Analysis of modified surface force pore flow model with concentration polarization and comparison with Spiegler-Kedem model in reverse osmosis systems

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Abstract

The Modified Surface Force Pore Flow (MD-SF-PF) model is used for predicting the performance of the sodium chloride-water and sodium sulphate-water reverse osmosis systems. Unlike the previous analysis available in literature on this model, the present work takes concentration polarization into account explicitly. The required mass transfer coefficient is estimated by relating it to the feed flow rate through two additional parameters. The model equations being non-linear are solved using the orthogonal collocation technique. The model solution code is validated by comparing results with those available in literature. Simulation studies indicate observed rejection versus flux has a similar trend to that predicted by the Spiegler-Kedem model. From some of the experimental observations of Murthy [Studies on membrane transport models, Ph.D. thesis, I.I.T. Delhi, July 1996], model solution and mass transfer parameters are estimated through a combination of the Downhill Simplex method and Monte Carlo search. Simulated results using above parameters are found to be in very good agreement with the remaining experimental observations. Prediction of the membrane performance and mass transfer coefficient are also found to be very close to those estimated through the Spiegler-Kedem model. The membrane specific parameters such as the membrane thickness and pore radius are calculated from experimental data for the two different systems on a similar cellulose acetate membrane. The closeness of these parameter values again shows the validity of MD-SF-PF model.

Keywords: Concentration polarization; Downhill simplex; Orthogonal collocation; Sodium chloride; Sodium sulphate; Spiegler-Kedem

1. Introduction

When a semi-permeable membrane (permeable to solvent, impermeable to solute) is placed between two compartments—one containing pure solvent and the other containing solution—due to high osmotic pressure in the solvent side, solvent tends to go to the solution side. But if a pressure gradient greater than the osmotic pressure is applied across the membrane, against the direction of the osmotic pressure gradient, then this tendency is reversed; i.e., the solution becomes more concentrated while the solvent in it passes to the solvent rich side.

Reverse Osmosis has become a very popular method for water purification. The major advantage of the process is its ability to perform direct separation at ambient conditions and allowing separation of heat sensitive materials. It is currently being used extensively in the production of potable and industrial water, treatment of domestic and industrial wastewater, and in food processing.

Development of a reliable membrane transport model for describing mass transport processes in a reverse osmosis membrane is a highly desirable goal since not only does this allow the analysis of performance characteristics of a membrane, but this can also assist in the design of new membranes. Onsager [1,2] used the principles of irreversible thermodynamics to relate the fluxes with the forces through phenomenological coefficients. However, a major limitation...
of irreversible thermodynamics is that it is valid for systems not far from equilibrium. The next step was the development of Kedem-Katchalsky model [1-5] for a dilute two-component system, consisting of water and a solute. The three adjustable parameters in this model are simple functions of the original phenomenological coefficients. In the Spiegler-Kedem model [6], the assumption on the applicability of the linear laws throughout the thickness of the membrane was resolved by rewriting the original linear IT equations in the differential form and then integrating them over the membrane thickness. Although the Spiegler-Kedem model [6] gives quite accurate results, it is not a mechanistic based model, i.e., it does not explain the mechanism of transport or the nature of the membrane structure.

Out of the mechanistic based models, the Solution Diffusion model [7,8] has been applied to many different systems as it is simple and has only two adjustable parameters and it is only appropriate for systems where the rejection is close to unity.

The three parameter Solution Diffusion Imperfection model [9] allowed for the presence of some imperfections, which permit the salt to pass undiluted, but dodged the difficulty of the explicit inclusion of the convection or viscous flow.

The four parameter Fineley Porous model [8,10,11] is based on a balance of applied frictional forces in a one-dimensional pore, while the Frictional model [5,6] has a very simple physical interpretation, which amounts to a heuristic derivation. Both these models keep all the mechanisms in their equations from the start but Mason and Lonsdale [12] felt the treatment of viscous flow was either misinterpreted or mishandled in both of them.

The Diffusion Viscous flow or the Highly Porous model [11] uses the Poisuielle's law to describe the total volume flow and the total solute flux is expressed as the sum of a contribution due to viscous and diffusive flow.

Mason and Lonsdale [12] reviewed all membrane transport models described above and compared them with the statistical mechanical theory of membrane transport. They concluded all these models are equivalent in the sense that they end up writing down the same transport equations. However, these models differ in their predictions about the transport coefficients. They finally recommended the Spiegler-Kedem model for describing and predicting the performance of reverse osmosis and ultra filtration membranes.

As the Spiegler-Kedem model relates the membrane surface concentration to the permeate concentration, it needs to be combined with concentration polarization if the permeate concentration is to be related to the bulk feed concentration which results in the combined film theory—Spiegler-Kedem or CFSK model. Murthy [13] also analyzed the predictions of the many membrane transport models with his experimental observations and found the CFSK model to give the closest results. On plotting the reciprocal of the observed rejection against volume flux, he observed that the $M^a$ value, where the observed rejection is maximum, is predicted more accurately by the CFSK model as compared to other models [13,14]. Thus, the CFSK model has been selected for comparing the predictions of our work.

The Surface Force Pore Flow model [15] is a relatively recent two-dimensional model for describing the transport processes in a reverse osmosis membrane. Since the model takes into account the membrane structure and various membrane-solute interactions, it is expected the model will present a more accurate description of the mass transfer process taking place outside the membrane.

Mehdizadeh and Dickson [16] pointed out the SF-PF model uses an incorrect form of the material balance, the potential function in the pore is inconsistent with the cylindrical geometry and the solute concentration just inside the pore is equal to that of the permeate. These corrections led to the development of the Modified Surface Force Pore Flow model. The model contains four parameters—namely, $\theta_1$ and $\theta_2$, required for estimating the potential function, $R_W$, the membrane pore radius, and $\eta/\tau$, the ratio of the membrane tortuosity to its porosity. Due to the complexity of the non-differential equations of the MD-SF-PF model, numerical techniques are required for obtaining the solution such as the orthogonal collocation scheme [17,18].

The paper in which the MD-SF-PF model was defined [16] assumed the solute bulk concentration is equal to the solute concentration on the membrane surface and used this concentration to compute the theoretically observed rejection. Their later work [19] mentions the concentration polarization model can also relate the bulk feed concentration to the membrane surface concentration. However, detailed analysis of the same was not carried out in their reference [20]. As concentration polarization effects are very important in reverse osmosis, they must be included for model prediction and parameter estimation analysis.

In order to incorporate the concentration polarization model into the MD-SF-PF model, the value of the mass transfer coefficient is required. The mass transfer coefficient is dependent on several factors like cell geometry, feed flow rate and temperature. Although its value can be computed for fully developed flow in well-established geometries like channels and pipes, in actual experimental set-up for reverse osmosis the exact cell geometry and flow regime are often unknown. This introduces the need to relate the value of the mass transfer coefficient to the flow rate for a specified solute-solvent system.

