FABRICATION OF ANION EXCHANGE MEMBRANE: A PRELIMINARY STUDY

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ABSTRACT

The objective of the work was to fabricate an anion exchange membrane, which can be used for electrodialysis process. The anion exchange membranes were fabricated by means of solution casting method using polysulfone as the binder and anion exchange resin as the polyelectrolyte. The membranes characteristics and performance of the fabricated membranes were evaluated and compared with the commercial anion exchange membranes. The membrane thickness, permselectivity, water content, ion exchange capacity, concentration of ion exchange group and morphological properties of the membranes were studied. The results showed that the percentage of anion exchange resin determine the capacity of ion exchange, percentage of permselectivity and capacity concentration of ion exchange group.

Keywords: Anion exchange membrane; Electrodialysis; Polysulfone; Ion exchange resin; Membrane characterisation

INTRODUCTION

Membranes separation process is becoming important for industrial and domestic applications. Various membranes have been developed for nanofiltration, pervaporation, microfiltration, ultrafiltration, reverse osmosis and electrodialysis. Ion exchange membranes are used in the electrodialysis membrane separation processes. An ion exchange membrane is the membrane that carries fixed positive and negative charges [1]. The ion exchange membranes consist of polymer matrix with three-dimensionally cross-linked construction and fixed charge groups. The basic polymer matrix and the fixed charge ion determine the properties of ion exchange membranes such as the mechanical, chemical and thermal stability of the membrane. The objective of this research was to develop ion exchange membranes using the ion exchange resin and evaluate their characteristic and performance.

EXPERIMENTAL

Materials

The following materials were used to prepare the membranes; all of them are used as received.

a) Polysulfone (Amoco Corp., Udel 1700).
b) 1, 1, 2, 2-Tetrachloroethane (Fluka) as solvent with a refractive index of 1.494 at 25°C.
c) Anion-exchange resin Amberlite IRA-410 Cl (Fluka), with an exchange capacity of 1.4 meq/ml (3.8 meq/g-dry resin) and screen grading 16 to 50 mesh.
d) Non-woven fabric (Asahi Kasei Corp., Japan)

Methods

Anion-exchange resin particles were dried in an oven at 65°C for 24 hour, powdered and sieved to the desired mesh size of 80 to 100 mesh. The finely powdered ion exchange resin was dispersed in solution of polysulfone and mixed into 1, 1, 2, 2-Tetrachloroethane. This resulting viscous solution was then cast on glass plate and overlapped by non-woven fabric. The prepared membranes were dried at room temperature for 3 hours. Different percentages resin was used to prepare the membranes. Six of anion exchange membranes samples were prepared based on the percentage in loading of resin and were labelled as BERL–A30, BERL–A40, BERL–A50, BERL–A60, BERL–A70 and BERL–A80.

Characterisation of Anion Exchange Membranes

The ion exchange membranes were characterized by evaluating their physico-chemical properties such as membrane thickness, permselectivity, ion exchange capacity, water content and concentration of ion exchange group. In addition, the membrane morphology was studied by using the scanning electron microscopy (SEM). The obtained results were compared with the properties of commercially available membranes. Detail of these measurements and methods of the characteristic of ion exchange membrane is outline in the following section.

Membranes thickness. The membrane thickness is an important property in the membrane study because it is directly influence the mechanical strength, electrical resistance, and permselectivity of the membrane. The thickness of ion exchange membranes was measured by a portable thickness meter. The thickness measurement device is accurate to 0.01 mm.

Membranes permselectivity. The permselectivity of ion exchange membrane is defined as the difference between the transports of electrical charges by specific counter-ions to the total transport of electrical charge through the membrane [1]. It is known that the cross-linking density, the concentration of electrolytes and the ion exchange capacity affect the degree of permselectivity in the membrane. A test equipment consists of two cells was used to determine the permselectivity. The ion exchange membrane was placed between the diluting and concentrating compartment. Under this arrangement a concentration gradient occurred across the membrane. The membrane potential was measured by two calomel reference electrodes, which were placed in the diluting and concentrating compartments. In the concentrating compartment, a 0.1 M KCl solution was circulated through the cell, while in the diluting compartment, 0.5 M KCl solution. All the measurements were carried out at 25°C. In this arrangement one of the ions in the solution would pass through the testing membrane until the both compartment reach equilibrium. The potential difference takes 10 - 20 minutes to reach a steady state value. Then, the permselectivity of the membrane (α) can be calculated according to Equation 1 [1, 2]:

