A quantification of diffusion dialysis process: Single electrolyte system (sodium chloride solution)

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A quantification of diffusion dialysis process in a single electrolyte system has been investigated in this study. Firstly, the volume of water which permeates from water side to feed side was to be quantified detailedy, and results showed that diffusate solution volume changes over time according with the characteristics of quadratic polynomial \((y = a_0 t^2 + a_1 t + a_2)\). Secondly, Permeability coefficients of membrane to \(H_2O\) \((P_{H_2O}, P_{H_2O})\) and \(NaCl\) \((P_{NaCl}, P_{NaCl})\) were used to quantify diffusion dialysis process. Results showed that with the increase of feed concentration, \(P_{H_2O}\) and \(P_{NaCl}\) decrease, while \(P_{H_2O}\) and \(P_{NaCl}\) increase. Furthermore, when modifying factor \(\lambda = 3.30\) and \(\sigma = 2.37\), comparisons of theoretical and experimental concentrations of \(NaCl\) in diffusate solution illustrated that both \(P_{H_2O}\) and \(P_{NaCl}\) are satisfactory coefficients for characterizing the diffusion dialysis process. In addition, the mathematical model discussed in this study can provide an effective method to deal with the mass transfer process of diffusion dialysis easily and conveniently, especially, is helpful to select an optimum ion exchange membrane to operate diffusion dialysis.

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1. Introduction

Diffusion dialysis is a membrane separation process which is driven by solution concentration gradient. Taking anion exchange membrane (AEM) diffusion dialysis process as an example, feed (acid and metal salt mixture) is fed on one side of AEM, while water is supplied to the other side of AEM as a counter flow. On one hand, acid in feed is recovered on the water side through AEM due to the acid concentration difference. On the other hand, metal ion is left in the feed side because of its large size and positive valence, which is repulsed by AEM. As a result, clean acid can be recovered effectively with a diffusion dialysis membrane module.

For diffusion dialysis has many advantages: low energy consumption, operational simplicity, high efficiency and so on [1–3], it has been used to recover hydrochloric acid, sulfuric acid and other acids from waste solutions in electropate, metal-refining, titanium white industries, etc. [4–7].

Along with deepening research on application of diffusion dialysis, theoretical study of diffusion dialysis is gradually in-depth. Based on Nernst–Planck equation and Teorell–Meyer–Sievers, Elmidaoui et al. [8] calculated the flux of HCl and NaCl respectively. Results showed that these values were in satisfactory agreement with experimental values. Kang et al. [9] established a lumped parameter model to predict hydrochloric acid recovery in diffusion dialysis process in terms of various operating parameters, and results illustrated that this model gave reasonably good agreement with experimental results in predicting recovery yield; however, since the solution volume change was not considered, the model was only applied to diffusion dialysis process of low concentration feed. Z. Pašaty research group has also made many theoretical contributions on diffusion dialysis, and the investigated system included: \(H_2SO_4\) + \(ZnSO_4\), \(HCl\) + \(FeCl_2\), \(HCl\) + \(FeCl_3\), \(HNO_3\) + \(NaNO_3\), etc. [10–14]. What is more, in most cases, the described diffusion dialysis processes are batch wise, i.e., a batch cell with an ion exchange membrane was investigated; time dependence of ions concentrations in both compartments was recorded, and then combined with an optimized procedure, some basic differential equations were integrated to quantify the diffusion dialysis process.

In our previous paper [15], it has been mentioned that water can permeate from water side to feed side during the diffusion dialysis process. And when the concentration of metal salt in feed is high and the effective membrane area is large, this phenomenon is particularly evident. Since the phenomenon makes against the proceeding of diffusion dialysis, it is necessary to carry out a study on it. During most antecedent literatures, study on this phenomenon was relatively less. And generally speaking, the dependence \((V(t) = f(t))\) was basically approximated to the time dependence of
Nomenclature

\[ J_{\text{NaCl}}, J_{\text{H}_2\text{O}} \] NaCl and H₂O flux through membrane, mol/(m² s)

\[ P_{\text{NaCl}}, P_{\text{H}_2\text{O}} \] NaCl and H₂O permeability coefficients of membrane, mol/(m² s J)

\[ \mu_{\text{NaCl}}, \mu_{\text{H}_2\text{O}} \] NaCl chemical potential at the membrane surfaces contacting the dialysis and diffusate solutions, J/mol

\[ \mu_{\text{NaCl}^0}, \mu_{\text{H}_2\text{O}^0} \] H₂O chemical potential at the membrane surfaces contacting the dialysis and diffusate solutions, J/mol

\[ C_{\text{NaCl}}, C_{\text{NaCl}^0} \] theoretical value and experimental value of NaCl concentration in diffusate solution, mol/L

\[ \mu_{\text{NaCl}^0}, \mu_{\text{H}_2\text{O}^0} \] standard chemical potential of M⁺⁺, X⁻⁻, and Mₓₓₓₓ, mol/L

\[ \mu_{\text{NaCl}^0}, \mu_{\text{H}_2\text{O}^0} \] real chemical potential of M⁺⁺, X⁻⁻, and Mₓₓₓₓ, J/mol