The objective of this work is to incorporate concentration polarization in the MD-SF-PF model and to develop a numerical solution for solving the differential equations of the model. The mass transfer coefficient may be related to flow rate through the use of two additional parameters—'a' and 'b'—increasing the number of parameters to be estimated to six. Thus, a numerical scheme is developed for estimating the parameters for a particular solute-solvent system. To evaluate the accuracy of the MD-SF-PF model predictions, the estimated parameter set is used to predict the membrane
2. Theory

2.1. Membrane mass transport models

The general purpose of a membrane mass transport model is to relate the performance (usually expressed in terms of fluxes of solute and solvent and observed rejection) to the operating conditions (usually expressed in terms of pressure and concentration driving forces). In a model, some coefficients emerge that must be determined based on some experimental data. The success of a model can be measured in terms of its ability to describe mathematically the data with coefficients that are reasonably constant over the range of operating conditions. Here, we briefly discuss two models: IT based Spiegler-Kedem model and mechanism based Modified-Surface force-pore flow model which are used for comparison in this study.

2.2. Spiegler-Kedem model

The Spiegler-Kedem [6] model predicts the following equations for volume flux, $J_V$, and actual rejection, $R_A$:

$$J_V = L_p(A_p - aA_t)$$  \hspace{1cm} (1)

$$R_A = \frac{J_V}{J_V(1 - \sigma)}$$  \hspace{1cm} (2)

where $L_p$ is the hydraulic permeability coefficient of the membrane; $P_M$ is the overall permeability coefficient and $\sigma$ is the reflection coefficient.

On combining the relationship between $R_A$, the actual rejection, and $RO$, the observed rejection, with the film theory, the following equations are obtained:

$$C_{A1} - C_{A2} = \frac{J_V}{k}$$

Eliminating $C_{A1}$, $C_{A2}$, and $C_{A4}$ in terms of the actual rejection, $KA$, and observed rejection, $RO$, we obtain

$$\frac{1 - R_A}{RO} = \frac{1}{R_A} \exp \left( \frac{J_V}{k} \right)$$  \hspace{1cm} (5)

$$\ln \left( \frac{1 - R_A}{RO} \right) = \ln \left( \frac{1 - \sigma}{\sigma} \right) \left( \frac{1}{1 - \exp(-P_e)} \right) + \frac{J_V}{k}$$  \hspace{1cm} (6)

The Eqs. (1), (2) and (6) are the basic equations of the combined film—Spiegler-Kedem model (CFSK). By using a non-linear parameter estimation technique, the unknown parameters, $P_M$, $\sigma$ and the mass transfer coefficient, $k$, can be determined from the given experimental data of observed rejection ratio versus volume flux.

2.3. Modified-surface force-pore flow model

This work is based on the equations proposed in the MD-SF-PF model [16]. A few key equations are reproduced below while their derivation can be found from the above-mentioned reference.

The differential equation for the velocity profile inside a pore can be found by a force balance in the $z$-direction on a fluid element in the annular region between $z$ and $z + dz$ and between $r$ and $r + dr$ inside a pore. The detailed derivation takes into account the net force due to difference in pressure, viscous shear stresses using Newton’s law of viscosity and the net force due to friction between the solute and the pore wall, leading to the following equation:

$$\frac{d\alpha(\rho)}{dp} + \frac{1}{\beta} \frac{d\alpha(\rho)}{dp} + \frac{AP - \Delta P(1 - \exp(-P_e))}{\beta_t} - \frac{\alpha(\rho)e^{-\theta(\rho)}}{\beta_t} \left( 1 + \frac{\Delta H}{\theta(\rho) - 1} \right) = 0$$  \hspace{1cm} (9)

where

$$\beta_t = \frac{D_{AB}}{R_w \tau_2}$$  \hspace{1cm} (10)
brane (charged or uncharged): pore cross-sectional area to obtain:

In the later papers [21,22] a modified form 'b' function, the pore wall. This friction is the result of the hydrodynamic

θ function and’ affects the radial slope of the potential. The

where

applied to any solute (electrolyte or non-electrolyte) and mem-

potential function coming to a peak at the pore centerline instead

In the above integration, the solute molecule has been as-

approximation [16,19] and has been used in our analysis.

Although the friction function should be a function of the

radial position, the modified Faxen equation is a reasonable

model, which describes the friction between the solute and

wall. After integrating solute and solvent fluxes over the area

of a single pore, they have been generalized over the sur-

face area of the membrane. In order to relate average solute

and solvent fluxes through a single pore to the flux through a

membrane, the fractional pore area on the membrane face, \( r \), is used. Thus, one gets:

\[
N_A = \int J_r
d\rho
\]

\[
N_s = e J_h
\]

Then, the total flux is given by:

\[
N_s = N_s + N_h
\]

The permeate concentration, \( C_{A3} \), is related to the solute and solvent fluxes as:

\[
C_{A3} = \frac{\int J_r}{J_e} + \frac{\int J_h}{J_e}
\]

The analysis in this paper assumes all pores on the membrane

surface have the same radius. However, in case a pore size

distribution is present, then the solute and solvent fluxes need to be integrated across all the possible pore sizes.

2.4. Incorporation of concentration polarization model in the MD-SF-PF model

During the membrane separation process when the membrane

rejects the solute, the solute concentration near the membrane surface increases. Hence, there is a difference in the feed concentration in the bulk, \( C_{up} \), and that at the membrane face, \( C_{up} \). The MD-SF-PF model assumes \( C_{up} \) is known [16,19]. But since it is not possible to measure \( C_{up} \), researchers have used the concentration polarization model to relate it to \( C_{up} \). The build up of solute concentration in the boundary layer region can be described by the film theory. Thus, on rewriting the first form of Eq. (8) in terms of concentrations, one obtains:

\[
C_{A2} = C_{A3} = (C_{A1} - C_{up}) \exp \left( \frac{N_A + N_s}{k C} \right)
\]

Although the concentration polarization can be easily inte-

grated with the MD-SF-PF model, it has not been done so far. After its addition, the computations become slightly more involved on account of two convergence loops that are now needed [23]. The algorithm describing the key steps for in-

corporating the concentration polarization in the MD-SF-PF model has been described in Jain [23].

2.5. Mass transfer coefficient

The film mass transfer coefficient has been found to be de-

pendent on feed flow rate, cell geometry, temperature and

solute system. A generalized correlation of mass transfer

suggests that the Sherwood number is related to the Reynolds

and Schmidt numbers as [24]:

\[
Sh = x_1 Re^{x_2} Sc^{x_3}
\]
values are used to predict \( D^\circ \) and then, assuming the solution be simplified to obtain:

\[
Nernst \text{ on the assumption of complete dissociation } [29]:
\]

where the value of diffusivity of strong electrolytes at infinite NaCl-H\(_2\)O in the above two papers also differed slightly.

the complete procedure used to obtain these values was tion for solving the membrane equation [27] and propos-

MD-SF-PF model can be used for different solute-solvent

Systems. These include estimating the solute radius and the

solute-solvent combination.