$$\alpha = \frac{\Delta V_{meas}}{\Delta V_{calc}} \times 100\,[\%] \qquad (1)$$

Where ΔV_{meas} and ΔV_{calc} is the measured potential difference between the calomel electrodes and the potential difference calculated for a 100% permselective membrane. For a system consisting of standardized aqueous solution of 0.1 and 0.5 M KCl solution, the calculated potential difference is 36.94 mV. It is calculated using the Nernst equation [1]:

$$\Delta V_{calc} = \frac{RT}{zF} \ln \frac{C_2 \gamma_2}{C_1 \gamma_1} \qquad (2)$$

Where R is the gas constant (8.13 J.mol^{-1}.K^{-1}), T is the temperature (K), z is the electrochemical valence, F is the Faraday constant (96,490 C.mol^{-1}), C_1 and C_2 are the concentrations of the solutions and γ_1 and γ_2 are the corresponding activity coefficients. It is important to note that before running the experiment, the ion exchange membrane should be equilibrated with a 0.1 M KCl solution for 24 hours.

Ion exchange capacity. The ion exchange capacity of ion exchange membrane was determined by acid-base titration method. For the anion exchange membrane, a dried sample of anion exchange membrane (2 × 2 cm^2) was initially brought in the OH^- form by immersion into a 1 M NaOH solution for 24 hours at room temperature with gentle agitation. After rinsing the sample with deionised water, it was placed in a 2 M NaCl solution to exchange the hydroxyl ions with the chloride ion. The amount of hydroxyl ions released was then determined by back titration with 1 M of HCl solution. The ion exchange capacity was calculated via the Equation 3 [2]:

$$\text{IEC} = \frac{\text{Volume of HCl (ml)} \times \text{Molarity of HCl}}{\text{Weighted dried membrane}} \left[\frac{meq}{g}\right] \qquad (3)$$

Water content. The membrane was initially equilibrated in a 0.5 M NaCl solution for 24 hours. This step will change the membrane into Na^+ and Cl^- form. The membrane was then immersed in deionised water for 3 days at the room temperature. After the soaking step its surface moisture was wiped and the wet membrane was weighed. The weighed wet membrane W_{wet} was dried at a constant

temperature (80°C) until a constant weight W_{dry} was obtained. The membrane water content can be calculated using Equation 4 [1, 2, 3]:

$$\text{Water content} = \left(\frac{W_{wet} - W_{dry}}{Wwet}\right) \times 100\,[\%] \tag{4}$$

Concentration of ion exchange group. The results of ion exchange capacity and water content were used to calculate the concentration of ion exchange group of the ion exchange membranes by using Equation 5 [5]:

$$\text{Concentration of ion exchange group, } A_w = \frac{\text{Ion exchange capacity, } IEC}{\text{Water content, } W} \left[\frac{\text{meq}}{\text{g.H}_2\text{O}}\right] \tag{5}$$

Membrane morphology. The morphology of ion exchange membranes was studied using scanning electron microscope (SEM). The sample of membrane with the membrane area size of 1 cm × 1 cm was mounted onto the aluminium stub. The sample was then sputter-coated with gold prior to macroscopic observation. Finally, the sample was put into the SEM apparatus for scanning the surface and cross section of the membrane structures.

RESULTS AND DISCUSSIONS

The physical characteristic of anion-exchange membranes, which were prepared from polysulfone and different resin loading, are presented in Figure 1.