\[ \lambda_{\text{NaCl}}, \lambda_{\text{H}_2\text{O}} \] standard chemical potential and real chemical potential of solvent (A), J/mol

\[ \Delta \mu_{\text{NaCl}^0}, \Delta \mu_{\text{H}_2\text{O}^0} \] NaCl and H₂O chemical potential difference of diffusate solution and dialysate solution, J/mol

\[ \sigma_{\text{NaCl}}, \sigma_{\text{H}_2\text{O}} \] activity of NaCl, mol/L

\[ \gamma_{\text{NaCl}}, \gamma_{\text{H}_2\text{O}} \] activity coefficient of NaCl, mol/L

\[ a_{\text{NaCl}}, a_{\text{H}_2\text{O}} \] activity coefficient, mean activity coefficient, osmotic coefficient

\[ \tau, \tau_{a}, \tau_{w} \] average osmotic coefficient, average osmotic coefficient of dialysate solution, average osmotic coefficient of diffusate solution

\[ \tau_{a}, \tau_{w} \] average mean activity coefficient, average mean activity coefficient of dialysate solution, average mean activity coefficient of diffusate solution

\[ M_{\text{NaCl}}, M_{\text{H}_2\text{O}} \] relative molecular weight: NaCl of H₂O mole fraction and A molecular

\[ c_{\text{NaCl}}, c_{\text{NaCl}^0} \] NaCl molar concentration and moal quantity in diffusate solution, mol/L, mol

\[ \rho_{\text{H}_2\text{O}} \] density of water, kg/m³

\[ \varphi \] volume of diffusate solution, L

\[ n_{\text{H}_2\text{O}^0} \] molar quantity of diffusate solution, mol

\[ Z_a, Z_x \] the chemical valence of anion and cation of solute molecule

\[ A \] the effective membrane area of diffusion dialysis membrane module, m²

\[ \tau \] time, s

\[ K \] absolute temperature, K

\[ v \] the number of ions which a molecular electrolyte ionizes

\[ m \] solute molality, mol/kg

\[ A_a \] Debye-Hückel constant for activity coefficient, 0.511 kg⁻¹/² mol⁻¹/² at 25 °C

\[ I \] ionic strength, mol/kg

\[ B, a \] constants in Eq. (10)

\[ b_0, b_1, c_0 \] coefficients of quadratic polynomial (y = a₀x² + b₀x + c₀)

\[ m_{\text{solute}}, m_{\text{diff}} \] solute molality of dialysate solution and diffusate solution, mol/kg

\[ c_{\text{NaCl}} \] NaCl molar concentration in feed at τ = 0, mol/L

\[ m_a, m_b \] molality of ion A, mol/kg

\[ Z_b \] chemical valence of ion B

\[ \lambda, \delta \] modifying factors of \( P_{\text{NaCl}} \) and \( P_{\text{H}_2\text{O}} \)

liquid volume at water side by the second order polynomial approximating directly [10,11,13,16]. What is more, at present, there is no further study on this phenomenon. In this paper, the phenomenon, i.e. the volume of water which permeates from water side to feed side during the diffusion dialysis process, was to be investigated detailedley. To simplify the investigation problem, single sodium chloride solution was used to operate AEM diffusion dialysis experiments. Moreover, chemical potential difference across the AEM was regarded as the mass transfer driving force. Besides, based on these, a novel mathematical model would be established to quantify the diffusion dialysis process for practical use.

2. Theoretical development

2.1. Mass transfer in diffusion dialysis process

Once feed and water were contacted by an AEM, diffusion dialysis process takes place. NaCl and H₂O flux through AEM \( J_{\text{NaCl}}, J_{\text{H}_2\text{O}} \) can be described by transformative Fick's law:

\[ J_{\text{NaCl}} = P_{\text{NaCl}} (\mu_{\text{NaCl}^0} - \mu_{\text{NaCl}}) \]

\[ J_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}} (\mu_{\text{H}_2\text{O}^0} - \mu_{\text{H}_2\text{O}}) \]

where \( \mu_{\text{NaCl}} \) and \( \mu_{\text{H}_2\text{O}} \) are NaCl chemical potentials in dialysate solution and diffusate solution respectively, while \( \mu_{\text{NaCl}^0} \) and \( \mu_{\text{H}_2\text{O}^0} \) are H₂O chemical potentials in dialysate solution and diffusate solution respectively. \( P_{\text{NaCl}} \) and \( P_{\text{H}_2\text{O}} \) are NaCl and H₂O permeability coefficients of the membrane, respectively. According to the law of mass conservation, \( J_{\text{NaCl}} \) can be correlated with the change of NaCl molar quantity in diffusate solution, while \( J_{\text{H}_2\text{O}} \) can be related to the change of solution volume in diffusate solution, and specific equations are illustrated as follows:

\[ J_{\text{NaCl}} = \frac{1}{A} \frac{d n_{\text{NaCl}}}{d \tau} = \frac{1}{A} \frac{d (c_{\text{NaCl}}^0 - c_{\text{NaCl}})}{dt} \]

\[ = \frac{1}{A} \left[ \nu \frac{d c_{\text{NaCl}}}{dt} + c_{\text{NaCl}}^0 \frac{d \varphi}{dt} \right] \]

