulk solvent viscosity, N s m$^{-2}$

$\gamma_i$  activity coefficient of ion $i$ within pore, dimensionless

$\lambda_i$  ratio of ion radius to pore radius, dimensionless

$\mu_i$  electrochemical potential of ion $i$, J mol$^{-1}$

$\phi_i$  steric partition coefficient of ion $i$, dimensionless

$\chi_i$  effective charge density, mol m$^{-3}$

$\zeta$  ratio of effective charge density to bulk feed concentration, dimensionless

$\psi$  potential within the pore, V

$\theta$  sum of square objective function in fitting, dimensionless
VIII.A.5. REFERENCES


Membrane Based Separation Processes for Effluent Treatment


INVESTIGATING THE PHYSICAL PROPERTIES OF NANOFILTRATION MEMBRANES USING EXPERIMENT AND THEORETICAL MODELS

ABSTRACT

Two commercial nanofiltration (NF) membranes viz., NF 300 MWCO and NF 250 MWCO was investigated experimentally using neutral and charged solutes viz., glucose, sodium chloride and magnesium chloride. The experimental rejection rates of solute were investigated using Donnan steric pore model (DSPM) and DSPM-dielectric exclusion (DSPM-DE) model. The radius of pore was found to be 0.62 nm and 0.56 nm. The permeability of both the membrane was almost same. Various radii viz., Stokes-Einstein, Born effective and Pauling radii were used in the theoretical simulation. It was concluded that these radii predicted accurately different charge densities. To access the dielectric exclusion, NF 250 membrane was investigated. The charge density decreased drastically for sodium chloride when dielectric exclusion was included in the theoretical model, which showed the real physical characteristics of the membranes employed. The divalent ion, magnesium chloride showed a shift from positive to negative charge density when dielectric exclusion was incorporated. The charge density and pore radius is thus an important physical parameter, which has influence in understanding fouling propensity of nanofiltration membranes.

Results of this chapter are submitted to Chemical Engineering Research and Design (2007)
VII.B.1. INTRODUCTION

In recent years, the use of membrane-based nanofiltration (NF) membrane technology has increased rapidly in chemical, petrochemical, biological and desalination industries, since it overcomes several operational problems that are associated with the conventional techniques. 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 the sieving effect, Donnan, dielectric exclusion and in addition, electromigration, which makes it useful to separate, both charged as well as organic solutes [1]. When NF membranes were used in the pretreatment section of conventional RO, the product recovery increased to 36.4% with a reduction in the operating pressure to 54 bar, which resulted in an enormous amount of energy reduction. The top-brine temperature in conventional multi-stage flash (MSF) was increased above 120 o C, when NF was used as a pretreatment, which reduced the scaling propensity of calcium and magnesium salts [2].

Besides desalination industry, the application of NF technology today includes disinfection by removal of organics [3] and recovery of high value organometallic catalysts from the reaction mixtures allowing the catalyst to be reused [4] (White, 2006). NF also can be used to separate inorganic salts with much smaller size than pore size according to electrostatic repulsions. Pharmaceutical applications includes the isolation of industrially important antiviral drug precursor, N-acetyl-D-neuraminic acid [5], clindamycin from fermentation waste water [6], sodium cefuroxime from cephalosporin-C [7] and Cephalexin [8], NF technique may be used in water softening, drinking water purification and other fields of medicine and engineering. The presently used NF membranes are mostly negatively charged or neutral.

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
Membrane Based Separation Processes for Effluent Treatment

ignoring the structure of the membrane or any transport mechanism. These models are utilized at high rejection of solutes, but fail to predict at lower rejection. Mechanistic models assume the membrane structure and the model equations account for effects of physical and chemical characteristics of both the membrane and the electrolyte solution. Most mechanistic models fall in to two categories: those based on space-charge (SC) model and Teorrell-Meyer-Sievers (TMS) model. The SC model is mathematically complicated and computationally expensive as compared to 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 the difference in dielectric constant between the bulk and nanocavity. Role of the difference existing between dielectric constant of the aqueous solution in the pores and dielectric constant of the membrane material is assumed to be dominant in determining the rejection mechanism related to dielectric effects [9]. It was clearly shown that the dielectric exclusion cannot be neglected in the analysis of filtration properties of NF membrane [10,11]. Experimental techniques such as nuclear magnetic resonance (NMR) and Fourier transform infrared spectra (FT-IR) show week signals at the surface of the membrane; the surface charge is generated due to the unreacted species at the surface during interfacial polymerization [12]. The influence of ion radii, namely, Stokes-Einstein, Born and Pauling has profound effect on the prediction of charge density at the surface of the membrane. Donnan steric pore model (DSPM) was investigated for various solutes such as sodium chloride, sodium sulfate, magnesium chloride and magnesium sulfate [13]. DSPM-dielectric exclusion was also investigated for various radii. The effect of pore size distribution was also investigated, which gave a different prediction for various radii [14,15]. The principal objective of the present study is to investigate the influence of ionic radii viz., Stokes-Einstein, Born and Pauling to predict the Donnan steric pore model (DSPM) and Donnan steric
Membrane Based Separation Processes for Effluent Treatment

