Diffusion and Osmotic Permeability of Ion Exchange Membrane MK-40 Using Sodium Chloride Solution

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ABSTRACT

Cation exchange membrane (MK-40) is a commercial membrane with a fixed group that is an important part of the electrodialysis (ED) process. Sodium chloride (NaCl) diffusion and osmotic permeability for MK-40 was studied. A cell containing two compartments was used to analyse the properties of the MK-40 membrane fixed between them. Furthermore, the influence of temperature, NaCl concentration, and operating time on MK-40 properties was investigated. The results showed that the highest diffusion permeability coefficient of NaCl was 7.37×10−9 (m²/s), and the maximum osmotic permeability coefficient of distilled water was 43.8×10−9 (m²/s) at NaCl solution concentration of 0.1 M and 50°C. Generally, the permeability was constant beyond 60 min of operational time. Additionally, the minimum diffusion permeability coefficients of the MK-40 membrane fell by about 22% over time when the concentration of NaCl solution was 1 M at 25°C. To conclude, membrane properties in the ED process depend on the two electrodes (a cathode and an anode), without the diffusion of salts particles. Meanwhile, the most important properties of cation exchange membranes (CEMs) used in electrodialysis are increased membrane efficiency when water and salts transport decrease through CEMs, which leads to a decrease in energy consumption. Thus, the MK-40 membrane showed a good
properties due to its low diffusion permeability for concentrated NaCl solution at elevated temperatures and minimum reduction in diffusion permeability of concentrated NaCl solution over time.

Keywords: Cation exchange membrane (MK-40), diffusion permeability, electrical conductivity, osmotic permeability, sodium chloride

INTRODUCTION

Industrial application of ion exchange membranes (IEMs) started with saltwater desalination, and membranes are widely used in many fields such as drinking water treatment, treated wastewater treatment, amino acid demineralisation, sugar liquor demineralisation, whey demineralisation, and purification of organic matter. Saline water desalination is the most appropriate and commonly used fundamental technology of these applications (Tanaka, 2011). Recent years have seen extensive use of IEMs in processes such as electrodialysis (ED), diffusion dialysis, dialysis of Donnan, and capacitive deionisation (Chaabouni et al., 2015). Owing to their chemical stability, water transport properties and desirable ion, IEMs have recently attracted considerable interest in membrane-based technologies (Geise et al., 2014a).

MK-40 is one of the heterogeneous cation ion exchange membranes in the form of a flat sheet (Vasil’eva et al., 2013). MK-40 composites are developed based on KU-2 cation exchange resins (a matrix of polystyrene (PS) cross-linked with divinylbenzene (DVB) and fixed groups), polyethylene and nylon (Melnikov et al., 2018). MK-40 rejects an ion with the same charge (co-ions) and enables the passage of oppositely charged ion (counter-ions) (Geise et al., 2014b). The main application of MK-40 in processes of water desalination (Andreeva et al., 2020). On the other hand, IEMs are considered a key component of electrodialysis (ED) systems. Their contribution to the process’s overall cost may be as large as 40 to 50 % (Mikhaylin & Bazinet, 2016). Therefore, the application of technologies utilizing IEMs is typically defined by the transport properties and costs of IEMs.