\[ J_{\text{H}_2\text{O}} = \frac{1}{A} \frac{d n_{\text{H}_2\text{O}}}{d \tau} = \frac{1}{A} \frac{d (\rho_{\text{H}_2\text{O}} c_{\text{H}_2\text{O}})}{dt} \]

\[ = \frac{1}{A} \left[ \nu \frac{d c_{\text{H}_2\text{O}}}{dt} + c_{\text{H}_2\text{O}}^0 \frac{d \varphi}{dt} \right] \]

where \( n_{\text{NaCl}} \) and \( n_{\text{H}_2\text{O}} \) are mole quantities of NaCl and H₂O in diffusate solution respectively. \( c_{\text{NaCl}}^0 \) and \( c_{\text{H}_2\text{O}}^0 \) are the NaCl concentration and solution volume in diffusate solution. A is the total effective membrane area of diffusion dialysis membrane module. \( \rho_{\text{H}_2\text{O}} \) and \( M_{\text{H}_2\text{O}} \) are the density and relative molecular weight of H₂O. Combining of Eqs. (1) and (3), and combining of Eqs. (2) and (4) give the following two equations:

\[ J_{\text{NaCl}} = P_{\text{NaCl}} (\mu_{\text{NaCl}^0} - \mu_{\text{NaCl}}) = \frac{1}{A} \left[ \nu \frac{d c_{\text{NaCl}}}{dt} + c_{\text{NaCl}}^0 \frac{d \varphi}{dt} \right] \]

\[ J_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}} (\mu_{\text{H}_2\text{O}^0} - \mu_{\text{H}_2\text{O}}) = \frac{1}{A} \frac{d (\rho_{\text{H}_2\text{O}} c_{\text{H}_2\text{O}})}{dt} \]

Combining the above two equation obtains the following equation.
\[
\frac{d\mu_{A}}{dt} = \frac{A_{F_{\text{react}}}(\mu_{A}^{\text{M}^+} - \mu_{A}^{\text{M}^-})}{\nu^+} \cdot \frac{C_{\text{M}^+}}{\nu^+} + \frac{A_{F_{\text{react}}}(\mu_{A}^{\text{M}^-} - \mu_{A}^{\text{M}^+})}{\nu^-} \cdot \frac{C_{\text{M}^-}}{\nu^-}
\]
(7)

2.2. The calculation of solution chemical potential

Solution is composed by solvent and solute, and these two parts have their own calculation formulas of chemical potential.

The calculation formula of solvent \( (A) \) chemical potential \( (\mu_{A}) \) is expressed as follows [17]:

\[
\mu_{A} = \mu_{A}^0 - 0.001 \varphi R T M_{A} \nu m
\]
(8)

where \( \mu_{A}^0 \) is the standard chemical potential of solvent \( (A) \). \( \varphi \) is the osmotic coefficient which is used to measure the deviation between real solution and ideal solution. \( R \) is gas constant, \( T \) is Kelvin temperature, and \( M_{A} \) is the relative molecular weight of solvent \( (A) \). \( \nu \) is the number of ions which a molecular electrolyte ionizes, while \( m \) is solute molality.

Compared with solvent chemical potential, the calculation process of solute chemical potential is relatively complicated. Take \( M_{A}X_{A} \) as a solute for example, the following equation set depicts the calculation expressions of \( M^+ \), \( X^- \), and \( M_{A}X_{A} \):

\[
\begin{align*}
\mu_{M^+} &= \mu_{M^+}^0 + \varphi RT n_{M^+} \nu^+ \\
\mu_{X^-} &= \mu_{X^-}^0 + \varphi RT n_{X^-} \nu^-
\end{align*}
\]

\[
\mu_{M_{A}X_{A}} = \mu_{M_{A}X_{A}}^0 + \varphi RT n_{M_{A}X_{A}}
\]

where \( \mu_{M^+}^0 \), \( \mu_{X^-}^0 \), and \( \mu_{M_{A}X_{A}}^0 \) denote the real chemical potentials of \( M^+ \), \( X^- \), and \( M_{A}X_{A} \), while \( \mu_{M^+} \), \( \mu_{X^-} \), and \( \mu_{M_{A}X_{A}} \) present the standard chemical potentials of them. \( n_{M^+} \), \( n_{X^-} \), and \( n_{M_{A}X_{A}} \) are the activities of \( M^+ \), \( X^- \), and \( M_{A}X_{A} \), respectively. As reported in literatures [18,19], thermodynamically, individual ion activity is not defined, and it is impossible to determine activities or activity coefficients of single-ion species. For this reason, it is necessary to define a mean activity \( (\bar{a}) \) and mean activity coefficient \( (\bar{\gamma}) \) of solute, and the definitions are expressed following:

\[
\begin{align*}
\bar{a}_i &= \text{def} \left( \frac{\sigma_{M^+}^{\text{M}^+} \cdot \sigma_{X^-}^{\text{X}^-}}{\sigma_{M^+}^{\text{M}^+} \cdot \sigma_{X^-}^{\text{X}^-}} \right)^\frac{1}{\nu^+} \\
\bar{\gamma}_i &= \text{def} \left( \frac{\sigma_{M_{A}X_{A}}^{\text{M}^+} \cdot \sigma_{M_{A}X_{A}}^{\text{X}^-}}{\sigma_{M_{A}X_{A}}^{\text{M}^+} \cdot \sigma_{M_{A}X_{A}}^{\text{X}^-}} \right)^\frac{1}{\nu}
\end{align*}
\]