pore model-dielectric exclusion (DSPM-DE). Two commercial membranes viz., NF 250 MWCO and NF 300 MWCO (from Permionics, India) were used in the study for comparative purpose. Sodium chloride and magnesium chloride was used as a simple solute. The effect of pH on rejection was studied to determine the NF isoelectric point of the membrane. The effect of radii on hindrance factor was also investigated. Physical properties of the membrane like radius of pore and charge densities were deduced from the theoretical models.

VII.B.2. RESULTS AND DISCUSSIONS

VII.B.2.1. Description of Different Ion Radii

The Born effective radii for hydrated ions are given in Table VII.B.1. The 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 [16].

<table>
<thead>
<tr>
<th>Solute</th>
<th>$D_{\text{io}} \times 10^{-9}$ (m$^2$ S$^{-1}$)</th>
<th>$V_i$ (cm$^3$ mol$^{-1}$)</th>
<th>$r_i$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stokes</td>
</tr>
<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>
<tr>
<td>Glucose</td>
<td>0.69</td>
<td>110</td>
<td>0.368</td>
</tr>
</tbody>
</table>

Table VII.B.1. Ion bulk diffusion coefficient, partial molar volumes and various ion radii for different solutes [16-21].
Figure VIII.B.1. Experimental and theoretical rejection as a function of pressure drop for sodium chloride of various bulk concentrations for Stokes-Einstein radius. (DSPM) for NF 300 membrane.

Figure VIII.B.2. Experimental and theoretical rejection as a function of pressure drop for sodium chloride of various bulk concentrations for Stokes-Einstein radius. (DSPM) for NF 250 membrane.
VII.B.2.2. Validation of Experimental Data with Donnan Steric Pore Model (DSPM)

Figures VIII.B.1 and VIII.B.2 shows the experimental rejection of sodium chloride for NF 300 and NF 250 membranes. Experiments were carried out at normal pH. The negatively charged membrane attracts the positively charged ions, but repels the negatively charged ions. This effect is the well-known Donnan effect. At lower concentration, the rejection of sodium chloride was high. As the concentration was increased, the rejection started to decline as shown in Figure VIII.B.1. At higher concentration, the effect of steric hindrance was also negligible due to shielding of charged solutes [22]. When NF membrane was placed in an ionic solution, due to the association and dissociation of functional group at the surface leads to the formation of charges.

VII.B.2.3. Determination of Membrane Permeability

Pure water was subjected to permeation at different operating pressures as shown in Figure VIII.B.3. to obtain the membrane permeability.
Figure VIII.B.3. Experimental volumetric flux, $J_v$ as a function of pressure drop for pure water for NF 300 MWCO membrane.

**VII.B.2.4. Determination of Radius of Pore**

The retention of glucose was performed as an uncharged solute to determine the radius of pore using the uncharged solute model. The rejection of glucose increased with pressure drop as shown in Figure 4.

Negative charge densities were fitted to the experimental data. Table VII.B.2 shows the results of charge density of sodium chloride with concentration for both the membranes. Stokes-Einstein radius predicted higher charge density when compared to Born and Pauling radii. Born radius predicted lower charge density, which can be considered physically realistic since the NF membrane carry low negative charge at its surface.

**Table VII.B.2.** Comparison of charge densities obtained by DSPM for Desal-NF membrane for sodium chloride with various radii.

<table>
<thead>
<tr>
<th>Radii</th>
<th>NF 300 MWCO Charge density (mol/m³)</th>
<th>NF 250 MWCO Charge density (mol/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Stokes Einstein</td>
<td>-30</td>
<td>-65</td>
</tr>
<tr>
<td></td>
<td>-230</td>
<td>-350</td>
</tr>
<tr>
<td></td>
<td>-1500</td>
<td>-2000</td>
</tr>
<tr>
<td>Born’s</td>
<td>-14.5</td>
<td>-30</td>
</tr>
<tr>
<td></td>
<td>-112</td>
<td>-150</td>
</tr>
<tr>
<td></td>
<td>-670</td>
<td>-900</td>
</tr>
<tr>
<td>Pauling</td>
<td>-24</td>
<td>-50</td>
</tr>
<tr>
<td></td>
<td>-185</td>
<td>-270</td>
</tr>
<tr>
<td></td>
<td>-1100</td>
<td>-1500</td>
</tr>
</tbody>
</table>

**Table VII.B.3.** Comparison of charge densities obtained by DSPM for Desal-HL NF membrane for magnesium chloride with various radii.

