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Preparation of diffusion dialysis membrane for acid recovery via a phase-inversion method

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Abstract. Herein, the preparation of anion exchange membrane (AEM) from brominated poly(2,6-dimethyl 1,6-phenylene oxide) BPPO and dimethylaniline (DMA) by phase-inversion process is reported. Anion exchange membranes (AEMs) are prepared by varying the DMA contents. Prepared AEMs show high thermal stability, water uptake (WR) around 202% to 226%, dimensional change ratios of 1.5% to 2.6% and ion exchange capacities (IECs) of 0.34 mmol/g to 0.82 mmol/g with contact angle of 59.18° to 65.15°. These membranes are porous in nature as confirmed by SEM observation. The porous property of membranes are important as it could reduce the resistance of transportation of ions across the membranes. They have been used in diffusion dialysis (DD) process for recovery of hydrochloric acid (HCl) from the mixture of HCl and ferrous chloride ($FeCl_2$). Presence of $–N+(CH_3)_2C_6H_5Br^-$ as a functional group in membrane matrix facilitates its applications in DD process. The dialysis coefficients of hydrochloric acid (U_H) of the membranes are in range of 0.0016 m/h to 0.14 m/h and the separation factors (S) are in range of 2.09 to 7.32 in the HCl/$FeCl_2$ system at room temperature. The porous membrane structure and presence of amine functional group are responsible for the mechanism of diffusion dialysis (DD).

Keywords: brominated poly(2,6-dimethyl 1,6-phenylene oxide); N,N-dimethylaniline; anion exchange membrane; phase-inversion

1. Introduction

In case of metal surface treatment using pickling process, for example, various acids such as hydrochloric acid, sulphuric acid and nitric-hydofluoric acid have been chosen (Moon *et al*. 2000). Such pickling process concerns with the electroplating resin regeneration, steel production, aluminium etching and metal refining etc. (Wu *et al*. 2009, Palatay and Zakova 2006, Negro *et al*. 2001). In these processes, large quantities of aqueous wastes containing metal ions and acids of high concentration have been produced. The accumulation of metal ions in the waste decreases the efficiency of the picking/etching agent. The waste could not be recycled and must be discarded. So

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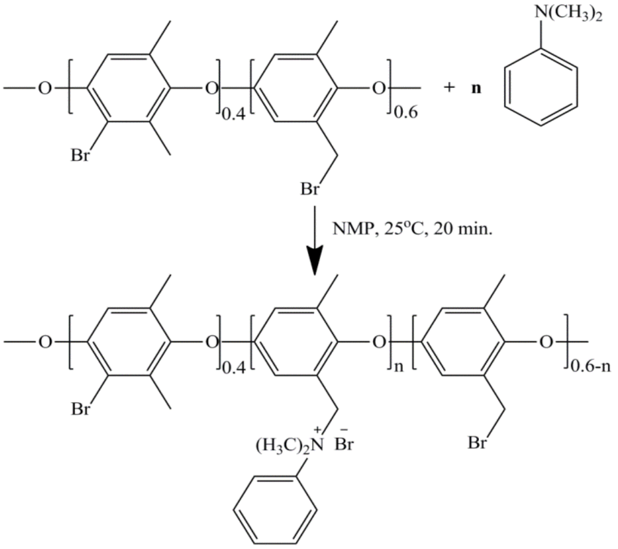
the related industries need to give serious attention in treating these wastes in a proper way. Diffusion dialysis (DD) process using anion exchange membrane is a useful separation technique for this purpose. The main driving force behind its working principle is concentration gradient (Strathmann 2004, Wu *et al.* 2011, Kang *et al.* 2001). This is an environment friendly and cost-effective process because no consumption of energy is needed as it totally depends upon the migration of ions from high concentration gradient to the lower one. Anion exchange membranes are very crucial for this process. Most of the anion exchange membranes used for recovery of acids are usually homogeneous and are synthesised from different polymers namely polystyrene (PS), polysulfone (PSf) and brominated poly(2,6-dimethyl 1,4-phenylene oxide) (BPPO) (Kang *et al.* 2001). The polymer can be post-quaternized after membrane preparation or pre-quaternized followed by solution casting, drying and heating process (Kariduraganavar *et al.* 2006). The polymer chain provides the required stability and strength while quaternary amonium group gives ion exchange capacity (IEC) and ion transport properties. Most of the the membranes used in DD process are compact and dense. Ions are adsorbed in the membrane matrix and then diffused through the membrane down to a concentration gradient (Wijmans and Baker 1995). The ions mobility and affinity with the membrane are used to measure the membrane permeability. Earlier attempts for membrane alteration, which increase membrane hydrophilicity, incorporate ion exchange groups and assistant functional groups, are eligible to increase the membrane affinity with the ions. The membrane stability such as swelling resistance in water decreases due to an increase in the hydrophilicity of membrane. Therefore, the main objective is to develop highly permeable and stable membranes for DD process.