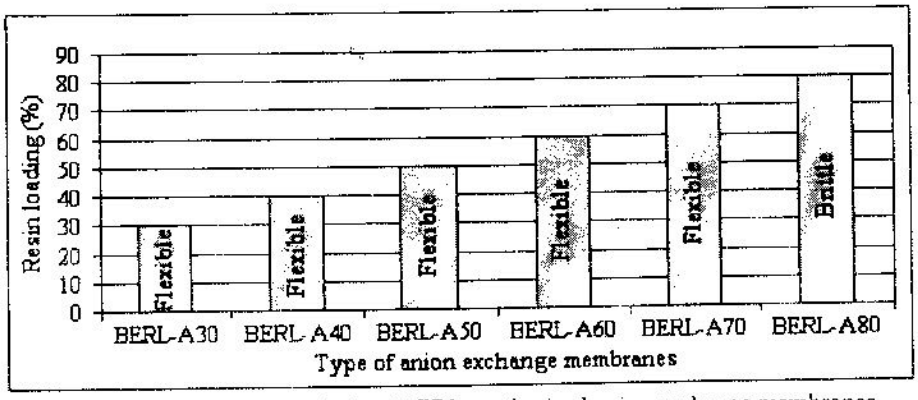


Figure1: Physical characteristic of BERL synthesized anion exchange membranes.

The results show that the membranes containing 80% and above of resin loading are brittle in nature. This indicates that the compatibility of resin-binder decrease with the increase in resin loading. In addition with the increase in resin loading, beyond a certain point phase inversion takes place, and cross-linked polystyrene particles tend to form the continuous phase and polysulfone as the discrete phase. Polystyrene being more brittle in nature compared to plasticized polysulfone, fails to act as an impact modifier and crack propagation becomes facile, resulting in a brittle membrane. At any particular blend ratio the finer the resin particles, the more homogeneous the blend is, resulting in a more flexible membrane. The maximum resin loading is in the region of 70% for the optimum physical characteristic of anion exchange membranes.

Ion exchange capacity is one of the most important coherent properties of ion exchange membranes. It represents the number of ionic sites that can transfer the ions through the membrane. It also controlled the hydrophilic and the swelling behaviour as well as the water content of the membranes. Figure 2 shows the relationship between the water content and the ion exchange capacity for different resin loading of anion exchange membranes. Based on the obtained results observed that with an increase of the resin loading, the ion exchange capacity and water content increased.

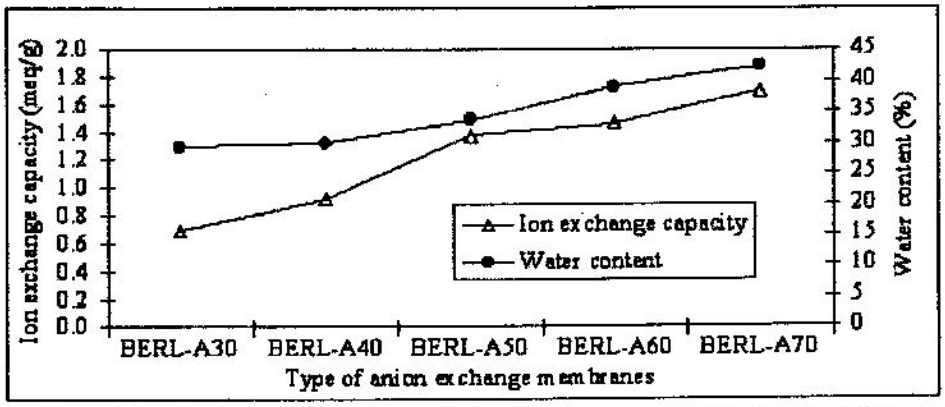


Figure 2: The relationship between the water content and the ion exchange capacity for different resin loading of anion exchange membranes.

This result shows that the fabricated anion exchange membranes possessed the ion exchange capacity in the range of 0.69 – 1.7 meq/g-dry-resin. The results are comparable with the range of ion exchange capacity of commercial anion exchange membranes, which is in the range of 1.00 to 1.50 meq/g.

The water content is an important behaviour in ion exchange membrane, since it would directly affect the electro-chemical properties of membrane. Such behaviour is due to the presence of the functional groups in the membranes. According to the data of commercial anion exchange membranes, the range of water content is from 29 to 44 g. H_2O/g. Thus, it was found out that the water content of the membranes synthesised in the laboratory are also in the similar range. The membrane water content depends on the ion exchange capacity of anion exchange membrane. The water content increases gradually with the increase in the ion exchange capacity.

