



## Preparation and characterization of high-performance anion exchange membranes for acid recovery

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### ABSTRACT

In this research, a series of homogeneous 3-(dimethylamino)-2,2-dimethyl-1-propanol (DMADMP)-functionalized anion exchange membranes (AEMs) were prepared via solution casting method. The successful preparation of AEMs was confirmed by employing Fourier transform infrared spectroscopy. The prepared membranes denoted homogeneous structure confirmed by utilizing scanning electron microscopy. The prepared AEMs were characterized in terms of water uptake ( $W_R$ ), linear swelling ratio (LSR), ion exchange capacity (IEC), thermal, chemical and mechanical stability. They exhibited water uptake of 23% to 68%, LSR of 8% to 31% and IEC of 1.46 to 2.66 mmol/g. They exhibited excellent thermal, chemical and mechanical stability. The acid recovery performance of the prepared DMADMP-functionalized membranes was evaluated using simulated mixture of HCl and FeCl<sub>3</sub> as model feed via diffusion dialysis at room temperature. The diffusion dialysis coefficient of acid ( $U_{H^+}$ ) was 9 ( $10^{-3}$  m/h) to 32 ( $10^{-3}$  m/h) whereas the diffusion dialysis coefficient of metal ( $U_{Fe^{2+}}$ ) was 0.02 ( $10^{-3}$  m/h) to 1.9 ( $10^{-3}$  m/h). For the prepared membranes, the separation factor was 17–456 at ambient temperature. The diffusion dialysis performance of the prepared membranes was higher than commercial membrane DF-120B ( $U_{H^+} = 0.004$  m/h,  $S = 24.3$ ) at room temperature. Results represented that the prepared DMADMP-functionalized membrane could be employed as excellent candidate for acid recovery.

*Keywords:* Diffusion dialysis; Anion exchange membrane; DMADMP; Acid recovery

### 1. Introduction

With rapid industrialization, wastewater treatment has become a global issue. During many industrial processes including smelting, electroplating, mining, and metal surface treatment, inorganic acids are required for metal surface washing or metal leaching, which produces a huge volume of waste acid possessing metal ions, such as Fe<sup>2+</sup>, Zn<sup>2+</sup>, and Cu<sup>2+</sup> [1–4]. The discharge of wastewater from acid washing into the environment without any treatment results in serious environmental issues including water and soil pollution

[5–8]. Waste acid recovery and treatment methods mainly include pyrohydrolysis, precipitation, crystallization, electrodialysis [9,10], diffusion dialysis [11,12], neutralization, oxidation [13], and distillation concentration [14].

Diffusion dialysis using ion exchange membranes has become outstanding as a distinguished separation method. It was used to separate hydrated species due to concentration gradient [15]. It is notorious due to its capability of recovering acids and alkali from waste solutions [16,17]. It is better than other separation processes because of several leverages including simple installation, cost effectiveness,

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low energy and environmental benefactions [18–21]. Even then diffusion dialysis process still requires more work to attain complete success in acid/alkali recovery because of equilibrium concentration of species in solutions. As we know that the properties of ion exchange membranes are significant for the recovery of acid/alkali from waste solution. Therefore, the workers endeavor seriously to fabricate new ion exchange membranes, which will exhibit high acid/alkali recovery performance during diffusion dialysis process.

Ion exchange membrane is a crucial component which controls the diffusion dialysis performance. It can be classified into anion exchange membranes (AEMs) and cation exchange membranes (CEMs) due to type of ionic moiety into the membrane matrix. AEM as an important component of diffusion dialysis process has got great interest [16,22]. It plays a crucial role to selectively permit the flow of cations, which allow the separation of acid from waste solutions [23]. Due to smaller size and electro-neutrality requirement, proton also passes through AEM [24,25]. Therefore, diffusion dialysis process has been largely used in the recovery of sulfuric acid [26], hydrochloric acid [27], nitric acid [28], and a mixed acid [29,30].

AEMs are usually synthesized by linking cationic head groups with polymer architecture [31,32]. An ideal AEM must fulfill all the requirements such as acid permeability, moderate selectivity, metallic ion resistance, and good thermal and mechanical stability [33]. Many attempts have been made to improve these properties of AEMs. To attain this, different polymer architectures such as polyvinyl alcohol (PVA), brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO), polysulfone (PSf) and polystyrene were employed to fabricate AEMs [34]. The main issue of polyvinyl alcohol is that its membranes exhibited higher swelling in water particularly at elevated temperature [35]. The high price of raw material for polysulfone polymer makes it difficult to enlarge for applications [36]. Contrarily, the polystyrene backbone exhibited poor stability at higher temperature [37]. Currently, brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) is attracting higher attention because of its cheapness, and excellent thermo-mechanical properties. The use of BPPO for membrane synthesis as polymer architecture will remove the use of toxic material such as chloromethyl ether (CME) [38]. BPPO possesses an excellent hydrolytic stability, high class of transition temperature, and high mechanical stability. It exhibits excellent formation and functionalizable properties due to existence of highly reactive  $-\text{CH}_2\text{Br}$  group [39]. Moreover, the hydrophobic surface of PPO can be easily changed to hydrophilic surface via hydrophilic functionality. Motivated by these discussed excellent properties, we selected BPPO as polymer architecture in this work.

Contrarily, the functional group linked to the polymer architecture, which deduces the anion permeability, is also very crucial. Until now, several AEMs bearing different functional groups such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [22], 4-dimethylaminopyridine (DMAP) [40], tris(2-(2-methoxyethoxy)ethyl)amine (TDA) [41],  $\text{N,N,N',N'}$ -tetramethylethylenediamine (TEMED) [42],  $\text{N}$ -methylpyrrolidine [43], 1,4-diazabicyclo[2.2.2]octane [44], etc. have been synthesized for diffusion dialysis applications. However, these membranes are still limited for diffusion dialysis

process. Therefore, we shall introduce a novel 3-(dimethylamino)-2,2-dimethyl-1-propanol as a cationic head group to prepare AEMs for diffusion dialysis process. It also possesses hydroxyl groups that will act as assistant functional groups to enhance the transport of  $\text{H}^+$  ions through hydrogen bonding across the AEM in diffusion dialysis process [45,46]. Moreover, the existence of hydroxyl group may encourage the formation of an intermolecular hydrogen-bond network that could increase the mechanical properties of the prepared AEMs. These side chains are also responsible for higher thermal stability of membranes. The hydrophilicity of the prepared AEM was increased due to the presence of side chains in 3-(dimethylamino)-2,2-dimethyl-1-propanol, which is responsible for higher acid recovery performance.