IEMs are mainly affected by several parameters: temperature, solution concentration, electrical conductivity, and flux time. Temperature is one of the most important characteristics that can affect the electrical conductivity and fluid flow, and the characteristics of IEMs. Therefore, it is very important to optimise the temperature (Karimi & Ghassemi, 2016). For instance, Guesmi et al. (2010) reported that different temperatures (10, 25, and 40°C) had significantly affected the ion exchange equilibrium of the system with CMX cation exchange membrane involving monovalent and divalent ions. Nevertheless, the salt concentration also influences the diffusion permeability, conductivity, and ion transport numbers (Sarapulova et al., 2019). For example, Geise et al. (2013) found that when the salt concentration increased from 0.58 to 58 g/L, the permeability of sodium chloride decreased by 16% in uncharged hydrogel and increased by more than 10% in charged polymers.
In this regard, diffusion and osmotic permeability are key indicators for IEMs characteristics. It can be measured by two-compartments cells used for calculating diffusion and osmotic permeability coefficients. The values of diffusion and osmosis depend on the size of the system, and on the concentration profiles of dilute and concentrate solutions, which are set by the application of the ED system (Chehayeb et al., 2019). Many methods have been used to determine the effect of solution properties on membrane diffusion permeability, such as solution concentration, temperature and flux time. For example, Kingsbury et al. (2018) studied the permeability of water and salt simultaneously using a two-chamber cell. One-half of the cells consisted of a NaCl solution, while the other half consisted of distilled water. In addition, a concentrated NaCl solution was selected to optimise the osmosis rate and promote water transport measurements. Furthermore, the non-flow two-chamber cell was used by Melnikov et al. (2018) to analyse the permeability of the diffusion. Half of the cell consisted of salt or acid, while the second half consisted of distilled water.

From the literature, permeation of co-ions of NaCl via diffusion and water by osmosis is a non-ideal movement that cannot be regulated by electrical fields and thus decreases the performance of electrochemical processes. Consequently, limiting non-ideal transport of water and salt (osmosis and salt diffusion) is a key objective to study the effect of some parameters on CEM (MK-40) performance (Gubari et al., In Press). To date, there are a few researchers who have evaluated the effect of discharged feed solutions and different distilled water temperatures on diffusion and osmotic permeability of CEMs in the ED process to verify the effectiveness of membrane separation. Therefore, this study aims to investigate the diffusion and osmotic permeability of MK-40 membrane, employing two compartments cell, using NaCl solution and distilled water, at different salt concentrations (0.1, 0.5 and 1 M) and different distilled water temperatures (25 and 50°C).

MATERIALS AND METHODS

Membranes and Reagents

The MK-40 membrane is effective for small-scale water desalination due to its low cost and long lifetime (Gubari et al., 2021). The copolymerisation of polystyrene obtained by Ion-exchange materials in the MK-40 membrane with divinylbenzene. “Shchekinoazot” (Russian) manufactured this membrane in the form of flat sheets (Vasil’eva et al., 2013). MK-40 membrane pore size distribution indicates two maxes, the first one approximately 10 nm and corresponding to micro and mesoporous, and the second relates to macropores around 1000 nm in sizes. The pores of the membrane MK-40 are positioned within the sulfonated ion-exchange particles (MK-40). The second pores type is the spaces in a membrane between various particles (Nikonenko et al., 2019). Table 1 collects the main features of commercial MK-40 membranes (Pismenskaya et al., 2012). In this study,
distilled water (electric conductivity of 4.5 µS cm\(^{-1}\); pH = 5.5; 25°C) and NaCl (≥99.7% purity) at different concentrations were used.

Table 1
Properties of commercial MK-40 membrane

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Cation exchange (MK-40)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion exchange groups, bulk</td>
<td>–SO(_3^−)</td>
</tr>
<tr>
<td>Idem, surface</td>
<td>–SO(_3^−)</td>
</tr>
<tr>
<td>Thickness, µm</td>
<td>480 ± 10</td>
</tr>
<tr>
<td>Ion exchange capacity, mM cm(^{-3}) wet</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>Ion exchange material surface fraction of, %</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>Contact angle, degrees</td>
<td>55 ± 3</td>
</tr>
<tr>
<td>Particular conductivity in solution 0.5 M NaCl, mS.cm(^{-1})</td>
<td>7.7 ± 0.3</td>
</tr>
<tr>
<td>Diffusion permeability, 10(^{-8}) cm(^2). s(^{-1})</td>
<td>6.7 ± 0.4</td>
</tr>
</tbody>
</table>