Thus, the calculation expression of solute \( M_{A}X_{A} \) chemical potential can be written into another form:

\[
\begin{align*}
\mu_{M_{A}X_{A}} &= \mu_{M_{A}X_{A}}^0 + (m + n) \varphi RT \bar{a}_i \\
&= \mu_{M_{A}X_{A}}^0 + (m + n) \varphi RT \bar{\gamma}_i
\end{align*}
\]
(9)

where \( C_{M_{A}X_{A}} \) is the molar concentration of solute in solution.

As seen from the Eqs. (8) and (9), it is easy to see that, to calculate the chemical potential, osmotic coefficient \( (\varphi) \) and mean activity coefficient \( (\bar{\gamma}) \) are necessary to be known in advance. Most calculation methods [19–23] for \( \varphi \) and \( \bar{\gamma} \) have been evolved by Debye–Hückel equation [24], and in this paper, in allusion to the situation of solution (strong electrolyte) in this study, calculation method reported in literature [25] is considered to be more appropriate. And specific computation formula is expressed as follows:

\[
\begin{align*}
1 - \varphi &= 2.303 \lambda \cdot (Z \cdot Z_{\text{eff}}) \cdot \frac{\rho^2}{\lambda^2} \cdot \sigma(\rho^2) - 2.303(0.06 + 0.68) \\
&= (Z \cdot Z_{\text{eff}}) \cdot \frac{\rho^2}{\lambda^2} \cdot \varphi(\alpha) - 2.303 \cdot \frac{1}{2} \\
\log \bar{\gamma}_A &= \frac{A_{\lambda}(Z \cdot Z_{\text{eff}}) \cdot \rho^2}{1 + \rho^2} = \frac{(80 - 81)}{(1 + \alpha)^2} + B I
\end{align*}
\]
(10)

\( (11) \)

where \( A_{\lambda} \) is a constant affected by the kind of solvent, temperature and so on. \( Z \) and \( Z_{\text{eff}} \) are the chemical valence of anion and cation, respectively. \( \lambda \) is solution ionic strength. \( \rho \) and \( \alpha \) are determined independently using data on heats of mixing and heat capacity for a number of salts including sea water treated as a single salt solution. And the result of plentiful experiments shows that \( \rho = 1.0 \) and \( 0.5 \leq Z_{\text{eff}} \leq 1.5 \) is satisfactory to within the accuracy of the data, even to 200 °C. The expressions of \( \sigma(\rho^2) \) and \( \varphi(\alpha) \) of Eq. (10) are written following:

\[
\begin{align*}
\sigma(\rho^2) &= \frac{3}{(\rho^2)^3} \left[ 1 + \rho^2 - \frac{1}{1 + \rho^2} - 2 \ln(1 + \rho^2) \right] \\
\varphi(\alpha) &= \frac{2}{\alpha} \left[ \frac{1 + 2\alpha}{1 \cdot [1 + \alpha]^{\frac{1}{2}}} \right] \\
&= \frac{2}{\alpha} \left[ \frac{1 + 2\alpha}{1 \cdot [1 + \alpha]^{\frac{1}{2}}} \right]
\end{align*}
\]
(12)

(13)

\( B_0 \) and \( B \) were found to depend on \( |Z \cdot Z_{\text{eff}}| \) as follows:

\[
(\frac{B_0 - B}{|Z \cdot Z_{\text{eff}}|}) = 0.06 + 0.68
\]

\( B \) is a constant which can be referred to corresponding table in literature [25].

2.3. Brief calculation steps

Summing up Sections 2.1 and 2.2 as stated above, calculation steps are described here briefly. Firstly, during the experimental operation process, time dependence of the volume and concentration of diffusate solution is easily determined, i.e., \( V(t), C_{\text{NaCl}}(t), \sigma(t) \) and \( \alpha(t) \) can be obtained. Secondly, osmotic coefficient \( (\varphi) \) and mean activity coefficient \( (\bar{\gamma}) \) can be calculated by Eqs. (10) and (11). Thirdly, chemical potential of solvent and solute can be gotten according to Eqs. (8) and (9). Finally, as known the \( V(t), C_{\text{NaCl}}(t), \sigma(t), \) \( \varphi(\alpha) \), \( \bar{\gamma}_A \) (\( \mu_{\text{NaCl}} - \mu_{\text{HCl}} \)) and \( \bar{\gamma}_A \) (\( \mu_{\text{HCl}} - \mu_{\text{HCl}} \)), it is relatively easy to obtain the permeability coefficients of the membrane \( (P_{\text{NaCl}} \) and \( P_{\text{HCl}} \) according Eqs. (5) and (6). In addition, modifying factors \( (\lambda, \alpha) \) can be determined by an optimized procedure according to Eq. (7) to revise the mathematical model.

