ELECTROKINETIC SALT REJECTION IN HYPERFILTRATION

THROUGH POROUS MATERIALS

by

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ABSTRACT

A theory is presented for the salt rejecting characteristics of porous membranes, whose pore size is large compared with molecular dimensions, under reverse osmosis conditions where the saline solution is moved through the membrane pores by an applied pressure gradient. The salt rejection mechanism is assumed to be an electrokinetic one resulting from charge built up on the interior surfaces of the material when in contact with the saline solution. The performance of the membrane is shown to depend on three basic similarity parameters: the ratio of Debye length to effective pore radius; a dimensionless wall potential related to the $\zeta$ potential; and a Peclet number based on the filtration velocity through the pore, the membrane thickness and the diffusion coefficient of the salts in the water. Depending on the number of ion species present in the feed solution, it is shown that additional parameters may be required to characterize the presence of these species. Comparison of the theory with available experimental data shows very good agreement. The membrane performance based on the simple cylindrical pore model is shown not to be markedly altered when compared with models based on more complex geometrical considerations, that is, pores with a statistical size distribution, pores of slit shape and pores of non-constant cross-section. Experiments performed on bentonite clay also show that the continuum model used may be expected to hold down to very small pore sizes (pore radii $\sim 20$ Å).

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NOMENCLATURE

(MKS units are given for illustration)

\( a \)  - pore radius, m
\( \bar{a} \)  - dimensionless pore radius, \( a/a_0 \)
\( a^* \)  - pore radius when all pores in membrane are identical and straight, m
\( a_0 \)  - most probable pore radius when pores in membrane have a statistical size distribution, m
\( a_L \)  - larger pore radius of variable cross-section pore, m
\( a_S \)  - smaller pore radius of variable cross-section pore, m
\( A \)  - pore cross-sectional area, \( m^2 \)
\( \bar{A} \)  - membrane surface area, \( m^2 \)
\( b \)  - half-width of slit pore, m
\( c \)  - salt concentration distribution along center, kg mole/\( m^3 \)
\( \bar{c} \)  - dimensionless salt concentration, \( c/c_i \)
\( c_i \)  - concentration distribution of ion type \( i \) along center, kg mole/\( m^3 \)
\( \bar{c}_i \)  - dimensionless ion concentration, \( c_i/(c_i)_i \)
\( C_i \)  - radial concentration distribution of ion type \( i \), kg mole/\( m^3 \)
\( C^+ \)  - radial concentration distribution of cations or anions, kg mole/\( m^3 \)
\( D \)  - diffusion coefficient of salt in water, \( m^2/sec \)
\( D_a \)  - diffusion coefficient of salt in water at temperature \( T_a \), \( m^2/sec \)
\( D_p \)  - diffusion coefficient of salt in water at temperature \( T_p \), \( m^2/sec \)
\( f_N \)  - normal distribution function defined by Eq. (3.1)
\( F \)  - Faraday's constant, 9.65 \( \times 10^7 \) coul/kg equiv
\( h \)  - membrane thickness, m
\( H \)  - dimensionless charge strength parameter, \( Z^*/Z \)
\( J_i \) - flux of ion type \( i \) per unit cross-sectional area of pore, kg mole/sec/m²

\( J_+ \) - flux of cations or anions per unit cross-sectional area of pore, kg mole/sec/m²

\( \bar{J} \) - total salt flux in membrane, kg mole/sec

\( J_i \) - total flux of ion type \( i \) in pore, kg mole/sec

\( J_s \) - total flux of dissociated salt in pore, \( J_+ + J_- \), kg mole/sec

\( J_+ \) - total flux of cations or anions in pore, kg mole/sec

\( K_j \) - integrals \( j = 1,2,3,4 \) defined by Eq.(1.8)

\( K_{jb} \) - integrals \( j = 1,2,3,4 \) defined by Eq.(3.32b)

\( K'_l \) - integrals defined by Eq.(2.10)

\( K''_l \) - integrals defined by Eq.(2.10)

\( L \) - pore length, m

\( n \) - total number of pores in membrane

\( N \) - total number of sections in variable cross-section pore

\( P_c \) - clay compaction pressure, kg/m²

\( Pe \) - Peclet number, VL/D

\( Pe^* \) - Peclet number when all cylindrical pores in membrane are identical and straight

\( (Pe)_L \) - Peclet number defined by Eq.(3.46)

\( (Pe)_S \) - Peclet number defined by Eq.(3.46)

\( \Delta P \) - pressure difference across membrane, kg/m²

\( q \) - water flux per unit membrane area, m³/sec/m²

\( Q \) - total water flux in pore, m³/sec

\( \bar{Q} \) - total water flux in membrane, m³/sec

\( r \) - radial coordinate, m
\( \bar{r} \) - dimensionless radial coordinate, \( r/a \)

\( R \) - universal gas constant, \( 8.31 \times 10^3 \) joule/\( ^\circ \text{K} \cdot \text{kg mole} \)

\( R \) - salt rejection coefficient (Eq.(1.10))

\( \hat{R} \) - scaled rejection coefficient defined by Eq.(1.26)

\( <R> \) - membrane rejection coefficient when pores have a statistical size distribution

\( R_i \) - rejection of ion type \( i \) (Eq.(2.14))

\( R_{\text{max}} \) - maximum salt rejection coefficient (Eq.(1.20))

\( S_0 \) - specific surface area, \( \text{m}^{-1} \)

\( t \) - tortuosity or ratio of length of equivalent cylindrical pore to membrane thickness

\( t^* \) - tortuosity when all cylindrical pores in membrane are identical and straight

\( T \) - temperature, \( ^\circ \text{K} \)

\( T_a \) - average ambient temperature during salt rejection experiment, \( ^\circ \text{K} \)

\( T_p \) - ambient temperature when streaming potential was measured, \( ^\circ \text{K} \)

\( u \) - velocity distribution in pore, \( \text{m/sec} \)

\( V \) - mean flow velocity, \( \text{Q/A, m/sec} \)

\( w \) - depth of slit channel, \( \text{m} \)

\( W \) - wave length of variable cross-section pore, \( \text{m} \)

\( x \) - axial coordinate, \( \text{m} \)

\( \bar{x} \) - dimensionless axial coordinate, \( x/L \)

\( y \) - transversal coordinate, \( \text{m} \)

\( \bar{y} \) - dimensionless transversal coordinate, \( y/b \)

\( Z \) - charge number when salts dissociate into ions of equal valence, or charge number of ion type 2 when salts dissociate into three
ion types

$Z^*$ - charge number of ion type 1 with same sign as ion type 2

$Z_1$ - charge number of ion type 1

$\gamma$ - membrane porosity

$\Gamma$ - contraction ratio, $a_S/a_L$

$\delta$ - dimensionless concentration ratio, $c_2/c_3$

$\delta_D$ - Debye sheath thickness, m

$\varepsilon$ - permittivity of water, farad/m

$\kappa_j$ - functions ($j = 1,2$) defined by Eq.(1.12)

$\kappa_j$ - functions ($j = 3,4$) defined by Eq.(1.15)

$\kappa_{jb}$ - functions ($j = 1,2$) defined by Eq.(3.32a)

$\lambda$ - Debye ratio, $\lambda_D/a$

$\hat{\lambda}$ - scaled Debye ratio defined by Eq.(1.28)

$\lambda^*_L$ - Debye ratio when all cylindrical pores in membrane are identical and straight

$\lambda_D$ - Debye length (Eq.(1.4) and Eq.(2.5)), m

$(\lambda^*_L)_L$ - Debye ratio, $\lambda_{DL}/a_L$

$\mu$ - viscosity of water, kg sec/m$^2$

$\mu_a$ - viscosity of water at temperature $T_a$, kg sec/m$^2$

$\mu_b$ - viscosity of water at temperature $T_b$, kg sec/m$^2$

$\sigma$ - mean deviation of normal distribution

$\Sigma$ - function equal to $\Sigma_1/\Sigma_2$

$\Sigma_1$ - function defined by Eq.(3.5a)

$\Sigma_2$ - function defined by Eq.(3.6a)

$\phi$ - electric potential distribution along pore center, V

$\bar{\phi}$ - dimensionless potential, $ZF\phi/\Omega_T$
\( \Delta \phi \) - dimensionless potential difference across membrane, \( \phi_{II} - \phi_I \)

\( \bar{\phi}_i \) - dimensionless potential, \( Z_i F \phi / kT \)

\( \phi \) - total electric potential, V

\( \psi \) - radial electric potential, V

\( \bar{\psi} \) - dimensionless radial potential, \( Z F \psi / kT \)

\( \bar{\psi}_w \) - dimensionless wall potential defined as \( \bar{\psi} \) at \( r = a \)

**subscripts**

\( i \) - ion type \((i = 1, 2, 3)\), also section number of variable cross-section pore \((i = 1, 2, \ldots, N)\)

\( I \) - condition at feed side of pore

\( II \) - condition at product side of pore

\( b \) - for slit pore

\( c \) - for variable cross-section pore
INTRODUCTION

It has long been known that many porous or relatively porous materials have the property of partially rejecting salt when a saline solution filters through them. Typical materials which have this property are clays\textsuperscript{1}, porous glass\textsuperscript{2}, cellophanes\textsuperscript{3}, ion exchange materials\textsuperscript{4} and porous dynamically formed membranes\textsuperscript{5}. The salt rejecting property of these porous materials suggests the possibility of fabricating membranes from such materials for reverse osmosis desalting applications. Though they may not have very high salt rejecting properties, these porous membranes could have very high flux rates and therefore could be very useful when applied to low salinity waters. Such fabrication, however, would be facilitated if a theory can be developed to indicate how the salt rejection depends on the physical properties of the membrane.

When in contact with a saline solution, many macroporous materials (where the pore size is large compared with molecular dimensions) acquire a charge on their pore walls. This surface charge gives rise to a potential field which extends from the walls a distance approximately equal to the Debye length into the liquid within the pores. Within this region, there is an excess of ions (counterions) having a charge opposite to that of the walls. If the salt solution is moved through the pores, say due to an applied pressure gradient, the excess of charge of one sign within the pore liquid causes a net transport of charge and the buildup of a streaming potential. The effect of the streaming potential is to set up an electric field parallel to the
surface which will increase the transport of the coions and reduce that of the counterions until there is an equal transport of both ions, or until there is no current flow. The net effect of the coion exclusion and the axial field is such to cause the ratio of the molar salt flux to the volume flux of water to be less than the molar salt concentration on the upstream side of the porous material. Such porous materials, therefore, tend to partially reject salt.

Related electrokinetic phenomena have been analyzed in a large number of works. In general, the earlier treatments were approximate and applied to the case where the Debye length was small compared with the pore radius and/or the surface charge was sufficiently small that the Poisson equation could be linearized. Dresner solved the problem without either of these assumptions, but he considered the special case where the flow of electrolyte is associated with gradients in pressure and electric potential across the membrane but with no concentration gradient. Without the axial concentration difference, the corresponding information on the salt rejection characteristics of the membrane was not obtained. Gross and Osterle solved the problem for the general case, assuming only that the Debye sheath can be described by the Chapman-Gouy model. However, the authors applied their model to some fundamental electrokinetic problems with small concentration gradients, and did not work out explicit solutions for desalting applications.

The present thesis derives explicit solutions for the salt rejection characteristics of different porous materials with differing feeds. The thesis consists mainly of four chapters. In Chapter 1,
the membrane is assumed to be made up of straight uniformly distributed cylindrical pores, and explicit solution of salt rejection is derived for the case where the salts in the feed solution dissociate fully into ions of equal valence. Excellent agreement is obtained between the theory and available experimental data. In Chapter 2, the same membrane model is applied to the case where the salts in the feed solution dissociate fully into ions of different valences, and the degree of rejection of each of the ion types is calculated. Only very limited experimental data is available, but they are found to be in very good agreement with the theory. In Chapter 3, the membrane is not assumed to be made up of simple cylindrical pores, but of various geometrical configurations, and this geometrical influence on the salt rejection characteristics of the membrane is evaluated. To investigate the effect of the pore size on the salt rejection characteristics of the membrane when the pore size is down to molecular dimensions, experiments were carried out on highly compacted bentonite clays and the results are discussed in Chapter 4.
CHAPTER 1 - SIMPLE CAPILLARY MODEL WITH SIMPLE SALT SOLUTION*

1.1 Model and Equations

Fluid flow through macroporous media is usually analyzed by considering that the fluid flows through the porous medium via a series of straight, uniformly distributed cylindrical pores. In this chapter, the same simple physical model is applied to derive explicit salt rejection characteristics for porous materials. Other geometrical considerations regarding the size distribution and shape of the pores will be discussed in Chapter 3. Also, the feed solutions considered in this chapter are those that have salts which dissociate into ions of equal valence. More complicated feed conditions where the salts dissociate into ions of different valences will be discussed in Chapter 2.

In this simple physical model where the porous material is assumed to consist of a series of identical pores, the performance of a single pore characterizes that of the whole porous material. The physical mechanism of salt rejection in each of these pores is as described in the Introduction, where the salt rejecting property of porous materials is attributed to the charge buildup on the interior surfaces of the pores when in contact with the saline solution. The charge buildup on the interior surface, however, is a very complex phenomenon as it can be caused by various reasons, for example, ion adsorption, surface chemical reactions and etc. 10.

A cylindrical coordinate system \((x,r)\), where \(x\) is positive in the direction of flow and \(r\) is the radial coordinate with origin in the

* Materials in this chapter have been published in Ref. 9.
axis of symmetry, will be used to derive explicit solution for the salt rejection characteristics of a single pore. Following Gross and Osterle\textsuperscript{8}, the total electric potential $\phi$ is split into two parts

$$\phi = \phi(x) + \psi(x,r)$$  \hfill (1.1)

The total electric potential $\phi$ is connected with the ion concentrations $C_\pm(x,r)$ through the Poisson equation, where the subscript $+$ refers to cations and $-$ refers to anions.

Because of the cylindrical symmetry of the problem, there is no net ion flux or bulk flow in the radial direction within the pore. The integration of the radial ion flux equation gives the radial ion concentration distribution in the form of Boltzmann distribution with respect to the radial component of the field $\psi$

$$C_+(x,r) = f_+(x) \exp [\tilde{\psi}](x,r)]$$  \hfill (1.2a)

$$\tilde{\psi} c(x) \exp [\tilde{\psi}(x,r)]$$  \hfill (1.2b)

Here $\tilde{\psi} = ZF\psi/kT$ is the dimensionless radial potential, with $Z$ the absolute value of the charge number of the ions, $F$ and $k$ the Faraday and gas constants, respectively, and $T$ the absolute temperature.

With $f_\pm(x)$ undetermined functions, Eq. (1.2a) applies at any station within the pore. For the case where the Debye length is very small compared with the pore radius, the potential in the central core
of the pore depends essentially on \( x \) alone, and is equal to \( \phi(x) \) with \( \psi \not\equiv 0 \). Also for this case, the positive and negative ion concentrations are equal in the central core and are equal to \( c(x) \). Eq. (1.2a) then takes the approximate form given by Eq. (1.2b)

Although Eq. (1.2b) is derived for conditions within the pore, it can also be taken outside the pore since it contains the conditions of equilibrium for the ionized species at the pore entrance and exit. It must be emphasized again that it is generally applicable only in the limit when the Debye length is small. However, when the Debye length is comparable with the pore radius or larger, Eq. (1.2b) still describes accurately the situation within the pore near either end of it. But inside the rest of the pore, it implies a certain axial distribution of charge either on the pore wall or in the solid wall material.