In this manuscript, the synthesis of a series of homogeneous AEMs with different physico-chemical properties was described by introducing varying quantity of 3-(dimethylamino)-2,2-dimethyl-1-propanol into the polymer matrix. The prepared membranes were tested for acid recovery via diffusion dialysis process employing the simulated mixture of HCl and  $\text{FeCl}_2$  as model feed at ambient temperature. The acid recovery performance of the prepared membranes was compared with commercial membrane DF-120B under identical experimental conditions. The variation in ion exchange capacity (IEC), water uptake, linear swelling ratio (LSR), morphology, chemical, thermal, and mechanical stability of the attained AEMs as a function of 3-(dimethylamino)-2,2-dimethyl-1-propanol was also revealed and discussed in detail.

## 2. Experimental setup

### 2.1. Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was kindly provided by Sigma-Aldrich Chemicals (Germany). 2,2'-Azo-bis-isobutyronitrile (AIBN), chlorobenzene, ethanol,  $\text{N}$ -bromo-succinimide (NBS), chloroform,  $\text{N}$ -methyl-2-pyrrolidone (NMP), 3-(dimethylamino)-2,2-dimethyl-1-propanol (DMADMP), sodium chloride (NaCl), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), potassium chromate ( $\text{K}_2\text{CrO}_4$ ), silver nitrate ( $\text{AgNO}_3$ ), hydrochloric acid (HCl), ferrous chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), and methyl orange (MO), were kindly provided by Sinopharm Chemical Reagent Co. Ltd., China, and used as received. Throughout this work, deionized water was employed.

### 2.2. Bromination of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)

Bromination of PPO was carried out according to the previously reported method [47]. Initially, 6 g of PPO (50 mmol) was added into chlorobenzene (50 mL) in a round-bottom flask possessing a magnetic stirrer and refluxed condenser. After its complete dissolution, NBS (4.45 g, 25 mmol), and AIBN (0.25 g, 1.5 mmol) were added into solution of PPO and reaction mixture was heated at  $135^\circ\text{C}$  for 3 h. The reaction mixture was precipitated into excess of ethanol after cooling at room temperature. Attained polymer was washed several times and dried under vacuum for 48 h at  $40^\circ\text{C}$ . The degree of bromination was confirmed by using  $^1\text{H}$  NMR spectroscopy.

### 2.3. Fabrication of AEMs

In this research, a series of homogeneous AEMs were prepared by using solution casting method as reported in literature [48]. For this purpose, 0.8 g of brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) was added into N-methyl-2-pyrrolidone to get 8% (w%) solution. AEMs with different physico-chemical properties were prepared by adding 0.2, 0.3, 0.35 and 0.40 g of 3-(dimethylamino)-2,2-dimethyl-1-propanol (DMADMP) into casting solution. Table 1 represents detailed composition and theoretical ion exchange capacities of the prepared AEMs. The reaction mixture was stirred vigorously at 40°C for 12 h and then casted onto a glass plate at 60°C for 24 h. The resultant

membranes were peeled off from glass plates and cleaned with deionized water. The prepared membranes were assigned as DMADMP-25, DMADMP-38, DMADMP-44, and DMADMP-50, where 25, 38, 44, 50 refer to the weight percentage (w%) of 3-(dimethylamino)-2,2-dimethyl-1-propanol (DMADMP) in the membrane matrix. The chemical structure of the prepared AEMs is represented in Fig. 1.

### 2.4. Characterizations

#### 2.4.1. <sup>1</sup>H NMR and Fourier transform infrared tests

<sup>1</sup>H NMR (DMX 300 NMR spectrometer operating at 300 MHz) was used to confirm the successful bromination

Table 1  
Composition and theoretical ion exchange capacity of the prepared anion exchange membrane

Membranes	DMADMP-25	DMADMP-38	DMADMP-44	DMADMP-50
BPPO (g)	0.8	0.8	0.8	0.8
DMADMP (g)	0.25	0.30	0.35	0.40
IEC <sub>t</sub> (mmol/g)	1.53	2.08	2.32	2.72