<table>
<thead>
<tr>
<th>Radii</th>
<th>NF 300 Charge density (mol/m³)</th>
<th>NF 250 Charge density (mol/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Stokes Einstein</td>
<td>1.45</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>16.3</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>115</td>
</tr>
<tr>
<td>Born’s</td>
<td>3.3</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>29.5</td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>340</td>
</tr>
<tr>
<td>Pauling</td>
<td>4.9</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>54</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>630</td>
<td>550</td>
</tr>
</tbody>
</table>

CHAPTER-VIIIB

193
With this influence of ions size, the radius, which predicts lower charge density, can be regarded as physical picture of the surface of the membrane. Table VII.B.3 shows the charge densities obtained by theoretical simulation. Pauling radius predicted higher charge density than the other radii. Stokes-Einstein radius predicted the lowest charge densities. It can be concluded that Stokes-Einstein radius can be used for magnesium chloride since it offers lower charge density and nearer to the surface characteristics of membrane, although there is a wide hiatus between obtained result and surface characteristics.

VII.B.2.5. Effect of pH

The rejection of sodium chloride as a function of pressure drop for various pH values for NF 250 was shown in Figure VIII.B.5. The rejection of sodium chloride depends strongly upon the operating pH. With increasing feed pH from 3 to 9, sodium chloride rejection shows minima around the pH range of 5-5.5. The point at which minimum rejection occurs is called "isoelectric
point,” which is attributed to the fact that electrostatic repulsion between charged membrane surface and solute performed the minimum because surface charges of the membrane increase and decrease with increasing pH.

Positive charge of the membrane grows when pH decreases and sodium ions are rejected more and more by amide groups of the membrane. Since the cation and anion cannot act independently, Cl- is also rejected to maintain electroneutrality. The charge effect is thus added to steric exclusion and retention increases. At pH higher than the isoelectric point, an increase in the negative charge will occur at the surface of the membrane due to which more of chloride ions are rejected. At pH 9.0, when the membrane pore is more negatively charged, the chloride ion experiences an electrostatic repulsion from the membrane pore and will be rejected by the membrane. Because the electroneutrality of permeate solution must be maintained, Na+ ions will also be rejected. As the pH decreases, the electrostatic and ion rejection also decreases. At pH 5.0, the rejection reaches a local minimum, since the lack of charge leads not only to no electrostatic repulsion, but also to increased pore size and salt passage.

DSPM model was used to the experimental data to study the effect of pH. Similar procedures were also followed for Born effective and Pauling radii, respectively. Tables VIII.B.4 and VIII.B.5 show the results obtained from simulation of both positive and negative charge densities.

Figure VIII.B.8 shows the experimental rejection of sodium chloride at isoelectric point for NF 250 membranes. DSPM-DE model was implemented. Steric and dielectric exclusion parameters were the only partitioning effect. The charge density was kept at zero, while the radius of the pore was determined through the uncharged solute in the model. Stokes-Einstein, Born and Pauling radii were all used. The only fitting parameter in the model was the pore dielectric constant, which was varied with the experimental data. The model fitting is also shown in Figure VIII.8. Each
radii predicted different dielectric constants as shown in Table VIII.5, but the magnitude of variation was small.

**Table VIII.B.4.** Comparison of charge density using DSPM for NF 250 membrane for sodium chloride with various radii (positive and negative charge densities).

<table>
<thead>
<tr>
<th>Radii</th>
<th>Charge density (mol/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.0</td>
</tr>
<tr>
<td>Stokes Einstein</td>
<td>45</td>
</tr>
<tr>
<td>Born’s</td>
<td>38</td>
</tr>
<tr>
<td>Pauling</td>
<td>88</td>
</tr>
</tbody>
</table>