Throughout their formulation for arbitrary Debye length, Gross and Osterle\(^8\) used Eq. (1.2b) rather than Eq. (1.2a). This approach is adopted here since the use of Eq. (1.2b) greatly simplifies the analysis and calculations for arbitrary Debye length. The results obtained for integrated quantities, such as salt rejection and streaming potential, are rigorous for small Debye length; and for the general case, they satisfy all the boundary conditions and represent a good approximation to the exact solution.

With \( a \) denoting the radius of the cylindrical pore, the potential \( \psi(x,a) = \psi_w \) is termed the wall potential. In the present development, the wall potential \( \psi_w \) is assumed to be constant, largely because it is
a reasonable assumption for a number of materials in typical aqueous solution. Also, as will be discussed later, the concentration does not vary that much along the pore, and the wall potential, if it is affected by the concentration of the solution, should not vary that much either. A constant $\psi_w$ assumption, therefore, represents a good approximation to the boundary condition, and the solution so obtained represents a good solution to the problem.

With the pore length large in comparison with the radius $a$, the Poisson equation governing the potential distribution can be shown to be expressible in the dimensionless form

$$\lambda^2 \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \bar{\psi}}{\partial r} \right) = \sinh \bar{\psi}$$

(1.3)

where $\bar{r} = r/a$ and $\lambda = \lambda_D/a$. The Debye length $\lambda_D$ is given by

$$\lambda_D = (\varepsilon_0 kT/2cZ^2F^2)^{1/2}$$

(1.4)

with $\varepsilon$ the permittivity. It must be emphasized that $\lambda$ is a local value which depends on $x$ through the dependence of $\lambda_D$ on the salt concentration $c(x)$. Equation (1.3) is solved subject to the constant wall potential condition $\bar{\psi} = \bar{\psi}_w$ at $\bar{r} = 1$ and to the symmetry condition on the pore axis $\partial \bar{\psi}/\partial \bar{r} = 0$ at $\bar{r} = 0$. Although analytic solution of this equation are available, as will be discussed later, for large and small values of the Debye ratio $\lambda$, Eq. (1.3) in general can only be solved by numerical means. To illustrate the behavior of $\bar{\psi}$, the potential
distribution across the pore is plotted in Fig. 1 for a wall potential \( \overline{\psi}(1) = 2.79 \) and for different values of the Debye ratio \( \lambda \). It can be seen that the influence of the potential, and hence the salt rejection characteristics, increases markedly with \( \lambda \). For a Debye ratio greater than about 2, the potential distribution is close to the constant value which it assumes when \( \lambda \to \infty \).

The equation which governs the ion fluxes is the Nernst-Planck equation. Employing Eq. (1.1) and (1.2), the flux equations can be written

\[
j_\pm = u c \exp(\overline{\psi}) - D \exp(\overline{\psi}) \frac{dc}{dx} + D c \exp(\overline{\psi}) \frac{d\overline{\psi}}{dx} \quad (1.5)
\]

where \( j \) denotes the ion flux per unit area, \( \overline{\psi} = Z F \phi / R T \), and \( D \) is the diffusion coefficient which is taken to be equal for the positive and negative ions.

Under hyperfiltration condition where the flow resulting from the applied pressure gradient is large in comparison with that resulting from either the concentration or potential gradients across the membrane, the velocity distribution in the cylindrical pore is given by the Poiseuille relation

\[
u = 2V(1 - r^2) \quad (1.6)
\]

Here, \( V = Q/A \) is the mean flow velocity with \( Q \) the total volume flow
rate and $A$ the pore cross-sectional area. It must be emphasized that when
the pressure gradient across the pore is not sufficiently large, the
modification to the Poiseuille relation due to the concentration and
potential gradients must be taken into account as, for example, in the
treatment of Gross and Osterle.

The total flux of each ion type can be obtained by integrating Eq.
(1.5) over the pore cross-sectional area. The total flux of dissociated
salt molecules is given by $J_s = J_+ + J_-$, and the total current is
$I = ZF(J_+ - J_-)$. In the present problem, there is no current through
the pore so that from Eqs. (1.2b), (1.5) and (1.6), the following
equations can be obtained:

\[
J_s = 2cQ K_1 - 2AD K_3 \frac{dc}{dx} + 2AD c K_4 \frac{d\phi}{dx} \quad (1.7a)
\]
\[
0 = -2cQ K_2 + 2AD K_4 \frac{dc}{dx} - 2AD c K_3 \frac{d\phi}{dx} \quad (1.7b)
\]

The $K$'s are definite integrals of functions of $\overline{\psi}$ over the pore cross-
section

\[
K_1 = 4 \int_{0}^{1} \cosh \overline{\psi}(1 - \overline{r}^2) \overline{r} d\overline{r}, \quad K_2 = 2 \int_{0}^{1} \cosh \overline{\psi} \overline{r} d\overline{r}
\]
\[
K_3 = 2 \int_{0}^{1} \cosh \overline{\psi} \overline{r} d\overline{r}, \quad K_4 = 2 \int_{0}^{1} \sinh \overline{\psi} \overline{r} d\overline{r}
\]

Since $\overline{\psi}$ is determined from the solution of Eq. (1.3), the $K$'s couple
the ion flux equations to that of the Poisson equation and are func-
tions of $\overline{\psi}_w$ and $\lambda(c)$.
The elimination of $\frac{d\bar{c}}{dx}$ in Eq. (1.7) leads to the following equation for the salt concentration

$$\frac{\kappa_1}{\text{Pe}} \frac{d\bar{c}}{dx} - \bar{c} = -\bar{c}_{\text{II}} \kappa_2$$  \hspace{1cm} (1.9)

Here $\text{Pe} = \frac{V L}{D}$ is the Peclet number and $\bar{x} = x/L$ with $L$ the pore length. $\bar{c} = c/c_1$ and

$$\bar{c}_{\text{II}} = \frac{c_{\text{II}}}{c_1} = 1 - R$$  \hspace{1cm} (1.10)

where $c_1$ is the feed concentration at $x = 0$ and $c_{\text{II}}$ is the product concentration at $x = L$ with

$$c_{\text{II}} = \frac{J}{G}$$  \hspace{1cm} (1.11)

The salt rejection coefficient $R$ defined in Eq. (1.10) is equal to 1 for complete salt exclusion by the membrane and 0 for no exclusion.

The functions $\kappa_1$ and $\kappa_2$ appearing in Eq. (1.9) depend on the $K$'s and are defined by

$$\kappa_1 = \frac{K_3^2 - K_4^2}{K_1 K_3 - K_2 K_4}$$

$$\kappa_2 = \frac{K_3}{K_1 K_3 - K_2 K_4}$$  \hspace{1cm} (1.12)
Since $\kappa_1$ and $\kappa_2$ depend on $\overline{\psi}$ and $\lambda(c)$ through the $K's$, it follows that Eq. (1.9) is coupled with the Poisson Eq. (1.3). These equations can be solved numerically, as, for example, by treating $\kappa_1$ and $\kappa_2$ as functions of $c$ and solving the system by a direct step-by-step forward marching procedure in $x$.

1.2 Parameters and Solutions

From the system of equations and boundary conditions defining the pore problem, it can be easily shown that the rejection coefficient $R$ depends on three dimensionless parameters. These parameters are the dimensionless wall potential $\overline{\psi}$, the Peclet number $Pe$, and the Debye ratio $\lambda_1$ which is the ratio of the Debye length evaluated at the feed concentration to the pore radius. The same general dependence can be shown to hold for the streaming potential $\Delta \phi$. The explicit solution dependence on these three parameters, however, can only be obtained in general by numerical means. But before presenting the numerical solutions, a number of analytic asymptotic solutions for limiting values of the dimensionless similarity parameters will be investigated first.

Such analytic solutions, apart from their own value, can serve as a guide to show how the numerical solutions should scale with changes in the parameters.

Two limiting cases of particular interest are for large and small values of the Debye ratio. For large values of $\lambda$, $\overline{\psi}$ becomes independent of $\lambda$; while for sufficiently small values, the Debye ratio may be taken constant and set equal, for example, to $\lambda_1$ so that $\overline{\psi} = \psi(r; \overline{\psi}, \lambda_1)$. It follows that in either case the $K's$ of Eq. (1.8), and hence $\kappa_1$ and
of Eq. (1.12), are constants dependent at most on $\bar{\psi}_w$ and $\lambda_I$. Eq. (1.9) is then easily integrated subject to the conditions that $\bar{c} = 1$ at $\bar{x} = 0$ and $\bar{c} = \bar{c}_{II}$ at $\bar{x} = 1$. This leads to the following general expression, valid in either the small or large Debye ratio limits, for the concentration ratio across the pore

$$\bar{c}_{II} = 1 - R = \frac{e^{\frac{Pe/\kappa_1}{(1 - \kappa_2) + \kappa_2 e^{\frac{Pe/\kappa_1}{\kappa_2}}}}}$$

Eliminating $dc/dx$ in Eq. (1.7b) by means of Eq. (1.9) and $c(x)$ by means of the solution of Eq. (1.9) just described, yields a simple quadrature for $\phi(x)$. In this manner, one can determine the corresponding streaming potential across the capillary. With some manipulation this result may be expressed in the form

$$\bar{\Delta \phi} = -\kappa_4 \ln\left[\frac{e^{\frac{-Pe/\kappa_1}{\kappa_2}}}{\kappa_3}\right]$$

where $\bar{\Delta \phi} = \bar{\phi}_{II} - \bar{\phi}_I$ is the dimensionless potential difference between the solutions at the pore ends (with the potential made dimensionless with respect to $RT/ZF$). The parameters $\kappa_3$ and $\kappa_4$ are here defined by

$$\kappa_3 = \frac{K_4}{K_2}, \quad \kappa_4 = \frac{K_4}{K_3}$$

For the case when the Debye ratio $\lambda$ is everywhere sufficiently large compared to one, the problem becomes physically a one dimensional one in $x$. It was shown in the last section that this large Debye ratio
behavior is already manifested at values of $\lambda \geq 2$. This is principally a consequence, as may be seen from Eq. (1.3), of the fact that the requirement for the limit is $\lambda^2 \gg 1$ which is a weaker one than $\lambda \gg 1$.

For this limit, it is readily apparent from Fig. 1 and Eq. (1.3) that $\overline{\psi}(r)$ is constant across the pore and the solution of Eq. (1.3) satisfying the boundary conditions is simply $\overline{\psi} = \overline{\psi}_w$. It follows that

$$K_1 = K_3 = \cosh \overline{\psi}_w \quad , \quad K_2 = K_4 = \sinh \overline{\psi}_w$$

(1.16)

and

$$\kappa_1 = 1 \quad , \quad \kappa_2 = \cosh \overline{\psi}_w$$

(1.17)

$$\kappa_3 = 1 \quad , \quad \kappa_4 = \tanh \overline{\psi}_w$$

Substituting these into Eq. (1.13) and Eq. (1.14) yields the following limiting forms for the rejection coefficient and streaming potential.

$$R = 1 - \frac{e^{Pe}}{(1 - \cosh \overline{\psi}_w) + e^{Pe} \cosh \overline{\psi}_w}$$

(1.18)

$$\Delta \phi = - \tanh \overline{\psi}_w \ln[(1 - \cosh \overline{\psi}_w) + e^{Pe} \cosh \overline{\psi}_w]$$

(1.19)

Figure 2 and Fig. 3 are plots of the rejection coefficient $R$ as a function of Peclet number $Pe$ for different values of the wall potential $\overline{\psi}_w$. The theoretical curves are calculated using Eq. (1.18). For a fixed wall potential $\overline{\psi}_w$, the rejection is seen to increase with the
Peclet number Pe as it should, since the Peclet number is a measure of the ratio of the convective to diffusive effects. At small Pe, diffusion is dominant with the result that there is a lower rejection; while at large values of Pe, convection is dominant and the rejection is increased. The maximum possible rejection for a fixed wall potential is given by the asymptotic limit

\[ R_{\text{max}} = 1 - \frac{1}{\cosh \psi_w} \]  

(obtained from Eq. (1.18) for Pe >> 1. The approach to this limit is characterized by a typical relaxation behavior so that the rejection is already an appreciable fraction of the asymptotic value for Peclet numbers as low as 2. That the rejection increases with increasing wall potential for all Pe is a direct consequence of the increased effect of the wall region on the charge distribution across the pore and hence on the rejection, as described earlier.

The experimental data on Fig. 2 and Fig. 3 were obtained by Jacazio et al.\(^9\) and Michelsen-Harriott\(^3\), respectively. The excellent agreement between the experiments and the theory confirms the validity of the theory in its prediction of the dependence of the rejection coefficient on the Peclet number and the wall potential when the Debye ratio is large. In the experiment by Jacazio et al.\(^9\), all the relevant parameters were measured and the comparison is therefore absolute. Whereas in the experiment by Michelsen and Harriott, the wall potential \(\psi_w\) was not measured and is assumed here to be 33.4 mV in order to provide the
best fit between the theory and the experiment. Although arbitrarily chosen, this value of 33.4 mV is nevertheless quite a reasonable value for cellophanes.

It was mentioned in Section 1.1 that the concentration profile along the pore in general does not vary that much, and therefore the wall potential should be quite constant. This is evident from Fig. 4 where the concentration profiles are plotted for different values of Peclet number $\text{Pe}$ with $\overline{\psi}_w = 1.22$. It can be seen from this figure that the concentration of the solution in most of the pore length is indeed very close to the feed concentration. If the wall potential is primarily determined by the interaction between the wall and the solution, the constant wall potential assumption would be a very reasonable one. The question whether a constant wall potential can be used to characterize the porous material against different feed concentrations is a different one. It all depends on the type of materials and the concentration range of the feed solutions. For cases where the range of feed concentrations is not too wide, and the wall potential is not very sensitive to the concentration of the solution, the use of a certain wall potential to characterize the porous material is not a bad one. If the wall potential does vary with the feed concentration, then other characterization parameters which do not change with the feed concentration would be more appropriate.

For the other limit when $\lambda << 1$ (or really $\lambda^2 << 1$), analytic solution is somewhat difficult. In this limit, the Debye sheath is very thin and hence the rejection is very low. Because of the thinness of
the Debye sheath, the transverse curvature term $-1(\partial \bar{\psi}/\partial \bar{r})$ in the Poisson equation may be neglected in comparison with $\partial^2 \bar{\psi}/\partial \bar{r}^2$. With $\lambda$ set equal to $\lambda_I$, Eq. (1.3) reduces to

$$\frac{d^2 \bar{\psi}}{d\bar{r}^2} = \frac{\sinh \bar{\psi}}{\lambda_I^2}$$  \hspace{1cm} (1.21)

This equation can be integrated to

$$\lambda_I^2 \left( \frac{d\bar{\psi}}{d\bar{r}} \right)^2 = 2 \left( \cosh \bar{\psi} - \cosh \bar{\psi}_0 \right)$$  \hspace{1cm} (1.22)

where $\bar{\psi}_0$ is the radial potential on the pore axis. When integrated again, Eq. (1.22) gives the expression for $\bar{r}(\bar{\psi}, \bar{\psi}_0)$ as an elliptic integral of the first kind.