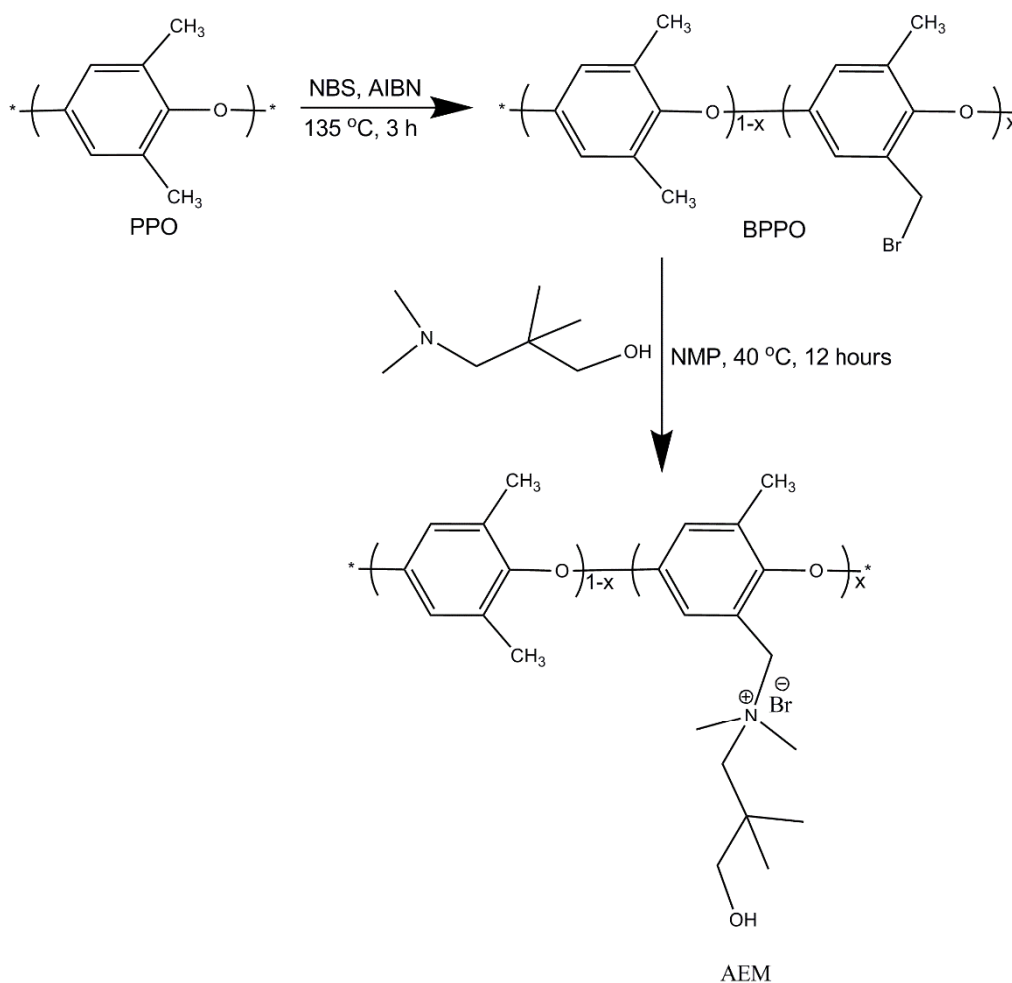


Fig. 1. Preparation of BPPO-based anion exchange membranes.

of PPO. The successful fabrication of AEMs was confirmed by attenuated total reflectance with Fourier transform infrared (FTIR) spectrometer (Vector 22, Bruker, Massachusetts, MA, USA) in the range of 4,000–400  $\text{cm}^{-1}$ .

#### 2.4.2. Ion exchange capacity

IEC of the prepared AEMs was determined by classical Mohr's method [44]. First, dried membrane samples were immersed in 1.0 M NaCl solution for 48 h such that all the charge sites were changed into the  $\text{Cl}^-$  form. The membrane samples were washed with distilled water to remove excessive NaCl, and then soaked in 0.5 M  $\text{Na}_2\text{SO}_4$  solutions for 48 h. The quantity of  $\text{Cl}^-$  ions released was measured by titration with 0.05 M  $\text{AgNO}_3$  employing  $\text{K}_2\text{CrO}_4$  as an indicator. It was measured by the equation given below:

$$\text{IEC} = \frac{C_{\text{AgNO}_3} V_{\text{AgNO}_3}}{m} \quad (1)$$

where  $m$ ,  $V$  and  $C$  show the dry mass of the membrane sample, titre value during titration and the concentration of  $\text{AgNO}_3$  solution, respectively.

#### 2.4.3. Water uptake and linear swelling ratio

Water uptake ( $W_R$ ) of the prepared AEMs was measured at room temperature by soaking dried membrane samples into deionized water. The wet weight of membranes was attained after removing surface water with a tissue paper. It was measured from difference in mass before and after drying the membranes by below relationship [49].

$$W_R = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (2)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  denotes wet and dry weights of the membrane, respectively.

LSR of the prepared AEMs was also revealed at room temperature. The membrane sample was cut into a ( $5 \text{ cm}^2 \times 5 \text{ cm}^2$ ) pieces for it. It was recorded from the following relationship [44]:

$$\text{LSR} = \frac{(L_{\text{wet}} - L_{\text{dry}})}{L_{\text{dry}}} \times 100\% \quad (3)$$

In Eq. (3),  $L_{\text{wet}}$  and  $L_{\text{dry}}$  represents wet and dry lengths of the prepared membrane samples, respectively.

#### 2.4.4. Morphology

Field emission scanning electron microscope (FE-SEM, Sirion 200, FEI Company, USA) was employed to reveal structural features of the prepared AEMs.

#### 2.4.5. Thermal and mechanical stability

Thermal stability of the prepared AEMs was elaborated by employing Shimadzu TGA-50H analyzer (Kyoto,

Japan) with a heating rate of  $10^\circ\text{C}/\text{min}$  within the temperature range of  $25^\circ\text{C}$ – $800^\circ\text{C}$  under nitrogen atmosphere. Mechanical stability of wet AEMs was studied by employing Q800 dynamic mechanical analyzer (DMA, TA Instruments, Kyoto, Japan) at a stretch rate of 0.5 N/min.

#### 2.4.6. Chemical stability

The chemical stability of the prepared AEMs was premeditated by immersing into  $\text{HCl}/\text{FeCl}_2$  feed solution at  $60^\circ\text{C}$ . It was recorded in terms of weight loss as a function of immersion time.

#### 2.4.7. Diffusion dialysis of $\text{HCl}/\text{FeCl}_2$ mixture

To evaluate acid recovery performance of the prepared DMADMP-functionalized AEMs, diffusion dialysis experiment was conducted in a two-compartment cell as reported in the literature [45,46]. It was separated by the membrane having an effective area of  $5.7 \text{ cm}^2$ . The prepared AEMs were conditioned in the feed solution ( $0.91 \text{ M HCl} + 0.25 \text{ M FeCl}_2$ ) for overnight and then washed with deionized water before utilizing into diffusion dialysis experiment. During diffusion dialysis experiment, one compartment of the cell was filled up with 100 mL feed solution while the other compartment with 100 mL deionized water. Then, both side solutions were stirred vigorously and equally to remove the concentration polarization. This experiment was conducted for 60 min for each sample. Finally, both feed and permeate were withdrawn from respective compartments of cell. The amount of  $\text{H}^+$  in both compartments was determined by titration method while  $\text{Fe}^{2+}$  amount was determined by inductive coupled plasma spectrophotometry (ICP, Optima 7300 DV).

