

Pervaporation Separation of Dimethyl Carbonate/Methanol Mixtures with Regenerated Perfluoro-Ion-Exchange Membranes in Chlor-Alkali Industry

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ABSTRACT: The waste perfluoro-ion-exchange membranes (PFIEMs) in chlor-alkali industry were regenerated and used to the separation of dimethyl carbonate (DMC)/methanol (MeOH) mixtures by pervaporation process. The energy-dispersive spectrum (EDS) demonstrates that the impurities on the surfaces of waste PFIEMs can be effectively cleared by the regeneration process. The degree of swelling, sorption, and pervaporation properties of the regenerated PFIEMs with different counter ions were investigated. The results indicate that the counter ions of PFIEMs conspicuously influence the degree of swelling, sorption, and pervaporation properties for DMC/MeOH mixtures. The degree of swelling and solubility selectivity both decreases with the alkali metal counter ions in the sequence: $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$. The degree of swelling increases with MeOH concentration increasing in feed liquid. The pervaporation measurements illustrate that the permeation flux decreases and the separation factor increases with the rising in ion radius of counter ions. The increase of feed concentration (MeOH) and feed temperature is advantageous to improve permeation flux while at the cost of separation factor decreasing. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3473–3481, 2013

KEYWORDS: perfluoro-ion-exchange membrane (PFIEM); pervaporation; dimethyl carbonate (DMC)/methanol (MeOH) mixtures; perfluorosulfonic acid (PFSA); nafion

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INTRODUCTION

Perfluoro-ion-exchange membrane (PFIEM) is widely used for caustic soda electrolysis in chlor-alkali industry owing to its superiorities such as energy efficient, environmental benign, high-product purity, and easy operation and is already recognized as the substitute of the mercury and diaphragm processes.^{1,2} PFIEM used in caustic soda electrolysis in chlor-alkali is ordinarily a bilayer composite membrane with perfluorosulfonic acid ionomer (PFSA) and perfluorocarboxylic acid ionomer (PFCA) layers reinforced by polytetrafluoroethylene (PTFE) fibers.^{2,3} Its typical cross-sectional structure can be described by the schematic diagram shown in Figure 1. The SEM image shown in Figure 2 is the cross-section of F-8020SP PFIEM, the Flemion membrane product from ASAHI Glass.

Commonly, the PFIEM used in chlor-alkali ordinarily has a life of 2–4 years in China.⁴ Thus, a great deal of waste PFIEM engenders because of the enormous product capacity of caustic soda in China. Burning and deep burying are two common methods to dispose the waste PFIEMs. Burning PFIEMs will produce poisonous gases of sulfide and fluoride⁵ which will lead

to severe environmental pollution. As the biodegradation of PFIEMs hardly occurs for ages owing to the special chemical stability, the deep burying also brings about environmental problem and land wastage. Thus, it is significant to recover and reuse the waste PFIEMs in chlor-alkali industry for other fields.

Pervaporation process is considered to be a promising alternative to conventional energy intensive technology like distillation for liquid separation owing to its advantages such as low-energy consumption, simple, and high separation efficiency. Besides, pervaporation process also has superiority in separating azeotropic mixtures as well as mixtures with adjacent boiling point compared to traditional distillation process because it can break through thermodynamic limit (azeotropic point). PFSA is the main ingredient of PFIEM. Besides its applications in chlor-alkali cell, pervaporation process is another important application field for PFSA membrane.^{6–16} Several reports revealed the dehydration of inorganic and organic acid^{6–9} by pervaporation process using PFSA (nafion) membrane because it has high chemical stability and preferential permeation for water. Furthermore, PFSA was also employed to the dehydration of small

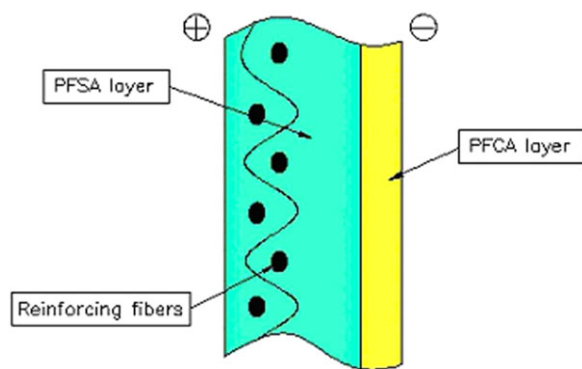


Figure 1. Schematic diagram of the cross-sectional structure of PFIEM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecular alcohol by pervaporation process or blended with other materials.^{10–13} PFSA has also been found to be highly selective for separating methanol (MeOH) from organic solutions in some separation process.^{14–16} DMC is an environmental benign chemical.¹⁷ The separation of MeOH and DMC is an important step in industrial DMC manufacturing because these two components easily form azeotropic mixtures in distilling process.¹⁸ Several researchers have revealed the separation of DMC/MeOH mixtures by pervaporation process.^{18–25}

In this article, the waste PFIEMs (F-8020SP) in chlor-alkali industry were regenerated and used to the pervaporation separation of DMC/MeOH mixtures. The equilibrium sorption and swelling properties of the regenerated PFIEMs with different counter ions in DMC/MeOH mixtures were measured. Effects of the counter ions of PFIEMs, MeOH concentration in feed liquid, feed temperature on the pervaporation performances were investigated in detail.