For the limits of large and small $\bar{\psi}$, Eq. (1.22) can be solved with explicit solutions in terms of elementary functions. For the case where $\bar{\psi}$ is everywhere sufficiently small (a condition which will be met, say, for $\bar{\psi}_w << 1$), Eq. (1.22) integrates to $\bar{\psi} = \bar{\psi}_w \cosh (\bar{r}/\lambda_I)/[\cosh (1/\lambda_I)]$. When $\lambda_I << 1$, this expression can be further reduced to

$$\bar{\psi} = \bar{\psi}_w e^{-(1 - \bar{r})/\lambda_I}$$  \hspace{1cm} (1.23)

This is the familiar one dimensional potential distribution in a Debye sheath. Even with this simple expression for the potential, it is still very difficult to get any explicit solution from Eq. (1.13) because of the complexity of the integrals in $\kappa_1$ and $\kappa_2$. However,
because of the low rejection characteristics expected, any analytic solution, even if it is possible to get, would have very limited applications. Instead of using Eq. (1.23) for attempting analytic solutions, it can very well be used as a guide for describing the solution characteristics when \( \lambda \ll 1 \), and also for scaling considerations as will be discussed in Section 1.3.

One other limit which has been already discussed for the case of \( \lambda \) large but which is of interest over the whole range of Debye ratios and \( \bar{\Psi}_w \) is the case of Pe \( \gg 1 \). From Eq. (1.13), it may be observed that the rejection coefficient has a relaxation behavior as a function of Pe, and the relaxation behavior is of the same type for both large and small Debye ratios. For the large Debye ratio case, it was shown earlier that when Pe \( \sim 2 \), the rejection is already an appreciable fraction of its asymptotic, Peclet number independent value. From Eq. (1.13), the same Peclet number independence is expected for the small Debye ratio case. If this condition holds for the small and large Debye ratio limits, it is reasonable to assume that the intermediate regime also manifests the same large Peclet number independent behavior at relatively low Peclet values. That this is the case can be seen in Fig. 5 where the rejection is plotted as a function of the Debye ratio \( \lambda_I \) for two different values of the wall potential \( \bar{\Psi}_w \). The theoretical curves were obtained from a complete numerical step by step integration with Pe \( \gg 1 \) (Ref. 10). Although not shown, exact numerical results for Pe = 2 are found to be only slightly below those of Pe \( \gg 1 \). The curves of Fig. 5 clearly indicate the increasing rejection with \( \lambda_I \),
which follows from the arguments given earlier. Furthermore, the rapid increase with $\lambda_I$ is seen to take place at $\lambda_I \sim 1$, which is also consistent with the expected exponential increase around this value (cf. Eq. (1.23)).

The experimental data were obtained by Jacazic et al. The excellent agreement between the theory and the experiment confirms the validity of the theory and shows that rejection does increase with the Debye ratio $\lambda_I$. It is noted that were the values of the Peclet number a little bit higher than they were, the experimental data might be closer to the theoretical curve.

### 1.3 Single Universal Correlation

The similarity of the family of the theoretical rejection curves as a function of Peclet number for different values of $\psi_w$ with $\lambda_I >> 1$ (Fig. 2 and Fig. 3) and the similarity of the family of rejection curves as a function of the Debye ratio for different values of $\psi_w$ with $\text{Pe} >> 1$ (Fig. 5) suggest that it might be possible to empirically correlate these solutions in the general case with a single universal correlation for the rejection coefficient $R$ in terms of three parameters $\lambda_I$, $\psi_w$, and Pe. The already derived asymptotic solution will be used as a guide to carry out this correlation.

Eq. (1.13), which is valid for both small and large Debye ratios, is used as a guide for the scaling of the family of solutions of $R$ as a function of $\lambda_I$ for different values of $\text{Pe}$ with $\psi_w$ constant. The parameters $\kappa_1$ and $\kappa_2$ in Eq. (1.13) were evaluated only in the large Debye ratio limit where they were found to be $\kappa_1 = 1$ and $\kappa_2 = \cosh \psi_w$. 

It is recognized however from Eq. (1.9), which is the equation for the axial salt concentration distribution, that \( \text{Pe}/\kappa_1 \) represents the ratio of the time for the salt to diffuse across the length of the pore in the sheath region compared to the time for it to be convected across (or alternatively the ratio of the axially convected to the axially diffused flux within the sheath). Recognizing that the average streamwise velocity along the pore in the sheath region is given approximately by \( V(\delta_D/a) \), where \( \delta_D \) is the "sheath thickness," then in order of magnitude

\[
(\text{Pe}/\kappa_1) \sim (VL/D) (\delta_D/a) \tag{1.24}
\]

with \( \kappa_1 \sim a/\delta_D \). For large Debye ratios when the sheath fills the pore, \( \kappa_1 = 1 \) and is consistent with previously obtained results.

From numerical solutions of the Poisson equation, the qualitative behavior of \( \delta_D/a \) is of the form

\[
\delta_D/a \sim 1 - \exp (-\alpha \lambda_I/\psi_w) \tag{1.25}
\]

where \( \alpha \) is a constant. It is to be noted that the calculations were carried out over a wide range of \( \lambda_I \) (0.1 to 2.0) but for only the relatively narrow range of \( \psi_w \) of interest (\( \approx 1.2 \) to 2.8). In any case, the empirical form of Eq. (1.25) is physically reasonable, approaches the proper limits for small and large \( \lambda_I \), and is consistent with all the derived asymptotic limits such as Eq. (1.23).
From Eq. (1.13) with \( \kappa_2 = \cosh \bar{\psi}_w \) and Eqs. (1.24) and (1.25), the Peclet number dependence can be shown to be scaled out of the rejection \( R \) by the relation

\[
\hat{R} = R\left[ \frac{\cosh \bar{\psi}_w \left( e^{\frac{\text{Pe}/\kappa_1}{(e^{\frac{\text{Pe}/\kappa_1}{1}} - 1)} \right)}{\cosh \bar{\psi}_w \left( e^{\frac{\text{Pe}/\kappa_1}{1}} - 1 \right)} \right]
\]

with

\[
\frac{\text{Pe}/\kappa_1}{1} = \text{Pe}[1 - \exp (-5\lambda_I/\bar{\psi}_w)]
\]

Here \( \hat{R} \) is the scaled rejection coefficient and the value of \( \alpha = 5 \) was determined empirically.

It is to be noted that when the Debye ratio \( \lambda_I \) is large, the scaled rejection coefficient \( \hat{R} \) has a maximum value equal to \( R_{\text{max}} \) of Eq. (1.20). If \( \hat{R} \) is referenced to \( R_{\text{max}} \), then the family of curves of \( \hat{R}/R_{\text{max}} \) as a function of the Debye ratio \( \lambda_I \) for different values of the wall potential \( \bar{\psi}_w \) would have a value of \( \hat{R}/R_{\text{max}} = 1 \) (or independent of \( \bar{\psi}_w \)) when \( \lambda_I >> 1 \).

To scale out the dependence on \( \bar{\psi}_w \) in general of the family of curves of \( \hat{R}/R_{\text{max}} \) as a function of \( \lambda_I \) it is necessary to determine what is the proper scale measuring the sheath thickness. As in all non-constant density boundary layer type problems, the appropriate normal scale is a length which is measured by the integral of the density over the normal coordinate, and not the value of the coordinate itself, which in this case is \( \lambda_I \) when measured in pore radii. For the present problem the appropriate "density" is the counter ion charge distribution in the
sheath, which is proportional to \( \exp(\bar{\psi}) \). Consistent with the derived asymptotic relations, a mean charge strength over the sheath may be estimated as \( \exp(\bar{\psi}_w \lambda_I/2) \) and a proper normal scale denoted by \( \hat{\lambda}_I \) can be concluded as

\[
\hat{\lambda}_I = \lambda_I \exp(\lambda_I \bar{\psi}_w / 2) \quad (1.28)
\]

Numerical calculations for the rejection coefficient for various ranges of the parameter \( \bar{\psi}_w \), \( \text{Pe} \) and \( \lambda_I \) are shown in Fig. 6. These results are plotted using the scaling relations of Eqs. (1.26) - (1.28). It can be seen that all the solutions collapse onto a single curve which to good approximation is given by

\[
\frac{\hat{R}}{R_{\text{max}}} = \exp(-0.4 \hat{\lambda}_I^{-1.05}) \quad (1.29)
\]

A slightly more accurate representation for small \( \hat{\lambda}_I \) is given by

\[
\frac{\hat{R}}{R_{\text{max}}} = 2.6 \hat{\lambda}_I^2 \quad (\hat{\lambda}_I^2 \ll 1) \quad (1.30)
\]

From the above results, it can be seen that the empirically correlated behavior has the correct asymptotic form in the small as well as in the large Debye ratio limit. When applied to membrane characterization, this single universal correlation of a three parameter family of solution should be very valuable.

Previous experimental data by Jacazio et al.\(^9\) and Michelsen-Harriott\(^3\) have been reduced and plotted in Fig. 7 as \( \hat{R} \) vs. \( \hat{\lambda}_I \). The
theoretical curve in this figure is the theoretical correlation discussed earlier. It can be seen that the comparison between the theory and the experiment is again very good. It should be noted that the apparent larger scatter of the data is misleading in the sense that it is due to the fact that the rejection coordinate has been stretched by referencing it with respect to the maximum rejection $R_{\text{max}}$. 
Figure 1. Dimensionless radial potential distribution across a cylindrical pore for different Debye ratios and a fixed wall potential ($\Psi_w = 2.79$).
Figure 2. Salt rejection coefficient of a cylindrical pore with a constant surface potential for large Debye ratio as a function of Peclet number, and comparison with experiments of Jacazio et al. on compacted clay.
Figure 3. Salt rejection coefficient of a cylindrical pore with a constant surface potential for large Debye ratio as a function of Peclet number, and comparison with experiments of Michelsen and Harriott on cellophane membranes.
Figure 4. Dimensionless axial concentration profile along a cylindrical pore with a fixed surface potential for large Debye ratio and for different Peclet numbers.
Figure 5. Salt rejection coefficient of a cylindrical pore with a constant surface potential for large Peclet number as a function of Debye ratio, and comparison with experiments of Jacazio et al. on compacted clay.
Correlating Equations

\[
\frac{\hat{R}}{R_{\text{max}}} = \exp\left\{-0.4 \, \lambda_{I}^{-1.05}\right\}
\]

\[
\frac{\hat{R}}{R_{\text{max}}} = 2.6 \, \lambda_{I}^2
\]

\[R_{\text{max}} = 1 - \frac{1}{\cosh \bar{\psi}_w}\]

Numerical Calculations

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<th>$\lambda_{I}$</th>
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<tr>
<td>$\times$ 1.22</td>
<td>10</td>
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Figure 6. Empirical universal correlation of salt rejection coefficient. \(\hat{R}\) and \(\hat{\lambda}\) are defined in Eqs. (1.26)-(1.28). Points represent exact numerical solutions.
Figure 7. Comparison with experiment of theoretical universal correlating function for salt rejection coefficient.
CHAPTER 2 - SIMPLE CAPILLARY MODEL WITH MULTIPLE SALT SOLUTION

In Chapter 1, the salt rejection capabilities of a porous material were calculated under the assumptions that the wall potential on the pore wall is a constant independent of the salt concentration, and that the feed solution is a dilute one containing a fully dissociated simple salt, i.e., one which dissociates into cations and anions of the same valence. Under these conditions it was shown that the salt rejection characteristics of a porous membrane could be determined in terms of three dimensionless similarity parameters: the ratio of the Debye length to pore radius; a dimensionless wall potential; and a Peclet number based on the filtration velocity through the pore, the pore length and the diffusion coefficient of the salt in the feed solution.

If the analysis of Chapter 1 is to be useful for characterizing the performance of a porous membrane for actual brackish water applications, then it must be extended to include the case where the feed solution contains multiple salts, that is, a mixture of salts which dissociate into ions with different valences. For this case, the salt rejection may be expected to depend also upon parameters which measure the relative concentrations and valences of the salt ions present in the feed solution. In this chapter, the analysis of Chapter 1 is extended to a feed containing multiple salts to derive explicit solutions for brackish water applications.

* Materials in this chapter have been published in Ref. 11.
2.1 Formulation

To investigate the rejection characteristics of a feed containing a mixture of salts which are fully dissociated, a particular case is used as an example. In this particular case, the feed is considered to have the present ions of charge number +Z and -Z, which characterize a fully dissociated simple salt and, in addition, ions of charge number Z*. The generalization to any additional number of ionic species is straightforward. In the analysis to follow, the three types of ions considered are differentiated through the subscripts $i = 1, 2$ and 3, where

$$Z_1 = Z^*, \quad Z_2 = +Z, \quad Z_3 = -Z$$

(2.1)

The charge numbers of type 1 and type 2 ions are considered here, by convention, to have the same sign. The charge number $Z$, however, can be either positive or negative.

As in Chapter 1, the flow through a straight cylindrical pore is analyzed first and then the results for such a pore are related to the real membrane through the identification of an effective pore radius and an effective pore length defined in terms of the measurable bulk properties of the membrane such as the permeability, porosity and thickness. Also, as in Chapter 1, a cylindrical coordinate system $(x,r)$, with $x$ positive in the direction of flow and $r$ in the radial direction with the origin at the axis of symmetry, is used. Following Gross and Osterle⁸ and also the analysis in Chapter 1, the total electric potential $\phi$ is split into two parts
\[ \phi(x,r) = \phi(x) + \psi(x,r) \]  

(2.2)

The potential \( \psi \) in Eq. (2.2) is related to the radial ion concentration distribution \( C_i \) through the condition that there is no ion flux in the radial direction, resulting in the following Boltzmann equilibrium form

\[ C_i(x,r) = c_i(x) \exp \left( -\frac{Z_i}{kT} \bar{\psi} \right) \]  

(2.3)

Here, \( \bar{\psi} = ZT/\mathcal{O} T \) is the same dimensionless radial potential as defined in Chapter 1. The potential \( \psi \) extends from the wall of the pore into the liquid a distance approximately equal to the Debye length \( \lambda_D \). When \( \lambda_D \) is small compared with the pore radius \( a \), then \( \phi \) and \( c_i \) are respectively the total potential and concentration of ion of type \( i \) in the center of the pore. When \( \lambda_D \) is comparable with or larger than \( a \), then \( \phi \) and \( c_i \) are undetermined functions which take on the definitions given for small \( \lambda_D \) only near the two ends of the pore. As in Chapter 1, Eq. (2.3) will be used as a good approximation for all values of \( \lambda_D \), although Eq. (2.3) is true only for small values of \( \lambda_D \).

With the length of the pore \( L \) large compared to the pore radius \( a \), the Poisson equation governing the potential distribution within the pore can be written as

\[ \lambda^2 \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \bar{\psi}}{\partial r} \right) = \frac{1}{2} \left[ \exp(\bar{\psi}) - \exp(-\overline{\psi}) \right] - \delta\left[ \exp(-\bar{\psi}) - \exp(-\overline{\psi}) \right] \]  

(2.4)
where \( \bar{r} = r/a \) and \( \lambda = \lambda_D/a \) is the Debye ratio parameter. Here, the Debye length \( \lambda_D \) is defined in terms of the concentration \( c_3 \)

\[
\lambda_D = \left[ \frac{\varepsilon \delta T}{2c_3 Z^2 F^2} \right]^{1/2}
\]  

(2.5)

with \( \varepsilon \) the permittivity.