In return to the challenge, the possibility of porous membrane from hydrophobic polymer may be attemped, since the hydrophobic polymer matrix can give membrane strength and the porous morphology may reduce the resistance of ions transport through the membranes. Though the porous membranes are employed for processes other than diffusion dialysis, the role of pores for DD can be reflected from casual reports. For example, porous membranes are oftenly uses in pressure-driven membrane processes such as ultrafiltration, nano filtration etc. Other research groups used two step phase inversion technique to prepare porous composite ion exchange membranes for desalination applications (Klaysom *et al.* 2011). The membranes with sponge-like cross-sectional pores can be applied for electrodialysis (ED) process. For instant, our previous work reveals the presence of 20-65 nm or 30-120 nm micropores in the PVA/QPPO membranes (Wu *et al.* 2013). In another investigation from our group, BPPO based porous anion exchange membranes have higher values of dialysis coefficients (0.020 m/h to 0.025 m/h at 25°C) and separation factor up to 45.5 for hydrochloric acid recovery from $HCl/FeCl_2$ (Wu *et al.* 2014). These micropores can support the diffusion of HCl significantly, resulting into high U_H value without much decline in selectivity. The step of membrane fabrication is a little complicated. It uses the post functional groups and needs silica as a crosslinking agent.

In this study, porous anion exchange membranes are prepared by phase-inversion method for diffusion dialysis from the reaction of BPPO and dimethylaniline (DMA). BPPO is used as a base material because of its higher stability, strength and easiness for quaternization (Xu *et al.* 2008). DMA is used as a solvent for BPPO because it has good affinity for BPPO. Different AEMs were prepared and characterized in terms of water uptake (WU), dimensional stability, ion exchange capacity (IEC), thermal stability and contact angle. These membranes are used in diffusion dialysis (DD) for acid recovery and the results are compared with commercial DF-120 dense membrane. The effect of amine contents on performance of membrane in DD is also discussed.



Scheme 1 The preparation of BPPO-based anion exchanged membranes

2. Experimentals

2.1 Materials

Brominated poly (2, 6-dimethyl-1, 4-phenyleneoxide) (BPPO) and commercial membrane DF-120 are supplied by Shandong Tianwei Membrane Technology Co. Ltd. (China). The membrane properties include: ion exchange capacity (IEC) = 1.96 mmol/g; water content (W_R) = 42%; transport number (t) > 0.98; membrane area resistance (R_m) < 3.0 Ω cm^2 and thickness 0.30-0.32 mm. The dimethylaniline (DMA) is of analytical grade and commercially obtained from Shanghai-Sinopham Chemical Reagent Co. Ltd. (China). Deionized water is used throughout the experiments.

2.2 Preparation of anion exchange membranes A-E

The preparation of anion exchange membranes A-E was carried out by using phase-inversion method. The casting solution was prepared by dissolving of 2.8 g brominated poly(2,6-dimethyl-1,6-phenylene oxide) (BPPO) into 10 mL N-Methyl-2-pyrrolidone (NMP) at room temperature. The membrane A was prepared from brominated poly(2,6-dimethyl-1,6-phenylene oxide) BPPO without amination but anion exchange membranes B-E were prepared by adding different amounts of dimethyaniline (DMA) into the casting solution to attain membranes with different properties. The casting solution was shaken for 20 minutes to accelerate the reaction between BPPO and amine. After that the solution was cast onto a glass plate and immediately immersed into water. The obtained membranes were washed by immersing in water for two days. The preparation route is shown in Scheme 1.

2.3 Membrane characterization

FTIR spectra of anion exchange membranes were recorded by FTIR spectrometer (Victor 22, Bruker) with a resolution of 2 cm-1 and a spectral range of 4000-400 cm-1. TGA was conducted by a Shimadzu TGA-50H analyzer under the air flow, with a heating rate of 10°C/min. The morphologies of membranes were observed using scanning electron microscopy (TM 3000 Tabletop Microscope, Hitachi).

