

## Pervaporation of *n*-Butanol Aqueous Solution Through ZSM-5-PEBA Composite Membranes

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**ABSTRACT:** Composite membranes were prepared by incorporating ZSM-5 zeolite into poly(ether-block-amide) (PEBA) membranes. These composite membranes were characterized by TGA, XRD, and SEM. The results showed that the zeolite could distribute well in the polymer matrix. And when the zeolite content reached 10%, the agglomeration of zeolite in the membranes was found. The composite membranes were used to the pervaporative separation of *n*-butanol aqueous solution. The effect of zeolite content on pervaporation performance was investigated. With the contribution of preferential adsorption and diffusion of *n*-butanol in the polymer matrix and zeolite channel, the 5% ZSM-5-PEBA membrane showed enhanced selectivity and flux. The effects of liquid temperature and concentration on separation performance were also investigated. All the composite membranes demonstrated increasing separation factor and permeation flux with increasing temperature and concentration. Incorporation of ZSM-5 could decrease the activation energy of *n*-butanol flux of the composite membrane. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 105–112, 2013

**KEYWORDS:** membranes; pervaporation; *n*-butanol; PEBA; ZSM-5 zeolite

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### INTRODUCTION

In recent years, using the acetone butanol ethanol (ABE) fermentation process to produce biobutanol as a biofuel has got more and more attention. As an advanced biofuel,<sup>1</sup> *n*-butanol has several advantages such as high energy content, low vapor pressure, higher octane rating, and better adaptability for the existing gasoline supply system than bioethanol. However, *n*-butanol has a severe inhibition to the traditional acetone-*n*-butanol-ethanol (ABE) fermentation process,<sup>2</sup> which resulted in the total solvent (acetone-*n*-butanol-ethanol, ABE) concentration cannot exceed 20 g L<sup>-1</sup> for different bacterial strains.<sup>3</sup> To make the fermentation process economically attractive, some separation techniques, such as distillation,<sup>4</sup> gas stripping<sup>5</sup> adsorption,<sup>6</sup> and pervaporation have been coupled with fermentation to recover *n*-butanol from fermentation broth. Among them, pervaporation is a novel and effective membrane technique that is favorable for separating liquid mixture especially small amount of organics from aqueous solution. Because of its simplicity to combine with fermentation process, high permselectivity, energy and cost saving, pervaporation has already been reported to recover *n*-butanol from ABE fermentation process by some researchers. Qureshi et al. have carried out a series of research on this field.<sup>3,7</sup> They used a kind of silicone membrane<sup>8</sup> to integrate pervaporation with fermentation process. The results showed solvent productivities were improved to 200% of the

control batch fermentation productivities. Then they<sup>9</sup> prepared silicalite-filled silicone membranes to pervaporate *n*-butanol from fermentation broth. Though the addition of silicalite did not significantly improve flux, it was able to increase the selectivity 2.2-fold. Izák et al.<sup>10</sup> prepared ionic liquid (IL)-polydimethylsiloxane (PDMS) composite membrane to remove *n*-butanol out of a *C. acetobutylicum* culture. And overall solvent productivity of fermentation connected with continuous product removal by pervaporation was 2.34 g L<sup>-1</sup> h<sup>-1</sup>.

As we know, membrane material has great effect on the pervaporation performance. Up to now several kinds of polymers were proved to be preferential permeation for organics, such as PDMS,<sup>11–13</sup> poly(1-trimethylsilyl-1-propyne)(PTMSP),<sup>14,15</sup> poly(vinylidene fluoride-co-hexafluoropropene) (P(VDF-co-HFP))<sup>16,17</sup> and poly(ether block amide) (PEBA).<sup>18,19</sup> Among them, PEBA is a thermoplastic elastomer and comprises of rigid polyamide as “hard segments” and flexible polyether as “soft segments.”<sup>20</sup> By changing the proportion of the two segments, PEBA with different physical and chemical properties could be gotten. Because of its organophilic property, some researchers prepared PEBA to pervaporative separation of *n*-butanol from dilute aqueous solution. Fouad and Feng<sup>21</sup> used PEBA membrane to recover *n*-butanol over the low feed concentration range (0.03–0.4 wt %). High permeation flux (about 400 g m<sup>-2</sup>·h at 60°C) and high separation factor (about 38 at 60°C) could be obtained, demonstrating

PEBA was a good *n*-butanol preferential permeation membrane material. Feng et al.<sup>22</sup> also prepared PEBA membrane to pervaporate acetone-*n*-butanol-ethanol (ABE) from dilute aqueous solutions. It was found that the membrane had the potential to recover ABE solvent from dilute solution and the permselectivity was in the order of *n*-butanol > acetone > ethanol.