The dialysis coefficients ( $U$ ) can be determined by using the below equation [33,45]:

$$U = \frac{M}{At\Delta C} \quad (4)$$

In Eq. (4),  $A$  shows the effective membrane area ( $\text{m}^2$ ),  $t$  depicts the time (h),  $M$  represents the concentration of component transported in (mol), and  $\Delta C$  shows the logarithm average concentration between the compartment chambers ( $\text{mol}/\text{m}^3$ ).  $\Delta C$  was calculated from below relationship [40]:

$$\Delta C = \frac{C_f^0 - (C_f^t - C_d^t)}{\ln \left[ C_f^0 / (C_f^t - C_d^t) \right]} \quad (5)$$

where  $C_f^0$  and  $C_f^t$  are feed concentrations at time 0 and  $t$ , respectively, and  $C_d^t$  is the dialysate.

Dialysis coefficients  $U_{\text{H}}$  and  $U_{\text{Fe}}$  can be determined using the above equations (Eqs. (4) and (5)). The separation factor ( $S$ ) is the ratio of dialysis coefficients ( $U$ ) of the two species present in the solution. It can be calculated by the following equation [33]:

$$S = \frac{U_{\text{H}}}{U_{\text{Fe}}} \quad (6)$$

### 3. Results and discussion

#### 3.1. Synthesis of BPPO

Fig. 2a represents  $^1\text{H}$  NMR spectrum of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). The successful bromination of PPO was achieved using NBS as a brominating agent and AIBN as an initiator. Depending on the reaction condition and reagents, the bromination can occur either at benzylic position or at the aromatic ring [47,50]. Herein, it occurred at the benzylic position of PPO in refluxing chlorobenzene solution at  $135^\circ\text{C}$  by employing above discussed conditions.  $^1\text{H}$  NMR spectroscopy was used to investigate the structure and degree of bromination of BPPO and attained  $^1\text{H}$  NMR spectrum is depicted in Fig. 2b.  $^1\text{H}$  NMR spectrum of BPPO shows that the characteristic benzyl bromide group was present at 4.3 ppm. The degree of bromination was 75% measured from the integral area ratio between benzyl bromide group and unreacted benzyl signal at 2.1 ppm.

#### 3.2. FTIR analysis of the prepared membranes

Herein, the FTIR analysis was employed to confirm the successful synthesis of DMADMP-functionalized AEM. Fig. 3 represents the FTIR spectrum of pristine BPPO as well as synthesized membrane DMADMP-50. When FTIR spectrum of synthesized membrane DMADMP-50 was compared with pristine BPPO, the prepared membrane DMADMP-50 exhibits a band at  $1,050\text{ cm}^{-1}$ . This band is associated to C–N stretching vibration representing the successful synthesis of AEMs. Because of the linkage of methyl group ( $-\text{CH}_3$ ) possessing DMADMP to BPPO architecture via quaternization reaction, the band at  $2,930\text{ cm}^{-1}$  became broader. The characteristic band associated to the quaternization reaction appeared at  $3,430\text{ cm}^{-1}$ , which is due to the stretching vibration of hydroxyl group ( $-\text{OH}$ ) present in DMADMP. Further, the characteristic band at  $750\text{ cm}^{-1}$  is attributed to C–Br stretching into the pristine BPPO membrane [51]. The signal for C–Br stretching in bromobenzyl groups at  $750\text{ cm}^{-1}$  disappeared in the DMADMP-functionalized membrane [51,52]. It represents that DMADMP is successfully attached to the BPPO architecture.

#### 3.3. Morphology of the prepared membranes

Herein, the detailed structural aspects of the prepared AEMs were revealed by employing (FE-SEM, Sirion 200, FEI Company, USA). Fig. 4 represents the micrographs of surfaces and cross-sections of the prepared DMADMP-functionalized AEMs. From the prepared membranes DMADMP-25 to DMADMP-50, it can be seen that the dense nature of the prepared AEMs is achieved by increasing the concentration of ion-exchange content (DMADMP) in the polymer matrix. The surfaces and cross-section of the prepared AEMs are free from holes or cracks representing their homogeneous structure. Moreover, the surfaces and cross-sections of the prepared membranes exhibited homogeneous structure but with little roughness on them. This attained dense structure of the prepared membranes is crucial to achieve higher acid recovery via diffusion dialysis process. From this, it was concluded that the prepared

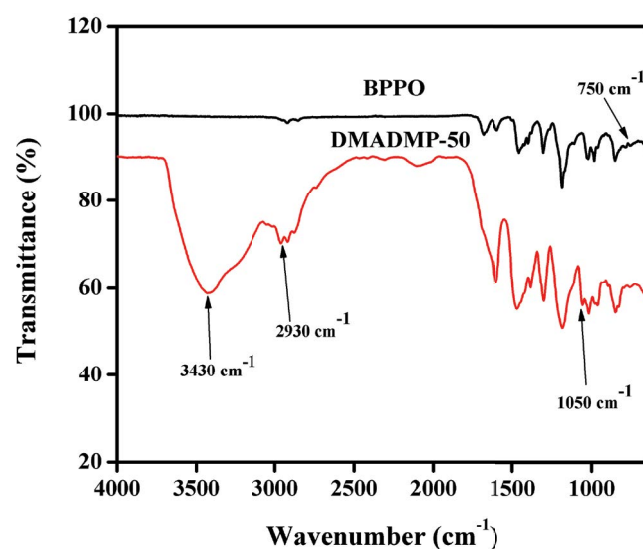


Fig. 3. IR spectrum of pristine BPPO and DMADMP-50 membranes.