Ion exchange capacities (IEC) were calculated by applying the Mohr method (Yan and Hickner 2010). The weight of dry membranes was precisely measured and the membranes were changed into chloride ion (Cl^-) form by dipping in 1.0 M NaCl solution for 2 days. After that membranes were washed off with deionized water to remove immoderate NaCl and then immersed them in 0.5 M Na_2SO_4 for 2 days. Anion exchange capacities were calculated by measuring the quantity of exchanged Cl^- by titration with 0.05 M $AgNO_3$.

Water uptake (W_R) was calculated to evaluate the hydrophilicity of membranes. It was calculated from the dry weight and wet weight by dipping the membrane samples in to deionized water for 2 days at room temperature. WR is calculated by following relation.

$$W_R = \frac{W_w - W_d}{W_d} \times 100 \tag{1}$$

where W_d is the weight of membrane in dry state, W_w is weight of membrane in wet form after dipping into deionized water.

The dimensional stability was measured by means of dimensional change ratio, which was determined from the geomatrical average values of linear change ratios in both x and y directions using the following relation.

$$\eta = \sqrt{\left(\frac{x - x_o}{x_o}\right)\left(\frac{y - y_o}{y_o}\right)} \tag{2}$$

where η is the final dimentional change ratio, x, y and x_o, y_o are the length of base membrane and a final membrane in x and y directions respectively which were calculated by a digital micrometer (0-150 mm, Shanghai, China).

2.4 Diffusion dialysis

During the DD process, the ion transport is driven mainly by the concentration gradient, with observation of the Donnan criteria of co-ion rejection and preservation of electrical neutrality (Stancheva 2008). The separation of HCl from feed solution is shown in Fig. 1 to explain the principle of DD. As shown in Fig. 1, HCl and its metal salts in feed solution tend to transport to the water side due to concentration difference across the membrane. Due to the presence of anion exchange membrane, the Cl^- ion is allowed to pass but metal ion (Fe^{2+}) is much less likely to pass. The H^+ ions, although positively charged, have higher competition in diffusion than metal ions due to their higher mobility, smaller size and lower valence state. Hence they can diffuse along with the Cl^- ions to meet the requirement of neutrality. The H^+ transport is key to the DD process (Stancheva 2008, Xu 2002, 2005). The properties of AEM including stability in acid solution, high H^+ permeability, poor water permeability, relatively high water uptake and strong rejection to metal are also necessary. DD was performed by employing a two-compartment cell of equal volume (100 ml) separated by the membrane (Luo *et al.* 2010, Wu *et al.* 2011, Wu *et al.* 2010a). The experimental setup for batch DD is shown in Fig. 2. The feed side of the cell was filled with a mixture of 1.0 M HCl and 0.25 M $FeCl_2$ and permeate side with deionized water. During the diffusion dialysis, both compartments were stirred with equal rate to reduce concentration polarization effect. The transport characteristics were measured from time dependences of the component concentration in both the compartments (Palaty and Bendova 2009). DD was carried out for 1 hour at room temperature and then feed/permeate solutions were removed from both sides of the cell. HCl concentration in the solution was calculated by titration with standard Na_2CO_3 while $FeCl_2$ concentration was determined by titration with $KMnO_4$. The separation fector (S) with respect to one species over another is given as the ratio of dialysis coefficients (U) of the two species present in the solution. U can be measured by following relation

$$U = \frac{M}{At\Delta C} \tag{5}$$

where M is the amount of component transported in moles, A is area in cm^2, t is time in h and ΔC logarithm average concentration between two chambers in moles per cubic meters and given as follows

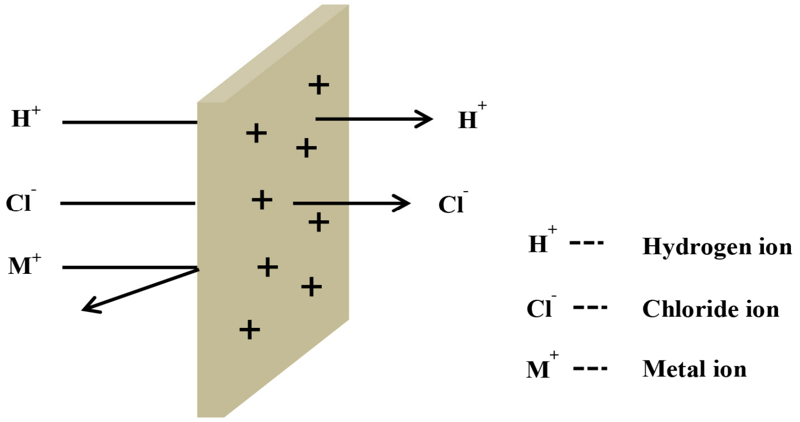


Fig. 1 Illustration of the diffusion dialysis principle through the HCl separation process from mixture of HCl and $FeCl_2$