The parameters \( H \) and \( \delta \) are defined by

\[
H = \frac{Z_1}{Z_2} = \frac{Z^*}{Z} \quad ; \quad \delta = \frac{c_2}{c_3}
\]  

(2.6)

It is to be noted that \( H \) which measures the relative charge strength of the type 1 and type 2 ions is always positive since the type 1 and type 2 ions are defined to have the same sign. The parameter \( \delta \) measures the relative molar percent of the additional ion type. In the limiting case of say a single dissociated salt, where ions of type 2 are absent but the valences of the two ions present are different, \( \delta = 0 \). In this case \( H \) is defined through the ratio of the absolute value of the charge numbers of the two ions, i.e., \( H = Z^*/Z \). In the absence of ions of type 1, when the single salt is also a simple one in the sense that it dissociates into ions of equal valence (e.g., NaCl), then \( \delta = 1 \), and the parameter \( H \), which in this case equals one, does not enter the problem.

The boundary conditions for Eq. (2.4) are that at \( \bar{r} = 1 \) (wall) the potential has a constant value \( \bar{\psi}_w \) termed the wall potential, while at \( \bar{r} = 0 \) (the axis of the pore) \( \partial \bar{\psi} / \partial \bar{r} = 0 \) from symmetry.

The ion transport in the pore is governed by the Nernst-Planck equation. With the potential distribution split following the definition
of Eq. (2.2), and with the ion concentration expressed in the Boltzmann form of Eq. (2.3), the Nernst-Planck equations for the flux per unit area of the ion type \( i \) can be written

\[
\bar{J}_i = uC_i - D \exp\left(\frac{Z_i}{Z} \bar{\psi}\right) \frac{dc_i}{dx} - DC_i \frac{d\bar{\phi}_i}{dx}
\]  

(2.7)

Here, \( \bar{\phi}_i = Z_i \bar{\phi}/R T \), \( D \) is the diffusion coefficient which is assumed equal for all the ion types, and \( u \) is the velocity distribution within the pore.

Under hyperfiltration conditions, where the flow resulting from the pressure gradient is much larger than the flows due either to the potential or concentration gradients, the velocity distribution can be obtained from the Poiseuille relation

\[
u = 2V(1 - \frac{r^2}{R^2})
\]  

(2.8)

The mean flow velocity \( V \) is equal to the total volume flow rate \( Q \) divided by the pore cross-sectional area \( A \).

The total ion flux \( J_i \) for each of the ion types can be obtained by substituting Eq. (2.8) into Eq. (2.7) and then integrating over the cross-sectional area of the pore

\[
J_i = c_i Q K_i^l - AD K_i^{ll} \frac{dc_i}{dx} - AD K_i^{ll} c_i \frac{d\bar{\phi}_i}{dx}
\]  

(2.9)

where
\[ K'_i = 4 \int_0^1 \exp \left( -\frac{Z_i}{Z} \psi \right) (1 - r^2) \overline{r} dr \]

\[ K''_i = 2 \int_0^1 \exp \left( -\frac{Z_i}{Z} \psi \right) \overline{r} dr \]

(2.10)

With the pore length \( L \) and the feed concentration of ion type 3, i.e., \( (c_3)_I \) as reference scales, Eq. (2.9) can be rearranged into the following non-dimensional form

\[ (\overline{c_i})_{II} = \overline{c_i} \frac{K''}{K'_i} \frac{dc_i}{dx} - \frac{K''}{Pe} \frac{dc_i}{dx} \frac{d\phi_i}{dx} \]

where \( \overline{x} = x/L, \overline{c_i} = c_i/(c_3)_I \), and \( Pe = VL/D \) is the Peclet number.

Here, and in what follows, the subscript I is used to denote conditions on the feed side and II conditions on the product side. The ion concentrations on the product side are defined in terms of the corresponding fluxes by the relation

\[ (c_i)_{II} = \frac{J_i}{Q} = \frac{J_i}{VA} \]

(2.12)

Also from the electro-neutrality condition

\[ Z_1 \overline{c_1} + Z_2 \overline{c_2} + Z_3 \overline{c_3} = 0 \]

(2.13)

With \( (c_i)_I \) the feed concentration of ion type \( i \), the rejection coefficient \( R_i \) for each ion type is given by
\[ R_i = 1 - \frac{(\overline{c}_i')_{II}}{(\overline{c}_i')_{I}} \]  

(2.14)

where \((\overline{c}_i')_{I} = (c_i I)/(c_3 I)\). The rejection coefficient \(R_i\) is seen to have a value of 1 for complete rejection and 0 for no rejection. It is the rejection coefficient which is of interest and it can be evaluated with the aid of the closed set Eqs. (2.2) - (2.6) and (2.10) - (2.13).

2.2 Solutions

It can be deduced from the set of equations derived in the preceding section that the rejection coefficients defined by Eq. (2.14) for each of the ion types depend in general on five parameters: \(Pe\), \(\lambda_i\), \(\overline{\psi}_w\), \(\delta_i\) and \(H_i\), with the subscript \(I\) indicating that the parameter is evaluated using the known feed concentration \((c_3)_{I}\). It turns out that the dependence of each of the salt rejection coefficients on \(Pe\), \(\lambda_i\) and \(\overline{\psi}_w\) is to a good approximation similar to that for the case of a simple salt treated in Chapter 1. Therefore, in order to make the presentation of numerical results more succinct, the present analysis will concentrate on showing the dependence of the coefficients in the other two parameters \(\lambda_i\) and \(H_i\). In a couple of cases, however, the dependence on \(\lambda_i\) will also be shown. In the limit \(\lambda_i >> 1\), an analytic solution will be given which shows the dependence on \(\overline{\psi}_w\).

The one parameter which will not be considered explicitly in its influence on the rejection characteristics is the Peclet number \(Pe\). From the solutions and experimental comparisons presented in Chapter 1 for the simple salt case, the salt rejection \(R\) (the same for the cations
and anions) was shown to increase with the Peclet number for a given value of the Debye ratio $\lambda_1$ and wall potential $\bar{\psi}_w$, and to reach an asymptotic limit for large Pe. One of the important results, which can be seen in Fig. 2 and Fig. 3, was that the large Peclet number independence actually occurred at relatively low Pe values, around 2. The increase in rejection with increasing Peclet number follows from the fact that the Peclet number is a measure of the convective to diffusive effects. At small Pe, diffusion is dominant with the result that there is a lower rejection, while at large Pe, convection is dominant and the rejection is increased. Because the same qualitative behavior is expected for the present case, and because of the relative independence of the rejection on Pe for values of Pe $\gtrsim 2$, the present analysis will consider only the large Peclet limit in order to simplify the presentation. It should be emphasized, however, that including this parameter only complicates the algebra and graphical results but introduces no basic difficulties.

Even with the elimination of the dependence on Pe, a solution can in general only be obtained by numerical means. One particular limit where an analytic result can be given is where in addition to Pe $\gg 1$, the Debye ratio is also large, i.e., $\lambda_1 \gg 1$. This situation was exploited in the simple salt case in Chapter 1, and corresponds to the physical limit where the potential is uniform across the pore and the rejection takes place in the thick sheaths formed outside the pore at its ends.

For the limit $\lambda_1 \gg 1$, the potential $\bar{\psi} = \bar{\psi}_w$ and the integrals $K'_1$ and $K''_1$ of Eq. (2.10) can be easily evaluated. Using the relation
\( \bar{\phi}_i = Z_i F \phi / R T \), the potential gradients in Eq. (2.11) can be eliminated between the equations for \( i = 1 \) and \( i = 2 \) or 3. This leads to two first order nonlinear differential equations, one in terms of \( c_1 + c_2 \), and the other in terms of \( c_1 + c_3 \). These two equations and the electroneutrality condition give three equations for the three unknowns, \( c_1 \), \( c_2 \) and \( c_3 \). When \( Pe \) is finite, the two nonlinear differential equations can not be integrated analytically, and must be solved by numerical means. However, when \( Pe \gg 1 \), the terms \( Pe^{-1} d c_i / dx \) in these two equations are small and can be neglected. The differential equations then reduce to two algebraic equations in the unknowns \( (c_i)_{II} \). These equations are linear in \( (c_i)_{II} \), so that with the equation of electroneutrality they provide three linear algebraic equations for the three unknowns. On solving these equations the rejection coefficients for each ion type Eq. (2.14) can be evaluated with the following results:

\[
R_1 = 1 - \frac{(H + 1) \exp(\overline{\psi}_w) - \delta \overline{\psi}_w (H - 1) \exp(- \overline{\psi}_w)}{\exp[(H + 1) \overline{\psi}_w] + \delta \overline{\psi}_w [(H - 1) \overline{\psi}_w] + (1 - \delta) H} \quad (2.15)
\]

\[
R_2 = 1 - \frac{2 + (1 - \delta) (H - 1) \exp[- (H + 1) \overline{\psi}_w] \exp(\overline{\psi}_w) + \delta \overline{\psi}_w [(H - 1) \overline{\psi}_w] + (1 - \delta) H \exp(- H \overline{\psi}_w)}{\overline{\psi}_w + \overline{\psi}_w (H - 1) \exp(- \overline{\psi}_w) + (1 - \delta) H \exp(- H \overline{\psi}_w)} \quad (2.16)
\]

\[
R_3 = R_1 - \delta (R_1 - R_2) \quad (2.17)
\]

It should be emphasized that Eqs. (2.15) - (2.17) for the rejection coefficients are valid in general when \( \overline{\psi}_w \) is positive. When \( \overline{\psi}_w \) is negative, corresponding to the case where the type 1 and type 2 ions are counterions, Eqs. (2.15) - (2.17) can give the physically
impossible result of a rejection greater than 1 for the larger charge
number counterion (type 1 when $H > 1$ or type 2 when $H < 1$) and a negative
rejection for the smaller charge number counterion. It may be seen from
Eqs. (2.15) and (2.16) that for $\psi_w < 0$ the rejections obtained are
generally greater than 1 unless $|\psi_w|$ is very small. This result has
been shown previously by Dresner

When the solution is such that Eqs. (2.15) - (2.17) give a rejec-
tion greater than 1, the problem is easily treated by considering that
the counterions of higher charge are completely rejected ($R = 1$) and
therefore do not enter the charge pore, and that the only ions which
enter the pore are the counterions of lower charge and the coions

Obtaining the rejection coefficients for these two ion types is
straight forward with the procedure the same as for the case when there
are three ion types.

Equations (2.15) - (2.17) are plotted in Fig. 8 for a wall poten-
tial $\psi_w = 1.22$, and two charge strengths $H = 2$ and 4. The results
confirm the physical argument that due to stronger electrostatic effects
ion species of higher charge number should be more strongly rejected
than those of lower charge number, and the increase in rejection should
increase for larger values of the charge strength parameter $H$. The
increased rejection of electrolytes with increasing valences of the
ionic species is a well known characteristic of hyperfiltration membranes.

For the case considered, where the wall potential $\psi_w$ is positive,
it is interesting to note that the rejections of the type 1 and 2 ions
depend only very weakly on the parameter $\delta_i$. Expanding
Eqs. (2.15) - (2.17) shows the slopes of $R_1$ and $R_2$ with respect to $\delta_1$ are of the order of $\exp(-2\bar{\psi}_w)$, which is usually quite small for any value of $\bar{\psi}_w \gtrsim 1$.

The weak dependence of $R_1$ and $R_2$ on $\delta_1$ enables the use of the maximum and minimum values of $R_3$ (when $\delta_1 = 0$ and $\delta_1 = 1$, respectively) as reference rejections when investigating the dependence of the rejections on the Debye ratio $\lambda_1$. These two values will indicate the rejection levels of $R_1$ and $R_2$, as well as indicate the maximum and minimum values of $R_3$. The dependence of these rejections on the Debye ratio $\lambda_1$ are obtained by solving the system of equations of preceding section numerically. It was done following the same procedure as in the limiting case $\lambda_1 >> 1$, when a set of nonlinear differential equations were reduced to a set of algebraic equations for $Pe >> 1$. The only exception in this case is that the integrals $K'_1$ and $K''_1$ had to be evaluated numerically. The results are plotted in Fig. 9 for a value of $\bar{\psi}_w = 1.22$ (≈ 30 mV at room temperature) and $H = 2$. The figure shows, as expected, that the difference in rejection among the three ion types diminishes with decreasing Debye ratio $\lambda_1$ and that the rejection characteristics are qualitatively similar to the simple salt case.

One limit of interest for which the theory will be compared with experimental data is where there is only a single salt which dissociates into two ions of different valence. In this case $\delta_1 = 0$, and Eqs. (2.15) and (2.17) become

$$R_1 = R_3 = 1 - \frac{(H + 1)}{\exp(H\bar{\psi}_w) + H \exp(-\bar{\psi}_w)} \quad (2.18)$$
Here the charge parameter \( H = Z^*/Z \).

For the case where the single salt is a simple salt, in the sense that on dissociating the two ions are of equal valence, \( \delta_1 = 1 \) and Eqs. (2.16) and (2.17) reduce to the result derived previously in Chapter 1.

\[
R_2 = R_3 = 1 - \frac{1}{\cosh \psi_w^*} \quad (2.19)
\]

This same result can be obtained from Eq. (2.15) and Eq. (2.16) by setting \( H = 1 \). It should be noted by comparing Eqs. (2.18) and (2.19) that the salt rejection, when the ions are of different valence, is greater than for a simple salt if \( H > 1 \), and is less than for a simple salt if \( H < 1 \).

**TABLE I**

Comparison of Theory with Experiment by Hoornaert et al.\(^{14}\) on the Rejection of two Different Salts by Dynamically Formed Membranes

<table>
<thead>
<tr>
<th>Salt</th>
<th>Conc. (N)</th>
<th>Conc. (ppm)</th>
<th>Flux ((cm^3/sec/cm^2))</th>
<th>Rejection Observed (%)</th>
<th>Rejection Calculated (^*) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl(_2)</td>
<td>0.025</td>
<td>1191</td>
<td>(3.43 \times 10^{-3})</td>
<td>79.8</td>
<td>80.7</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.025</td>
<td>1462</td>
<td>(4.18 \times 10^{-3})</td>
<td>52.0</td>
<td>51.5</td>
</tr>
</tbody>
</table>

Hyperfiltration rejection data for a divalent salt (MgCl\(_2\)) and a univalent salt (NaCl) have been obtained by Hoornaert et al.\(^{14}\) using high flux dynamically formed hydrous zirconium oxide membranes. Their data for low feed concentrations (\(< 1,200 - 1,500\) ppm) and high feed recirculation rates (49 - 62 l/hr) are shown in Table I. The operating pressure was relatively low, around 20 Kg/cm\(^2\) (\(< 20\) atm), and the temperature was about 25°C.

\(^*\) For assumed wall potential \( \psi_w^* = 1.35 \) (35 mV)
The salts tested correspond to the limiting case of \( \delta_1 = 0, \ H = 2 \) for the divalent single salt (\( \text{MgCl}_2 \)) and \( \delta_1 = 1 \ (H = 1) \) for the simple salt (\( \text{NaCl} \)). Assuming for the moment that both the Peclet number \( Pe \) and the Debye ratio \( \lambda \) are sufficiently large, then the theoretical rejections of these two salts can be calculated using Eqs. (2.18) and (2.19). However, the wall potential \( \psi_w \) was not determined experimentally by Hoornaert et al.\(^{14} \) by carrying out the proper zeta-potential measurements, nor is the zeta-potential of zirconium oxide membrane known from other works. The calculated rejections in Table I were obtained by assuming a value of \( \psi_w = 1.35 \), corresponding to a wall potential of 35 mV. The value was chosen to give a best match with the data. Clearly, the theory can be brought into excellent agreement with the experiments by the choice of a single unknown parameter.