EXPERIMENTAL

Materials

The waste PFIEMs were kindly provided by Shanghai Chlor-Alkali Chemical (China). The PFIEM is the product of F-8020SP (Flemion[®]) ion-exchange membrane of Asahi Glass Group (Japan). MeOH and DMC were purchased from Shanghai Heqi Chemical (China). Hydrochloric acid (HCl), lithium chloride (LiCl), sodium chloride (NaCl), potassium chloride (KCl), and cesium chloride (CsCl) used to get PFIEMs with different counter ions were all in reagent grade and purchased from Shanghai Aladdin Chemistry Co. Ltd. (China).

Regeneration and Characterizations of Waste PFIEMs

The regeneration process of the waste PFIEMs can be described as follows. First, the waste PFIEMs were immersed with 8 wt % HCl at 80°C for 24 h. Second, the waste membranes were further cleaned in the ultrasonic water bath for 30 min. Then, the regenerated membranes were rinsed with deionized water. Thus, the regenerated PFIEM in acid type was obtained. The regenerated PFIEMs with different counter ions were prepared by ion-exchange method. It was realized by immersing the acid-form-regenerated PFIEM in 1M chloride aqueous solution for

24 h and rinsing with deionized water. The elements of the anodic surfaces (PFSA side; the anodic surface refers to the surface toward the anodic side of the electrolyzer cell in industrialized chlor-alkali process, the same below) of the waste and regenerated PFIEMs were measured by energy-dispersive spectrum (EDS) technology. The appearances of the waste and regenerated PFIEMs were shot with a digital camera.

Pervaporation Separation of DMC/MeOH Mixtures

The pervaporation process was performed on a stainless steel permeation cell. The effective membrane area was 24.6 cm² (diameter, 5.6 cm). The membrane was supported on a polypropylene porous plate. The feed liquid was pumped through the permeation cell by a peristaltic pump. The feed temperature was controlled by a thermostat system. The permeate side pressure was controlled below 100 Pa by a vacuum pump. The permeate liquid was collected in a cold trap cooled with liquid nitrogen. To minimize error, each sample membrane was tested for at least two times. The mean value of the two times was used as the final value. The deviation of pervaporation values was <5%.

The compositions of both feed and permeate liquid were analyzed by a gas chromatography (GC9800) equipped with a flame ionization detector and a capillary column (SE54 50 m × 0.32 mm × 0.5 mm).

The total permeation flux (J) is obtained as follows:

$$J = \frac{w}{At} \quad (1)$$

where w is the mass of permeate (g), A is the effective membrane area (m²), and t is the periodical time (h).

The separation factor (α) is defined as

$$\alpha = \frac{P_{\text{MeOH}}/P_{\text{DMC}}}{X_{\text{MeOH}}/X_{\text{DMC}}} \quad (2)$$

where X_{MeOH} and X_{DMC} are the weight fractions of MeOH and DMC in feed liquid, respectively, P_{MeOH} and P_{DMC} are the weight fractions of MeOH and DMC in permeate liquid, respectively.

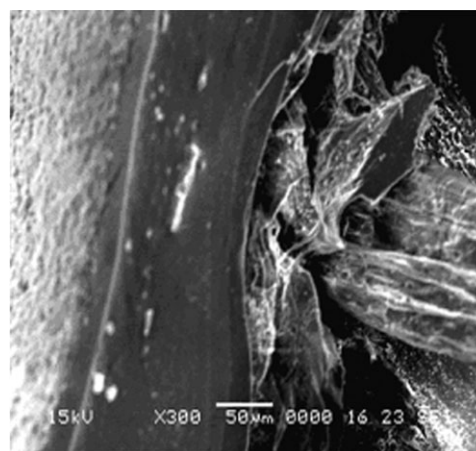


Figure 2. SEM image of the cross-section of F-8020SP membrane.