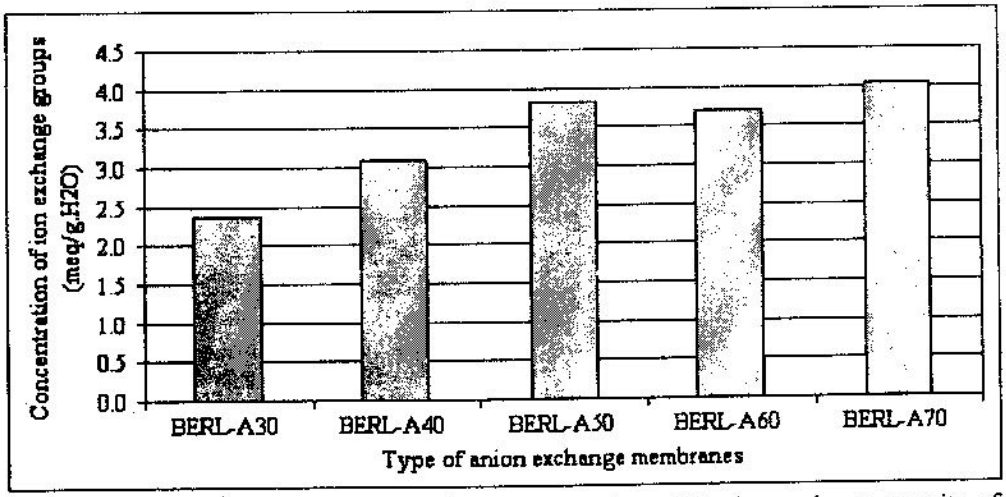


Figure 3: The relationship between the fixed ion concentration and the ion exchange capacity of the prepared anion exchange membranes at different resin loading.

Figure 3 illustrates the relationship between the fixed ion concentration and the anion exchange capacity of the prepared anion exchange membranes. An increase in the fixed ion concentration in the membrane, the ion exchange capacity is increased. In general, increasing the fixed ion concentration leads to an increase in ion exchange capacity. From the data in Figure 3, it indicates that to obtain a higher ion exchange capacity, the membrane should have a high fixed ion concentration.

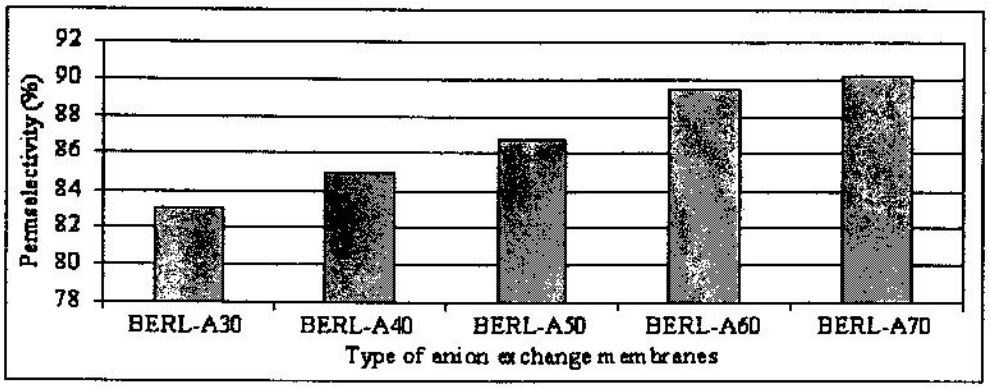


Figure 4: The relationship between the membrane permselectivity with the resin loading.

The permselectivity of ion exchange membrane is defined as the difference between the transports of electrical charges by specific counter-ions to the total transport of electrical charge through the membrane [1]. For a 100% perm-selective ion exchange membrane, all the current in the membrane is carried by the counter-ions. The results of the permselectivity of the fabricated anion exchange membranes are in the range of 83 – 91% as shown in Figure 4. It indicates that the leakage of co-ions through the membrane occurred during the electrodialysis process. Subsequently it would affect the purity of the product stream.

Table 1: Properties of commercial and synthesised ion exchange membranes.