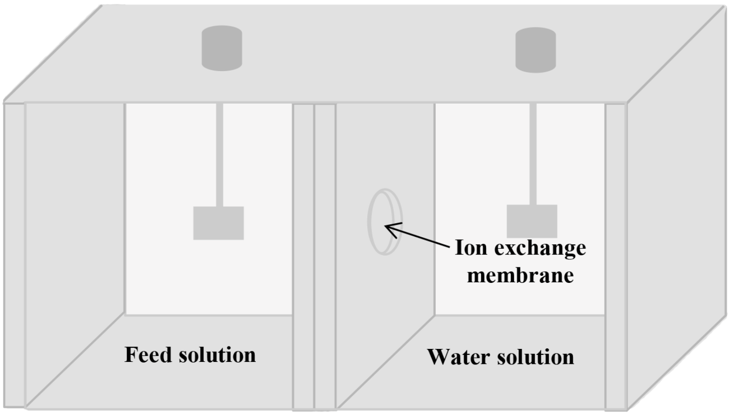


Fig. 2 Experimental setup of batch diffusion dialysis for the acid recovery

$$\Delta C = \frac{(C_f^o - C_d^t - C_f^t)}{\ln[(C_f^o - C_d^t)/C_f^t]} \tag{6}$$

where C_f^o and C_f^t are feed concentrations at time 0 and t respectively, and C_d^t is the dialysate concentration at time *t*. It should be noted that ($C_f^o - C_d^t - C_f^t$) is not equal to zero beacause water transport through membrane will cause volumetric change in the cell chamber during the experiment (Xu and Yang 2001).

3. Results and discussion

3.1 FTIR Spectra

BPPO is thermally and mechanically stable polymer and has been used for preparation of porous membranes by phase inversion technique (Wu *et al.* 2009, 2010b). The FTIR spectra of BPPO anion exchange membranes are represented in Fig. 3. The bands in range of 2850-2985 $\mathrm{cm^{-1}}$ and 1446 $\mathrm{cm^{-1}}$ are because of stretching of $-CH_3$, $-CH_2$ and –CH groups (V and δ) (Wu *et al.* 2010a). The band in region of 1020-1250 $\mathrm{cm^{-1}}$ is due to stretching vibration of C-N group indicating the successful amination reaction. The adsorption peaks of symmetrical and asymmetrical stretching vibration of C-O are at 1200 $\mathrm{cm^{-1}}$ and 1306 $\mathrm{cm^{-1}}$ and those of phenyl group at 1463 $\mathrm{cm^{-1}}$ and 1603 $\mathrm{cm^{-1}}$ respectively as shown in Fig. 3.

3.2 Morphologies

Morphologies of membranes B-E have been observed through scanning electon microscopy (SEM). The SEM images of membranes C and E have been selected as example, as shown in Fig. 4. The SEM images (C1, C2, C3) of membrane C and images (E1, E2, E3) of membrane E represent the bottom, top and cross section of these membranes respectively. All the membranes

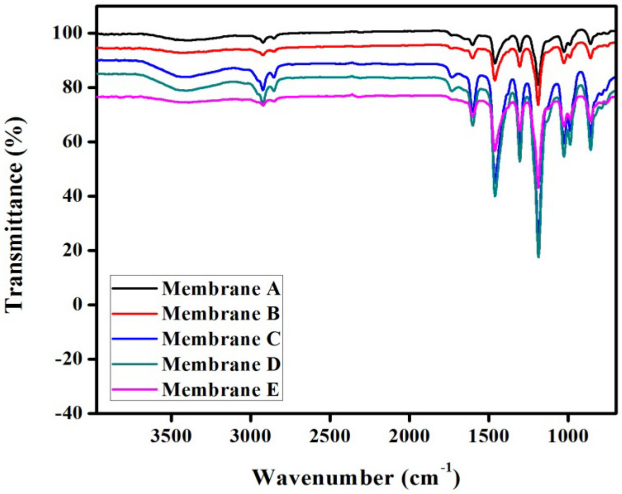


Fig. 3 The FTIR spectra (a) of BPPO based membrane and (B-E) are FTIR spectra of BPPO and amine