Of course, the meaningfulness of the comparison shown in Table I depends in large part on the accuracy of the wall potential \( \psi_w \) assumed, not only on its absolute value, but also on the sign of the potential. A positive potential for the dynamically formed hydrous zirconium oxide membrane was chosen on the grounds that for the pH range of the experiment (3 - 4.5) the membrane has the property of excluding cations, corresponding to a positive potential on the membrane\(^ {14,15} \). The absolute value of 35 mV, although chosen because of the good agreement it gave, is nevertheless quite reasonable for this type of material (see Chapter 1).

In order to determine the sensitivity of both the absolute values of the salt rejection and the ratio of the rejections to change in the
assumed values of the wall potential \( \overline{\psi}_w \), calculations have been carried out for a range of \( \overline{\psi}_w \) from 1 (\( \sim 26 \text{ mV} \)) to 2 (\( \sim 52 \text{ mV} \)). The results of these calculations, which are based on Eqs. (2.18) - (2.19), are shown in Fig. 10. It can be seen that the behavior of the absolute values of the rejections is moderately dependent on the value of the wall potential \( \overline{\psi}_w \), though not markedly so when it is recognized that a change in \( \overline{\psi}_w \) of but 0.1 corresponds to an absolute change in potential of around 2.5 mV. However, it can also be seen that the relative rejections, that is, the ratio of the divalent to univalent rejections, is reasonably insensitive to changes in wall potential with a doubling of the potential from 1 to 2 resulting in a change in the rejection rates of less than 28%. Of course, for large \( \overline{\psi}_w \) both rejections approach 1 with the difference between them tending to zero. The excellent agreement for \( \overline{\psi}_w = 1.35 \) is evident and it may be that such types of comparisons could eventually serve to evaluate \( \overline{\psi}_w \).

The calculated rejections shown in Table I and Fig. 10 assume that in the experiments the Peclet number Pe and the Debye ratio \( \lambda_1 \) are both large enough to justify the use of Eqs. (2.18) and (2.19). In addition, it is of course assumed that the effective pore radius \( a \) is large enough that the continuum model of the present theory is applicable. What follows is the derivation of the definitions of these parameters Pe, \( \lambda_1 \), \( a \) in terms of the measurable bulk properties of the porous material; and then through these relationships the estimate of their magnitude for the experiment considered.

In the flow through a cylindrical pore, the mean velocity \( V \), according to Poiseuille relation, is
\[ V = \frac{a^2}{8} \frac{1}{\mu} \frac{\Delta p}{L} \]  

(2.20)

where \( \mu \) is the viscosity of water and \( \Delta p \) is the applied pressure difference across the pore. If the porous membrane consists of a uniform distribution of these cylindrical pores, then the flow rate per unit membrane area \( q \) can be easily expressed as

\[ q = \frac{\gamma a^2}{8t} \frac{1}{\mu} \frac{\Delta p}{h} \]  

(2.21)

Here \( t = L/h \) is the tortuosity with \( L \) the thickness of the membrane, and \( \gamma \) is the porosity of the membrane. From Eq. (2.20) and (2.21), the Peclet number can be expressed as

\[ Pe = \frac{VL}{D} = qht^2 \frac{\gamma}{D\gamma} \]  

(2.22)

and the Debye ratio based on the feed condition \( \lambda_I \) is

\[ \lambda_I = \frac{\lambda_{DI}}{a} = \lambda_{DI} \left( \frac{8t^2 \mu h q}{\Delta p \gamma} \right)^{-1/2} \]  

(2.23)

Here the Debye length \( \lambda_{DI} \) is given by Eq. (2.5) with \( c_3 \) identified with its feed value. It should be noted that these same expressions for \( Pe, \lambda_I \) and \( a \) were derived by Jacazio et al. \(^9\)

In the experiment by Hoornaert et al. \(^14\), not all the constants needed to evaluate the parameters \( Pe, \lambda_I \) and \( a \) were measured. Those measured were the water flux per unit area \( q \) which ranged from \( 3.4 \times 10^{-3} \)
to $4.2 \times 10^{-3}$ cm$^3$/sec/cm$^2$ ($\approx 73 - 89$ gal/ft$^2$/day) and the applied pressure difference $\Delta p$ was around 20 kg/cm$^2$ ($\approx 20$ atm). In order to estimate these parameters, it is necessary to employ values for some of the constants known to be typical for the membrane used. For example, $h$ is assumed to be of the order of 5$\mu$, a value typical for dynamically formed membranes$^{15}$, while $\tau$ is taken to be $\approx 1.58$ which holds for a wide variety of porous materials$^{16}$ (see also Chapter 1). The porosity $\gamma$ is taken to be around $1/3$ which is a characteristic value for most ion exchange materials$^{17}$. For the temperature of the experiment $D = 1.5 \times 10^{-9}$ m$^2$/sec, and $\mu = 0.89$ centipoise.

Using the values of the constants indicated the effective radius was found to be about 20 Å, thus ensuring the applicability of the basic continuum model discussed in Chapter 1. The parameters $Pe$ and $\lambda_1$ both turn out to have values around 1. Although not very large, it may be seen from Figs. 2, 3 and 5 in Chapter 1 that they are large enough to apply the $\lambda_1 \gg 1$ and $Pe \gg 1$ solutions as represented by Eqs. (2.18) - (2.19). Of course it should be emphasized that there is no difficulty in obtaining the solutions for finite $Pe$ and $\lambda_1$. However, these parameters are not known with sufficient accuracy for the experiments reported in the literature to enable a meaningful comparison with the theory to be carried out.
Figure 8. Rejection coefficients for multiple salts which dissociate into three ion types with two different charge strength parameters. Cylindrical pore with a constant surface potential, large Debye ratio and large Peclet number.
Figure 9. Maximum and minimum rejection coefficients for multiple salts which dissociate into three ion types as a function of Debye ratio. Cylindrical pore with a constant surface potential and large Peclet number.
Figure 10. Rejection coefficients for a divalent and a univalent salt as a function of surface potential. Cylindrical pore with large Debye ratio and large Peclet number. Experimental data from Ref. 14 using dynamically formed hyperfiltration membranes (wall potential not measured but matched for best agreement with theory).
CHAPTER 3 - EFFECT OF GEOMETRY ON THE SIMPLE CAPILLARY MODEL

In the simple capillary model discussed in the previous two chapters, the porous membrane is considered to be made up of a series of uniformly distributed cylindrical pores. In any actual porous membrane, the pore geometry is undoubtedly more complicated than this simple arrangement. The usefulness of this simple capillary model, therefore, depends on how well it can characterize the actual performance of a porous membrane. From the excellent agreement between the theory and the experiments indicated so far in Chapters 1 and 2, this simple capillary model does seem to work very well. What makes this simple capillary model such a good one is, however, not very clear, and it is precisely the aim of the present chapter to investigate this question. In what follows, the performance of a porous membrane based on different geometrical configurations will be analyzed and compared with that of the simple capillary model. If the differences among these various models are small, which they turn out to be, then it will explain why the theory based on the simple capillary model agrees so well with experimental observations.

3.1 Statistical Size Distribution

In this section the porous membrane is considered to be made up of cylindrical pores of various sizes, and the performance of such a membrane is analyzed and compared with those based on the simple capillary model where all the pores are identical. In the analysis to follow, the pore sizes in the non-uniform model are assumed to be distributed according to the Normal Distribution function.
\[ f_N(\overline{a}) = \Lambda_N \exp \left[ - \frac{(\overline{a} - 1)^2}{2\sigma^2} \right] \quad (3.1) \]

with
\[ \int_0^\infty f_N(\overline{a}) \, d\overline{a} = 1 \quad (3.1a) \]

and
\[ \Lambda_N^{-1} = (\frac{\pi}{2})^{1/2} \sigma \left[ 1 + \text{erf} \left( \frac{1}{\sqrt{2} \sigma} \right) \right] \quad (3.1b) \]

Here \( \sigma^2 = (\Delta a/a_0)^2 \) is the mean square deviation referred to the most probable pore radius \( a_0 \) for which the distribution function has a maximum, and \( \overline{a} = a/a_0 \) is a dimensionless pore radius. Whereas in the uniform model, all the pores have the same pore radius equal to \( a^* \). It should be noted that for any porous membrane, the uniform pore radius \( a^* \) based on the uniform model and the most probable radius \( a_0 \) based on the non-uniform model are not the same.

The relationship between \( a^* \) and \( a_0 \), however, can be easily established. This relationship is required, as will be seen later, in order to be able to compare the membrane rejection performances based on these two models. According to Hagen-Poiseuille relation, the mean velocity \( V \) through a single pore with pore radius \( a \) is

\[ V = \frac{a^2 \Delta p}{8 \mu \, L} \quad (3.2) \]

where \( \Delta p \) is the applied pressure difference across the pore, \( L \) is the length of the pore and \( \mu \) is the water viscosity. If the total number of the pores inside the membrane is \( n \) and their sizes distributed according to the Normal Distribution function defined by Eq. (3.1),
then the total flow rate $\bar{Q}$ through the membrane is

$$\bar{Q} = \frac{n \pi a_0^4 \Delta p}{8 \mu L} \left( \int_0^\infty f_N a^4 \, da \right)$$  \hspace{1cm} (3.3)

The porosity of the membrane $\gamma$ by definition is

$$\gamma = \frac{n \pi a_0^2 L}{\bar{\Lambda} h} \left( \int_0^\infty f_N a^{-2} \, da \right)$$  \hspace{1cm} (3.4)

where $\bar{\Lambda}$ is the membrane surface area and $h$ the membrane thickness.

Substituting Eq. (3.4) into Eq. (3.3), the water flux per unit membrane area, $q = \bar{Q} / \bar{\Lambda}$, can be expressed as

$$q = \left( \frac{a_0^2 \Sigma_1^{1/2}}{8 \tau^2} \right) \frac{\gamma \Delta p}{\mu h}$$  \hspace{1cm} (3.5)

where

$$\Sigma_1 = \left[ \int_0^\infty f_N a^{-4} \, da \right]^{1/2}$$  \hspace{1cm} (3.5a)

and $\tau = L / h$ is the tortuosity of the non-uniform pores. Denoting $S_0$ as the specific surface area, which by definition is the wetted surface area per unit solid volume, then $S_0$ can be expressed in terms of $a_0$ and $\gamma$ as
\[ S_0 = \frac{2\gamma}{(1 - \gamma) a_0 \bar{L}_2} \]  \hspace{1cm} (3.6)

where

\[ \bar{L}_2 = \frac{\int_{0}^{\infty} f_N a^{-2} \, da}{\int_{0}^{\infty} f_N a^{-3} \, da} \]  \hspace{1cm} (3.6a)

Substituting Eq. (3.6) into Eq. (3.5), the flow rate per unit area \( q \) can be expressed in another form with \( a_0 \) replaced by \( S_0 \)

\[ q = \frac{\gamma^2}{2t^2} \frac{\gamma^3 \Delta p}{S_0^2 (1 - \gamma)^2 \mu h} \]  \hspace{1cm} (3.7)

where

\[ \bar{\Sigma} = \bar{\Sigma}_1 / \bar{\Sigma}_2 \]  \hspace{1cm} (3.7a)

If the pore sizes in the membrane are uniformly distributed, the expression for the flow rate per unit area \( q \) corresponding to Eq. (3.5) for the non-uniform case is

\[ q = \frac{(a^*)^2}{8(t^*)^2} \frac{\gamma \Delta p}{\mu h} \]  \hspace{1cm} (3.8)

where \( t^* = L/h \) is the tortuosity of the uniform pores. The other expression for \( q \) corresponding to Eq. (3.7) is

\[ q = \frac{1}{2(t^*)^2} \frac{\gamma^3 \Delta p}{S_0^2 (1 - \gamma)^2 \mu h} \]  \hspace{1cm} (3.9)
Since the bulk properties $\gamma$, $S_0$, $\Delta p$, $\mu$, $h$, $q$ are the same for both the uniform and non-uniform models, the comparison of Eq. (3.9) and Eq. (3.7) shows that the relationship between $t$ and $t^*$ is

$$ t = t^* \Sigma $$

(3.10)

With Eq. (3.10), the comparison of Eq. (3.8) and Eq. (3.5) shows that the relationship between $a_0$ and $a^*$ is

$$ a_0 = a^*/\Sigma_2 $$

(3.11)

The rejection property of each of the pores in the membrane, as analyzed in Chapter 1, depends on three similarity parameters. They are the constant wall potential $\overline{\Psi}_w$, the Debye ratio $\lambda_I = \lambda_{DI}/a$ and the Peclet number $Pe = VL/D = a^2 \Delta p/(8\mu D)$. In any given situation where the membrane operating conditions are specified, the values of these similarity parameters are defined for each of the pores within the membrane. The wall potential parameter $\overline{\Psi}_w$, according to the present assumption, takes on a certain value independent of the size of the pore or the feed concentration. The other two parameters $Pe$ and $\lambda_I$, however, may or may not have the same values for all the pores depending on whether the pores are of the same size or of different sizes. For the uniform model where all the pores are identical, all the pores have the same set of values of Peclet number and Debye ratio. In this
case, the Debye ratio $\lambda^*_I = \lambda_{DI}/a^*$ and the Peclet number $Pe^* = (a^*)^2 \Delta p/(\delta u D)$.

For the non-uniform model, each pore is different, and therefore each pore has a different set of values of $Pe$ and $\lambda^*_I$. These values of $Pe$ and $\lambda^*_I$ in each of the pores, however, can be defined in terms of those based on the uniform model. From Eq. (3.11) and the definition of these parameters, it is easy to obtain

$$\lambda^*_I = \lambda^*_I L^2 / a^*$$

(3.12)

$$Pe = Pe^* a^2 / L^2$$

The significance of Eq. (3.12) is that it allows all the rejection calculations, for both the uniform and non-uniform models, to be performed based on one set of similarity parameters $\overline{\psi}, Pe^*, \lambda^*_I$, whose values are defined in a given situation.