Experimental observations on NaCl-H\(_2\)O system using Cellulose Acetate

incremented. A sample data set collected on experimental
data is gradually increased, and at each flow rate, pressure is

is kept at 2020, 3030, 4040, 6060, 8080 and 10,100kPa

where \( x_1 \), \( x_2 \) and \( x_3 \) are system and flow regime dependent coefficients.

In literature, Hwang and Kammermeyer [25] used the

above equation for turbulent flows and Porter [26] in fully
developed and laminar regimes. All of them they took \( x_3 \) = 0.33 which makes us believe that \( x_3 \) can be taken as a con-

stant across flow regimes. With this in mind, Eq. (26) can be

simplified to obtain:

\[
k = aQ^b
\]

where ‘a’ and ‘b’ are the unknown parameters for a particular

solute-solvent combination.

Murthy [13] has shown the value of ‘a’ depends on the

solute-solvent system, while the value of ‘b’ ranges from

0.33 to 0.8.

2.6. Physical properties estimation

Some physical properties need to be estimated before the

MD-SF-PF model can be used for different solute-solvent systems. These include estimating the solute radius and the
diffusivity. While discussing the use of orthogonal colloca-
tion for solving the membrane equation [27] and propos-
ing the MD-SF-PF model [16], the values of diffusivity and solute radius for sodium chloride were specified. However, the complete procedure used to obtain these values was not stated. Moreover, it was observed the DAB values for NaCl-H\(_2\)O in the above two papers also differed slightly. In the present work, the solute molecular radius has been estimated using the Stokes-Einstein equation (28):

\[
R_s = \frac{kT}{6\pi\eta D_{\text{ab}}}
\]

where the value of diffusivity of strong electrolytes at infinite
dilution may be calculated from an equation obtained by

Nernst on the assumption of complete dissociation [29]:

\[
D^\circ \text{NaCl-H}_2\text{O} = 8.931 \times 10^{-1} \times \frac{Z^+Z^-}{c_+ + c_-}
\]

A useful tabulation of ionic conductance at infinite dilution
in water at 25 °C is given in Lange’s Handbook of Chemistry [30], which has been used in the above equation. These values are used to predict \( D^\circ \) and then, assuming the solution to be diluted infinitely, equated to \( D^\circ \) for estimation of the solute radius. Values of the above parameters for NaCl-H\(_2\)O and Na2SO4-H\(_2\)O systems are shown in Table 1.

At 25 °C and 1 atm, the density of water is taken as

1000kg/m\(^3\) (1g/cm\(^3\)) and viscosity as 1 x 10\(^{-5}\)Pas (1cP) [31]. These values are assumed to be constant throughout the operating conditions. Meh dizadeh and Dickson [27] used the value of viscosity of water as 8.965 x 10\(^{-4}\) Pa s (0.8965 cP).

2.7. Experimental observations

In order to estimate the parameters of any membrane transport model, experimental data are required. For the present work, experimental data available in literature [13,32] has been used. This section briefly mentions the experimental conditions at which the above data was ob-
tained. More details of experimental set-up and conditions can be obtained from the above references.

The experimental data was obtained in sets of inlet con-
centrations of 17.10, 103.18 and 207.62mol/m\(^3\) (1000, 6000, 12,000ppm) for NaCl-H\(_2\)O and 7.00, 42.51, 85.53, 158.42 and 217.80 mol/m\(^3\) (300, 600, 900, 1200 and 1500ml/min). For each flow rate, pressure is kept at 2020, 3030, 4040, 6060, 8080 and 10,100kPa (20, 30, 40, 60, 80 and 100 atm). These three conditions, taken together, specify one set of operating conditions. For a specific solute-solvent system, the concentration is ini-
tially kept constant. For each concentration, the flow rate is gradually increased, and at each flow rate, pressure is incremented.

A sample data set collected on experimental observations on NaCl-H\(_2\)O system using Cellulose Acetate

membrane is shown in Table 2.

3. Solution of membrane transport equations

3.1. Orthogonal collocation method

The SF-PF model used the Runge-Kutta technique to solve the nonlinear differential equations [15]. This tech-
nique has been found to be slow, inefficient and expensive

where \( x_1 \), \( x_2 \) and \( x_3 \) are system and flow regime dependent coefficients.
Table 2
Sample experimental data

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Pressure (Pa)</th>
<th>C (mol/m³)</th>
<th>J (m/s)</th>
<th>RO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.02 × 10⁷</td>
<td>4.8844</td>
<td>1.62 × 10⁻⁷</td>
<td>0.7613</td>
</tr>
<tr>
<td>2</td>
<td>3.03 × 10⁷</td>
<td>2.8353</td>
<td>2.81 × 10⁻⁷</td>
<td>0.8343</td>
</tr>
<tr>
<td>3</td>
<td>4.04 × 10⁷</td>
<td>2.1355</td>
<td>4.48 × 10⁻⁷</td>
<td>0.8752</td>
</tr>
<tr>
<td>4</td>
<td>5.06 × 10⁷</td>
<td>1.6596</td>
<td>6.97 × 10⁻⁷</td>
<td>0.9050</td>
</tr>
<tr>
<td>5</td>
<td>6.08 × 10⁷</td>
<td>1.5075</td>
<td>9.44 × 10⁻⁷</td>
<td>0.9119</td>
</tr>
<tr>
<td>6</td>
<td>7.01 × 10⁷</td>
<td>1.3980</td>
<td>1.28 × 10⁻⁷</td>
<td>0.9183</td>
</tr>
</tbody>
</table>

System: NaCl-H₂O; C₁: 17.1111 mol/m³; Q: 5.0 × 10⁻⁶ m³/s.

for solving the SF-PF model equations [27]. The orthogonal collocation of weighted residuals is used to provide an accurate and efficient solution to the nonlinear differential equations in the SF-PF and MD-SF-PF models. A brief mention of the relevant details is made below and further details can be obtained elsewhere [17,18].