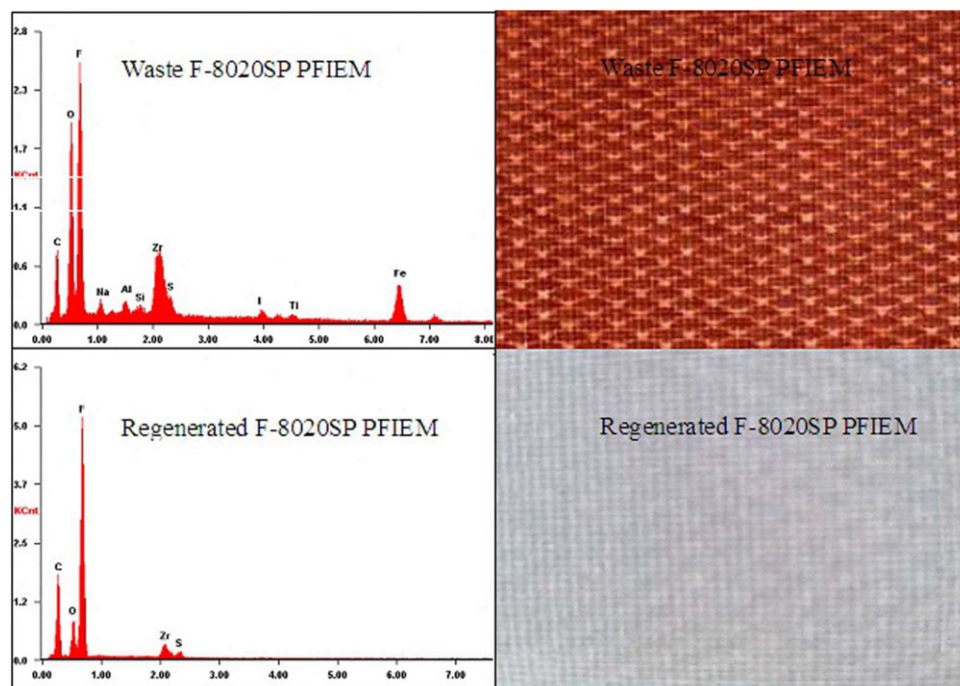


Figure 3. EDS spectra and image of the anodic surfaces of the waste and regenerated F-8020SP PFIEMs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Sorption and Swelling Measurements

The predried membranes were weighed and then soaked in DMC/MeOH mixtures for 48 h at 25 and 40°C, respectively, to attain sorption and swelling equilibrium. Then, the swollen samples were taken out and quickly weighed again after wiping off the free liquid on the membrane surface. The degree of swelling (DS) of membrane is determined upon the weight difference before and after swelling. It is defined as

$$DS = \frac{W_w - W_d}{W_d} \times 100\% \quad (3)$$

where W_d and W_w are the weights of dry and swollen membranes, respectively.

After being weighed, the swollen samples were placed immediately in a sealed tank. The sorbed liquid was collected in a liquid nitrogen trap by desorbing the equilibrated sample. The compositions were also analyzed by gas chromatography.

The solubility selectivity (S) is defined as

$$S = \frac{M_{\text{MeOH}}/M_{\text{DMC}}}{X_{\text{MeOH}}/X_{\text{DMC}}} \quad (4)$$

where M_{MeOH} and P_{DMC} are the weight fractions of MeOH and DMC in the equilibrated membrane, respectively.

RESULTS AND DISCUSSION

Regeneration of the Waste PFIEMs

PFIEM (Flemion, Nafion, etc.) has been widely applied to produce caustic soda by electrolyzing NaCl aqueous solution in chlor-alkali industry. Impurities such as Fe, Ca, Mg, and so on,

in fine brine are one important factor on the decline of the electrochemical properties of PFIEM. The impure metal elements are commonly deposited as hydroxide or oxide on the membrane surface during the long-term electrolysis process. Hence, strong acid solution like HCl aqueous solution should be an ideal reagent for the regeneration of waste PFIEM. The regeneration or washing process of waste PFIEM in chlor-alkali industry has been revealed in the previously published literatures.^{26,27} In this research, 8 wt % HCl aqueous solution was used to regenerate the waste PFIEM at 80°C.

Figure 3 shows that the EDS analysis of the anodic surface (PFSA side) of the waste and regenerated PFIEMs. It can be seen that the several elements such as C, F, O, Na, Al, Zr, Si, Fe, Ti, S, and I were detected on the surface of the waste membrane. Among them, C and F are the main elements of PFIEM; O is ascribed to the groups of $-\text{SO}_3^-$ and ZrO_2 which is the component of hydrophilic layer; Na is counter ion of polyelectrolyte; Zr is from hydrophilic ZrO_2 layer. Besides the own ingredients of PFIEM, the elements of Al, Si, Fe, Ti, and I are ascribed to the pollutants on the surface of PFIEM. As shown in Figure 3, these impurities like Al, Zr, Fe, Ti, S, and I are not found on the surface of the regenerated PFIEM, which demonstrates the regeneration process of combining acid immersing and ultrasonic washing is effective. The regeneration efficiency can be further illustrated by comparing the appearance pictures of the waste and regenerated PFIEMs shown in Figure 3.

Sorption and Swelling Behaviors of the Regenerated PFIEM

The DS and S of the regenerated PFIEMs with different counter ions (H^+ , Li^+ , Na^+ , K^+ , and Cs^+) for DMC/MeOH mixtures (MeOH, 10 wt %) are investigated at 25 and 40°C. The results