The rejection property of a membrane is a collective result of the rejection properties of all its pores. In the exceptional case where all the pores are identical, the membrane property equals that of each of its pores. In the non-uniform case, however, all the pores must be taken into consideration. The salt flux in each of the pores, by definition, is

$$j = c_I (1 - R) V \pi a^2$$

(3.13)

where $c_I$ is the feed concentration and $R = R(\overline{\psi}, Pe, \lambda^*_I)$ is the rejection
coefficient of the pore. If \( n \) is the total number of pores in the membrane, then the total salt flux through the membrane is

\[
\overline{J} = \int_{0}^{\infty} c_I (1 - R) \sqrt{\pi} a^2 n f_N \, da
\]  

(3.14)

and the total water transport through the membrane is

\[
\overline{Q} = \int_{0}^{\infty} \sqrt{\pi} a^2 n f_N \, da
\]  

(3.15)

Denoting \( c_{II} = \overline{J} / \overline{Q} \) as the product concentration and \( \langle R \rangle = 1 - c_{II} / c_I \) as the membrane rejection coefficient, then Eqs. (3.14) and (3.15) give

\[
\langle R \rangle = \frac{\int_{0}^{\infty} R f_N^{-4} \, da}{\int_{0}^{\infty} f_N^{-4} \, da}
\]  

(3.16)

Since the rejection coefficient for each pore \( R \) is determined in general by numerical methods, as discussed in Chapter 1, the membrane rejection coefficient \( \langle R \rangle \) can only be evaluated in general by numerical methods. To do this, the integral in Eq. (3.16) is replaced by the finite sum

\[
\langle R \rangle = \frac{\sum_{a_1}^{a_2} R(\psi_w, \text{Pe}, \lambda_I) f_N^{-4} \, \Delta a}{\sum_{a_1}^{a_2} f_N^{-4} \, \Delta a}
\]  

(3.17)
where the limits of the sum, \( \overline{a}_1 \) and \( \overline{a}_2 \), represent the points over which the contribution to the result is negligible. Assuming a certain mean deviation \( \sigma \), the membrane rejection coefficient \( <R> \) can be evaluated for different values of \( \overline{\psi}_w \), \( Pe^* \), and \( \lambda^{**}_I \). It should be emphasized that the parameters \( Pe \) and \( \lambda^{**}_I \) for determining the rejection coefficient \( R \) are related to \( Pe^* \) and \( \lambda^{**}_I \) through Eq. (3.12).

For the comparison of the non-uniform model to the uniform model, the membrane rejection coefficient \( <R> \) was calculated for two different limiting cases: \( \lambda^{**}_I >> 1 \) and \( Pe^* >> 1 \). For the limiting case of \( \lambda^{**}_I >> 1 \), membrane rejection coefficient \( <R> \) is plotted in Fig. 11 as a function of \( Pe^* \) for three different values of \( \sigma \) with \( \overline{\psi}_w = 1.22 \), and the results are compared with those based on the uniform model (i.e., \( \sigma = 0 \)). In these calculations the values for the pore rejection coefficient \( R \) were obtained from previous results in Chapter 1 for large \( \lambda^{**}_I \) (Eq. (1.18)) where \( R \) is independent of \( \lambda^{**}_I \) and dependent on \( \overline{\psi}_w \) and \( Pe \) only. It is assumed, of course, in this case that \( \lambda^{**}_I \) is large enough such that within the integrating limits \( \overline{a}_1 \) and \( \overline{a}_2 \) all the pores have large values of \( \lambda \). The three different values of the mean deviation \( \sigma \) are 0.2, 0.4 and 0.8. The values of \( \sigma = 0.2 \) and \( 0.4 \) represent possible narrow spreads of the distribution of pore sizes, whereas \( \sigma = 0.8 \) represents a possible wider spread. Measurement of porous glass tubes have shown that the size distribution is very narrow and is well within the narrow spread range considered (\( \sigma = 0.4 \)). It is anticipated that in the event of fabricating actual membranes for desalting applications, it is possible, if uniformity in pore sizes is intended, to construct membranes of the very narrow
spread type. For example, silica-alumina beads manufactured by the Mobil Research and Development Corporation with homogeneity in mind have a spread of well within $\sigma = 0.2^{19}$. In any case, the results in Fig. 11 show that the curves of $\sigma = 0.2$ and 0.4 are very close to the uniform model, and the curve of $\sigma = 0.8$, though it starts to show difference, is only slightly different from the uniform model. This concludes that in the evaluation of membrane rejection performance, there is very little difference, at least in this large Debye ratio limit, between using the uniform or the non-uniform model as long as the spread of the pore sizes for the non-uniform model is not too wide ($\sigma < 0.8$).

For the other limiting case of $Pe^* \gg 1$, the rejection $<R>$ is plotted in Fig. 12 as a function of $\lambda_1^*$ for the three different values of $\sigma$ with $\bar{\psi}_w = 1.22$. The values for the pore rejection coefficient $R$ were again obtained from previous numerical results in Chapter 1 for large $Pe$. The same condition holds that $Pe^*$ is large enough such that, within the integrating limits, all the pores have large values of $Pe$. The results in Fig. 12 again show that all the curves, except for $\sigma > 0.8$, are very close to the uniform model and therefore indicate that there is very little difference between the two models. Considering the similar dependence behavior of the rejection coefficient $R$ on $\lambda_1$ and $Pe$ as in the limiting case (see Chapter 1), it is reasonable to assume that the good comparison between the two models is true for all values of $\lambda_1^*$ and $Pe^*$. It can therefore be concluded that in the evaluation of membrane rejection performance, the difference between using a uniform
or a non-uniform distribution model is very small as long as the spread
of pore sizes for the non-uniform model is not too wide.

3.2 Slit Pores

In any porous material where the constituting particles have shapes
like platelets, it is very likely that the pores that exist in the
material are of narrow rectangular shape, or of slit shape. In this
section, the porous membrane is considered to be made up of identical
pores of slit shape, and the performance of such a membrane is analyzed
and compared with those based on the simple capillary model where the
pores are considered to be of cylindrical shape. In the analysis to
follow, the depth of the slit channel w is considered to be much
larger than the width of the slit channel 2b.

For any membrane, the size of the slit pores based on the slit
model and the size of the cylindrical pores based on the cylindrical
model are related and can be easily obtained. This relationship is re-
quired, as was in the previous section, in order to be able to compare
the membrane rejection performances based on these two models. Accord-
ing to Plane Poiseuille flow, the mean velocity \( V_b \) through a narrow
channel with width equal to 2b is

\[
V_b = \frac{b^2 \Delta p}{3\mu L_b}
\]  

(3.18)

where \( \Delta p \) is the applied pressure difference across the slit pore, \( L_b \) is
the length of the slit pore and \( \mu \) is the water viscosity. If \( n \) is the
total number of pores in the membrane, then the total flow \( Q \) through

the membrane is

\[ \bar{Q} = \frac{2n \omega b^3}{3\mu L_b} \Delta p \]  

(3.19)

The porosity of the membrane \( \gamma \) by definition is

\[ \gamma = \frac{n(2b\omega) L_b}{Ah} \]  

(3.20)

where \( A \) is the membrane surface area and \( h \) is the membrane thickness.

Substituting Eq. (3.20) into Eq. (3.19), the flow rate per unit membrane area, \( q = \bar{Q}/A \), can be expressed as

\[ q = \left( \frac{b^2}{3t_b} \right) \frac{\gamma \Delta p}{\mu h} \]  

(3.21)

where \( t_b = L_b/h \) is the tortuosity of the slit pores. Denoting \( S_0 \) as the specific surface area, which by definition is the wetted surface area per unit solid volume, then \( S_0 \) can be expressed in terms of \( b \) and \( \gamma \) as

\[ S_0 = \frac{\gamma}{b(1 - \gamma)} \]  

(3.22)

Substituting Eq. (3.22) into Eq. (3.21), the flow rate per unit area \( q \) can be expressed in another form with \( b \) replaced by \( S_0 \)

\[ q = \left( \frac{1}{3t_b} \right) \frac{\gamma^3 \Delta p}{S_0^2(1 - \gamma)^2 \mu h} \]  

(3.23)
For the cylindrical model, the expression for the flow rate per unit area \( q \) corresponding to Eq. (3.21) for the slit model is

\[
q = \frac{(a^*)^2}{8(t^*)^2} \frac{\gamma \Delta p}{\mu h}
\]  

(3.24)

where \( t^* = L/h \) is the tortuosity of the cylindrical pores, and \( a^* \) is the pore radius. The other expression for \( q \) corresponding to Eq. (3.23) is

\[
q = \frac{1}{2(t^*)^2} \frac{\gamma^3 \Delta p}{S_0^2(1 - \gamma)^2 h}
\]

(3.25)

Since the bulk properties \( \gamma, S_0, \Delta p, \mu, h \) are the same for both models, the comparison of Eq. (3.23) and Eq. (3.25) shows that the relationship between \( t_b \) and \( t^* \) is

\[
t_b = (\frac{2}{3})^{1/2} t^*
\]

(3.26)

With Eq. (3.26), the comparison of Eq. (3.21) and Eq. (3.24) shows that the relationship between \( b \) and \( a^* \) is

\[
b = \frac{1}{2} a^*
\]

(3.27)

The rejection property of a membrane where the pores are uniformly distributed is characterized by the rejection property of a single pore. As discussed previously in Chapter 1, the three similarity parameters
which govern the rejection property of a single pore are the constant wall potential, the Debye ratio and the Peclet number. In any given situation where the operating conditions are specified, the values of these similarity parameters are defined for each of the pores within the membrane. Except for the wall potential parameter which takes on a certain value independent of the pore shape or feed concentration, the values of the other two parameters depend on whether the shape of the pore is cylindrical or slit. For a cylindrical pore, the Debye ratio is defined as \( \lambda^* = \lambda_{DI}/a^* \) and the Peclet number \( Pe^* \equiv VL/D = (a^*)^2 \Delta \rho/(8\mu D) \) (see Eq. (3.2)). Whereas for a slit pore, the Debye ratio is defined as

\[ (\lambda^*_{DI})_b = \lambda_{DI}/b \]

and the Peclet number \( (Pe)_b \equiv V_b L_b /D = b^2 \Delta \rho/(3\mu D) \). Because of Eq. (3.27) these similarity parameters based on two different models are related

\[ (\lambda^*_{DI})_b = 2\lambda^*_I \]

\[ (Pe)_b = \frac{2}{3} Pe^* \]  

(3.28)

Equation (3.28) therefore allows all the comparisons to be performed based on one set of similarity parameters \( \bar{\psi}_w, Pe^*, \lambda^*_I \) which are defined in a given situation.

In a porous membrane where the pore sizes are uniformly distributed, the rejection property of a single pore governs that of the whole porous membrane. For a cylindrical pore, the rejection property has been discussed in detail in Chapter 1. Whereas for a slit pore, the rejection
property can be similarly obtained as those for the cylindrical pore. In the analysis to follow, a Cartesian coordinate system \((x,y)\) is used for the slit pore case where \(x\) is positive in the direction of flow and \(y\) the transverse coordinate with origin at the center plane of the slit channel. In this case, the ion fluxes are still governed by the Nernst-Planck equation (c.w., Eq. (1.5) in Chapter 1).

\[
\mathbf{j}_x = uc \exp(\overline{\psi}) - D \exp(\overline{\psi}) \frac{dc}{dx} + Dc \exp(\overline{\psi}) \frac{d\overline{\phi}}{dx} \tag{3.29}
\]

where \(u\) is the velocity distribution, \(c\) is the salt concentration along the pore, \(\overline{\psi}\) is the dimensionless transverse potential and \(\overline{\phi}\) is the dimensionless longitudinal potential. The velocity distribution \(u\), however, is now governed by the Plane Poiseuille relation

\[
u = \frac{3}{2} \nu_b \left(1 - \overline{y}^2\right) \tag{3.30}
\]

where \(\nu_b = Q/A\) is the mean flow velocity through the slit channel and \(\overline{y} = y/b\) is the dimensionless transverse coordinate. Also, the transverse potential is now governed by a Poisson-Boltzmann equation of the following form

\[
(\lambda)^2 \frac{d^2 \overline{\psi}}{d\overline{y}^2} = \sinh \overline{\psi} \tag{3.31}
\]

where \((\lambda) = \lambda_D/b\) is the dimensionless Debye ratio.

Following the same procedure as for the cylindrical pore case and with the same requirement that there is no electric current through the
pore (see Chapter 1), the same concentration equation as for the cylindrical case (Eq. (1.9)) can be obtained, except with different definitions for the coefficients

\[
\frac{K_{1b}}{(Pe)_b} \frac{dc}{dx} - \bar{c} = \kappa_2 \bar{c}_{II}
\]  
(3.32)

Here

\[
K_{1b} = \frac{K_{3b}^2 - K_{4b}^2}{K_{1b} K_{3b} - K_{2b} K_{4b}}
\]  
(3.32a)

\[
K_{2b} = \frac{K_{3b}}{K_{1b} K_{3b} - K_{2b} K_{4b}}
\]

and

\[
K_{1b} = \frac{3}{2} \int_0^1 \cosh \bar{\psi} \left(1 - \bar{y}^2\right) \, d\bar{y}
\]

\[
K_{2b} = \frac{3}{2} \int_0^1 \sinh \bar{\psi} \left(1 - \bar{y}^2\right) \, d\bar{y}
\]  
(3.32b)

\[
K_{3b} = \int_0^1 \cosh \bar{\psi} \, d\bar{y}
\]

\[
K_{4b} = \int_0^1 \sinh \bar{\psi} \, d\bar{y}
\]

In Eq. (3.32) \(\bar{c} = c/c_\bar{I}\) is a dimensionless concentration with \(c_\bar{I}\) defined as the feed concentration. The dimensionless product concentration is defined as \(\bar{c}_{II} = c_{II}/c_\bar{I} = J_s/[2V_b(2bw) c_\bar{I}]\) with \(J_s = J_+ + J_-\) as the total
salt flux. The total ion flux is defined as
\[ J_+ = 2 \int_{b}^{0} j_+ \, dy \]  
(3.32c)

Equation (3.32), as described in detail in Chapter 1, can only be solved in general by numerical methods, except for the limiting case when \( \lambda_b^+ \ll 1 \) where analytic solution is possible.

For the comparison of the slit model to the cylindrical model, the membrane rejection coefficient \( R = 1 - \frac{c_{II}}{c_I} \) was calculated for two limiting conditions: \( \lambda_1^+ \gg 1 \) and \( Pe^* \gg 1 \). For the limiting case where \( \lambda_1^+ \gg 1 \), or \( (\lambda_1)^*_b \gg 1 \), Eq. (3.32) can be integrated analytically with the following explicit result for the membrane rejection coefficient \( R \) for the slit model

\[ R = 1 - e \frac{(Pe)_b}{(1 - \cosh \frac{\psi}{\psi_w}) + e^{(Pe)_b} \cosh \frac{\psi}{\psi_w}} \]  
(3.33)

where \( (Pe)_b \) is related to \( Pe^* \) through Eq. (3.28). From Eq. (3.33) \( R \) is plotted in Fig. 13 as a function of \( Pe^* \) with \( \frac{\psi}{\psi_w} = 1.22 \), and the results are compared with those of the cylindrical model which were previously obtained (Eq. (1.18) in Chapter 1). The results in Fig. 13 show that the membrane performances based on the slit model are very close to those based on the cylindrical model, and therefore suggests that in the evaluation of membrane performance there is very little difference, at least in the large Debye ratio limit, between using the slit model and the cylindrical model.
For the other limiting case of Pe* \(>>\) 1, the results are plotted in Fig. 14 as a function of \(\lambda^*_I\) with \(\bar{\psi}_w = 1.22\). It is assumed in this case that Pe* is large enough such that \((Pe)_b >> 1\) (see Eq. (3.28)). The results for the slit case were obtained by solving Eq. (3.32) numerically (same as in Chapter 1) and those for the cylindrical case were obtained from previous results. Figure 14 again shows that the results between the slit model and the cylindrical model are very close to each other. Considering the similar dependence behavior of the rejection coefficient R on the Debye ratio \(\lambda^*_I\) and the Peclet number Pe* as in the limiting case (discussed in detail in Chapter 1), it is reasonable to assume that the good comparison between the two models is true for all values of \(\lambda^*_I\) and Pe*. This suggests again that the simple cylindrical model is a good model.