**VII.B.2.6. Validation of Experimental Data with Donnan Steric Pore Model-Dielectric Exclusion (DSPM-DE)**

Dielectric exclusion arises as a consequence of the difference between the dielectric properties of aqueous solution and the membrane pore. Thus, there will be a decrease in dielectric constant inside the nano pore. Dielectric exclusion results in the repulsion of ions of whatever charge it carries. However, equilibrium and dynamic properties of a solvent in the confined geometry like pores of NF membranes can differ significantly from those in the bulk (i.e., outside pores) because solvent molecules in such an environment exhibit a greater degree of spatial and orientation order. This ordered structure reduces the ability of solvent molecules to respond to an external electric field and hence, leads to a decrease in solvent dielectric constant. These results have been confirmed by the molecular dynamic simulations albeit some contradictory results do exist in the literature [23,24].
In the present investigation, the nano pore carries a charged surface and dielectric constant was around 33 to 35. The effect of electrostatic interaction and confinement decreases the dielectric constant of the solvent from 80 to 35. In this investigation, the electric field generated by the fixed charges at the pore walls is expected to produce some additional ordering of solvent dipoles and then a decrease in the effective dielectric constant inside the nano pores [25]. There is an experimental evidence for it that ion changes water structure in the pore [26].
Figure VIII.B.6. Experimental and theoretical rejection of sodium chloride of (0.01M concentration) for various pH values for Stokes-Einstein radius (DSPM positive charge density). NF 250 membrane

Figure VIII.B.7. Experimental and theoretical rejection of sodium chloride of (0.01M for various pH values for Stokes-Einstein radius (DSPM negative charge density). NF 250 membrane
Figure VIII.B.8. Rejection versus pressure drop for reassessed dielectric constant using different radii for NF 250 membrane.

Table VIII.B.6. Comparison of charge densities obtained by DSPM-DE for NF 250 membranes for sodium chloride with various radii

<table>
<thead>
<tr>
<th>Radii</th>
<th>Charge density (mol/m^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td></td>
</tr>
<tr>
<td>Stokes Einstein</td>
<td>-7.0</td>
</tr>
<tr>
<td>Born’s</td>
<td>-6.0</td>
</tr>
<tr>
<td>Pauling</td>
<td>-4.0</td>
</tr>
</tbody>
</table>

Figure VIII.B.10 show the experimental rejection of magnesium chloride with operating pressure. Stokes Einstein, Born and Pauling radii were all used in the theoretical simulation along with dielectric constants. The model fittings are shown in Figure VIII.B.10. The model fitted the experimental data in an excellent manner. Similar procedure was adopted for Born’s and Pauling radii. At dilute concentration, Born’s radii did not predict the experimental data and at high concentration, it predicted the experimental data perfectly. Pauling
radius could not predict the experimental data, since the rejection was high i.e., more than 99%. This may be due to the either sudden decrease in dielectric constant inside the nano pore or solvation energy kept the rejection high. Born radius predicted lower charge density at the surface than the Stokes-Einstein radius as shown in Table VIII.B.7.

One important thing is that the surface charge predicted by DSPM-DE in magnitude is less than that predicted by DSPM. If the image force contribution is included, there can be a change in the prediction. Result of DSPM-DE model shown in Table 8 can be compared with DSPM calculation shown in Table 3. DSPM needs positive charge density to fit the experimental data. Due to the introduction of reassessed dielectric exclusion, it resulted in lower negative charge. The positive charge obtained from DSPM was altered to lower negative charge by the DSPM-DE.

**Table VIII.B.7.** Comparison of charge densities obtained by DSPM-DE for NF 250 membranes for magnesium chloride with various radii.

<table>
<thead>
<tr>
<th>Radii</th>
<th>Charge density (mol/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>1</td>
</tr>
<tr>
<td>Stokes Einstein</td>
<td>-0.14</td>
</tr>
<tr>
<td>Born’s</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

It may thus be concluded that pore radius and dielectric constant have a great significance influence in the prediction of charge density. Pauling radius can be used in the simulation of dielectric exclusion, since it offers a less negative charge for sodium chloride, but will be close to the real physical properties of the membrane. In the case of magnesium chloride, the membrane predicted negative charge for magnesium chloride.
Figure VIII.B. 9. Experimental and theoretical rejection as a function of pressure drop for magnesium chloride of various bulk concentrations for Stokes-Einstein radius (DSPM-DE) for NF 250 membrane.

VII.B.3. CONCLUSIONS

The present investigation compares two different commercial NF membranes prepared by different procedures. DSPM was applied to the experimental data of sodium chloride rejection. Charge density at the surface of the membrane was used as a fitting parameter to experimental data of sodium and magnesium chloride rejection. Each radii predicted different charge densities. Correlations were developed relating charge density with concentration. Correlations were developed relating the charge density with pH. DSPM-DE was also applied to the experimental data of sodium and magnesium chloride rejections. The pore dielectric constant was obtained for different radii. This sort of detailed investigation is scarce in the literature. Image force contribution and dispersion free energy can be added to the present model to see its influence in the prediction.
VII.B.4. REFERENCES