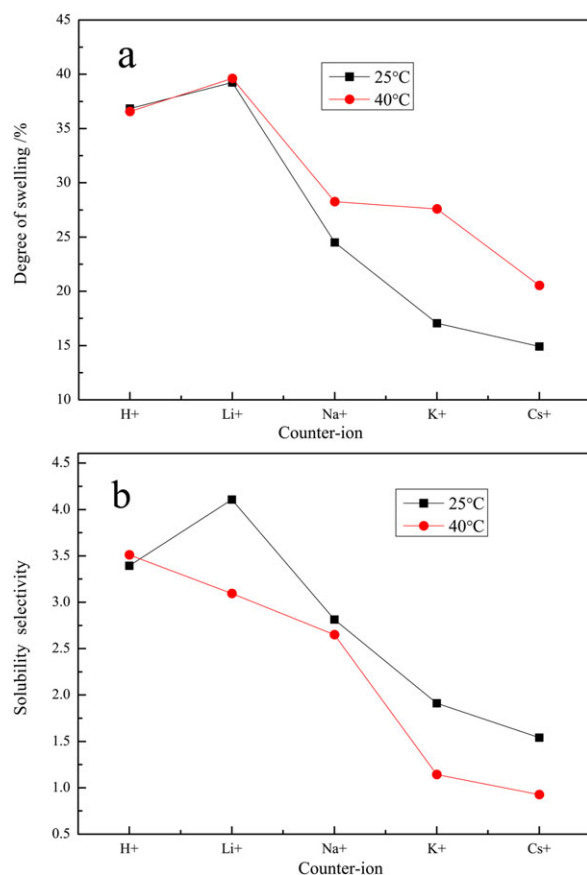


Figure 4. Effect of counter ion on the DS and sorption behaviors of PFIEM (MeOH concentration in feed liquid: 10 wt %, a: DS, b: S). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are shown in Figure 4. It can be seen that both the DS and the *S* decrease with the alkali metal counter ions in the following sequence: Li⁺ > Na⁺ > K⁺ > Cs⁺. The decrease of the *S* of PFIEM with the rising in ion radius indicates that the smaller alkali metal ions with relative low radius have higher affinity with MeOH than with DMC molecules. It can be explained that higher polar MeOH molecule is easily combined with the smaller alkali metal ions. The similar variation trend in the DS of PFSA (Nafion) membrane relating to the ion radius of counter ions was also observed in the previously published literatures.^{28–30} Randová's investigation revealed that the swelling extent of Nafion membrane in MeOH–water–alkali metal chloride solution decreased from LiCl > NaCl > KCl > CsCl.²⁸ Also, Jalani and Datta²⁹ measured the sorption behavior of Nafion membrane with different counter ions in vapor phase containing varied activity of MeOH, ethanol, and propanol. The nearly same swelling tendency was found. Nandan et al.³⁰ also found that the MeOH sorption in Nafion membranes in terms of counter ions follows the sequence: Li⁺ > Na⁺ > K⁺ > Cs⁺.

Figure 5 shows the effect of MeOH concentration in feed liquid on the DS and *S* of acid-form PFIEM. It can be seen that the DS increases and *S* decreases with the increase of MeOH concentration. As PFIEM has higher affinity with MeOH compared

with DMC, the increase of MeOH concentration in feed liquid must promote sorption and swelling. Nevertheless, a part of DMC molecules will also be sorbed in this process for their good association with MeOH molecules. As shown in Figure 5, it is also found that the DS of PFIEM at 40°C is higher than that in 25°C especially at higher MeOH concentration. It illustrates that increasing feed temperature can enhance the swelling of PFIEM. Higher DS of PFIEM indicates the prospective higher permeation flux at higher MeOH concentration. However, the results shown in Figure 5(b) indicate that the feed temperature has no evident influence on the *S* of the regenerated PFIEMs for DMC/MeOH mixtures.

Pervaporation Separation of DMC/MeOH Mixtures

Orientation of PFIEM in Pervaporation Process. Flemion ion-exchange membrane used in chlor-alkali industry is a PFSA/PFCA bilayer membrane supported by PTFE fibers. The PFSA and PFCA layers have different permeation performances. Therefore, the influence of membrane orientation on the pervaporation performances of the regenerated PFIEM is first measured and shown in Figure 6. As shown in Figure 6, the regenerated PFIEM membrane has better pervaporation performances in both separation factor and total permeation flux when the

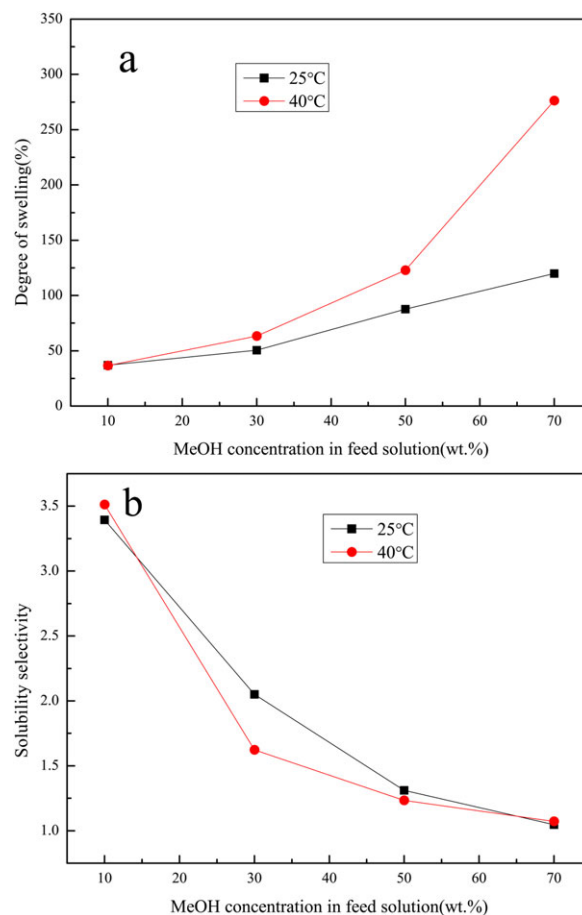


Figure 5. Effect of MeOH concentration in feed liquid on the DS and *S* of acid form PFIEM for DMC/MeOH mixtures (a: DS, b: S). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