3.3 Variable Cross-Section Pores

In this section the porous membrane is considered to be made up of identical cylindrical pores whose cross-sections are not constant, and the performance of such a membrane is analyzed and compared with those based on the simple capillary model where the pores are considered to have constant cross-sections. In the analysis to follow the variable cross-section pore is considered to have a geometrical configuration as shown in Fig. 15, where the cross-section of the pore is shown to vary in the form of a square wave with a wave length of \(W\). The length of the pore is \(L_c\), and the radii of the large and small cross-sections are \(a_L\) and \(a_S\) respectively.

For any membrane, the size of the pores based on this variable cross-section model, and the size of those based on the constant cross-section
model, are related. This relationship, as has been discussed before, is required in order to compare the membrane performances based on these two models. Under hyperfiltration conditions where the viscous forces are dominant, the pressure losses due to inertia forces at the entrance and exit of each section in the variable cross-section pore are negligible. Hence, according to Hagen-Poiseuille flow, the total flow rate $Q_c$ through a single variable cross-section pore is

$$Q_c = \frac{\pi a_i^4 \Delta p_i}{8\mu L_i}$$

(3.34)

where the subscript $i$ denotes any one of the $N$ sections in the pore with $N = (2L_c/W) + 1$. $a_i$, $\Delta p_i$, $L_i$ are the corresponding pore radii, pressure drop and length of that section denoted by the subscript $i$.

If $\Delta p$ is the pressure drop across the pore, then

$$\sum_{i=1}^{N} \Delta p_i = \Delta p$$

(3.34a)

Also

$$\sum_{i=1}^{N} L_i = L_c$$

(with $L_2 = L_3 = \ldots = L_{N-1}$)

(3.34b)

(\quad L_1 = L_N = L_2/2 \quad)

If $n$ is the total number of these pores in the membrane, then with the help of Eqs. (3.34) - (3.34b), the total flow rate through the membrane can be expressed as

$$\bar{Q} = nQ_c = \frac{n\pi \Gamma^4 a_L^4 \Delta p}{4\mu(1 + \Gamma^4) L_c}$$

(3.35)
where $\Gamma = a_s/a_l$ is the contraction ratio of the two sections. The
porosity of the membrane by definition is

$$\gamma = \frac{n\pi(a_l^2 + a_s^2) L_c}{2Ah}$$

(3.36)

where $A$ is the membrane surface area and $h$ is the membrane thickness.
Substituting Eq. (3.36) into Eq. (3.35), the flow rate per unit mem-
brane area $q$ can be expressed as

$$q = \left[\frac{\Gamma^4 a_l^2}{2(1 + \Gamma^2)(1 + \Gamma^4) t_c^2}\right] \frac{\gamma \Delta p}{\mu h}$$

(3.37)

where $t_c = L_c/h$ is the tortuosity of the variable cross-section pore.
Denoting $S_0$ as the specific surface area, then $S_0$ can be expressed as

$$S_0 = \frac{2\gamma (1 + \Gamma)}{(1 - \gamma)(1 + \Gamma^2) a_l}$$

(3.38)

Substituting Eq. (3.38) into Eq. (3.37), the flow rate per unit area $q$
can be expressed in another form

$$q = \left[\frac{2\Gamma^4 (1 + \Gamma)^2}{(1 + \Gamma^2)^3 (1 + \Gamma^4) t_c^2 S_0^2 (1 - \gamma)^2}\right] \frac{\gamma^3 \Delta p}{\mu h}$$

(3.39)

For the constant cross-section model, the expression for the flow
rate per unit area $q$ corresponding to Eq. (3.37) for the variable cross-
section model is
\[ q = \frac{(a*)^2 \gamma \Delta p}{8(t*)^2 \mu h} \]  
\[ (3.40) \]

where \( a^* \) is the pore radius and \( t^* = L/h \) is the tortuosity. The other expression for \( q \) corresponding to Eq. (3.39) is

\[ q = \frac{1}{2(t*)^2} \frac{\gamma^3 \Delta p}{s_0^2(1 - \gamma)^2 \mu h} \]  
\[ (3.41) \]

Since the bulk properties \( \gamma, s_0, \Delta p, \mu, h, q \) are the same for both the variable and constant cross-section models, the comparison of Eq. (3.39) and Eq. (3.41) shows that the relationship between \( t_c \) and \( t^* \) is

\[ t_c = \frac{2t^2 (1 + \Gamma)}{(1 + \Gamma^2)^{1/2} (1 + \Gamma^4)^{1/2} t^*} \]  
\[ (3.42) \]

With Eq. (3.42), the comparison of Eq. (3.37) and Eq. (3.40) shows that the relationship between \( a_L \) and \( a^* \) is

\[ a_L = \frac{1 + \Gamma}{1 + \Gamma^2} a^* \]  
\[ (3.43) \]

These relationships, Eqs. (3.42) - (3.43), will be used later on for the comparison of membrane performances based on the two models.

In a porous membrane where all the pores are identical, the rejection property of a single pore governs that of the whole porous material. For a constant cross-section cylindrical pore, the rejection property has been discussed in Chapter 1, whereas for a variable cross-section cylindrical pore, the rejection property can be similarly
obtained. In this case the governing concentration equation is still the same as that for a constant cross-section cylindrical pore (Eq. (1.9) in Chapter 1), except that the Peclet number and the Debye ratio must be based on the local radius of the pore (i.e., $a_L$ or $a_S$). Thus, the governing equation is

$$\frac{K_1}{(Pe)_I} \frac{dc}{dx} - \overline{c} = -c_{II} \kappa_2$$

(3.44)

where $\overline{c} = c/c_I$ is a dimensionless concentration with $c_I$ defined as the feed concentration, and $c_{II} \equiv c_{II}/c_I = J_s/(2Q_c c_I)$ is the dimensionless product concentration with $J_s = J_+ + J_-$ as the total salt flux and $Q_c$ as the total water flux through the pore.

The coefficients of Eq. (3.44) are defined as the following

$$K_1 = \frac{K_3^2 - K_4^2}{K_1K_3 - K_2K_4}$$

(3.44a)

$$K_2 = \frac{K_3}{K_1K_3 - K_2K_4}$$

with

$$K_1 = 4 \int_0^1 \cosh \overline{\psi} (1 - \overline{r}^2) \overline{r} \, d\overline{r}$$

$$K_2 = 4 \int_0^1 \sinh \overline{\psi} (1 - \overline{r}^2) \overline{r} \, d\overline{r}$$

(3.44b)

$$K_3 = 2 \int_0^1 \cosh \overline{\psi} \overline{r} \, d\overline{r}$$

$$K_4 = 2 \int_0^1 \sinh \overline{\psi} \overline{r} \, d\overline{r}$$
where
\[
\bar{r} = \frac{r}{a_L} \quad \text{when radius} = a_L
\]  \hspace{1cm} (3.44c)
\[
\bar{r} = \frac{r}{a_S} \quad \text{when radius} = a_S
\]

The dimensionless radial potential \( \bar{\psi} \) is still governed by the same Poisson-Boltzmann equation derived for the single cylindrical pore case (Eq. (1.3)).

\[
(\lambda)_{i}^{2} \frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} (\bar{r} \frac{\partial \bar{\psi}}{\partial \bar{r}}) = \sinh \bar{\psi} \]  \hspace{1cm} (3.45)

where
\[
(\lambda)_{i} = \frac{\lambda_D}{a_L} = (\lambda)_L \quad \text{when radius} = a_L
\]  \hspace{1cm} (3.45a)
\[
(\lambda)_{i} = \frac{\lambda_D}{a_S} = (\lambda)_S \quad \text{when radius} = a_S
\]

and \( \lambda_D \) is the Debye length (defined in Eq. (1.4)). Equation (3.45) is solved subject to the same boundary conditions of \( \bar{\psi} = \bar{\psi}_w \) at \( \bar{r} = 1 \) and \( \frac{\partial \bar{\psi}}{\partial \bar{r}} = 0 \) at \( \bar{r} = 0 \). Also in Eq. (3.44) the Peclet number \((Pe)_i\) is defined as

\[
(Pe)_{i} = \frac{Q_{C}}{\pi a_L^2 D} = (Pe)_L \quad \text{when radius} = a_L
\]  \hspace{1cm} (3.46)
\[
(Pe)_{i} = \frac{Q_{C}}{\pi a_S^2 D} = (Pe)_S \quad \text{when radius} = a_S
\]

where \( Q_C \) is the total water flux through the pore.

The relationship between the Peclet number \((Pe)_L\) of the variable cross-section model and that of the constant cross-section model can
be easily established. Substituting Eq. (3.35) into Eq. (3.46), \((\text{Pe})_L\) can be expressed as

\[
(\text{Pe})_L = \frac{\Gamma^4 a_L^2 \Delta P}{(1 + \Gamma^4) 4 \mu D}
\]  

(3.47)

The corresponding Peclet number for the constant cross-section model \(\text{Pe}^*\) can be expressed as

\[
\text{Pe}^* = \frac{(a^*)^2 \Delta P}{2 4 \mu D}
\]

(3.48)

From Eqs. (3.47) and (3.48) and using Eq. (3.43), the relationship between \((\text{Pe})_L\) and \(\text{Pe}^*\) is

\[
(\text{Pe})_L = \frac{2 \Gamma^4 (1 + \Gamma)^2}{(1 + \Gamma^2)^2 (1 + \Gamma^4)} \text{Pe}^*
\]  

(3.49)

Defining \((\lambda_\text{I})_L = \lambda_{\text{DI}}/a_L\) and \(\lambda^*_\text{I} = \lambda_{\text{DI}}/a^*\) as the feed Debye ratios for the two different models, the relationship between \((\lambda_\text{I})_L\) and \(\lambda^*_\text{I}\) can also be established through Eq. (3.43)

\[
(\lambda_\text{I})_L = \frac{1 + \Gamma^2}{1 + \Gamma} \lambda^*_\text{I}
\]  

(3.50)

Equations (3.49) and (3.50) therefore allow the comparison of membrane performances to be based on one set of similarity parameters: \(\overline{\psi}_w\), \(\text{Pe}^*\), \(\lambda^*_\text{I}\). It should be noted that the wall potential \(\overline{\psi}_w\) is the same for both models.
For the variable cross-section model, the membrane performance does not depend only on the three similarity parameters $\bar{\psi}_w$, $Pe^*$ and $\lambda_1^*$ mentioned, but also on two geometrical parameters: the contraction ratio $\Gamma$ and the number of sections in each pore $N$. However, in the present comparison of the two models, the membrane rejection performances are compared at two limiting conditions: $Pe^* \gg 1$ and $\lambda_1^* \gg 1$, and for these two limiting conditions the rejection coefficient of the membrane based on the variable cross-section model does not depend, as will be seen later, on the parameter $N$. Therefore, of the two geometrical parameters, only the contraction ratio $\Gamma$ enters into the problem, and for the present analysis, two values of the parameter $\Gamma$ will be used: $\Gamma = 0.8$ and $\Gamma = 0.6$. These two values represent possible reasonable small variations from the constant cross-section case. Also, from Eq. (3.42), the corresponding tortuosity values for $\Gamma = 0.8$ and $\Gamma = 0.6$ are $t_c = 0.92t^*$ and $t_c = 0.68t^*$, respectively, which are reasonable tortuosity values as $t^*$, the tortuosity for the constant cross-section model, has a value of about 1.6 for most porous materials\(^{16}\). Any values for $\Gamma < 0.6$ implies that $t_c \gtrsim 1$ and therefore would be unrealistic.

For the comparison of the two models, the membrane rejection coefficient $R = 1 - c_{II}/c_I$ were calculated for two limiting conditions: $\lambda_1^* \gg 1$ and $Pe^* \gg 1$. For the limiting case of $\lambda_1^* \gg 1$, or $(\lambda_1)_{II} \gg 1$, Eq. (3.44) can be integrated analytically with the following explicit result

$$
R = 1 - \frac{e^{-n \bar{\psi}_w}}{1 - \cosh \bar{\psi}_w + e^{-n \cosh \bar{\psi}_w}}
$$

(3.51)
where

\[(Pe)_n = \frac{1 + \Gamma^2}{2\Gamma^2} (Pe)_L\]  

(3.51a)

with \((Pe)_L\) related to \(Pe^*\) through Eq. (3.49). From Eq. (3.51), the membrane rejection coefficient \(\Gamma\) is plotted in Fig. 16 as a function of \(Pe^*\) for \(\Gamma = 0.8\) and 0.6 with \(\psi^* = 1.22\), and the results are compared with those based on the constant cross-section model (\(\Gamma = 1\)), which were obtained previously in Chapter 1 (Eq. (1.18)). The results in Fig. 16 show that the rejection coefficient based on the variable cross-section model are slightly less than those based on the constant cross-section model. However, the differences are not that large, especially for the case of \(\Gamma = 0.8\), and therefore indicate that the constant cross-section model is indeed a good model, at least in this large Debye ratio limit.

For the other limiting case of \(Pe^* >> 1\), the results are plotted in Fig. 17 with \(\Gamma\) as a function of \(\lambda^*\) for the two values of \(\Gamma\) with \(\psi^* = 1.22\). It is assumed in this case that \(Pe^*\) is large enough such that \((Pe)_L >> 1\) (see Eq. (3.49)). When \((Pe)_L >> 1\) the term \(\frac{1}{(Pe)_L} \frac{dc}{dx}\) in Eq. (3.44) is small and can be neglected with the result that \(\overline{c}_{II}\) (or indirectly the membrane rejection coefficient \(\Gamma\)) depends only at the inlet condition of the pore (in this limit \(\Gamma\) does not depend on the parameter \(N\) although in general it does, when Eq. (3.44) has to be integrated through all \(N\) sections). Under this condition, the rejection property of the variable cross-section pore is the same as those of a constant cross-section pore with the same inlet radius. Thus, the
rejection property of the variable cross-section pore can be obtained from those of constant cross-section pore with radius equal to \( a_L \). The results are then compared with those based on the constant cross-section model, where the pore radius is equal to \( a^* \). Figure 17 shows that the rejection curves of the two models are very close to each other. Considering again the similar dependence behavior of the rejection coefficient on the Debye ratio and the Peclet number as in the limiting cases (discussed in detail in Chapter 1), it is reasonable to assume that the good agreement between the two models is true for all values of \( \lambda^*_1 \) and \( Pe^* \). This suggests once again that the simple capillary model is a good model.
Figure 11. Comparison of salt rejection coefficient based on uniform distribution model (mean deviation $\sigma = 0$) with those based on non-uniform distribution model ($\sigma \neq 0$) as a function of Peclet number for large Debye ratio with constant surface potential.
Figure 12. Comparison of salt rejection coefficient based on uniform distribution model (mean deviation $\sigma = 0$) with those based on non-uniform distribution model ($\sigma \neq 0$) as a function of Debye ratio for large Peclet number with constant surface potential.
Figure 13. Comparison of salt rejection coefficient based on cylindrical pore model with that based on slit pore model as a function of Peclet number for large Debye ratio with constant surface potential.
Figure 14. Comparison of salt rejection coefficient based on cylindrical pore model with that based on slit pore model as a function of Debye ratio for large Peclet number with constant surface potential.
Figure 15. Geometrical configuration of variable cross-section cylindrical pore.
Figure 16. Comparison of salt rejection coefficient based on constant cross-section model (contraction ratio $\Gamma = 1$) with those based on variable cross-section model ($\Gamma \neq 1$) as a function of Peclet number for large Debye ratio with constant surface potential.
Figure 17. Comparison of salt rejection coefficient based on constant cross-section model (contraction ratio $\Gamma = 1$) with those based on variable cross-section model ($\Gamma \neq 1$) as a function of Debye ratio for large Peclet number with constant surface potential.
CHAPTER 4 -- EXPERIMENTS ON FINE PORE EFFECTS

4.1 Object of the Experiment

The effect of fine pores on the present continuum model is investigated experimentally on bentonite clay. The results of such an investigation will indicate not only the range of applicability of the present physical model, but also how the present theory may be extended to relatively fine pore applications. From the results which have been obtained in the present experiment (details will be discussed later), it is very clear that there is a gradual departure of the theory from experimental observations when the pores are down to a size comparable to molecular dimensions. This departure is undoubtedly caused by various molecular effects which are now important. One example of these is the effect of the pore walls on the mobility of the ions, which is an effect that has been evidenced in the study of diffusion of solutes through small neutral pores\textsuperscript{19,20}. Or in the case of a charged pore, the departure of the continuum theory could have been caused by the influence of the Stern layer\textsuperscript{21,22} which is a layer of counterions permanently adsorbed to the pore wall and which exerts short-range repulsive forces to the mobile counterions in the solution. Whatever these molecular forces may be, however, no attempt is made here to investigate the detailed nature of all these forces as it would require a much bigger effort than the present work allowed. What is intended in the present experiment is just to show the range of applicability of the present continuum theory and to see how far down in pore size the continuum theory is expected to hold.