3. Experimental

3.1. Materials

DF-120 AEM provided by Shandong Tianwei Membrane Technology Co., Ltd., China was used in this study, and its main characteristics were: IEC (ion exchange capacity) = 1.82 mol/kg. Wf (water content) = 42.34%. MEK (membrane area resistance) = 3.4 Ω cm² (16 °C) or 2.7 Ω cm² (25 °C). All the reagents were neutralized.
were purchased from domestic chemical reagents company and of analytical grade. Deionized water was used throughout.

3.2. Diffusion dialysis experimental apparatus

To be convenient to investigate the volume of water which permeates from water side to feed side, diffusion dialysis experiments were conducted with a conventional plate and frame diffusion dialysis (PFDD) membrane module, and it was composed of five pieces of DF-120 AEMs. The effective area of each membrane is 40 × 100 mm². Compartments were separated by AEMs, silicone gaskets (thickness ≈ 1.5 mm) and plastic partition nets (thickness ≈ 0.8 mm). And experimental set-up used in this study is shown in Fig. 1. At the very start of experiment, diffusate solution flask (2) was filled with 0.5 L deionized water, and dialysate solution flask (3) was full of 0.5 L 0.9–5.6 mol/L NaCl solution. Two submersible pumps (AP1000, Zhongshan Zhenghua Electronics Co., Ltd., China, with the maximal speed of 27 L/h) were placed in the two flasks to circulate the corresponding solution. During the diffusion dialysis process, Cl⁻ can diffuse through the anion exchange membrane from dialysate solution to diffusate solution freely, and because of the requirement of electric neutrality, then partial Na⁺ can also diffuse through the anion exchange membrane (generally speaking, selective permeability of membrane is less than 10%). So as time goes by, the NaCl concentration in diffusate solution increases. Diffusion was allowed to occur for 10 h. The entire device was placed in a water bath kettle in which the water temperature is constant at 25 ± 1 °C.

The samples in both diffusate solution and dialysate solution were analyzed with pre-determined time interval respectively. NaCl solution concentration was determined by measuring the solution conductance with a conductivity meter (DDS–307 Conductivity Meter, INESA Scientific Instrument Co. Ltd., China). Subtracting the conductance of deionized water, the relationship between NaCl solution concentration and conductance is a straight line through origin as shown in Fig. 2, and the linearity confirms the validity of the method. When the NaCl concentration exceeds the concentration scope in Fig. 2, sample should be diluted before determining.

4. Data treatment and discussion

4.1. Diffusate solution volume changes over time

Fig. 3 depicts the volume changes of diffusate solution over time at different feed concentrations. It is clear to see that diffusate solution volume decreases with an increase in feed concentration. With the passage of time, the diffusate solution volume is becoming less and less, and if time is enough, it can be deduced that the volume would reach a stable equilibrium state eventually. In allusion to the five curves in Fig. 3, some fitting works have been down; results indicate that the five curves accord with the characteristics of quadratic polynomial \( y = a_0 \tau^2 + b_0 \tau + c_0 \), and the detailed fitting results are shown in Table 1. As seen from Table 1, the five correlation coefficients are all close to 1.0 considerably, thus it can be concluded that the fitting result is appropriate and satisfactory. It can be also deduced that conclusion on time dependences of liquid volumes drawn by Z. Palaty research group [10–14] was suitable.

With regard to each coefficient \((a_0, b_0, c_0)\) of quadratic polynomial, it is clear to find that the value of \(a_0\) and \(b_0\) increase along with the feed concentration, while \(c_0\) is constant all the time. From the value of \(c_0\) (0.5 L), it is not difficult to find that \(c_0\) represents the initial volume of diffusate solution, and with regard to each case, the initial volume of diffusate solution is equal. What is more, what is the meaning of \(a_0\) and \(b_0\)?

To the quadratic polynomial \(y = a_0 \tau^2 + b_0 \tau + c_0\), its first derivation and second derivation are depicted as follows:

\[
\frac{dy}{d\tau} = y' = 2a_0 \tau + b_0, \quad \frac{d^2y}{d\tau^2} = y'' = 2a_0
\]

As seen from the two equations, it can be found that \(b_0\) is the value of \(y'\) at \(\tau = 0\), while \(a_0\) equals to the half of \(y''\), and they are expressed in further as:

\[b_0 = y'(0), \quad a_0 = \frac{y''}{2}\]

As stated in Section 2.1, Eq. (6) can be transformed into:

<table>
<thead>
<tr>
<th>Item (mol/L)</th>
<th>(a) (L²/s²)</th>
<th>(b) (L/s)</th>
<th>(c) (L)</th>
<th>Correlation coefficient ((R^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.06</td>
<td>2.50E−11</td>
<td>−3.54E−06</td>
<td>0.5</td>
<td>0.9993</td>
</tr>
<tr>
<td>4.33</td>
<td>4.43E−11</td>
<td>−5.64E−06</td>
<td>0.5</td>
<td>0.9995</td>
</tr>
<tr>
<td>3.08</td>
<td>5.02E−11</td>
<td>−9.16E−06</td>
<td>0.5</td>
<td>0.9995</td>
</tr>
<tr>
<td>1.85</td>
<td>1.47E−10</td>
<td>−1.32E−05</td>
<td>0.5</td>
<td>0.9995</td>
</tr>
<tr>
<td>0.95</td>
<td>1.70E−10</td>
<td>−1.35E−05</td>
<td>0.5</td>
<td>0.9986</td>
</tr>
</tbody>
</table>
\[
\frac{dy^\mu}{dz} = -p_{H_2O}(\mu_{H_2O}^\mu - \mu_{H_2O}^\mu) \cdot \frac{M_{H_2O}}{\rho_{H_2O}} \tag{6b}
\]