PEBA 2533, one of the commercialized PEBA copolymers with 80 wt % poly(tetramethylene oxide) and 20 wt % nylon 12,<sup>23</sup> has excellent chemical, mechanical property, and thermal stability as well as good pervaporation performance toward alcohol.<sup>21,22,24</sup> At the same time, ZSM-5 zeolite with high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, as a kind of inorganic filler, could enhance the permselectivity and mechanical strength of the polymer membrane.<sup>25,26</sup> Therefore, in this article, ZSM-5-filled PEBA 2533 membranes were prepared to separate *n*-butanol from aqueous solution by pervaporation. The selectivity and permeability of the mixed matrix membrane in the pervaporation process were discussed. The physical and chemical properties of the prepared membranes were characterized. The effects of feed concentration, temperature and zeolite content on the separation performance were investigated.

## EXPERIMENTAL

### Materials

PEBA 2533 was supplied by Arkema Group. HZSM-5 with particle size of 3 μm and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 300 was purchased from Shanghai Fuxu Molecular sieve Limited Company. *n*-butanol of analytical purity was supplied by Sinopharm Chemical Reagent. Deionized water was self-made.

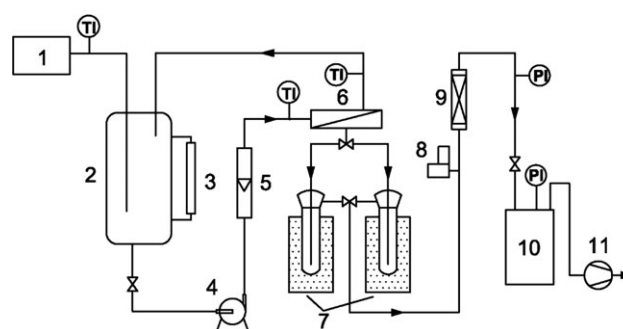
### Membrane Preparation

ZSM-5 zeolite was weighed and roasted in muffle furnace at 400°C for 4 h to remove the adsorbed water and carbon dioxide. The pretreated zeolite was then cooled in the desiccator to room temperature.

Plain PEBA membrane was prepared by dissolved the PEBA 2533 granule in *n*-butanol solvent at 70°C. After the polymer dissolved completely by stirring, the prepared 8 wt % casting solution was toppled on a horizontal glass plate and cast with a scraper. The solvent was evaporated in the atmosphere for 12 h. And then the membrane was further dried at 60°C in an oven. The ZSM-5 zeolite-filled membrane was prepared by ultrasonic dispersing ZSM-5 zeolite in *n*-butanol for 1 h when dissolving PEBA 2533 granule simultaneously. Then the two mixtures were stirred and mixed uniformly. The casting and drying steps were the same as plain PEBA membrane. The obtained plain PEBA and zeolite-filled membranes were labeled as PEBA, 2% ZSM-5-PEBA, 5% ZSM-5-PEBA, and 10% ZSM-5-PEBA for 0, 2, 5, and 10 wt % zeolite content.

### Membrane Characterization

X-ray powder diffraction (XRD, D8FOUCUS, Bruker AXS) was used to study the crystalline diffraction characteristics of the ZSM-5, PEBA, and ZSM-5-PEBA samples (with 2, 5, and 10% ZSM-5 content). The radiation was generated using Cu Kα (λ = 0.154 nm) from a graphite monochromator at 40 kV and 100 mA. Scanning rate was 6° min<sup>-1</sup> and scanning range was 4–70°.



**Figure 1.** Schematic diagram of the pervaporation experimental equipment. 1. thermal controller; 2. liquid reservoir; 3. level gauge; 4. liquid pump; 5. rotameter; 6. membrane cell; 7. cold trap; 8. pressure sensor; 9. dryer; 10. buffer tank; 11. vacuum pump.