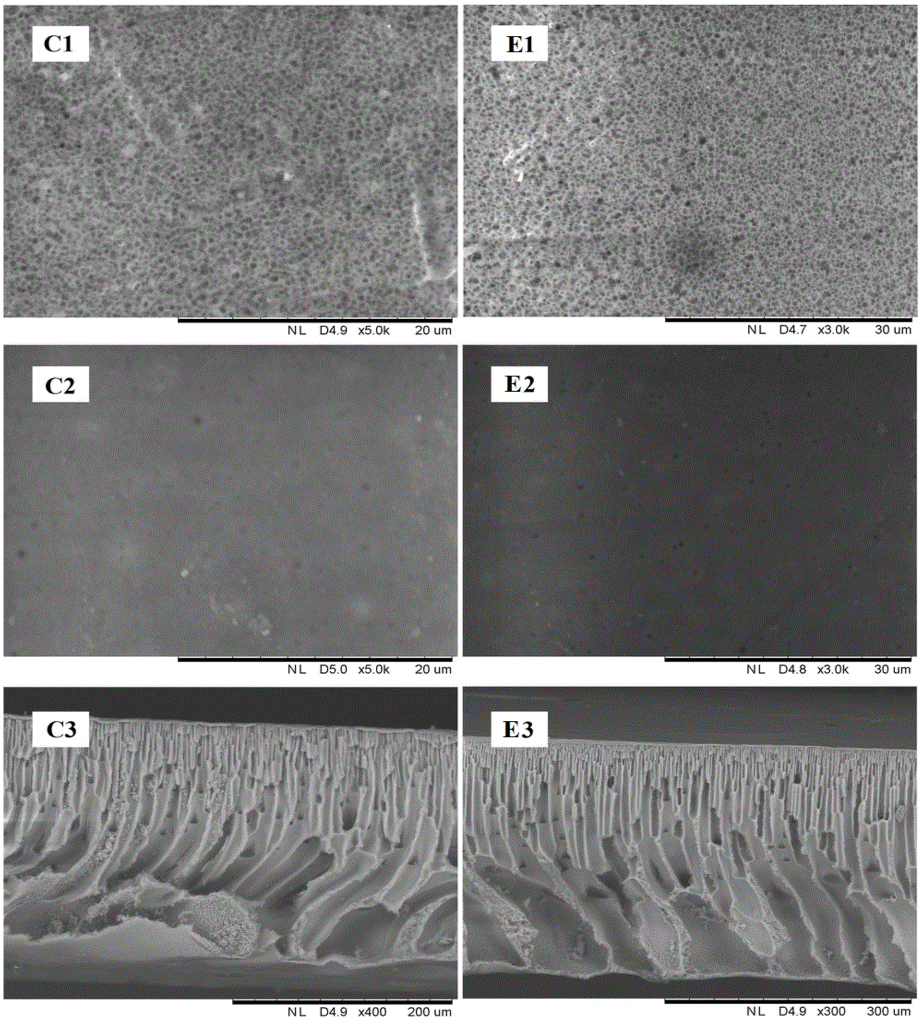


Fig. 4 SEM images bottom (C1), top (C2), and cross section (C3) of membrane C, and bottom (E1), top (E2), and cross section (E3) of membrane E

have asymmetrical structure containing a dense top layer and porous bottom layer. No particle appears in any of the membranes B-E, showing good compatibility of BPPO and amine (DMA). All of the membranes were smooth which represented that BPPO reacted completely with DMA. The SEM images of cross sections of all the membranes have been shown in Fig. 4. Finger-like pores are observerd through the bottom layer. These porous morphologies may reduce the resistance of ions during their passing across the membranes and thus are favourable for separation of mixtures. Therefore, these porous morpholgies may be useful for diffusion dialysis (DD) process.

3.3 Thermal stability (*TGA*)

TGA graphs of membranes A-E are given in Fig. 5. Weight loss before 130°C is due to loss of water and should be neglected. Initial decomposition temperature (IDT) and thermal decomposition (T_d, defined as the temperature at 5% weight loss) measured from TGA graphs are given in Table 1.

The IDT values of membranes B-E are in the range of 219-256°C and T_d values are in the range of 244-272°C. Similarly IDT and T_d values of BPPO blank membrane A are 171°C and 233°C respectively. Higher IDT and T_d values indicate better thermal stability of B-E anion exchange membranes. These values are similar to the IDT values of anion exchange membrane from partial hydrolysis, quaternization and sol-gel process (IDT = 237-254°C) (Wu *et al*. 2009). Therefore, these prepared AEMs have higher stability than BPPO membrane as DMA (dimethyl aniline) was incorporated in the membrane matrix, hence the inherent stability of BPPO polymer chain increased to some extent. Therefore, we obtain higher IDT and Td values for DMA incorporated BPPO membranes in comparison with the blank BPPO membrane. Moreover, the preparation process of these anion exchange membranes does not involve any radiation-grafting and hence no destruction of BPPO polymer chain occurs. These factors may contribute to the higher stability of these prepared anion exchange membranes.