3.1.1 Interior collocation
In order to estimate a dependent variable, in the present case—dimensionless velocity, it is approximated by a series of expansion containing n undetermined parameters. For a symmetric second-order boundary value problem in one variable—in the present case the dimensionless velocity—as a function of the dimensionless radial position, a suitable form is:

\[ y = y(1) + \sum_{i=0}^{n-1} a_i \phi_i(\rho^2) \]  

In the present case, as \( a(1) = 0 \), assuming the validity of the no slip boundary condition, the above equation reduces to:

\[ u = (1 - \rho^2) \sum_{i=0}^{n-1} a_i \phi_i(\rho^2) \]  

Using the values of the polynomials \( \phi_i(\rho^2) \) as given in Table 1 [17], for cylindrical geometry and \( n = 3 \), i.e. 3 undetermined constants \( a_0, a_1 \) and \( a_2 \), the velocity profile becomes:

\[ a(\rho^2) = (1 - \rho^2)a_0 + a_1 (1 - 3 \rho^2) + a_2 (1 - 8 \rho^2 + 10 \rho^4) \]  

3.1.2 Interior formulae
The gradient and laplacian operators, in cylindrical coordinates, for the \( a(\rho^2) \) of Eq. (32) are given by:

\[ \frac{da(\rho^2)}{d\rho} \bigg|_{\rho=ho_0} = \sum_{i=0}^{n-1} B_i a(\phi_i^2) \]  

\[ \frac{1}{\rho} \frac{d}{d\rho} \left( \frac{1}{\rho^2} \frac{da(\rho^2)}{d\rho} \right) \bigg|_{\rho=\rho_0} = \sum_{i=0}^{n-1} B_i a(\phi_i^2) \]  

for \( i = 1, 2, \ldots, n + 1 \). The coefficients \( A_i \) and \( B_i \) which have been used in this work (for symmetrical cylindrical geometry) can be obtained from Table 3 of Villadsen and Stewart [17].

3.1.3 Residual function
For the system under consideration, the residual function at the \( i^{th} \) collocation point becomes:

\[ R_i = \sum_{i=0}^{n-1} \left[ A_i a(\phi_i^2) \right] + \frac{AP - A^2 T \left[ 1 - \exp(-P(\phi_i)) \right]}{\rho_i^3} - a(\phi_i \exp(-P(\phi_i))) \left( 1 - \frac{1}{\rho_i^2} \right) \]  

\[ \left[ 1 + \frac{A^2}{\exp(a(\phi_i)) - 1} \right] \]  

(35)

Theoretically, the value of the above function should be zero at all collocation points. However, as the values of the parameters \( a_0, a_1 \) and \( a_2 \) are not known a priori, the residual function will have some finite value. As the iterations progress and the parameters approach their optimal value, the residues tend to zero.

3.1.4 Updating guess
The Newton-Raphson technique is employed to update the guess of the parameters used for the velocity profile:

\[ \mathbf{x}_{n+1} = \mathbf{x}_n - \mathbf{J}(\mathbf{x}_n)^{-1} \mathbf{F}(\mathbf{x}_n) \]  

In the above equation, ‘\( \mathbf{x} \)’ represents the vector set of unknown parameters \( a_0, a_1 \) and \( a_2 \), ‘\( n \)’ the iteration number, ‘\( \mathbf{F} \)’ the residual function value matrix and ‘\( \mathbf{J} \)’ the Jacobian matrix.

3.1.5 Termination condition
Iterations to obtain the optimal set of parameters are continued until the residues at all the collocation points are within the tolerance limit of \( 10^{-10} \) and the maximum change in the value of any of the unknown parameters is also within the tolerance limit of \( 10^{-10} \).

3.2. Analytical solutions
Analytical solutions have been used to test the validity of the MD-SF-PF model [16,27]. In the present work, we too used the formulae under the Poiseuille flow and total rejection conditions to test our velocity profile trends under identical operating conditions as specified in the above papers and found that our estimates matched those published excellently [23].

4. Parameter estimation
The modified surface force pore flow model along with the concentration polarization model contains six parameters—\( k_0, k_2, \tau, c, RW \) and \( a, b \). These parameters are determined by the Downhill Simplex method as described below.
Table 3
Data analysis for NaCl-H2O system

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Parameters used for data analysis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>θ₁</td>
<td>m</td>
<td>1.5007 × 10⁻⁹</td>
</tr>
<tr>
<td>2.</td>
<td>θ₂</td>
<td>m</td>
<td>4.8739</td>
</tr>
<tr>
<td>3.</td>
<td>R_W</td>
<td>m</td>
<td>9.9917 × 10⁻³</td>
</tr>
<tr>
<td>4.</td>
<td>τ/ε</td>
<td>m</td>
<td>1.2644 × 10⁻⁸</td>
</tr>
<tr>
<td>5.</td>
<td>a</td>
<td>(m/s)//(mol/m³)</td>
<td>0.7766</td>
</tr>
<tr>
<td>6.</td>
<td>b</td>
<td>(m/s)//(mol/m³)</td>
<td>1.0733</td>
</tr>
<tr>
<td>(B) Data analysis using above parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Operating condition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1.</td>
<td>C_A1</td>
<td>(mol/m³)</td>
<td>17.11</td>
</tr>
<tr>
<td>1.2.</td>
<td>Condition</td>
<td>BC</td>
<td>103.18</td>
</tr>
<tr>
<td>2.</td>
<td>Error analysis (% rms averaged)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1.</td>
<td>C_A3</td>
<td></td>
<td>10.27</td>
</tr>
<tr>
<td>2.2.</td>
<td>J_V</td>
<td></td>
<td>21.71</td>
</tr>
<tr>
<td>2.3.</td>
<td>R_O</td>
<td></td>
<td>2.35</td>
</tr>
<tr>
<td>2.4.</td>
<td>k</td>
<td></td>
<td>2.18</td>
</tr>
<tr>
<td>2.5.</td>
<td>E</td>
<td></td>
<td>16.55</td>
</tr>
</tbody>
</table>

Note: These parameters are averaged parameters obtained from observations at 17.11 and 103.18 mol/m³.

4.1. Optimization problem

Experimental values are available in terms of operating conditions (inlet concentration, pressure drop and flow rate), permeate solute concentration and flux. The model equations are solved from initial guesses of the six parameters and the results compared with the experimental observations. Two optimization functions are formed, first one, E₁, from minimization of the fractional difference in the calculated and experimental permeate concentration and the other, E₂, from minimizing the fractional difference between the calculated and experimental flux:

\[ E_1 = \sqrt{\sum_{i=1}^{n} \left( 1 - \frac{C_{Expt}}{C_{Sim}(C_A)} \right)^2} \]  

\[ E_2 = \sqrt{\sum_{i=1}^{n} \left( 1 - \frac{J_V}{J_{Sim}(C_A)} \right)^2} \]

The fractional errors are used instead of absolute differences, as this would make the values independent of the units used, thus preventing a bias towards any one parameter. On combining these two functions, the overall objective function becomes:

\[ E = \frac{E_1 + E_2}{2} \]

The aim of the optimization procedure is to find out the values of θ₁, θ₂, R_W, τ/ε, a and b at which E is very small, i.e., the theoretical predictions match the experimental ones with minimum error.

4.2. Downhill simplex method

At this stage we have a six-parameter non-linear optimization problem. We could not identify a technique that would guarantee the global minimum solution to the problem, so we combined an approach giving a local minimum and developed a search technique that would optimize the solution [23]. We selected the Downhill Simplex method [33]. As starting with any initial guess, this approach almost always converges to a local minimum.