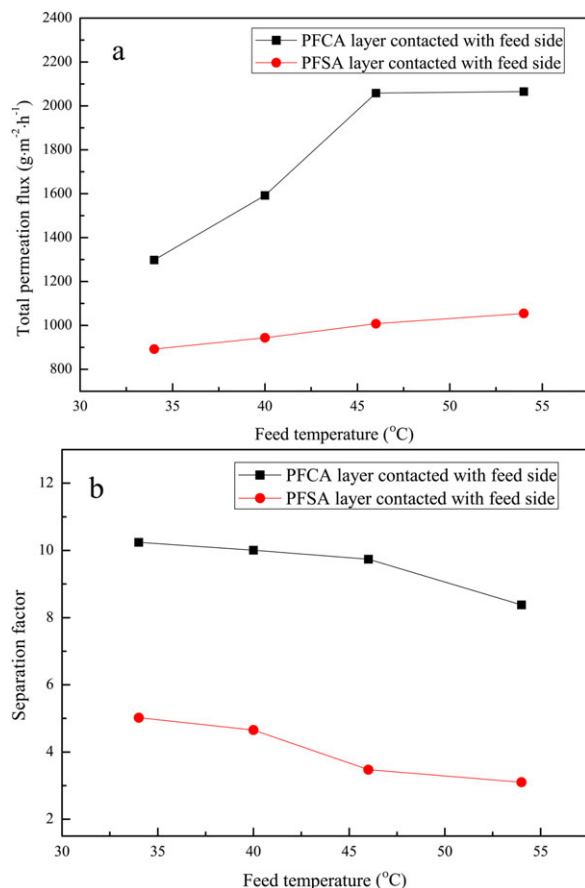


Figure 6. Effect of membrane orientation on the permeation flux and separation factor (a: total permeation flux, b: separation factor). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PFCA layer is contacted with feed side. The similar findings were also obtained by Sportsman⁹ for the dehydration of nitric acid with PFSA/PFCA bilayer membrane. Sportsman claimed that the configuration by orientating PFCA layer directly faced feed liquid allows it to become fully swollen, whereas PFSA is easily swollen. Upon these experimental results, the following pervaporation tests were carried out by orientating the PFCA layer directly contacted with feed liquid.

Effect of Counter Ion of PFIEM. Figure 7 shows the effect of counter ion on the pervaporation performances of the regenerated PFIEM for DMC/MeOH mixtures. The pervaporation experiments were conducted with 10 wt % MeOH concentration in feed liquid at 40°C. It can be seen that the permeation flux decreases with counter ion in the sequence of H⁺ > Li⁺ > Na⁺ > K⁺ > Cs⁺ varying from the highest value 1591.5 to 17.3 g·m⁻²·h⁻¹; meanwhile, the separation factor increases in this sequence from 10.0 for acid-form PFIEM to the highest value 30.0 for Cs form PFIEM. The preferential permeation of MeOH in PFIEM membrane can be understood in terms of the widely accepted the ion-cluster network model of Gierke³¹ in which the ionic sites of the pendant groups phase separate from the hydrophobic PTFE backbone to form clusters that are about 4

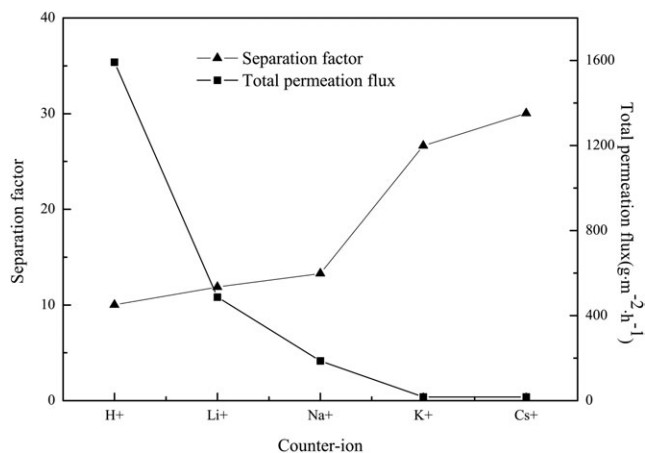


Figure 7. Effect of counter ion of PFIEM on the pervaporation performances of PFIEM for DMC/MeOH mixtures (MeOH concentration in feed liquid: 10 wt %, feed temperature: 40°C).

nm in diameter and are connected by short, narrow channels. As well, PFCA should have the similar microstructure with PFSA. Small molecules such as water and lower aliphatic alcohols can easily pass through the ionic channels in preference to large and low-polar molecules such as DMC. With the increase in size of the counter ion, the free volume of ion cluster decreases and causes the decrease of the permeation flux. The similar tendencies of the separation selectivity and permeation flux with counter ions were also found in the pervaporation separation of alcohol/H₂O mixtures.^{10–12}

According to the solution–diffusion mechanism, the separation factor of pervaporation process is the combination of solubility and diffusion selectivity. Comparing the experimental results in Figures 4 and 7, it is found that the varying trends of the separation factor of pervaporation process with counter ion is conspicuously different from that of the *S*. Therefore, the diffusion rates of MeOH and DMC molecules in the membrane should act as the dominant role in the pervaporation separation process rather than the solubility in the membrane. The diffusion