NOVA NANOSEM 450 scanning electron microscopy (FEI Company) was used to observe the surface and cross-section morphologies of the membranes.

The thermal stability of the membranes was measured by thermogravimetric analyzer (Q600SDT, TA Instrument) at a heating rate of 30°C min<sup>-1</sup> from 20 to 900°C in nitrogen atmosphere.

### Swelling Studies

The dried ZSM-5-PEBA membrane was weighed and immersed in *n*-butanol aqueous solution at 35°C. Then the membrane sample was periodically taken out and wiped carefully with Kimwipes (Kimberly–Clark) to remove the liquid on surface. After weighed, the sample was put back into aqueous solution again until the sample weight was unchanged. The degree of swelling (DS) was determined by

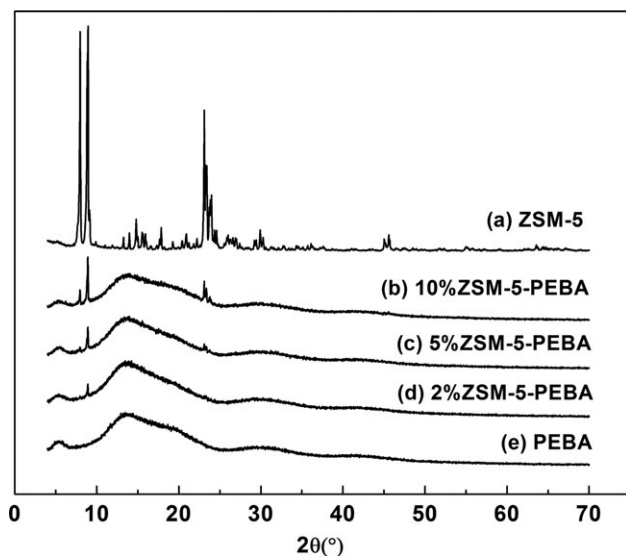
$$DS(\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where  $W_s$  and  $W_d$  are the mass of swollen and dry membranes, respectively.

### Pervaporation Experiment

The pervaporation apparatus was shown in Figure 1. The feed liquid storing in the reservoir was sent to the membrane cell by a liquid pump. Part of the feed went through the membrane and evaporated in vacuum environment on the downstream side. The permeate vapor was condensed and collected in the cold trap with liquid nitrogen. The retentate was recirculated to the liquid tank. During the experiments, the upstream side of the membrane cell was maintained at atmospheric pressure and the downstream side pressure was kept 320 Pa all the time. The feed temperature is controlled through a temperature-controller and the feed rate was monitored by a rotameter. The temperatures at the entrance and exit of the membrane cell are measured with two thermocouples. The effective membrane area is  $3.6 \times 10^{-3} \text{ m}^2$ .

The concentrations of permeates and feed were determined by gas chromatography (GC7890F, TECHCOMP (HOLDINGS) LIMITED) equipped with a FID detector and using HP-FFAP capillary column. The weight of permeates was weighed by electronic balance (with accuracy of 0.1 mg).



**Figure 2.** XRD patterns of (a) ZSM-5 zeolite, (b) 10% ZSM-5-PEBA membrane, (c) 5% ZSM-5-PEBA membrane, (d) 2% ZSM-5-PEBA membrane and (e) PEBA membrane.

The pervaporation performance of a membrane is usually evaluated in terms of separation factor  $\alpha$  and permeation flux  $J$ , which are determined as follows:

$$\alpha = \frac{(C_i/C_j)_{\text{Permeate}}}{(C_i/C_j)_{\text{Feed}}} \quad (2)$$

$$J = \frac{W}{At} \quad (3)$$

where  $C_i$  and  $C_j$  are the mass fractions of the  $n$ -butanol and water components, respectively;  $W$  is the mass of the permeate, g;  $A$  is the effective membrane area,  $m^2$ ;  $t$  is the permeation time, h.