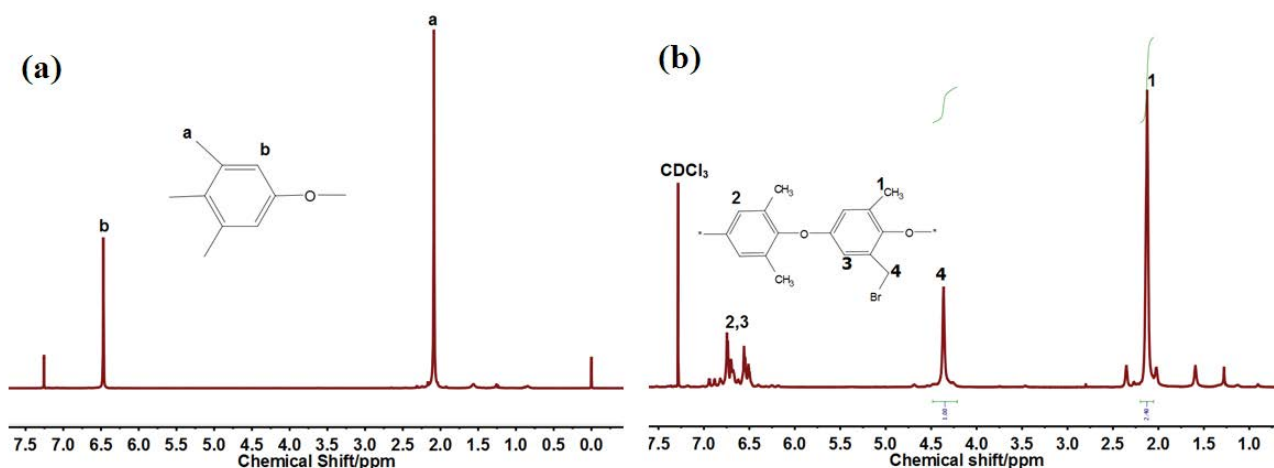


Fig. 2. (a)  $^1\text{H}$  NMR spectrum of PPO and (b)  $^1\text{H}$  NMR spectrum of BPPO.

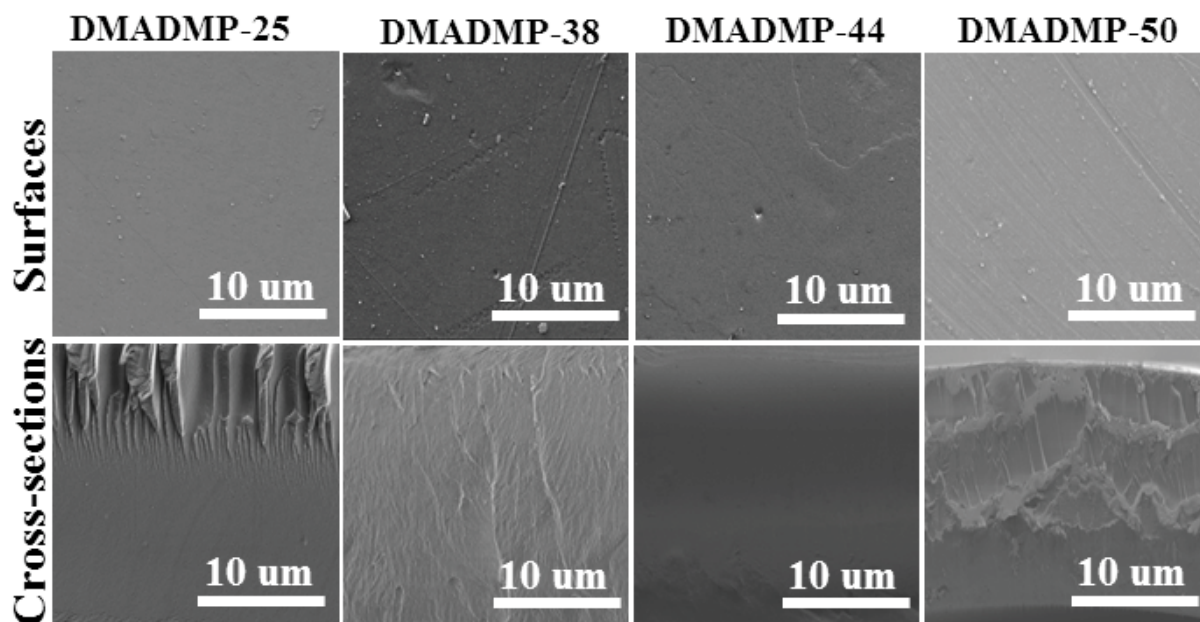


Fig. 4. SEM micrographs of surface and cross-section of the prepared anion exchange membranes represent homogeneous morphology.

DMADMP-functionalized AEMs could be employed for excellent acid recovery performance.

### 3.4. Water uptake and linear swelling ratio

Water uptake ( $W_R$ ) is a significant endowment which depicts the water holding capacity of ion exchange membranes (IEM). It depends on the amount of ion-exchange content in the polymer matrix [53]. It plays a crucial role in the transport of ion across the ion exchange membranes and modest water uptake is needed for higher permeability of anion [22]. It was measured at room temperature and attained results are shown in Fig. 5a. From the prepared membranes DMADMP-25 to DMADMP-50, it was found that water uptake enhanced from 23% to 68% with increasing amount of DMADMP in the polymer matrix. It depicts the slow increase in hydrophilicity of the prepared AEMs with enhancing the concentration of DMADMP in the membrane matrix.

Linear swelling ratio (LSR) is a significant property of AEMs. For the prepared DMADMP-functionalized AEMs, it was calculated at room temperature and obtained results are represented in Fig. 5b. At room temperature, the value of LSR for the prepared DMADMP-functionalized membranes was found to be 8%–31%. It has been observed that the value of LSR increased with increasing the amount of ion-exchange content in the membrane matrix. From here, it was concluded that the prepared DMADMP-functionalized membranes possess good swelling resistance essential for diffusion dialysis process.

### 3.5. Ion exchange capacity

IEC of AEMs shows the concentration of cationic groups in the membrane matrix. It represents the charged form of

the prepared ion exchange membrane (IEMs) [45]. It may expend an important effect on the membrane properties such as water uptake and swelling ratio. Fig. 5c depicts IEC of the fabricated DMADMP-functionalized AEMs. It was calculated by classical Mohr's method. From membrane DMADMP-25 to DMADMP-50, it was found that IEC increased from 1.46 to 2.66 mmol/g with enhancing the amount of DMADMP in the polymer matrix. Higher concentration of DMADMP in the polymer matrix results in higher IEC and vice versa. It has significant influence on diffusion dialysis performance of the prepared AEMs.