The manner in which the optimization operations are carried out and estimation of intermediate values has been carried out follow the development in literature [33,34].

These following sub-sections briefly describe some of the important issues we had to address while using the Downhill Simplex method. More details can be found in Jain [23].

4.2.1. Initial guess

Ideally, an optimization technique should be independent of the initial guess. However, since the Downhill Simplex method is a local optimization technique, it is important to have a very good initial guess. At first, the order of magnitude of each of the parameters is determined (θ₁: 10⁻⁹, θ₂: 5, R_W: 1(T), τ/ε: 10⁻⁸, a: 1.0 and b: 0.7). This is followed by simulation runs in which intermediate steps are analyzed to check for any physical inconsistency. In case none is observed, then the set is selected for preliminary simulation purposes. This initial guess is then updated as more simulations are carried out in an attempt to improve the overall error. The automated initial guesses update algorithm can be found in Jain [23].
4.2.2. Convergence criterion

The convergence of the Downhill Simplex method depends on the values of arbitrary constants in the reflection, contraction and expansion operations. It has been observed that fast convergence is obtained by taking \( a = 1 \), \( \beta = 0.5 \) and \( y = 2 \) [33, 34]; therefore, we adopted the same values for the present analysis.

The convergence criterion is not applied with respect to the changes in each optimization parameter but to the value of the total functions, \( E_1 \) and \( E_2 \), represented as a whole in \( E \). The reasoning behind this approach is that in statistical analysis, the value of 'b' was maintained as the upper limit of the potential function, meaning increasing \( \theta_1 \) and \( \theta_2 \) of both the error functions—\( E_1 \) and \( E_2 \)—was fixed at the centroid of \( E \). It is observed its value comes within 0.2 well before 30 iterations of the Downhill Simplex loop. Further iterations are not carried out since no change is observed in the parameters and the error is a constant. The above approach is acceptable since using the Downhill Simplex method often leads to local minima.

4.2.3. Interdependent parameters

Another issue to be considered is that all the five parameters affect both the error functions—\( E_1 \) and \( E_2 \). Incase either flux or permeate concentration is to be decreased, one could think of increasing the potential function, meaning increasing \( \theta_1 \) and/or \( \theta_2 \). However, as soon as the initial guess of the parameter is changed, in the orthogonal collocation convergence, the coefficients \( a_0, a_1 \) and \( a_2 \) will change. This would imply change in \( \theta_2 \), thus affecting \( \theta_1 \) and ultimately \( \theta_3 \). Thus, it is very difficult to predict the actual affect of changing a selected parameter.

4.2.4. Space constraints

In addition to the convergence criterion, there are constraints on the operational space as well; i.e., all the parameters are non-negative. This is incorporated by writing each parameter in the objective function as the square of its root. It is also ensured the parameters have physical correlations throughout the simplex operations. A simple check is maintaining the values of key physical quantities—\( C_{A1}, C_{A2}, N_A, N_B, NT \) and \( JV \) as non-negative. Additionally, the lower limit of \( CA_2 \) is fixed at \( CA_1 \), upper limit of \( CA_2 \) as twice \( CA_1 \), upper limit of \( CA_3 \) as \( CA_1 \), and in accordance with experimental observations, value of 'b' was maintained in the range of 0.33-0.8.

4.3. Monte Carlo search

It is often observed that the Downhill Simplex method attained local minima after a few iterations itself. As the parameters do not vary, the objective function \( I^{-1} \) becomes a constant. In order to explore the nearby surface, with small variations in the values of the parameters, an approach similar to that adopted in genetic algorithms has been developed along with the Downhill Simplex loop [23]. The algorithm of the Monte Carlo search technique has been described in Appendix A.

5. Results

5.1. Validation

The first aspect of the project is to solve the differential equation for the velocity profile using the orthogonal collocation method. The present model solution code is validated by comparing results with those presented by Mehdizadeh and Dickson [27] under identical conditions. For this section, the same values of physical properties; i.e., diffusivity, solute radius and viscosity are taken which were used in the original work [27]. Since, in the present code, the concentration polarization is taken into account while Mehdizadeh and Dickson [27] had neglected it, \( CA_2 \) is forced to be nearly equal to \( CA_1 \) by making mass transfer coefficient quite large. This is achieved by fixing ‘a’ at 1000, about 10 times the value normally observed when predicting the mass transfer coefficient from experimental data, and ‘b’ as 0, which makes the mass transfer coefficient independent of flow rate and its value sufficiently high for it to be considered infinite.

Our computed velocity profiles, actual rejection ratios and flux ratios are found to be in excellent agreement [23] with those published by Mehdizadeh and Dickson [27] validating the present orthogonal collocation code.

5.2. Concentration polarization model

The effect of introducing concentration polarization to relate \( C_{A2} \) and \( C_{A2} \) as seen in Figs. 1 and 2. Parameters used are \( a_1: 5.4434 \times 10^{-5} \cdot \text{m}^2 \cdot \text{s}^{-1} \cdot \text{m}^{-1} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \); \( b: 1.3 \times 10^{-3} \cdot \text{m} \); \( a: 1000 \); and \( b: 0 \). The operating conditions include temperature at 298 K, pressure as 4000 kPa and the bulk feed concentration as 75 mol/m^3. For these simulations, viscosity of water is taken as 0.001 kg/m/s (1 cP), diffusivity as 1.56 x 10^{-9} m^2/s and solute (NaCl) radius as 1.555 x 10^{-9} m (1.555 Å).

It is desired to represent a range of values for the mass transfer coefficient for all flow regimes—turbulent, laminar and intermediate. This is achieved by maintaining parameter ‘b’ as 0, making mass transfer coefficient equal to ‘a’. The value of ‘a’ is changed from 10^8 to 5.0 x 10^{-12} m/s which covered the above flow regimes. Figs. 1 and 2 depict the effect of increasing bulk feed concentration, with the mass transfer coefficient as a parameter, on rejection ratio and volume flux respectively. The decreasing trends of rejection ratio and volume flux with increasing feed concentration are along the expected lines. On the other hand, at a particular value of the bulk feed concentration, both rejection ra-
Fig. 1. Effect of bulk feed concentration on observed rejection ratio with the mass transfer coefficient as a parameter. Operating conditions: $T = 298$ K, $P = 4000$ kPa and $C_{A1} = 75$ mol/m$^3$ for NaCl-H$_2$O system. Model parameters: $\theta_1 = 5.4434 \times 10^{-9}$ m, $\theta_2 = 0.4910$, $\tau/\varepsilon = 1.0 \times 10^{-4}$ m and $R_w = 1.3 \times 10^{-9}$ m.

tio and volume flux increase with increasing mass transfer coefficient, which obviously is due to the reduced concentration polarization at higher mass transfer coefficients. The above graphs reflect the effect of mass transfer coefficient from $5 \times 10^{-6}$ to $10^{-1}$ m/s. For higher values of the mass transfer coefficients than $10^{-1}$ m/s the concentration polarization has already become insignificant and lower values than $5 \times 10^{-5}$ m/s are not present in real reverse osmosis operations.