3.4 Ion exchange capacity, water uptake and dimensional stability

All of the four anion exchange membranes (AEMs) contain $-N+(CH_3)_2C_6H_5Br-$ group which is formed by quaternization of BPPO matrix. The ion exchange capacities (IEC_A) values are given in Table 2. The values are in range of 0.34 mmol/g to 0.82 mmol/g. They increases as the amount of DMA increases from membrane B-E.

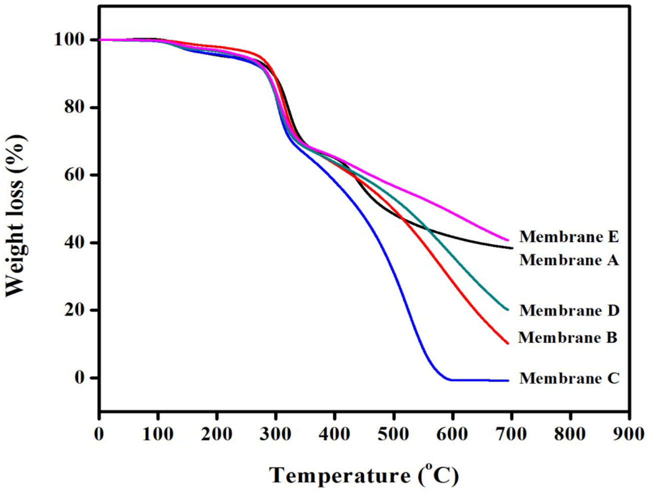


Fig. 5 The TGA diagram of anion exchange membranes A-E under air flow, with a heating rate of 10°C/min

Table 1 Initial decomposition temperature and final decomposition temperature of anion exchange membranes A-E

Membranes	A	B	C	D	E
IDT (°C)	171	256	230	219	220
T_d (°C)	233	272	245	249	244

Table 2 Properties of anion exchange membranes B-E

Membranes	B	C	D	E
IEC (mmol/g)	0.34	0.53	0.66	0.82
Water Uptake (%)	202	210	222	226
Dimensional Stability (%)	1.50	1.60	1.80	2.60
Fixed group conc. (mol/L·10^{-3})	1.6	2.50	2.95	3.63
contact angle (°)	65.15	64.81	61.69	59.18

Water uptake (W_R) which is important term in the ion and water transfer, is mainly depend on the membrane cross linking degree and functional groups (Berezina *et al.* 2008). It is represented in Table 2, WR for anion exchange membranes B-E followed the increasing order from 202.9% to 226.8%, representing the gradual increase of hydrophilicity as the IEC is increased. It is due to the increased amount of DMA. Both IEC and WR are important to describe membrane hydrophilicity. WR is greatly influenced by the amount of dimethylaniline (DMA). As the amount of DMA increases, the W_R also increases from 202.9% to 226.8%. It should be noted that the water content is high as compare to dense ion exchange membranes. The reason is that the pores in the membrane matrix can uptake a portion of water. The dimensional change ratios of anion exchange membranes B-E are 1.5% to 2.6% as given in Table 2, suggesting high stability of membranes. The dimensional change ratios of anion exchange membranes B-E increases as the quantity of DMA increases from membrane B-E as shown in Table 2. Thus, a high water uptake does not affect any of the dimensional stability.

3.5 Fixed group concentration (C_R) and water contact angle

The fixed group concentration (C_R) values of the membranes B-E were measured at room temperature. The measurement of C_R values have been calculated as the ratio of ion exchange capacity (IEC) to water uptake (WR) as given in Table 2. The fixed group concentration (C_R) values increases from 0.0016 mol/L to 0.0036 mol/L as the amount of dimethylaniline (DMA) increases from membrane B-E. According to earlier researchers (Xu and Yang 2001, 2004), the change of CR values can affect DD performance of membrane distinctively. Water contact angle is an impotant parameter to measure the hydrophilicity of IEMs. It was measured for membranes B-E at room temperaure. The results are represented in Table 2. It is clear, the ion exchange capacity (IEC) values and water uptake (W_R) increases as the amount of dimethylaniline (DMA) inreases from membrane B-E, but the water contact angle decreases, respresenting the increase in hydrophilicty of the membranes.