## RESULTS AND DISCUSSION

### Membrane Characterization

**XRD Analysis.** Figure 2(a) shows that there are two sharp characteristic diffraction peaks of ZSM-5 in the range of  $7^\circ$ – $9^\circ$  and  $23^\circ$ – $25^\circ$  for ZSM-5 zeolite.<sup>27</sup> Figure 2(b–e) shows the XRD patterns of PEBA membrane, 10% ZSM-5-PEBA, 5% ZSM-5-PEBA, and 2% ZSM-5-PEBA membranes. There is no sharp diffraction peak but four wide diffraction peaks appeared at the range of  $4^\circ$ – $50^\circ$  in PEBA membrane, which proves that PEBA is a kind of amorphous polymer.<sup>28</sup> The XRD pattern of ZSM-5-PEBA composite membrane is the superposition of ZSM-5 zeolite and PEBA samples. The sharp diffraction peaks at the range of  $7^\circ$ – $9^\circ$  arose in the XRD pattern of 2% ZSM-5-PEBA composite membrane. When the zeolite content increased, more and higher characteristic diffraction peaks of ZSM-5 appeared for 5% ZSM-5-PEBA and 10% ZSM-5-PEBA membranes, which demonstrates that ZSM-5 zeolite distributes well in the PEBA polymer matrix.

**SEM Analysis.** Figure 3 shows the SEM images of the surface layer and cross section of PEBA and ZSM-5-PEBA composite

membranes. The plain PEBA membrane is very smooth [Figure 3(a,e)]. It can be seen from Figure 3(b–d) that the zeolite particles are distributed without defect throughout the polymer matrix of ZSM-5-PEBA composite membranes. Based on membrane surface SEM images merely, the situation of zeolite distribution was not easy to find, because most zeolites situated underneath the membrane skin layer. According to the information of the cross section SEM images of 2% ZSM-5-PEBA and 5% ZSM-5-PEBA membranes, it was found that the zeolite distributes homogeneously in the polymer matrix [Figure 3(f,g)]. While in the 10% ZSM-5-PEBA membrane matrix, small zeolite particles and some bigger particles can be found simultaneously [Figure 3(h)], indicating the agglomeration of ZSM-5 zeolite.

**Thermogravimetric Analysis.** Figure 4 shows the thermogravimetric curves of PEBA and 5% ZSM-5-PEBA sample. The decomposition temperature (about  $210^\circ\text{C}$ ) of 5% ZSM-5-PEBA membrane is almost the same as that of PEBA membrane. However, silicalite particle is helpful to adsorb thermal energy, protecting PEBA from thermal attack.<sup>29</sup> Thus the weight loss rate induced by thermal decomposition of 5% ZSM-5-PEBA ranged from  $210$  to  $360^\circ\text{C}$  is slower than that of PEBA.