When using the Spiegler-Kedem model [6], on increasing $J_V$, $1/RO - 1$ initially decreases, attains a minimum, and then starts increasing (Section 2.2). To test this trend, the model

Fig. 2. Effect of bulk feed concentration on flux with the mass transfer coefficient as a parameter. Operating conditions: $T = 298$ K, $P = 4000$ kPa and $C_{A1} = 75$ mol/m$^3$ for NaCl-H$_2$O system. Model parameters: $\theta_1 = 5.4434 \times 10^{-9}$ m, $\theta_2 = 0.4910$, $\tau/\varepsilon = 10 \times 10^{-9}$ m and $R_w = 13 \times 10^{-9}$ m.
solution code is run at a temperature of 298 K for a bulk feed concentration of 75 mol/m$^3$ of the NaCl-H$_2$O solution with pressure being incremented in steps of 1000 kPa from 1000 to 4000 kPa. The model parameters used are: $\theta_1$: 5.4434 x 10$^{-9}$ m, $\theta_2$: 0.4910, $\tau/\varepsilon$: 1.0 x 10$^{-4}$ m, and $R_w$: 1.3 x 10$^{-9}$ m with the mass transfer coefficient having been varied from 5.0 x 10$^{-6}$ to 10$^{-3}$ m/s. Observations at mass transfer coefficient of greater than 2.5 x 10$^{-5}$ m/s show no discernible change from the trend at 2.5 x 10$^{-5}$ m/s and so have not been included in the graph (Fig. 3).

Looking at the above graphs, it can be said the concentration polarization becomes significant when the mass transfer coefficient lies in 10$^{-6}$-10$^{-4}$ m/s range—essentially the regime in which most of the experimental data sets lie.

5.3. Model evaluation

Parameter estimation has been done in two steps. In the first step, all the experimental observations at some selected bulk feed concentrations are used to estimate the parameters. These parameters are then used to back calculate the experimental observations from which they are produced in order to study the consistency of the original experimental observation.

In the second step, the above estimated parameters are averaged to obtain the 'average parameters'. These parameters are then used to predict the membrane performance of all available experimental conditions including those, which were not used in any way for parameter estimation.

For data analysis, we have preferred to examine error functions 'E1', 'E2' and 'E', rather than the parameters individually. $\tau/\varepsilon$ has been selected as the single point error function encompassing the effects on both observed rejection ratio and the volume flux. This approach is followed as parameters like $\theta_1$ and $\theta_2$ must be examined together, and not individually, for potential function evaluation. As the optimization process is fairly random, while $\theta_1$ may be affected in some iterations, others times $\theta_2$ may be changed. With just 2 or 3 data sets being used for computing averaged parameter sets, we felt carrying out an error analysis would make more sense.

For the case of NaCl-H$_2$O system, all experimental data at 17.11 and 103.18 mol/m$^3$ have been used separately for parameter estimation. When these parameters are used for analysis of the same set of experimental data, the back calculation errors (E) are 13.05 and 16.55% for 17.11 and 103.18 mol/m$^3$, respectively. The averaged parameters for these two concentrations are given in Table 3. As shown in this table, using these averaged parameters to estimate the membrane performance at 207.62 mol/m$^3$, the results are found to be in excellent agreement with the experimental observations with $E$ being 16.98%. Subsequently, these parameters are used to further predict the membrane performance and the detailed results are discussed below (Section 5.4).

When a similar procedure is repeated for Na$_2$SO$_4$-H$_2$O system, with the parameters being estimated at 42.51 and 158.42 mol/m$^3$, the back calculation errors (E) are 15.51 and 14.24%, respectively. The averaged parameters for these two concentrations are shown in Table 4. Using these parameters, the errors (E) between the predicted and the experimental observations for concentrations 7.00, 85.53 and 217.80 mol/m$^3$ are estimated and found to be 18.74, 12.90 and 16.98% respectively. The above values in $E$ clearly in-
3.2. Comparison of membrane specific parameters

Table 5

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$\theta_1$</td>
<td>m</td>
<td>2.6144 x 10^{-9}</td>
</tr>
<tr>
<td>2.</td>
<td>$\theta_2$</td>
<td>m</td>
<td>7.3203</td>
</tr>
<tr>
<td>3.</td>
<td>$\nu$</td>
<td>m</td>
<td>1.2000 x 10^{-9}</td>
</tr>
<tr>
<td>4.</td>
<td>$\nu$</td>
<td>m</td>
<td>1.0404 x 10^{-9}</td>
</tr>
<tr>
<td>5.</td>
<td>$\nu$</td>
<td>m</td>
<td>0.7769</td>
</tr>
<tr>
<td>6.</td>
<td>$\epsilon$</td>
<td>(m/s)/(mol/m^3)^{0.5}</td>
<td>0.8620</td>
</tr>
</tbody>
</table>

(B) Data analysis using above parameters

(1) Operating condition

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Condition</th>
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<th>$P$</th>
<th>$P$</th>
<th>$P$</th>
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<tr>
<td>1.</td>
<td>BC</td>
<td>42.51</td>
<td>158.42</td>
<td>70.0</td>
<td>85.53</td>
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</table>

(2) Error analysis (% rms averaged)

<table>
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<th>$\theta_1$</th>
<th>$\theta_2$</th>
<th>$\nu$</th>
<th>$\epsilon$</th>
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<tr>
<td>BC</td>
<td>10.99</td>
<td>10.60</td>
<td>13.60</td>
<td>8.27</td>
<td>15.33</td>
</tr>
<tr>
<td>3</td>
<td>19.15</td>
<td>17.13</td>
<td>22.75</td>
<td>16.26</td>
<td>18.49</td>
</tr>
</tbody>
</table>

Note: These parameters are averaged parameters obtained from observations at 42.51 and 158.42 mol/m^3.