The calculation formula of chemical potential difference (Eq. (19), stated in Section 4.2) would be substituted into above equation, getting the following equation:

\[
y' = -p_{H_2O} \cdot \frac{\Delta m_{H_2O}}{\rho_{H_2O}} - 0.001RT \cdot 18 \cdot 2 \cdot (\bar{\sigma}_T \cdot m_f - \bar{\sigma}_W \cdot m_w) = -0.0322 \cdot p_{H_2O} \cdot (\bar{\sigma}_T - \bar{\sigma}_W) \cdot m_f - \bar{\sigma}_W \cdot m_w \tag{6c}
\]

When \( t = 0 \), Eq. (6c) can be simplified into:

\[
b_0 = y'(0) = -0.0322 \cdot p_{H_2O} \cdot \bar{\sigma}_0 \cdot C_0
\]

where \( C_0 \) is the initial feed concentration. From the above relationship, it could be concluded that \( b_0 \) is influenced by \( p_{H_2O}, \bar{\sigma}_0, C_0 \) these three factors as plain as print. Strictly speaking, \( b_0 \) is also affected by temperature, effective membrane area, property of AEM and so on.

The derivative of Eq. (6c) can be presented as follows:

\[
y'' = -0.0322 \cdot p_{H_2O} \cdot \left( \bar{\sigma}_T \cdot m_f - \bar{\sigma}_W \cdot m_w \right)'' = -0.0322 \cdot p_{H_2O} \cdot \left( \bar{\sigma}_T \cdot m_f - \bar{\sigma}_W \cdot m_w \right) \tag{14}
\]

Supposing that \( \bar{\sigma}_T \approx \bar{\sigma}_W \), the above equation can be simplified as:

\[
y'' = -0.0322 \cdot p_{H_2O} \cdot (\bar{\sigma}_T \cdot m_f - \bar{\sigma}_W \cdot m_w)'' = -0.0322 \cdot p_{H_2O} \cdot \bar{\sigma}_T \cdot m_f - \bar{\sigma}_W \cdot m_w \tag{14b}
\]

In addition, Eqs. (15) and (16) can be obtained by the relationship of mass conservation.

\[
y'^{\mu} \cdot m_w + m_w \cdot y'' = V' \cdot m_f + m_f \cdot y' \tag{15}
\]

\[
m_f = 0.5C_0 - m_w \cdot V'^{\mu} = 0.5C_0 - m_w \cdot V' \tag{16}
\]

Thus, considering Eqs. (14b), (15), (16) comprehensively, calculation formula of \( a_0 \) can be expressed as follows:

\[
a_0 = \frac{y'}{y''} = -0.0322 \cdot p_{H_2O} \cdot \bar{\sigma}_T \cdot m_f - \bar{\sigma}_W \cdot m_w \tag{14b}
\]

\[
= -0.0322 \cdot p_{H_2O} \cdot \bar{\sigma}_0 \cdot \left[ \frac{0.5C_0}{1 - V'} - m_f \cdot \frac{y'}{y''} \right] \tag{14b}
\]

As seen from the calculation formula, it is obvious to see that \( a_0 \) is affected by many factors, such as \( p_{H_2O}, \bar{\sigma}_0, C_0, \).

4.2. Average mean activity coefficient (\( \bar{\gamma}_T \)) and average osmotic coefficient (\( \bar{\varphi} \))

In this study, NaCl aqueous solution was used as the model system, so \( Z_+ = 1, Z_- = -1 \) and \( |Z_+, Z_-| = 1 \). The entire experiment was operated at 25 ± 1°C, so \( A_1 \) is equaled to 0.511 kg^{1/2}mol^{1/2} approximately. And as stated in the reference [29], result of plentiful experiments shows that \( \rho = 1.0 \) and \( \rho Z_+, Z_- = 1.5 \) is satisfactory to within the accuracy of the data, even to 200°C. Therefore, sum it up, in Eqs. (10)-(13), these specific parameters can be assigned as follows:

\[
|Z_+, Z_-| = 1, B = 0.0574, a = 1.5, A_1 = 0.511, \rho = 1.0 \tag{17}
\]