### 3.6. Thermal and chemical stability

Fig. 6a represents thermal stability of the prepared DMADMP-functionalized AEMs as well as pristine BPPO membrane. It was investigated via thermogravimetric analysis (TGA) within the temperature range of 30°C–800°C under a nitrogen atmosphere. From Fig. 6a it can be seen that the weight loss of studied AEMs took place in three steps [40]. The weight loss below 140°C is due to the loss of residual water and solvent. The second weight loss step observed in range of 190°C–250°C is attributed to the degradation of quaternary ammonium group in the polymer matrix [54]. The final weight lost around 450°C is due to the degradation of polymer backbone [48]. This analysis showed that the prepared DMADMP-functionalized AEMs possess higher thermal stability.

The chemical stability of the prepared AEM DMA-DMP-50 was investigated in terms of weight loss. It was revealed by immersing it into the feed solution (1 M HCl + 0.25 M FeCl<sub>3</sub>) for 240 h at 60°C and attained results are represented in Fig. 6b. It can be seen that the percentage weight loss of the prepared AEM DMADMP-50 was found to be 14% after 10 d soaking into feed solution at 60°C. Further,



the color of the prepared membrane DMADMP-50 was kept unchanged. From this, we concluded that the fabricated DMADMP-functionalized AEMs are good for acid recovery via diffusion dialysis process.

### 3.7. Diffusion dialysis performance of the prepared membranes

After detailed characterization of the fabricated DMA-DMP-functionalized AEM, their acid recovery performance was evaluated via diffusion dialysis process. It was conducted in two compartment cell employing simulated mixture of HCl/FeCl<sub>2</sub> (1 M HCl + 0.25 M FeCl<sub>2</sub>) as model feed at ambient temperature. Fig. 7 represents diffusion dialysis coefficient of acid ( $U_{H^+}$ ) and metal ( $U_{Fe^{2+}}$ ) at 25°C. The values of  $U_{H^+}$  and  $U_{Fe^{2+}}$  for the developed DMADMP-functionalized AEMs were 9 ( $10^{-3}$  m/h) to 32 ( $10^{-3}$  m/h) and 0.02 ( $10^{-3}$  m/h) to 1.9 ( $10^{-3}$  m/h), respectively. At 25°C, the value of  $U_{H^+}$  for

the prepared membranes was much higher than commercial membrane DF-120B ( $U_{H^+} = 0.004$  m/h) [55]. With increasing the amount of DMADMP in the polymer matrix, the value of  $U_{H^+}$  was enhanced from 0.009 to 0.032 m/h at ambient temperature. Table 2 represents an interesting comparison of the synthesized AEMs with membranes reported in the literature. From this, we concluded that the prepared AEMs are excellent candidate for acid recovery. The migration of ion through the ion exchange membrane is associated to water uptake, IEC, structure of the membrane and hydrogen bonding. From Fig. 7, it was observed that the values of both  $U_{H^+}$  and  $U_{Fe^{2+}}$  for the prepared AEMs were increased with enhancing the concentration of DMADMP in the membrane matrix. It was associated to the enhancement in IEC and water uptake with increasing the amount of DMADMP in the polymer matrix resulting in increase in hydrophilicity of the prepared AEMs. Moreover, the presence of free