In hyperfiltration through porous materials the salt rejection coefficient $R$ as well as the streaming potential $\Delta \phi$, according to the
present continuum theory, depend, in the limiting case of large Debye ratio $\lambda_I$, only on two similarity parameters: the wall potential $\bar{\psi}_w$ and the Peclet number $Pe$. In the present experiment, the values of $Pe$ and $\bar{\psi}_w$ were kept relatively constant with $\lambda_I$ kept relatively large, and only the pore size was reduced to see its effect on the values of $R$ and $\Delta \bar{\phi}$. It is obvious that the value of $\bar{\psi}_w$ can not be controlled, but it is considered here constant mainly because it was found that with $Pe$ = constant and $\lambda_I >> 1$, the values of $R$ and $\Delta \bar{\phi}$ were not affected by any change in feed concentration, and therefore $\bar{\psi}_w$ had to be constant. Under this condition of constant $Pe$ and $\bar{\psi}_w$ and with $\lambda_I >> 1$, the values of $R$ and $\Delta \bar{\phi}$, according to the present continuum theory, should remain constant independent of the pore size, and therefore any otherwise experimental behavior would indicate a departure of the theory.

It should be noted that in the measurement of steady state streaming potential across a porous clay bed, it has been found that the potential tends to drift continuously and is very difficult to estimate its exact value. Instead of measuring the steady state streaming potential, the present experiment measures the change in streaming potential with respect to a sudden change in flow condition $\Delta \bar{\phi}/Pe^{23}$, when the flow through the porous bed is suddenly applied or stopped. Under this condition, the concentration across the membrane, and therefore the Donnan potential, will remain the same, and any change in streaming potential across the membrane is due to convection only and not due to diffusion. The equation that governs the ion flux for such a suddenly-changed flow and large Debye ratio case, according
to the present continuum theory, is

\[ J_+ = c \exp(\psi) Q + ADc \exp(\psi) \frac{d\phi}{dx} \]  \hspace{1cm} (4.1)

where \( J \) is the total ion flux through the pore, \( c \) is the salt concentration along the pore, \( Q \) is the total flow rate and \( A \) is the cross-sectional area of the pore. For the condition of no electric current through the pore, \( J_+ = J_- \) and Eq. (4.1) can be integrated with the streaming potential \( \Delta \phi \) due to a sudden flow change \( Q \) expressed in the following form

\[ \frac{\Delta \phi}{Pe} = \frac{(\phi)_{II} - (\phi)_{I}}{Pe} = -\tanh \psi \]  \hspace{1cm} (4.2)

According to this expression, the value of \( \Delta \phi/Pe \) when \( \psi \) is constant should remain constant independent of pore radius, and the measurement of \( \Delta \phi/pe \) at small pores therefore would provide very valuable information on how far down in pore size the present continuum theory is expected to hold.
4.2 Experimental Apparatus

Experiments were performed on salt rejection and streaming potential in sodium chloride (NaCl) solution filtered through a thin bed of Wyoming bentonite, 200 mesh, clay. The clay was chosen mainly because it is a substance where electrokinetic effects are known to be significant, and where salt rejection has previously been observed by other investigators\(^1\). Clay beds are also relatively very easy to prepare in a wide range of thicknesses and porosities. The clay sample was obtained from Nispel Inc. with a grain density of 2.8 gm/cm\(^3\) quoted from pycnometer measurements by the clay supplier.

The clay sample, 11.09 cm in diameter, was held between porous disks which were compressed by pistons as shown in Fig. 18. On each side of the clay membrane, there were two porous disks with the finer one (5\(\mu\) pores) on the face of the clay membrane. The other more porous disk (120\(\mu\) pores) acts as a backing support for the finer porous disk and also, on the feed side, provides a space for circulation of the feed solution. The side walls of the chamber were lined with Teflon and the feed and the product solutions were in electric contact only through the clay membrane itself. The two stainless steel pistons were held together by bolts through the flanges, and compression on the pistons was obtained by tightening the bolts. The compaction stress exerted by the pistons was always larger than the applied fluid pressure drop across the membrane. This compaction pressure could be read from a pressure gauge which connects to an oil reservoir beneath the lower piston. The amount of clay used in each test was 50 grams which, depending on the compaction
pressure, provides a clay membrane with a thickness from 0.29 cm to 0.61 cm. The thickness of the clay membrane was measured using a large micrometer having an accuracy of 1/1000 inch, which measured the increased separation of the two cylinders when clay was embedded. The porosity of the membrane could be easily obtained since the membrane volume and the solid volume were known in each test.

Figure 19 is a schematic of the experimental apparatus. A reservoir with a volume of about 160 in$^3$ held the saline feed solution which was pressurized via an inflatable balloon, and the pressure could be read from a pressure gauge. Different pressure gauges with different ranges were used to ensure that the applied pressure could be read to an accuracy of within $\pm$ 5%. The feed solution was circulated by convection (one of the connecting tubes was heated and the other cooled) over the feed side of the clay membrane so as to prevent concentration polarization. All metal parts of the system, including the porous disks which supported the clay, were made of stainless steel. The product water in the experiment was collected by a 10 cc graduated cylinder with each test collecting 8 to 9 cc implying an accuracy of within $\pm$ 1%. Silver-silver chloride reversible electrodes were fitted on either side of the clay membrane for the measurement of streaming potential.

The NaCl feed concentrations in these tests were in a range from 0.001M to 0.004M. The product concentrations were measured by an Orion Ionalyzer (chloride electrode model 94-17, reference electrode model 90-02) with concentration readings given in terms of millivolts which were read by an electrometer (Keithley model 610B). In the concentration
range of the experiment, 0.001M to 0.004M, it was possible to read the concentration to an accuracy within \( \pm 2\% \).

The change in streaming potential when the flow was applied or stopped was measured by the same Keithley electrometer and was recorded in a chart recorder (Hewlett Packard model 135). In order to increase the sensitivity of the measurement, the steady state part of the streaming potential was suppressed by a D.C. mV generator (Electronic Development Corporation model MV 100N) and the changing of the streaming potential could be magnified and read from the recorder with an accuracy of within \( \pm 1\% \).

4.3 Experimental Results

Experimental results are shown in Tables II and III with the raw data shown in Table II and reduced data shown in Table III. In each test run, sufficient product water with the equivalent of at least one void volume of the clay bed was filtered through the membrane before the product water was collected for flow rate and concentration measurements. Since the flow rate through the membrane was extremely slow, requiring a whole day just to collect a few cc of product water, the solution temperature was considered the same as the ambient temperature. Product concentration was carried out in each run when sufficient product water was collected, usually around \( 5 \) to \( 9 \) cc. After the concentration measurement, the streaming potential measurement was carried out by measuring the change in streaming potential when the flow through the membrane was suddenly applied or stopped.
In Table II, \( c_I \) is the feed concentration which was prepared by mixing known quantity of salt (NaCl) with known quantity of distilled water. \( T_a \) is the average ambient temperature for the whole test period when the product water was collected for flow rate and concentration measurements. \( P_c \) is the compaction pressure with \( h \) the thickness of the membrane and \( \gamma \) the porosity of the membrane. \( \Delta p (= p_I - p_{II}) \) is the applied pressure and \( \overline{Q} \) is the resulting flow rate. \( T_p \) is the ambient temperature when the streaming potential was measured, and \( \Delta \phi/Pe \) is the change in streaming potential \( \Delta \phi (= \phi_{II} - \phi_I) \) per applied pressure \( \Delta p \).

The reduced parameters are shown in Table III. In this table the parameters were calculated according to expressions which were discussed in detail in Chapters 1 and 2. From Eq. (1.4), the average Debye ratio throughout the test run \( \lambda_{DI} \) is defined as

\[
\lambda_{DI} = (\frac{\epsilon_0 \sigma T_a}{2c_I \gamma Z^2 F^2})^{1/2} \tag{4.8}
\]

The pore radius \( a \), following Eq. (2.21), can be expressed as

\[
a = (\frac{8 t^2 k}{\gamma})^{1/2} \tag{4.9}
\]

where the permeability \( k \) is defined as

\[
k = \frac{u_a h q}{\Delta p} \tag{4.10}
\]

with \( q \) the total flow rate \( \overline{Q} \) per unit membrane area. In these
calculations, the tortuosity \( t \) for clay is taken to be 1.58 \(^{16}\), and the water viscosity is based on the average ambient temperature \( T_a \). The Debye ratio \( \lambda_\text{I} = \lambda_{\text{DI}} / a \). The average Peclet number throughout the test run, following Eq. (2.22), is

\[
\text{Pe} = \frac{K \Delta p t^2}{\mu_a D_a \gamma} \tag{4.11}
\]

where the salt diffusion coefficient \( D_a \) is based on the temperature \( T_a \). The rejection coefficient is simply \( R = 1 - c_{\text{II}}/c_\text{I} \). Since the streaming potential was measured when the solution temperature was \( T_p \), the parameter \( \Delta \phi/\text{Pe} \) by definition is

\[
\frac{\Delta \phi}{\text{Pe}} = \frac{ZF \mu_p D_p \gamma}{R T K t^2} \frac{(\Delta \phi)}{\text{Pe}} \tag{4.12}
\]

where the water viscosity \( \mu_p \) and the salt diffusion coefficient \( D_p \) are based on temperature \( T_p \).

The experiments were conducted to obtain data on rejection coefficient and streaming potential for the condition \( \lambda_\text{I} \gg 1 \) and small constant \( \text{Pe} \). The values of the Debye ratio \( \lambda_\text{I} \) in the experiment ranged from 2.1 to 15.8 and, as discussed in Chapter 1, are large enough for the experimental condition to be considered the same as that of the limiting case \( \lambda_\text{I} \gg 1 \). It was, however, very difficult to control the value of the Peclet number \( \text{Pe} \), and the values of \( \text{Pe} \) in the experiment scattered slightly from a value of 0.088 with a maximum deviation of \( \pm 26\% \), but in most cases within \( \pm 10\% \).
The experimental data of the salt rejection coefficient \( R \) and the streaming potential \( \Delta \phi / Pe \) are plotted in Figs. 20 and 21, respectively, as a function of pore radius \( a \). The constant-value lines of the continuum theory are plotted according to previously obtained solutions for the salt rejection coefficient (Eq. (1.18)) and for the streaming potential (Eq. (4.2)). The value of 3.60 for the wall potential \( \psi_w \) is chosen such that both the rejection and the streaming potential lines match well with the experimental data at large pore radii when the continuum model is applicable. From these two figures, it can be seen that the experimental data, of both salt rejection and streaming potential, stay quite constant and match well with the continuum theory when the pore radius is larger than approximately 20 \( \AA \), but tend to increase and depart from the continuum theory when the pore radius is smaller than approximately 20 \( \AA \). Although it may seem that there are not enough experimental data at the larger pore radius range, it should be noted that the object of the present experiment is to find out at what pore size range the continuum theory may be expected to break down, rather than to confirm its validity at the larger pore radius range which have already been done as was shown in Chapter 1. The results therefore indicate that for the case of a NaCl feed solution, the theory is generally applicable down to a pore size of about 20 \( \AA \). Considering the fact that in any actual macroporous membranes the pore size is undoubtedly much larger than 20 \( \AA \), the present experimental findings become significant as they indicate that the present continuum model is applicable in general for practically all macroporous membranes.
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<th>( h ) (mm)</th>
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Figure 18. Experimental apparatus: detail of cell.
Figure 19. Experimental apparatus for measurements of salt rejection and streaming potential.
Figure 20. Experimental result of salt rejection coefficient as a function of pore radius and comparison with continuum theory for large Debye ratio, constant Peclet number and constant surface potential.
Figure 21. Experimental result of streaming potential as a function of pore radius and comparison with continuum theory for large Debye ratio and constant surface potential.
CONCLUSIONS

A theory of salt rejection by hyperfiltration through macroporous membranes has been presented. The theory is based on a relatively simple capillary model wherein the membrane is assumed to consist of a uniform distribution of cylindrical pores whose interior surfaces acquire a constant potential when in contact with the saline solution. Although the flow phenomena in actual porous membranes are undoubtedly more complex, the simple model appears to provide a theory in excellent agreement with salt rejection data from experiments on bentonite clay and cellophane. Theoretical calculations indicated that the predicted membrane characteristics based on this simple model differ only slightly from those based on more complex geometrical configurations. Furthermore, the theoretical characterization of the rejection in terms of a dimensionless wall potential, the ratio of the Debye length to an effective pore radius, and a Peclet number based on the filtration velocity and an effective membrane thickness seem appropriate for many materials observed so far. The constant wall potential assumption along the pore wall, which was made in the present theory, has been found to be a reasonable assumption for the boundary condition of the problem, especially for the case when the Peclet number is large. It is realized, however, that the characterization of a porous membrane in terms of a constant wall potential parameter independent of the feed condition may not always be useful, and depending on the membrane materials and feed conditions, other characterization parameters such as
a constant surface charge density parameter may be more suitable.

The effect of fine pores on the present macroscopic, continuum model has been investigated by experiment on bentonite clay. The experimental results indicated that, with the feed solution containing NaCl salt, the present theory holds down to a pore size of about 20 Å, and departs from experimental observations significantly only when the pore size is well below 10 Å. Considering the fact that any actual macroporous membrane would have a pore size greater than 20 Å, the present continuum theory does seem to be applicable for practically all macroporous membranes.

The present simple theory has been extended to the case more representative of brackish waters, where the feed solution contains multiple salts. For the particular case where the salts in the solution dissociate into three types of ions, explicit solutions have been presented. Excellent agreement was indicated between the theoretically calculated rejections and hyperfiltration rejection data of Hoornnaert et al. for the limiting case of single salts which dissociate into divalent and univalent ions. The comparison did, however, require an assumption, albeit a reasonable one, as to the value of the membrane wall potential.

Although the results so far obtained are encouraging, it is evident that a much wider range of membrane materials and operating conditions must be investigated experimentally before the full utility of the theory can be properly assessed.
REFERENCES