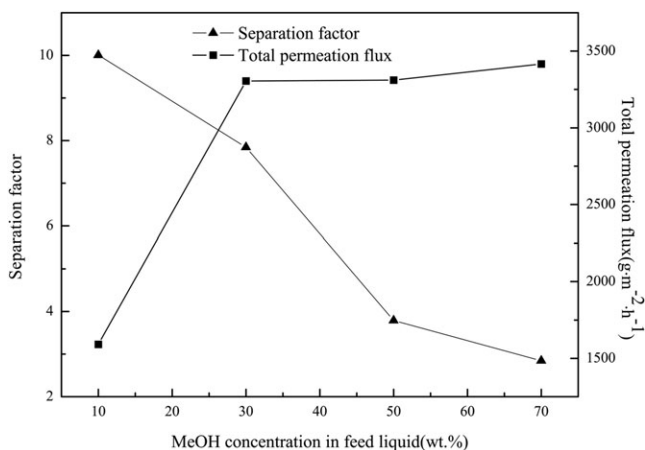


Figure 8. Effect of MeOH concentration in feed liquid on the pervaporation performances of the acid-form-regenerated PFIEM (feed temperature: 40°C).

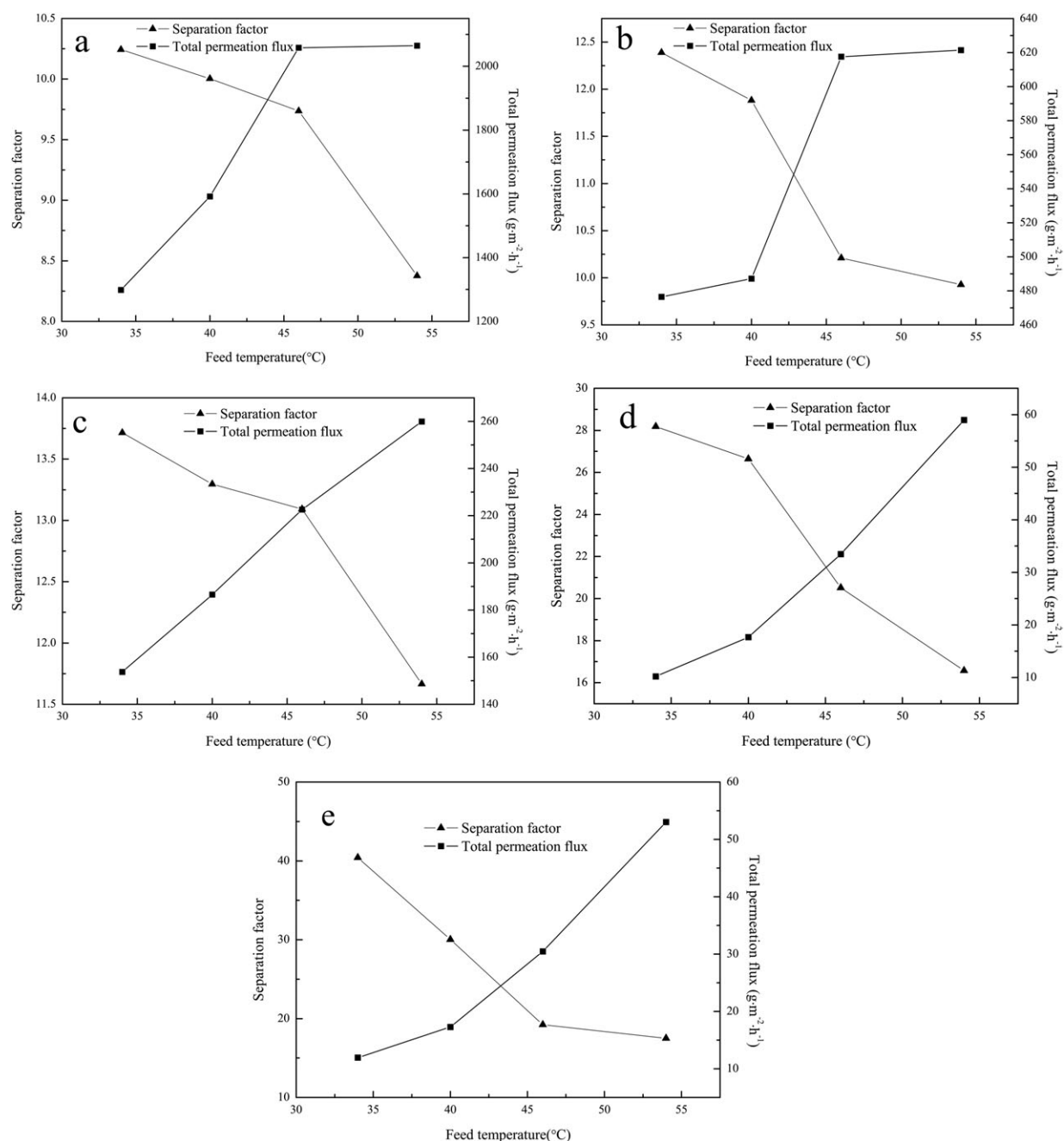


Figure 9. Effect of feed temperature on the pervaporation performances of the regenerated PFIEMs with different counter ions for the separation of DMC/MeOH (MeOH concentration in feed liquid: 10 wt %; counter-ion of PFIEM: a: H⁺, b: Li⁺, c: Na⁺, d: K⁺, and e: Cs⁺).

rate of MeOH molecules should be much higher than those of DMC molecules in membrane, especially for the membrane with large counter ions such as K and Cs.