**Salt and Water Penetration Measurements**

The coefficients of salt diffusion were determined from the calculation of the self-diffusion, taking into account the diluting effects of osmosis in the gradient of salt concentration. In other word, the flow of water from the distilled water compartment dilutes the salt concentration in the other compartment over time, and reduces the driving force of diffusion and osmosis (Kingsbury et al., 2018). The permeability of diffusion was established by the amount transferred by the membrane of a substance over a surface unit per unit of time. Thus, the permeability coefficients of membranes for salt diffusion can be determined by the formula given in Equation 1 of the experimental salt permeability obtained from the reference for a steady flow of liquid from the salt compartment to the distilled water compartment (Alekseeva et al., 2012).

\[
P_s = \frac{C_2 \cdot V_2 \cdot X}{(C_1 - C_2) \cdot S \cdot t}
\]  

(1)

where: \(P_s\) is NaCl diffusion permeability, (m\(^2\)/s); \(C_1\) and \(C_2\) are the total concentration of the components in salt solution and water, respectively (mol/m\(^3\)); \(V_2\) is the volume of water at the end of the experiment (m\(^3\)); \(S\) is membrane operating area (m\(^2\)); \(X\) is the membrane thickness (m); \(t\) is the test time (s).

The water flow from compartment filled with distilled water to compartment filled with NaCl solution is measured by the change in the amount of solution in horizontal capillaries over a given period. The osmotic permeability coefficient is determined by Equation 2 (Alekseeva et al., 2012).

\[
P_w = \frac{n_w \cdot X}{(C_1 - C_2) \cdot S \cdot t}
\]  

(2)
where: $P_w$ is distilled water osmotic permeability (m$^2$/s); $n_w$ is the moles of distilled water transferred (mol). It was measured from volume change in the distilled water compartment.

**Experimental Setup**

Before the operational process, MK-40 is cleaned with a carbon tetrachloride solution and wait 15 minutes for the membrane to dry, and then cleaned with an ethanol solution and wait 15 minutes for the membrane to dry. After that, the membranes are placed in a saturated solution of sodium chloride (NaCl) for 24 hours and then placed in distilled water for 24 hours. Subsequently, MK-40 is placed in (0.1 M) of NaOH solution for 24 hours and then placed in distilled water for 24 hours. Then, the MK-40 is placed in (0.1 M) of HCl solution for 24 hours and then placed in distilled water until a neutral reaction. In the operational process, membrane coupons were fixed in the cell for 24 hours before operation to achieve pseudo-stable osmosis and diffusion.

In this experiment, a two-compartment cell was employed to study the permeability characteristics of MK-40, as shown in Figure 1. In order to do so, NaCl as a salt solution and distilled water as solvent were used. The volumes of the left half-cell contained NaCl solution, and the right half-cell contained distilled water were 550 cm$^3$ each. The membrane area was 31.4 cm$^2$, and its thickness was 1 mm. The cell was connected to the

![Figure 1. Schematic experiment diagram of two-compartment cell](image)
thermostat box to maintain the cell temperature, and each compartment was connected to the thermocouple to measure temperature of the compartments. Different concentrations of NaCl (0.1, 0.5 and 1 M) and temperatures of distilled water (25 and 50°C) were selected to monitor diffusion and osmotic rates.

The two compartments were immediately filled with new solutions and distilled water. Once an operation began, the NaCl solution chamber and the distilled water chamber were stirred at 300 rpm with magnetic stir bars. The salt diffusion coefficient and osmotic water coefficient were determined due to water moving into the high concentrated compartment due to the osmosis process, while the salt diffused through the membrane into the distilled water compartment due to a concentration gradient. Each compartment of the cell was sealed and connected to a capillary tube, which made it possible to measure the volume change in the compartment with high accuracy. Then, the conductivity of distilled water compartment was measured over 15 min transition periods for each experiment, and the calibration curve using NaCl standard solutions converted these conductivity measurements to salt concentration. Finally, the salt diffusion coefficient and distilled water osmotic coefficient were measured using Equations 1 and 2, respectively.

RESULTS AND DISCUSSION

There are many properties of ion exchange membrane that influence salt diffusions, such as membrane chemical structure and water content. Diffusion of salt and osmosis of solvent are key factors that lead to variations in permeability of commercial MK-40 membrane. This study used, NaCl as a salt and water as a solvent, and the results were discussed below.