3.6 Diffusion dialysis (DD) performance

3.6.1 Diffusion dialysis coefficients (U_H and U_{Fe})

Four pieces of anion exchange membranes B-E were used in DD performance. Here HCl/$FeCl_2$ solution has been taken as an example to evaluate the DD performance, for waste solution containing acids and metal ions may come from metallurgical industries, acid cleaning processes and electrolysis, etc. (Agrawal and Sahu 2009). The DD performance data including dialysis coefficient of HCl (U_H) and dialysis coefficient of $FeCl_2$ (U_{Fe}) are represented in Figs. 6-7

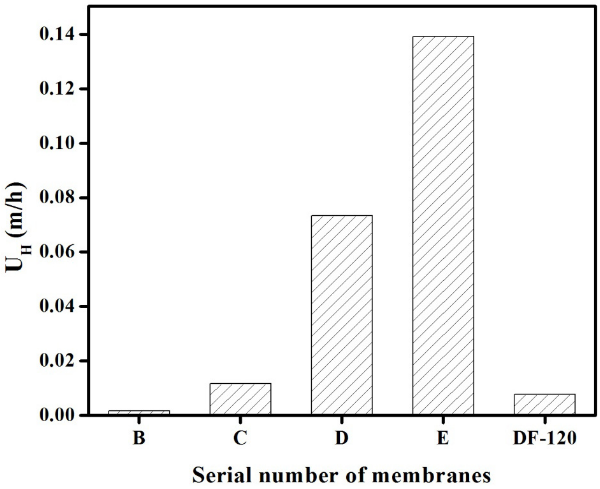


Fig. 6 Dialysis coefficient of HCl of anion exchange membrane B-E and DF-12 membrane

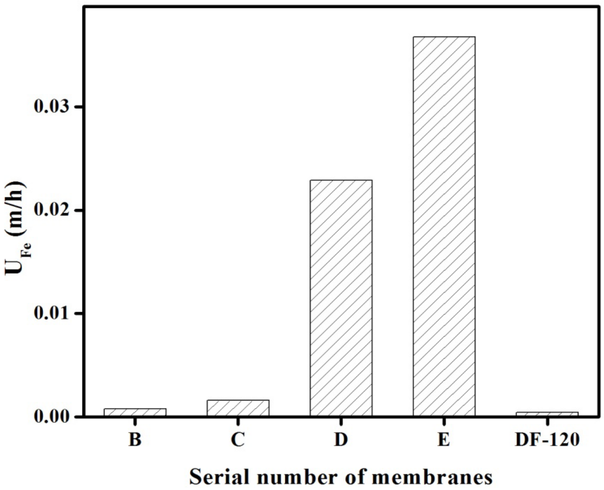


Fig. 7 Dialysis coefficient of $FeCl_2$ of anion exchange membrane B-E and DF-120 membrane

respectively. The U_H values are in the range of 0.0016 m/h to 0.14 m/h for anion exchange membranes B-E at room temperature. Similarly U_{Fe} values are in the range of 0.00079 m/h to 0.037 m/h for anion exchange membranes B-E at room temperature. The values of both U_H and UFe increase from membranes B-E with increasing amine contents at room temperature. This trend can be studied in the prospective of the membranes structure and acid transport mechanism. The anion exchange membranes B-E contain porous morphologies as indicated by SEM observations in Fig. 4. This porous morphology reduces the resistance during ions transport process. The porous morphology of anion exchange membranes is responsible for higher value of U_H. Thus, acid permeability depends on the porous morphology and anion exchange property of membranes. Moreover, all the membranes B-E contain active region or ion exchange group such as $-N+CH_3)_2C_6H_5Br^-$ which is reponsible for transport of ions across the membranes. As the amine

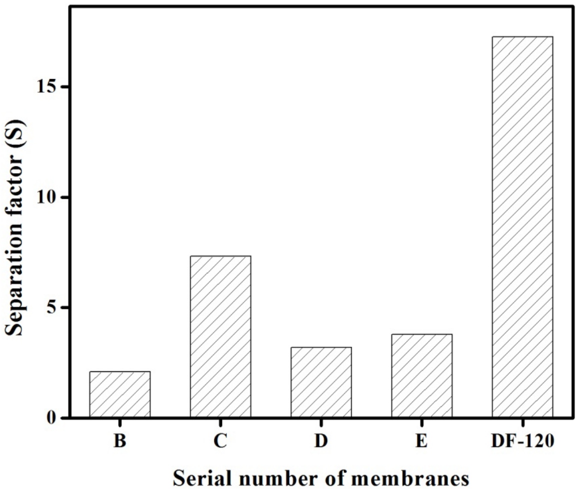


Fig. 8 Separation factor (*S*) of anion exchange membranes B-E and commercial DF-120 membrane