Effect of MeOH Concentration. The effect of MeOH concentration in feed liquid on pervaporation performances of the acid-form-regenerated PFIEM at 40°C is shown in Figure 8. As MeOH concentration increases from 10 to 70 wt %, the separation factor decreases from 10.0 to 2.8, whereas the permeation flux increases gradually from 1591.6 to 3415.7 g·m⁻²·h⁻¹. When

Table I. The Apparent Activation Energy of PFIEMs with Different Counter Ions

Counter ion	H ⁺	Li ⁺	Na ⁺	K ⁺	Cs ⁺
ΔE_{Total} (kJ·mol ⁻¹)	31.23	12.84	22.03	74.35	63.60
ΔE_{MeOH} (kJ·mol ⁻¹)	29.28	9.51	20.04	66.05	53.77
ΔE_{DMC} (kJ·mol ⁻¹)	4.30	1.66	4.18	23.32	18.57

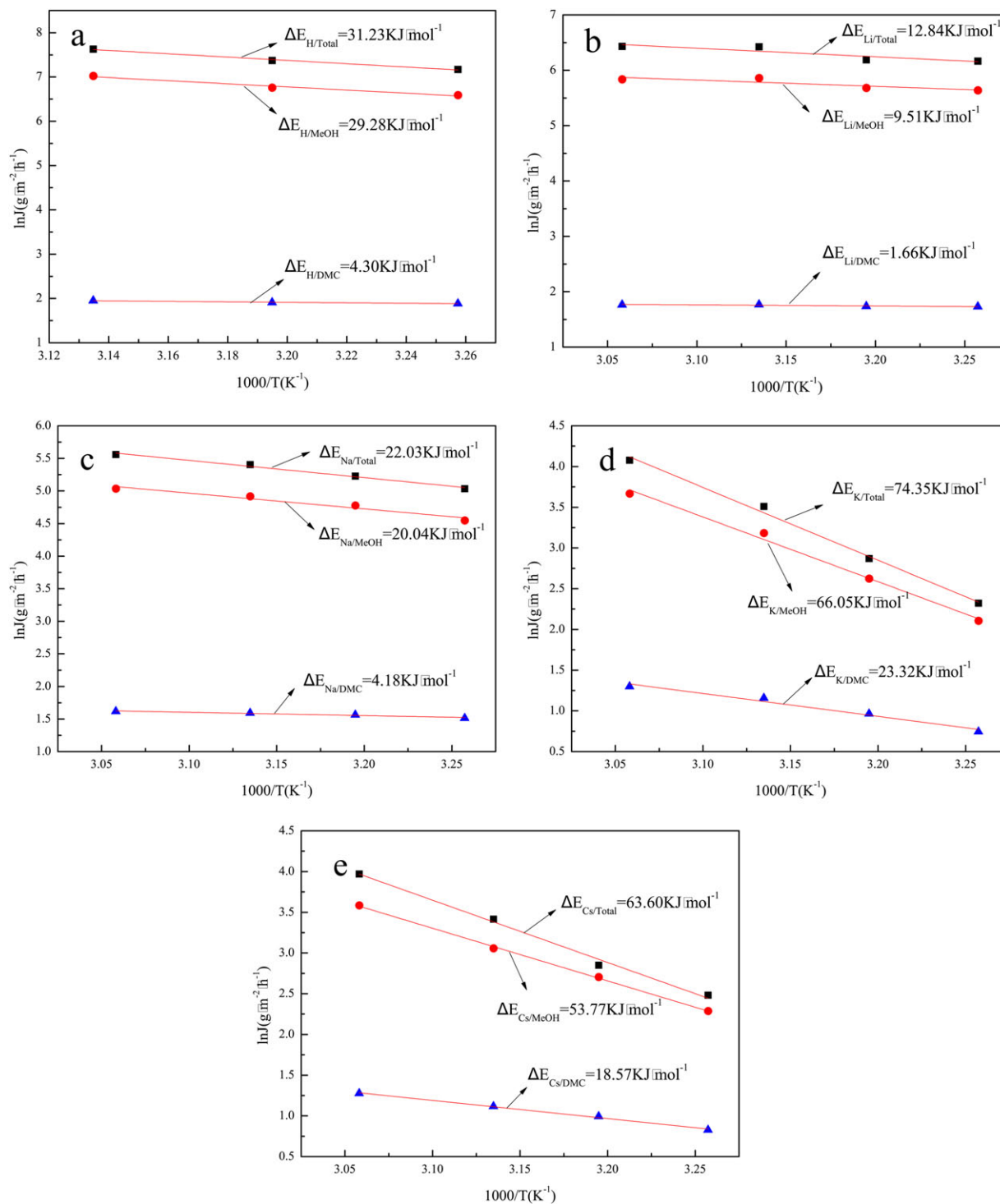


Figure 10. The activation energy required for pervaporation permeation of DMC/MeOH solution through PFIEMs with different counter ions (MeOH concentration: 10 wt %; counter-ion of PFIEM: a: H^+ , b: Li^+ , c: Na^+ , d: K^+ , and e: Cs^+). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