Based on these, Eqs. (10)-(13) can be further simplified:

\[
\phi = \frac{1}{\bar{\varphi}} = \frac{1}{3} \cdot \frac{\sigma(\bar{\varphi})}{1 - \sigma(\bar{\varphi})} \cdot (\sigma(1.5\bar{\varphi}) - 0.0661) \tag{10a}
\]

\[
\log y'_{\bar{\gamma}} = \frac{\sigma(\bar{\varphi})}{1 + \bar{\varphi}} \cdot \frac{0.941}{1 + (1.5\bar{\varphi})^2} + 0.0574l \tag{11a}
\]

\[
\sigma(\bar{\varphi}) = \frac{3}{\bar{\varphi}} \left[ 1 + \bar{\varphi} - \frac{1}{1 + \bar{\varphi}} - 2ln(1 + \bar{\varphi}) \right] \tag{12a}
\]

\[
\varphi(1.5\bar{\varphi}) = \frac{4}{3} \left[ \frac{1 + 3\bar{\varphi}}{(1 + (1.5\bar{\varphi})^2)} \right] \frac{ln(1 + 1.5\bar{\varphi})}{1.5\bar{\varphi}} \tag{13a}
\]

As seen from Eqs. (10a, 11a, 12a, 13a), the four equations are all only related with ionic strength (I). The calculation formula of ionic strength is expressed as follows:

\[
I = \frac{1}{2} \sum m_t \cdot (Z_t)^2 \tag{17}
\]

where \( m_t \) and \( Z_t \) are molality and chemical valence of ion \( B \), respectively. Here a prior statement is needed: strictly speaking, molar concentration and molality are two different concepts, and their values are popularly not equal; and in this study, to simplify the research process, the value of molar concentration is regarded as the same as that of molality approximately. In order to confirm the validity, a numerical comparison between them is made and the result is shown in Table 2. It can be observed that the relative deviation is relatively small, especially at the case of low concentration, the deviation equals to zero basically.

Based on above discussions, once the solution molar concentration is known, it is convenient to calculate the mean activity coefficient and osmotic coefficient. During the diffusion dialysis process, the concentrations of diffusate solution and dialysate solution change with time, as a result, mean activity coefficient and osmotic coefficient of the two solutions change over time accordingly. So in order to simplify the problem, average mean activity coefficient (\( \bar{\gamma}_{\bar{T}} \)) and average osmotic coefficient (\( \bar{\varphi} \)) were used, and Table 3 shows average mean activity coefficient and average osmotic coefficient of dialysate solution and diffusate solution (\( \bar{\gamma}_{\bar{T}} \), \( \bar{\varphi} \), \( \bar{\varphi} \)) at different feed concentrations, respectively. As known the average mean activity coefficient and average osmotic coefficient, the chemical potential difference can be calculated out:

\[
\Delta H_{H_2O} = \mu_{H_2O}^\mu - \mu_{H_2O}^\mu = 0.001RT_{H_2O}(m_f \bar{\sigma}_T - m_w \bar{\sigma}_W) = 0.002RT_{H_2O}(m_f \bar{\sigma}_T - m_w \bar{\sigma}_W) \tag{18}
\]

\[
\Delta H_{NaCl} = \mu_{NaCl} - \mu_{NaCl} = 2RT \ln(\bar{\gamma}_{\bar{T}} \cdot m_f - \bar{\gamma}_{\bar{T}} \cdot m_w) = 2RT \ln(\bar{\gamma}_{\bar{T}} \cdot m_f - \bar{\gamma}_{\bar{T}} \cdot m_w) \tag{19}
\]

4.3. Permeability coefficients

Substituting Eqs. (18) and (19) into Eqs. (5) and (6) can be drawn to calculate the permeability coefficients:

\[
R_{H_2O} = -\frac{1}{2} \frac{V' \cdot \frac{\partial^2 \bar{\varphi}}{\partial z^2} + \frac{\partial \bar{\varphi}}{\partial \bar{T} \cdot m_f}}{2RT \ln(\bar{\gamma}_{\bar{T}} \cdot m_f - \bar{\gamma}_{\bar{T}} \cdot m_w)} \tag{5a}
\]

\[
R_{NaCl} = -\frac{1}{2} \frac{m_t \cdot \frac{\partial \varphi}{\partial \bar{T} \cdot m_f}}{0.002RT_{H_2O}(m_f \bar{\sigma}_T - m_w \bar{\sigma}_W)} \tag{6a}
\]

During the calculation process, it can be wondrously found that the two coefficients change with operation time. However, theoretically speaking, once a diffusion dialysis process, including the ion

<table>
<thead>
<tr>
<th>Item</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molality (mol/kg)</td>
<td>0.02</td>
<td>0.04</td>
<td>0.08</td>
<td>0.12</td>
<td>0.16</td>
<td>0.20</td>
<td>0.24</td>
<td>0.28</td>
</tr>
<tr>
<td>Mole concentration (mol/L)</td>
<td>0.02</td>
<td>0.04</td>
<td>0.08</td>
<td>0.12</td>
<td>0.16</td>
<td>0.20</td>
<td>0.24</td>
<td>0.28</td>
</tr>
<tr>
<td>Relative deviation (%)</td>
<td>0.40</td>
<td>0.25</td>
<td>0.28</td>
<td>0.34</td>
<td>0.46</td>
<td>0.54</td>
<td>0.60</td>
<td>0.68</td>
</tr>
</tbody>
</table>
exchange membrane used and feed disposed, was fixed, permeability coefficient would be a constant. The reason is that there exist experimental deviations in actual experimental operation inevitably. Eqs. (18) and (19) provide the calculation method of experimental value of chemical potential difference, while Eqs. (5) and (6) represent the calculation method of theoretical value. An optimal value of $P_{\text{NaCl}}$ and $P_{H_2O}$ should be found to make the value of $F(P_{\text{NaCl}})$ and $F(P_{H_2O})$ in Eqs. (20) and (21) minimum. The sixth and eighth columns of Table 3 depict the optimal $P_{\text{NaCl}}$ and $P_{H_2O}$ at different feed concentrations.