content increases from membrane B-E, both IEC and W_R of the membranes also increases which results in higher hydrophilicity of membranes and U_H values of membranes B-E also increases. The U_H values depend on cationic group $-N+CH_3)_2C_6H_5Br^-$ group. Cl^- ions are allowed to pass due to the presence of cation ion exchange $-N+CH_3)_2C_6H_5Br^-$. To attain electrical neutral condition, H^+ ions can also passes with Cl^- through the membranes. Transport of Fe-related component such as Fe^{2+} and $FeCl^+$ is less likely to occur due to their larger size and lower mobility (Palaty and Bendova 2009). As a result, the acid transport mainly depends on the ion exchange group such as $-N+CH_3)_2C_6H_5Br^-$. Therefore, these membranes can be potentially used for the separation of HCl from $HCl/FeCl_2$ waste mixture.

3.6.2 Separation Factor (*S*)

Separation factors are the ratio of U_H to U_{Fe}. The *S* values of membranes B-E are in range of 09 to 7.32 which is lower than the commercial DF-120 membrane (18.5 at 25°C) (Wu *et al.* 2010a) and the previous BPPO-SiO_2 membranes (24.5-30.5 at 25°C (Luo *et al.* 2010). The *S* values of membranes B-E are shown in Fig. 8. Previous research has shown that membrane morphology and functional groups play important role for determining the selectivity. It is explained as follows, the pore size of membranes is important in the selectivity. The lower values of S may be due to larger pore size in the membranes because both H^+ and Fe^{2+} can pass through these pores without much resistance. The porous structure of membranes is also responsible for higher water uptake resulting in lower *S* value. Thus, larger pore size is disadvantageous to selectivity. Moreover, as the amount of amine content increases from membrane B-E, both IEC and W_R of AEMs also increase. The increased IECs are useful, but the increased W_R is not beneficial for the selectivity of different ions (H^+ and Fe^{2+}). Moreover, the electrostatic repulsion between fixed group $-N+CH_3)_2C_6H_5Br^-$ and counter-ion (H^+ and $Fe^{2+)}$ is also important (Palaty and Bendova 2009, Kujawski and Narebska 1991, Elmidaoui *et al.* 1991, Narebska *et al.* 1995, Paddison *et al.* 2002). By increasing amine concentration from membrane B-E, the electrostatic repulsion between ions (H^+ and Fe^{2+}) and $-N+(CH_3)_2C_6H_5Br^-$ become stronger and all these factors leads to lower *S* values. This is well known that, *S* values can be correlated to the ion selectivity of membrane.

5. Conclusions

BPPO based anion exchanged membranes (AEMs) were prepared using different amount of dimethylaniline (DMA) content by phase-inversion technique. As the amount of DMA increases, anion exchange capacity (IEC) of membranes also increases from 0.34 mmol/g to 0.82 mmol/g, water uptake (W_R) increases from 202% to 226%, fixed group concentration increases from 0.0016 mol/L to 0.0036 mol/L but the contact angle decreases from 65.15° to 59.18°. The membranes have initial decomposition temperature (IDT) in the range of 219-256°C and thermal decomposition temperature in the range of 244-272°C. The SEM investigation shows that the membranes have dense top layer and porous bottom layer. These membranes can be applied for diffusion dialysis process for the recovery of HCl from the mixture of HCl and ferrous chloride at room temperature. The acid dialysis coefficient (U_H) and ferrous chloride dialysis coefficient (U_{Fe}) of anion exchange membranes B-E increases with amine content beacause the hydrophilicity of membrane increases. The separation factor (S) from anion exchange membranes C-E follows the decreasing trend as the amine content increases. The separation factor (S) for anion exchange membrane C is highest (7.32) among all the membranes, but a little lower than that of commercial DF-120 membrane. Further investigation will be performed by tuning pore size of membrane dense layer to improve S value of membrane.

Acknowledgments

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Nomenclature

Code	Full name
AEM	Anion exchange membrane
BPPO	Brominated poly(2,6-dimethyl-1,4-phenylene oxide)
DMA	Dimethylaniline
NMP	N-Methyl-2-pyrrolidone
W_R	Water uptake
IEC	Ion exchange capacity
SEMT	Scanning electron microscopy
IDT	Initial decomposition temperature
T_d	Thermal decomposition temperature
C_R	Fixed group concentration
η	Dimensional change ratio
DD	Diffusion dialysis
U_H	Diffusion dialysis coefficient of HCl
U_{Fe}	Diffusion dialysis coefficient of $FeCl_2$
DF-120	Commercial DD membrane based on quaternized BPPO
S	Separation factor