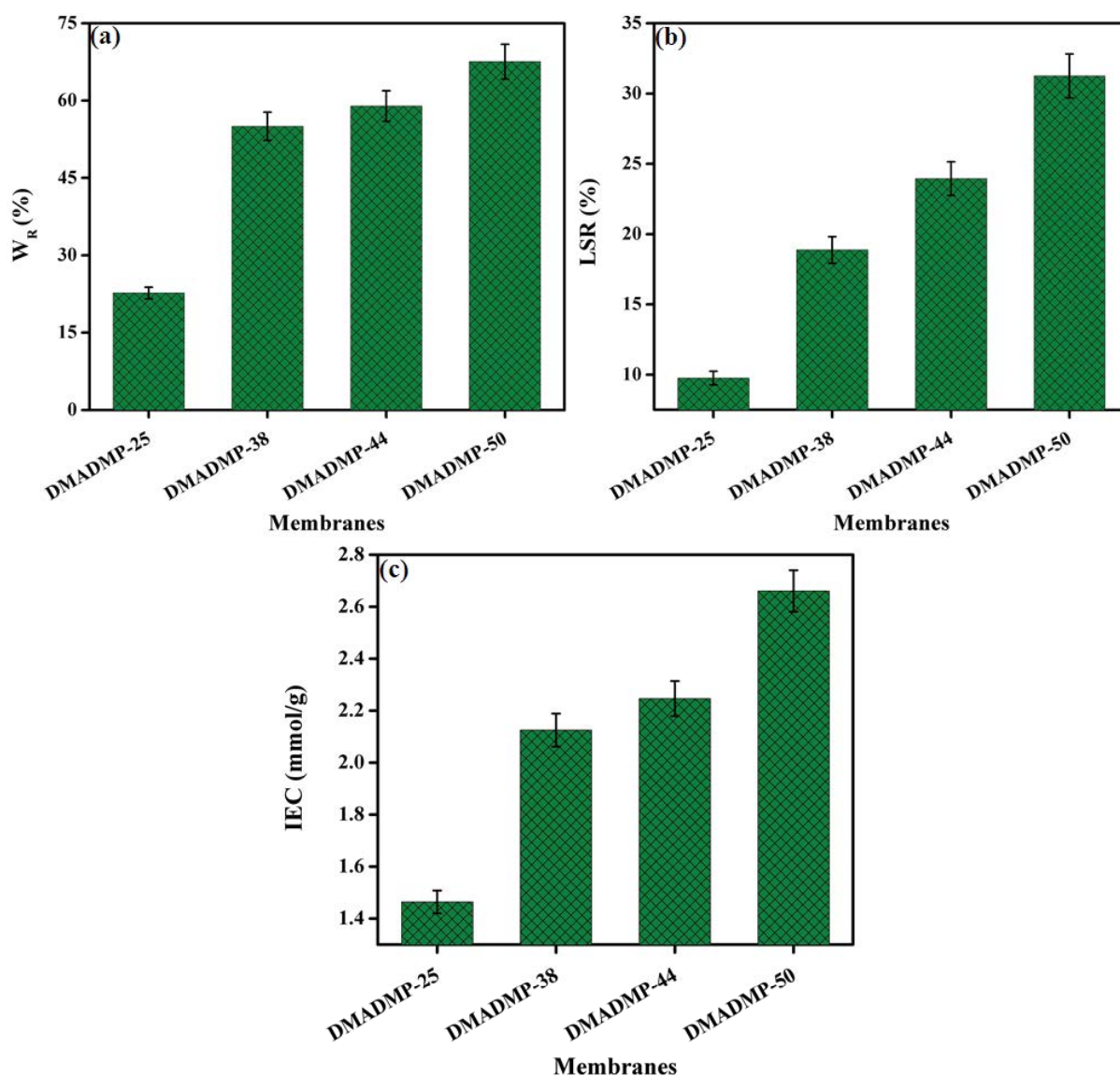


Fig. 5. (a) Water uptake, (b) linear swelling ratio, (c) ion exchange capacity of prepared membrane increase with enhancing amount of DMADMP in the membrane matrix.

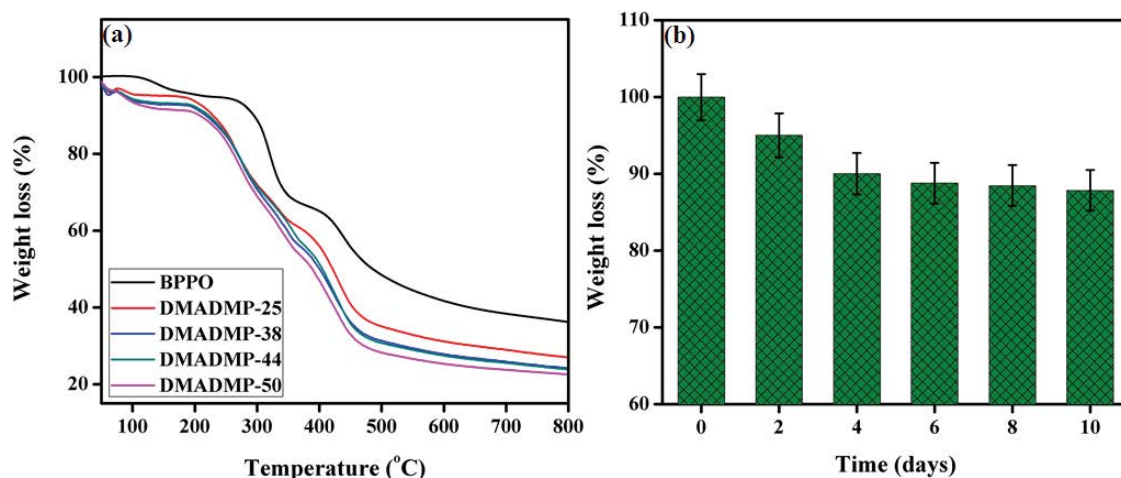


Fig. 6. (a) TGA curves of pristine BPPO and the prepared anion exchange membrane (AEM) and (b) weight loss of the prepared AEM DMADMP-50 after immersion in HCl/FeCl<sub>2</sub> feed solution for 10 d at 60°C.