$$F(P_{\text{NaCl}}) = \sum_{i=1}^{n} \left( \frac{\Delta \mu_{\text{NaCl,exp}}^{i} - \Delta \mu_{\text{NaCl,th}}^{i}}{J_{\text{NaCl,exp}}^{i}} \right)^{2}$$ (20)

$$F(P_{H_2O}) = \sum_{i=1}^{n} \left( \frac{\Delta \mu_{H_2O,exp}^{i} - \Delta \mu_{H_2O,th}}{J_{H_2O,exp}^{i}} \right)^{2}$$ (21)

As known the value of optimal $P_{\text{NaCl}}$ and $P_{H_2O}$, the next step is to investigate the accuracy of the mathematical model. Analyzing the calculation process of optimal $P_{\text{NaCl}}$ and $P_{H_2O}$, it is not difficult to find that the entire process is based on an idealistic experimental condition: no mass transfer boundary layer exists, the flow state of solution is thoroughly turbulent, and the experimental deviation is too small to be ignored, and so on. However, in the actual experiment process, mass transfer boundary layer and experimental deviation inevitably exist, that the seriously turbulent flow state cannot be guaranteed absolutely, and also there are some non-idealized factors exist. As a result, modifying factors $\lambda$ and $\varphi$ were defined to describe the deviation between actual case and ideal case, and Eq. (7) can be transformed into another form as follows:

$$\frac{d\mu_{\text{NaCl}}^{i}}{dt} = \frac{A_{\text{NaCl}}}{V_{g}} \left( J_{\text{NaCl,exp}}^{i} - \frac{\mu_{\text{NaCl,exp}}^{i}}{R T} \right) \frac{\frac{\Delta \mu_{\text{NaCl}}^{i}}{J_{\text{NaCl,exp}}^{i}}}{\frac{\mu_{\text{NaCl,exp}}^{i}}{R T}}$$

$$= -A_{\text{NaCl}} J_{\text{NaCl}}^{i} \left( \frac{\mu_{\text{NaCl,exp}}^{i}}{R T} - \frac{\mu_{\text{NaCl,th}}^{i}}{R T} \right) \frac{\frac{\Delta \mu_{\text{NaCl,exp}}^{i}}{J_{\text{NaCl,exp}}^{i}}}{\frac{\mu_{\text{NaCl,exp}}^{i}}{R T}}$$

(7a)

As stated in literature [16], in this study, a similar method was used to determine the value of $\lambda$ and $\varphi$ in Eq. (7a). In order to understand easily, the detailed calculation process is summarized as follows:

(1) A numerical calculation of diffusate solution volume. As represented in Section 4.1, the curve of diffusate solution volume changes over time accords with the characteristics of quadratic polynomial approximately ($y = ax^2 + bx + c_0$).

(2) The estimation of $\lambda$ and $\varphi$ values and calculation of theoretical value of NaCl concentration in diffusate solution, i.e. $c_{\text{NaCl,th}}$, at the same time intervals as those during the actual experimental process. In order to calculate the value of $c_{\text{NaCl,th}}$, Eq. (7a) is numerically integrated through the Rung–Kutta fourth-order method.

5. Conclusions

In this study, diffusion dialysis process of single electrolyte (sodium chloride) solution was conducted in a conventional PFDD membrane module with DF-120 anion exchange membrane. Time dependence of volume and concentration of diffusate solution were determined. Chemical potential difference of solution was used as the mass transfer driving force in the transformative Fick’s law.
Firstly, the volume of H$_2$O which permeated through ion exchange membrane was investigated quantitatively, and results showed that diffusate fluid volume changes over time according with the characteristics of quadratic polynomial ($y=a_0+ a_1t^2 + b_{01} t + c_0$).

Secondly, the permeability coefficients of membrane to H$_2$O ($P_{H_2O}$, $P_{H_2O}^n$) and NaCl ($P_{NaCl}$, $P_{NaCl}^n$) were used to quantify the diffusion dialysis process, and results illustrated that with an increase in feed concentration, $P_{NaCl}$ and $P_{NaCl}^n$ decreases, while $P_{H_2O}$ and $P_{H_2O}^n$ increases. In addition, when modifying factors $\lambda = 3.30$ and $\phi = 2.37$, the comparisons of theoretical and experimental concentrations of NaCl in diffusate solution showed that both $P_{H_2O}$ and $P_{NaCl}^n$ are satisfactory coefficients for characterizing the diffusion dialysis process.

In brief, the mathematical model discussed in this study can provide an effective method to deal with the mass transfer process of diffusion dialysis, especially, is helpful to select an optimum AEM to operate diffusion dialysis. Also since the solution volume change is considered, the mathematical model can be applied to diffusion dialysis process of whatever concentration feed. Further studies will focus on a binary electrolyte system.

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References