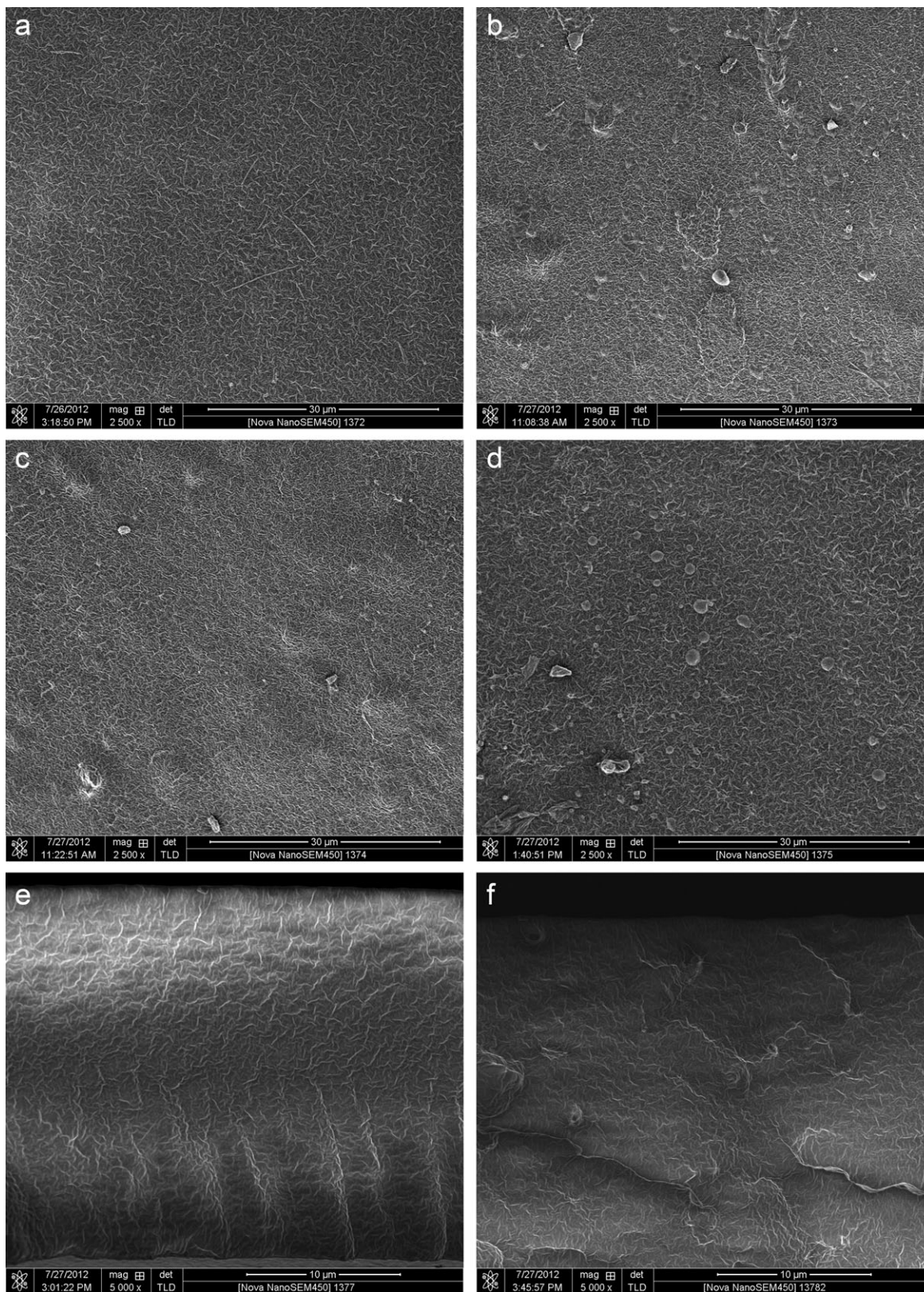
### Swelling and Sorption Properties of Composite Membrane

The swelling behavior of zeolite-filled PEBA composite membranes are showed in Figures 5 and 6. Figure 5 shows the effect of ZSM-5 zeolite content on the DS. The DS of all the zeolite-filled membranes are higher than that of the plain PEBA membrane. And the DS first increases and then decreases with the increasing zeolite content. 5% ZSM-5-PEBA membrane presents the highest DS value. Qureshi's<sup>30</sup> paper once reported that silicalite could be used to concentrate  $n$ -butanol from dilute solutions. Similarly, ZSM-5 zeolite, a kind of MFI zeolite with high hydrophobicity, is preferentially adsorptive to  $n$ -butanol. Therefore, the composite membrane could adsorb more  $n$ -butanol than plain PEBA membrane. On the other hand, inorganic zeolite also has a swelling suppression effect to polymer matrix,<sup>24</sup> which could weaken the motion of polymer segments and resulted in smaller free volume. As the zeolite content exceeded 5 wt %, this swelling suppression effect played a more important role than preferential adsorption effect. Thus the DS of 10 wt % ZSM-5-PEBA membrane decreases.

The effect of  $n$ -butanol concentration on swelling behavior was also investigated. From Figure 6, the DS increases obviously with increasing  $n$ -butanol concentration for both PEBA membrane and PEBA composite membranes. The reason lies in that PEBA and ZSM-5 zeolite are both organophilic and preferential adsorptive to  $n$ -butanol. As  $n$ -butanol concentration increase, more  $n$ -butanol molecules can enter the membrane matrix and then the DS increases. Earlier research<sup>31</sup> produced similar findings, i.e., when  $n$ -butanol concentration increased from 0.1 to 0.5 wt %, the DS changed from 2.9 to 16% at  $40^\circ\text{C}$ .