Diffusion Permeability of NaCl

Diffusion permeability coefficients of NaCl were calculated using Equation 1. Figure 2 presents the NaCl diffusion permeability coefficients at two distilled water temperatures (25 and 50°C), NaCl concentrations (0.1, 0.5 and 1 M), and 20 min transition periods. Over operational time of 20 to 100 min, when NaCl concentration was 0.1, 0.5 and 1 M, Figure 2 (a) showed that NaCl diffusion permeability coefficient decreased from $2.31 \times 10^{-9}$ to $1.76 \times 10^{-9}$ (m$^2$/s), $2.19 \times 10^{-9}$ to $1.62 \times 10^{-9}$ (m$^2$/s) and $1.97 \times 10^{-9}$ to $1.53 \times 10^{-9}$ (m$^2$/s) at temperatures of 25°C, respectively. During the same operational period, at NaCl concentration of 0.1, 0.5 and 1 M, Figure 2 (b) illustrated that NaCl diffusion permeability coefficient declined from $7.37 \times 10^{-9}$ to $3.88 \times 10^{-9}$ (m$^2$/s), $6.41 \times 10^{-9}$ to $3.54 \times 10^{-9}$ (m$^2$/s) and $5.41 \times 10^{-9}$ to $3.15 \times 10^{-9}$ (m$^2$/s), when temperature was 50°C, respectively.

Drop-in NaCl diffusion permeability coefficients could be due to water flux from diluted water compartment to salt solution compartment, lowering the driving force for diffusion and osmosis (Kingsbury et al., 2018). After about 60 min of operational time, NaCl diffusion permeability coefficients were approximately constant for both temperatures...
because of concentration polarisation resulting from increased salt concentration in the boundary layer near the surface of the membrane (Melnikov et al., 2018). It prevents salt penetration through the membrane, explaining why the diffusion permeability was approximately constant after 60 minutes of operation.

MK-40 membrane showed low permeability to NaCl, which results in minimising energy losses in the electrodialysis process. In comparison, Kamcev et al. (2018) investigated NaCl diffusion permeability coefficients of cation exchange membrane (CR61), using a high NaCl concentration of 1 M. They found that diffusion permeability coefficients were $1.7 \times 10^{-10}$ (m²/s).

Figures 2(a) and 2(b) both revealed that a higher temperature of 50°C has led to higher permeability than 25°C. It could be because the higher temperature can enhance the permeation rate and accelerate the ions transport across membranes (Luo et al., 2010). To date, there are very few studies reporting the diffusion permeability of membranes at high temperatures. It can be noticed that higher salt concentration has significantly decreased the diffusion permeability coefficients of MK-40 membrane. Over an operational period of 20-100 min, when the NaCl concentration increased from 0.1 M to 1 M, NaCl diffusion permeability coefficients of the MK-40 membrane fell by about 24%-22% and 47%-41%, for the temperature of 25 and 50°C, respectively. It indicates that the MK-40 membrane is uncharged due to decreased polymer’s water content as salt concentration increases. In contrast to charged membranes, when salt concentration increases, the salt diffusion permeability coefficients increase (Geise et al., 2013).

Tanaka (2011) investigated that when the temperature of ion exchange membranes such as Selemion CMR/ASR and Neoepta CIMS/ACS3 increased from 25°C to 50°C, the overall hydraulic permeability was increased from $(1.116 \times 10^2$ to $1.937 \times 10^2)$ cm^4.eq.^{-1}.s^{-1} and $(1.254 \times 10^2$ to $1.835 \times 10^2)$ cm^4.eq.^{-1}.s^{-1}. It confirms that when using a higher operating temperature, the membrane’s diffusion permeability will increase, which will
lead to a decrease in the efficiency of the MK-40 membrane. According to Gatapova et al. (2020), an ion-exchange membrane (MK-40) diffusion permeability coefficient for a NaCl solution under thermostatic and thermodynamic conditions has been investigated. They found a significant difference in diffusion coefficient values when operating at the same temperature compared to the temperatures difference on both sides.