4. Membrane performance prediction

In addition to the objective error function 'E', the membrane performance predictions are also carried out for the volume flux and permeate concentration against pressure

Table 6

<table>
<thead>
<tr>
<th>S. no.</th>
<th>System</th>
<th>$\theta_1$</th>
<th>$\theta_2$</th>
<th>$\nu$</th>
<th>$\epsilon$</th>
</tr>
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<tr>
<td>1.</td>
<td>NaCl-H_2O</td>
<td>9.9917</td>
<td>2.6144</td>
<td>0.7769</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Na_2SO_4-H_2O</td>
<td>1.2000</td>
<td>1.0404</td>
<td>0.8620</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Error (%)</td>
<td>17.36</td>
<td>-21.53</td>
<td></td>
<td></td>
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</table>

Error analysis compares experimental observations to and simulation estimations for CA_3, JV, and RO. "k" values are compared with CEFSK model predictions. $E$ is the overall objective error function.
1. Effect of pressure on rejection ratio and flux for NaCl-H2O system with flow rate (m³/s) as a parameter. 'S' represents simulated results and 'E' the experimental observations of Murthy [13]. Operating conditions: T = 298 K and CA1 = 207.62 mol/m³ (1000 ppm). Model parameters: θ1 = 1.5007 x 10⁻⁹ m, θ2 = 4.8739, τ/ε = 1.2644 x 10⁻⁴ m, R_W = 9.9917 x 10⁻¹⁰ m, b = 0.7786 and a = 1.0733 (m/s)/(m³/s)⁰.7786.

5.5. Mass transfer coefficient

Mass transfer coefficient and its parameters 'a' and 'b' are computed from the present parameters estimation analysis and compared with the values obtained from the combined film theory—Spiegler-Kedem (CFSK) model. Murthy [13] estimated the mass transfer coefficient and the coefficient parameters from the CFSK model using the Box-Kanemasu method [35]. When the mass transfer coefficient parameters from the two different methods are compared for both NaCl-H2O and Na₂SO₄-H₂O systems in Table 6, the maximum error in any parameter, for any system, is around 3% implying the predicted values from MD-SF-PF and the CFSK models are in excellent agreement.

5. Effect of pressure on rejection ratio and flux for Na₂SO₄-H₂O system with flow rate (m³/s) as a parameter. 'S' represents simulated results and 'E' the experimental observations of Murthy [13]. Operating conditions: T = 298 K and CA1 = 85.53 mol/m³ (1000 ppm). Model parameters: θ1 = 2.6144 x 10⁻⁹ m, θ2 = 7.3283, τ/ε = 1.0404 x 10⁻⁴ m, R_W = 1.2090 x 10⁻¹⁰ m, b = 0.7769 and a = 0.8620 (m/s)/(m³/s)⁰.7769.
5.6. Extrapolated results

When the reciprocal of the observed rejection is plotted against volume flux for both NaCl-H$_2$O and Na$_2$SO$_4$-H$_2$O systems under consideration, minima is not found within the experimental region. This necessitated the need to study the system in an extrapolated region; i.e., beyond the experimental region. As the experimental data are limited to 10,100 kPa (100 atm), the simulations are carried out to cover the pressure range of 2,000-0,000 kPa (19.8-396.0 atm). Plots for the systems under consideration are shown in Figs. 8 and 9. Our results indicate the $J_{V,m}$ would occur at 23,500 kPa (232.67 atm) for NaCl-H$_2$O and at 11,500 kPa (113.86 atm) for Na$_2$SO$_4$-H$_2$O.

The value of $\mathcal{A}_{m}$ estimated through the MD-SF-PF model for NaCl-H$_2$O system is $2.41 \times 10^{-5}$ m/s and for the Na$_2$SO$_4$-H$_2$O system is $2.01 \times 10^{-5}$ m/s. Corresponding values for these systems estimated using the CFSK

---

Fig. 6. Effect of bulk feed concentration on permeate concentration and flux for NaCl-H$_2$O system with flow rate (m$^3$/s) as a parameter. 'S' represents simulated results and 'E' the experimental observations of Murthy [13]. Operating conditions: $T = 298$ K and $P = 4,040$ kPa. Model parameters: $\theta_1 = 1.5007 \times 10^{-9}$ m, $\theta_2 = 4.8739$, $\tau/\varepsilon = 1.2644 \times 10^{-4}$ m, $R_W = 9.9917 \times 10^{-10}$ m, $b = 0.7786$ and $a = 0.0733$ (m/s)/(m$^3$/s)$^{0.7786}$.

Fig. 7. Effect of bulk feed concentration on permeate concentration and flux for Na$_2$SO$_4$-H$_2$O system with flow rate (m$^3$/s) as a parameter. 'S' represents simulated results and 'E' the experimental observations of Murthy [13]. Operating conditions: $T = 298$ K and $P = 10,100$ kPa. Model parameters: $\theta_1 = 2.6144 \times 10^{-9}$ m, $\theta_2 = 7.3283$, $\tau/\varepsilon = 1.0404 \times 10^{-4}$ m, $R_W = 1.2090 \times 10^{-10}$ m, $b = 0.7769$ and $a = 0.8620$ (m/s)/(m$^3$/s)$^{0.7769}$.
Fig. 8. Effect of flux on rejection ratio for NaCl-H_2O system. '*' represents simulated results using MD-SF-PF model, 'CFSK' are values obtained through combined film—Spiegl-Kedem model and '*' the experimental observations of Murthy [13]. Operating conditions: T = 298K, CA_1 = 103.18mol/m^3, Q = 1.5 x 10^{-6} m^3/s and P = 2,000-40,000kPa. MD-SF-PF model parameters: $\theta_1 = 1.5007 \times 10^{-9}$ m, $\theta_2 = 4.8739$, $\tau/\epsilon = 1.2644 \times 10^{-4}$ m, RW = 9.9917 x 10^{-10} m, $\delta = 0.7766$ and $\alpha = 1.0733$ (m/s)/(m^3/s)^0.779. Spiegl-Kedem model parameters: $\sigma = 0.9395$, $P_M = 4.168 \times 10^{-9}$ m/s, $\delta = 0.7763$ and $\alpha = 1.0355$ (m/s)/(m^3/s)^0.779 [13].

Assuming the CFSK model estimated values as the base, this means an error of -5.36% for the NaCl-H_2O system and an error of 8.08% for the Na_2SO_4-H_2O system. Looking at the above error calculations and the overall trends displayed in the figures, the MD-SF-PF model predictions of $J_m$ are in excellent agreement with the CFSK estimations.