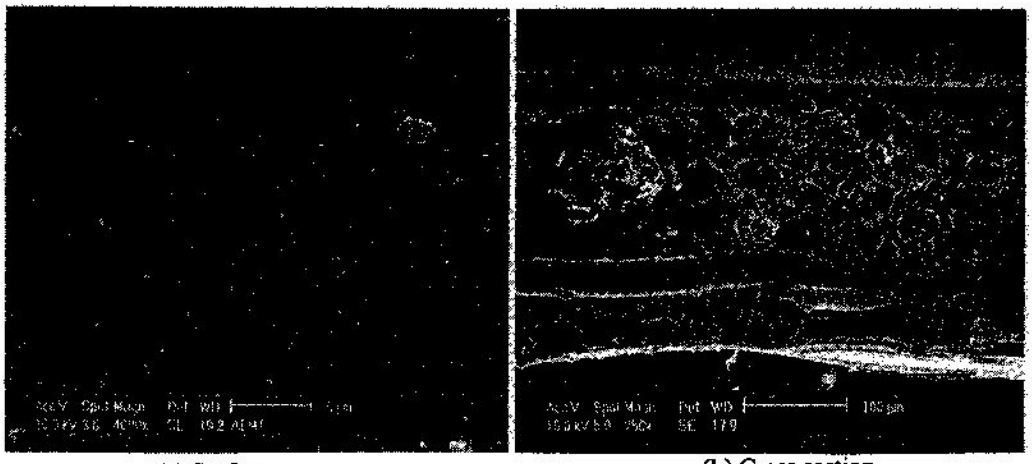
Types of anion exchange membranes	Resin loading (%)	Thickness of membrane (mm)	Perm-selectivity of membrane (%)	Ion exchange capacity (meq/g)	Water content (g. H_2O/g)	Concentration of ion exchange groups (meq/g. H_2O)
BERL-30[a]	30	0.33	83.0	0.69	29.20	2.36
BERL-40[a]	40	0.33	85.0	0.92	29.70	3.09
BERL-50[a]	50	0.34	86.8	1.38	33.60	3.83
BERL-60[a]	60	0.34	89.5	1.47	38.87	3.78
BERL-70[a]	70	0.37	90.2	1.70	42.42	4.05
AMI-701[b]	-	0.43	95.0	1.10	23.75	4.62
AHA[c]	-	0.19	95.0	1.37	28.09	4.91
AM1[c]	-	0.13	99.1	1.95	38.60	5.07
AM3[c]	-	0.12	99.5	1.98	31.53	6.31

[a] BERL-30, BERL-40, BERL-50, BERL-60, BERL-70 from Universiti Teknologi Malaysia;
[b] AMI-701 from Membranes International Inc., USA;
[c] AHA, AM3, AM1 from Tokuyama Soda, Japan.

Table 1 shows the properties of commercial and fabricated ion exchange membranes. Micrographs of the surface and cross section of the membrane obtained with a scanning electron microscope (SEM) are shown in Figure 5. The cross section was obtained by breaking the membrane at liquid nitrogen temperature. Its cross section consist of four layers: the polysulfone on the top and the bottom of the membrane, the anion exchange resin in the middle of the membrane and the non-woven fabric is below the resin for improving the membrane mechanical strength. It was seen that the fabricated membrane is an asymmetric membrane.

CONCLUSIONS

The results show that the fabricated ion exchange membranes are comparable with the commercial membranes. The fabricated anion exchange membranes, which was prepared from polysulfone does not require multiple preparation steps. The work indicates that the membrane properties are significantly affected by the percentage of resin loading: with an increase of resin loading will bring about an increase in ion exchange capacity, water content and permselectivity.



(a) Surface (b) Cross section

Figure 5: SEM photographs of the surface and cross section of the fabricated anion-exchange membrane.

LIST OF SYMBOLS

W_{wet}	Weight of wet resin, g
W_{dry}	Weight of dry resin, g
Wc	Water content, g-H_20/g-dry-resin
IEC	Ion exchange capacity, Meq/g
SEM	Scanning electron microscope
A_w	Concentration of ion exchange group
α	Permselectivity
M	Molar

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