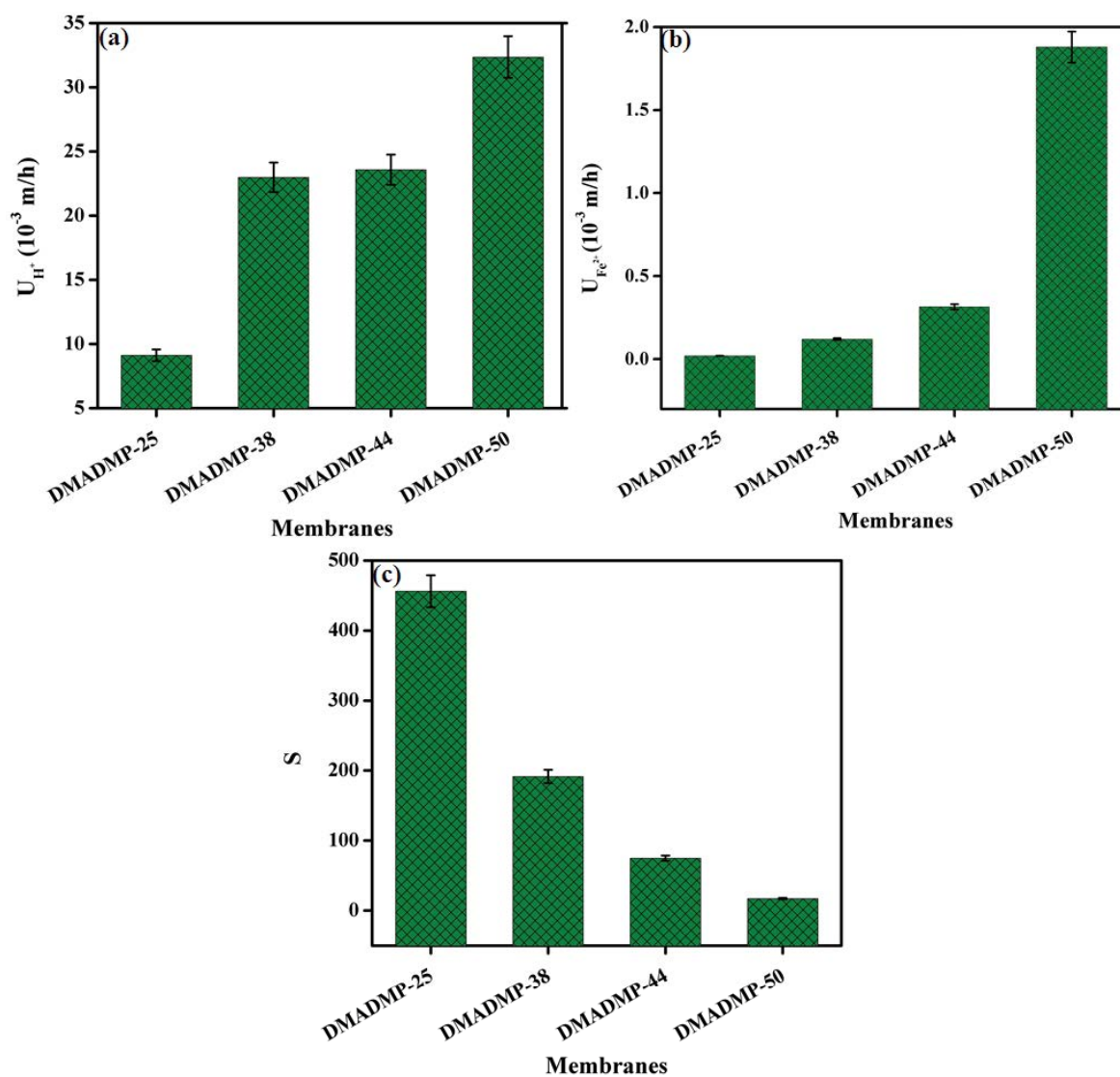


Fig. 7. (a) Diffusion dialysis coefficient of acid ( $U_{H^+}$ ), (b) diffusion dialysis coefficient of metal ( $U_{Fe^{2+}}$ ), (c) separation factor ( $S$ ) of the prepared AEMs from DMADMP-25 to DMADMP-50 at 25°C.



Table 2

Structure, ion exchange capacity, diffusion dialysis coefficient and separation factor of the prepared AEMs and reported membrane employing HCl/FeCl<sub>2</sub> as the model acidic waste solution at 25°C

Membranes	Structure	IEC (mmol/g)	$U_{H^+}$ (10 <sup>-3</sup> m/h)	S	References
DMADMP-50 membrane	Dense	1.46–2.66	9–32	17–56	This work
PVA-based hybrid membranes	Dense	0.58–1.15	11–18	18.5–21	[58]
PVA-silica anion exchange hybrid membranes	Dense	0.52–1.01	8–10	15.9–21	[59]
Quaternized bionic multisilicon copolymers	Dense	0.46–1.25	7.20–7.50	26.9–42.8	[60]
PVA-based anion exchange hybrid membranes	Dense	0.34–0.76	10–17	12–35	[61]
Quaternized PPO based hybrid membranes	Dense	1.70–2.20	5–11	17–32	[62]
Quaternized PPO based membranes	Dense	1.10–1.80	6–18	16–28	[63]

Table 3

Tensile strength (TS) and elongation at break ( $E_b$ ) of the prepared anion exchange membranes from DMADMP-25 to DMADMP-50 representing excellent mechanical stability

Membranes	DMADMP-25	DMADMP-38	DMADMP-44	DMADMP-50
TS (MPa)	41.70	34.89	27.07	19.10
$E_b$ (%)	7.37	8.99	14.71	16.58

hydroxyl group (–OH) in DMADMP can speed up the migration of H<sup>+</sup> through hydrogen bonding because it can easily form hydrogen bonding with H<sup>+</sup> [54]. The migration of H<sup>+</sup> and Fe<sup>2+</sup> through the prepared DMADMP-functionalized AEMs enhanced due to increase in IEC, water uptake and hydrogen bonding. It results to enhance the values of  $U_{H^+}$  and  $U_{Fe^{2+}}$  for the prepared AEMs at room temperature. The concentration of H<sup>+</sup> was higher than Fe<sup>2+</sup> due to difference in ionic radii. Hence, the value of  $U_{H^+}$  was higher than  $U_{Fe^{2+}}$  at room temperature. It showed that the prepared DMADMP functionalized AEMs possess good potential for diffusion dialysis application.

Fig. 7c depicts the separation factor (S) of the prepared DMADMP-functionalized AEMs at room temperature. For the prepared AEMs, the value of S was 17–456 which was higher than commercial membrane DF-210B [55] and other reported membranes [41,56]. For the prepared DMADMP-functionalized AEMs, the value of S was decreased from 456 to 17 with enhancing the concentration of DMADMP in the polymer matrix. Both H<sup>+</sup> and Fe<sup>2+</sup> ions were transported through the prepared membrane along with Cl<sup>-</sup> ion. Because of larger ionic radii and lower mobility of Fe<sup>2+</sup>, the transport of H<sup>+</sup> was higher than Fe<sup>2+</sup>. Moreover, the migration of Fe<sup>2+</sup> through the membrane was disturbing its selectivity [57]. Therefore, the value of S was decreased from the prepared membrane DMADMP-25 to DMADMP-50.

### 3.8. Mechanical stability

Herein, mechanical stability of the prepared membranes was studied in wet state by using dynamic mechanical analyzer (DMA). Tensile strength (TS) and elongation at break ( $E_b$ ) of the prepared membranes is given in Table 3. TS of the prepared membrane was decreased whereas elongation at break was increased from DMADMP-25 to DMADMP-50 with increasing IEC. It was observed that the

prepared membrane DMADMP-25 exhibited higher TS but lower  $E_b$ . In contrary, the prepared membrane DMADMP-50 exhibited lower TS but higher  $E_b$  representing excellent flexibility of the prepared membranes. TS of the prepared membranes was higher than previously reported IEM [55] representing that the prepared membranes possess excellent mechanical stability.  $E_b$  was in range of 7.37%–16.58%, which seems to be lower than hybrid AEMs [45].

## 4. Conclusions

In this article, a series of homogeneous DMADMP-functionalized AEMs were successfully prepared via solution casting method. The synthesis of the prepared membrane was confirmed by FTIR spectroscopy. Morphological analysis showed that the prepared membranes showed homogeneous structure. These membranes exhibited satisfactory thermal, chemical and mechanical stability necessary for diffusion dialysis process. Water uptake, LSR and IEC of the prepared membranes was enhanced with enhancing the amount of DMADMP in the membrane matrix. For the prepared membranes, diffusion dialysis performance was evaluated in two-compartment cell by employing HCl/FeCl<sub>2</sub> mixture as model feed at 25°C. The diffusion dialysis coefficient of acid ( $U_{H^+}$ ) was in the range of 9 (10<sup>-3</sup> m/h) to 32 (10<sup>-3</sup> m/h) and separation factor was in the range of 17–456 at ambient temperature. Hence, the prepared DMADMP-functionalized AEMs are good candidates for diffusion dialysis application.

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