MeOH concentration in feed liquid increases, the DS of PFIEM increases [Figure 5(a)], which will enhance the permeation process owing to the increasing in driving force. Certainly, with the swelling of membrane, DMC can also diffuse easily through the swollen membrane because the free volume becomes larger and

the polymer chains become more flexible. Meanwhile, MeOH molecules in the permeation process carry some DMC molecules because of the association between the two types of molecules. In addition, as shown in Figure 5(b), the S decreases with the MeOH concentration increasing in feed. The decline of

separation factor with the MeOH concentration in feed can be ascribed to the above factors. The similar tendency as a function of feed concentration also found for other polymeric membranes for the pervaporation of DMC/MeOH mixtures.^{19,20}

Effect of Feed Temperature. The pervaporation separation of DMC/MeOH mixtures of the regenerated PFIEMs with different counter ions was conducted at feed temperature of 34, 40, 46, and 54°C. The results are shown in Figure 9. It is found that the pervaporation performances of PFIEMs greatly depend on feed temperature. The total permeation flux of acid form PFIEM increases from 1298.4 to 2064.9 g·m⁻²·h⁻¹, whereas the separation factor slightly decreases from 10.2 to 8.4 as the feed temperature increases from 34 to 54°C. The similar trend is also found for the regenerated PFIEMs with other alkali metal counter ions. The varying tendencies can be explained as follows. First, the PFIEMs have higher sorption capacity for DMC/MeOH mixtures at higher temperature [Figure 5(a)], which is advantageous to obtain higher permeation flux. In addition, at higher feed temperature, permeate components have higher activity and higher diffusion rate, which can promote them to pass through the membrane. Furthermore, increasing feed temperature raises the vapor pressure of the permeating components on the upstream side of membrane; meanwhile, the vapor pressure on the downstream side is constant. Hence, the transport driving force is improved when the feed temperature increases, which also leads to the increase of permeation flux. The previous descriptions have pointed out that the feed temperature has no evident influence on the *S* of the PFIEMs for DMC/MeOH mixtures [Figure 5(b)]. Comparing the data shown in Figures 5(b) and 9, it can be concluded that the diffusion process should dominate the varying trends of separation factor with feed temperature.

Permeation Activation Energy. The relationship between the feed temperature and the permeation flux follows the Arrhenius law, which can be expressed as

$$\ln J = \ln J_0 - \frac{\Delta E}{RT} \quad (5)$$

where J_0 is a constant and ΔE is the permeation activation energy of permeate component through membrane. The logarithmic plots of total permeation flux versus the reciprocal of absolute feed temperature for the PFIEMs with different counter ions are shown in Figure 9. The ΔE values of the PFIEMs with different counter ions for the pervaporation separation of DMC/MeOH mixtures (10 wt % MeOH concentration) are obtained from the plot slopes. The activation energy values for MeOH, DMC, and total permeate components are listed in Table I.

As shown in Figure 10, typical linear relationships are achieved for the total and partial fluxes for all PFIEMs with different counter ions. It can be seen that the total and partial permeation activation energy for the PFIEMs with alkali metal counter ions increases from Li⁺ to K⁺, and then slightly decreases to Cs⁺ with the rising in the size of counter ions. The permeation through acid-form PFIEM has a medium activation energy value between Na⁺ and K⁺. As summarized in Table I, it can be

seen that the activation energy of MeOH permeation is higher than that of DMC permeation through the PFIEM for all counter ions. It demonstrates that the influence of feed temperature on DMC permeation is higher than on MeOH permeation. It causes the decline of the separation factor of PFIEM for DMC/MeOH mixtures with the feed temperature increasing.

CONCLUSIONS

The regeneration and reuse of the waste PFIEM in chlor-alkali industry were confirmed in this study. The regeneration efficiency of PFIEMs was proved by EDS technique and digital pictures. The regenerated PFIEMs were successfully reused in the pervaporation separation of DMC/MeOH mixtures. The experimental results illustrate that the counter ions of PFIEMs evidently influence the DS and *S*, and pervaporation separation of DMC/MeOH mixtures. The DS and *S* of the PFIEMs for DMC/MeOH mixtures both decrease with counter ions in the sequence of Li⁺ > Na⁺ > K⁺ > Cs⁺. The acid-form PFIEM has a medium DS between counter-ions Li⁺ and Na⁺. The DS increases and *S* decreases with MeOH concentration increasing in feed liquid, which is closely related to the rising in the size of counter ions. In pervaporation process, the permeation flux decreases in the sequence of H⁺ > Li⁺ > Na⁺ > K⁺ > Cs⁺, whereas the separation factor is converse to this sequence. For the separation of DMC/MeOH mixtures with acid-form PFIEM, the separation factor decreases from 10.0 to 2.8, whereas the permeate flux increases gradually from 1591.6 to 3415.7 g·m⁻²·h⁻¹ as MeOH concentration increases from 10 to 70 wt % at 40°C. The permeate flux increases from 1298.4 to 2064.9 g·m⁻²·h⁻¹, whereas the separation factor decreases from 10.2 to 8.4 when the feed temperature increases from 34 to 54°C.

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