Fig. 9. Effect of flux on rejection ratio for Na_2SO_4-H_2O system. '*' represents simulated results using MD-SF-PF model, 'CFSK' are values obtained through combined film—Spiegl-Kedem model and '*' the experimental observations of Murthy [13]. Operating conditions: T = 298K, CA_1 = 103.18mol/m^3, Q = 1.5 x 10^{-6} m^3/s and P = 2,000-40,000kPa. MD-SF-PF model parameters: $\theta_1 = 2.6144 \times 10^{-9}$ m, $\theta_2 = 7.3283$, $\tau/\epsilon = 1.0404 \times 10^{-4}$ m, RW = 1.2090 x 10^{-9} m, $\delta = 0.7769$ and $\alpha = 0.8620$ (m/s)/(m^3/s)^0.779. Spiegl-Kedem model parameters: $\sigma = 0.9982$, $P_M = 1.508 \times 10^{-9}$ m/s, $\delta = 0.7769$ and $\alpha = 0.8395$ (m/s)/(m^3/s)^0.779 [13].
versus osmosis membranes. Being a mechanism based model, the authors would also like to thank the two faculty members in the Chemical Engineering department, is also gratefully acknowledged. Rajesh Khanna and Dr. Kamal K. Pant, faculty members in the coding aspects. Assistance and support extended by Dr. Om Vir Singh from the Department of Chemical Engineering and Mr. Deepak Garg from the Department of Computer Science & Engineering who assisted us with the experimental observations. The membrane specific parameters of NaCl-H$_2$O and Na$_2$SO$_4$-H$_2$O systems on a similar cellulose acetate membrane have been shown to be very close to each other. The rejection ratio versus the flux trend and the predicted flux values for the system under consideration show agreement with the predictions of Spiegler-Kedem model. All other observations indicate the success of MD-SF-PF model as its predictions are found to be in agreement with the Spiegler-Kedem model—the model recommended by Mason and Lonsdale [12] for reverse osmosis membranes. Being a mechanism based model, the advantage of the MD-SF-PF model when combined with concentration polarization over the Spiegler-Kedem model is that its parameters can be related to the membrane structure, the solute-solvent and solute-membrane interactions.

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### Table 6

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Property</th>
<th>NaCl-H$_2$O</th>
<th>Na$_2$SO$_4$-H$_2$O</th>
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<tbody>
<tr>
<td>1.</td>
<td>Parameters</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>2.</td>
<td>Units</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>3.</td>
<td>Prediction</td>
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<td>0.7786</td>
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<tr>
<td>4.</td>
<td>CFSK</td>
<td>1.0335</td>
<td>0.7783</td>
</tr>
<tr>
<td>5.</td>
<td>Error (%$\chi^2$)</td>
<td>-1.16</td>
<td>-0.29</td>
</tr>
</tbody>
</table>

*Values from simulation based on the MD-SF-PF model in the present work.*

6. Conclusions

The addition of concentration polarization to the MD-SF-PF model resulted in a six-parameter estimation problem which has been solved by using Monte Carlo search and automatic guess updation combined with the Downhill Simplex technique. The estimated parameters are used to predict the membrane performance over a range of operating conditions, and the simulated results compare very well with the experimental observations. The membrane specific parameters of NaCl-H$_2$O and Na$_2$SO$_4$-H$_2$O systems on a similar cellulose acetate membrane have been shown to be very close to each other. The rejection ratio versus the flux trend and the predicted flux values for the system under consideration show agreement with the predictions of Spiegler-Kedem model. All other observations indicate the success of MD-SF-PF model as its predictions are found to be in agreement with the Spiegler-Kedem model—the model recommended by Mason and Lonsdale [12] for reverse osmosis membranes. Being a mechanism based model, the advantage of the MD-SF-PF model when combined with concentration polarization over the Spiegler-Kedem model is that its parameters can be related to the membrane structure, the solute-solvent and solute-membrane interactions.

### Nomenclature

- $a$ unknown in film mass transfer equation (Eq. (27)), (m/s)/(m$^2$/s)$^2$
- $a_x$ unknown parameter for velocity profile (Eq. (32))
- $a_1$ unknown parameter for velocity profile (Eq. (32))
- $a_2$ unknown parameter for velocity profile (Eq. (32))
- $a_3$ unknown parameter for the estimation of the velocity profile (Eq. (30))
- $\lambda_{ij}$ first derivative coefficient matrix for orthogonal collocation (Eq. (33))
- $b$ unknown in film mass transfer equation (Eq. (27))
- $b_0$ frictional parameter (Eq. (18))
- $b_0$ second derivative coefficient matrix for orthogonal collocation (Eq. (34))
- $C$ molar density of solution (mol/m$^3$)
- $C_f$ solute concentration at $i$th position (mol/m$^3$)
- $C_q$ solute concentration in permeate solution during $i$th observation (mol/m$^3$)
- $D_{f}$ solute diffusivity in infinitely diluted solution (m$^2$/s)
- $D_{s}$ solute diffusivity in solution (m$^2$/s)
- $E_i$ error in permeate concentration (Eq. (54))
- $E_2$ error in flux (Eq. (55))
- $F(x,\lambda)$ residual function value matrix (Eq. (36))
- $\beta$ radially averaged solute flux through a single pore (mol/m$^3$/s)
- $\gamma$ radially averaged solvent flux through a single pore (mol/m$^3$/s)
- $\dot{\lambda}(x,\mu)$ Jacobian matrix (Eq. (36))
- $J^f$ volume flux (m/s)
- $J^f$ volume flux at $i$th observation (m/s)
- $J_{f}$ value of flux, $J_{f}$, when $I/B_0$ - 1 is minimum when plotted against $J^f$ (m/s)
- $k$ film mass transfer coefficient (m/s)
- $k_p$ Boltzmann’s constant (J/K)
- $k_c$ cationic conductance at infinite dilution (mho/equivalent)
- $\alpha$ anionic conductance at infinite dilution (mho/equivalent)
- $l_{m}^{+}$ electro-osmotic conductance at infinite dilution (mho/equivalent)
- $l_{m}^{-}$ hydraulic permeability coefficient of the membrane (m$^2$/kg)
- $n$ number of experimental observations
- $N_{f}$ total flux during $i$th observation (mol/s)
Appendix A. Monte Carlo search algorithm

The Downhill Simplex method converges to a minimum, which is most likely, a local one. In an attempt to identify the global minima of the problem, the nearby surface solution needs to be explored. This is accomplished by adding a Monte Carlo search algorithm [23]. The integration of the Monte Carlo search with the Downhill Simplex routine has been done in the following manner:

1. This procedure is activated at every third iteration of the simplex loop to start after four iterations of the simplex loop have been completed. The objective of this step is to examine the nearby area of a potential local minima already identified by the downhill simplex method.

2. Values of \( \chi^{+1} \) for the past three iterations are compared. If error becomes constant, or consistently increases, it in-
indicates possible local minima might have been attained. For all other cases the Downhill Simplex routine is permitted to continue without any deviations.

3. Only the first six simplex vertices of the total seven are examined as a six-parameter combination is being handled. This is done to prevent any undue weightage being assigned to any parameter. In case the parameter serial number is equal to the vertex serial number, it is further tested (serial order of parameters: 01, 02, RW, ?>>a and b).

4. The variation probability of a parameter’s value has been accepted only if the error after the above described change is less than what it was before it carrying out the algorithm.

5. A multiplication change factor is randomly generated in the range of 0.0 to 1.0, for the parameter under consideration. The new value of the parameter is determined by multiplying the old one by this factor.

6. The resulting values of simplex vertices and the set of parameters is accepted only if the error after the above described change is less than what it was before it carrying out the algorithm.

References