**Osmotic Permeability of Solvent**

Various experiments were performed to investigate the transport of solvents in ion-exchange membranes (Alekseeva et al., 2012, Kingsbury et al., 2019). In this study, the water transport occurs as free water (osmosis), not as bound water (electro-osmosis). The osmotic permeability coefficients of distilled water were calculated using Equation 2. Over an operational period of 20-100 min, Figure 3 showed the osmotic permeability coefficients of distilled water at two distilled water temperatures (25 and 50°C), NaCl concentrations (0.1, 0.5 and 1 M), and 20 min transition periods. Over operational time of 20 to 100 min, when NaCl concentration was 0.1, 0.5 and 1 M, Figure 3 (a) showed that NaCl osmotic permeability coefficient decreased from 3.57×10^{-9} to 1.58×10^{-9} (m²/s), 2.09×10^{-9} to 0.8338×10^{-9} (m²/s) and 0.948×10^{-9} to 0.2×10^{-9} (m²/s) at temperatures of 25°C, respectively. On the other hand, under the same operating conditions, at NaCl concentration of 0.1, 0.5 and 1 M, Figure 3 (b) illustrated that the NaCl diffusion permeability coefficient declined from 43.8×10^{-9} to 21.13×10^{-9} (m²/s), 29.66×10^{-9} to 9.75×10^{-9} (m²/s) and 10.53×10^{-9} to 3.73×10^{-9} (m²/s), when the temperature was 50°C, respectively.

Decreasing osmotic permeability coefficients could be due to high salt concentration gradients lead to increase water flux from diluted water compartment to salt solution compartment due to osmosis (Kingsbury et al., 2018). Therefore, it is concluded that salt concentration’s gradients should be essentially low to minimise the distilled water’s flow

![Figure 3](image-url)

*Figure 3. Water permeability coefficients at two different distilled water temperatures, (a) 25°C and (b) 50°C, using different NaCl concentrations, 0.1, 0.5, and 1 M, over 100 min operational time*
due to osmosis, which increases the osmotic permeability coefficient. Furthermore, it could be due to concentration polarisation resulting from increased NaCl concentration in the membrane boundary layer (Melnikov et al., 2018). Osmotic permeability coefficients were also approximately constant for both temperatures (25°C and 50°C) after 60 minutes of operation.

A few studies have examined the influence of temperature on osmotic performance. Zhao and Zou (2011) studied the effect of temperature on membrane performance during osmosis desalination, and their results confirmed that the flux increases with increasing temperature. Kingsbury et al. (2018) investigated the water permeability coefficient of CEM (Nafion N115) using 4 M of NaCl solution; the results were $1.13 \times 10^{-10}$ (m$^2$/s). It can be concluded that the CEM membrane type (MK-40) has a low permeability to water, which results in minimising energy losses. It is noted that an increase in the overall NaCl solution concentration and an increase in distilled water temperature significantly affect osmotic permeability coefficient. Eventually, the findings showed that higher permeability of water was correlated with higher permeability of salt.

CONCLUSION
The diffusion and osmotic permeability have been successfully studied to characterize the heterogeneous cation exchange membrane (MK-40) using different concentrations of NaCl solution and distilled water temperatures. Salt concentration and water temperature were among the most important parameters affecting the diffusion and osmotic permeability of MK-40. The uncharged MK-40 membrane had low permeability to salt, which results in minimising energy losses. Nevertheless, the MK-40 membrane revealed that as the salt concentration of the external solution decreases, the diffusion permeability of the membrane increases. Since osmotic pressure is a linear function of solution concentration, osmotic water transfer increases linearly with increasing salt concentration. On the other hand, the temperature and flux time affected the diffusion and osmosis permeability of the membrane. For example, at a distilled water temperature of 50°C, the osmotic permeability coefficient of MK-40 was significantly higher than at 25°C.

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REFERENCES