### Pervaporation Performance of Composite Membrane

**Effect of Zeolite Content.** Figure 7 shows the effect of zeolite content on the pervaporation performance for the separation of 2.5 wt %  $n$ -butanol aqueous solution at  $35^\circ\text{C}$ . The permeation fluxes of all the composite membranes are higher than the plain PEBA membrane for improved preferential adsorption and



**Figure 3.** SEM images of: (a) PEBA surface, (b) 2% ZSM-5-PEBA surface, (c) 5% ZSM-5-PEBA surface, (d) 10% ZSM-5-PEBA surface, (e) PEBA cross section, (f) 2% ZSM-5-PEBA cross section, (g) 5% ZSM-5-PEBA cross section, and (h) 10% ZSM-5-PEBA cross section.

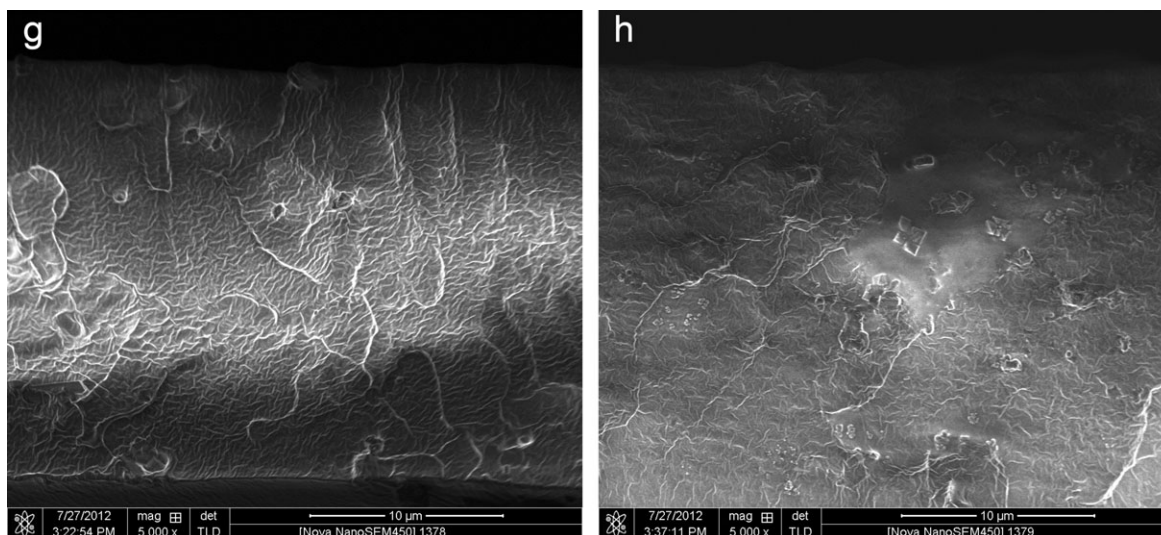


Figure 3. (Continued)

diffusion of *n*-butanol by zeolite incorporation. At first the separation factor increases with the increasing zeolite content and then it decreases. Similar to the changing trend of DS with zeolite content, 5% ZSM-5-PEBA presents the highest separation factor. The ZSM-5 zeolite is a kind of high silica zeolite and thus exhibits hydrophobic property. Though the molecular kinetic diameters of *n*-butanol (5.05 Å) and water (2.8 Å) are both less than the channel size of ZSM-5 zeolite (5.5 Å × 5.3 Å and 5.3 Å × 5.6 Å), the zeolite creates a preferential pathway for alcohol permeation due to alcohol preferential sorption, forcing water molecules to move around the zeolite and primarily permeate through the polymer phase.<sup>32</sup> The separation factor of the composite membrane increases with zeolite content firstly. But when the zeolite content increases to 10 wt %, it decreases. From the SEM image we could find the zeolite agglomeration in the 10% ZSM-5-PEBA membrane and some defects might appear in this membrane, influencing the effect of separation. Water molecule can get through these defects more easily than *n*-butanol. Therefore, a lower separation factor is got for the 10% ZSM-5-PEBA membrane.

**Effect of Temperature.** Figures 8 and 9 show the effect of different feed temperature (30, 35, 40, and 45°C) on the separation

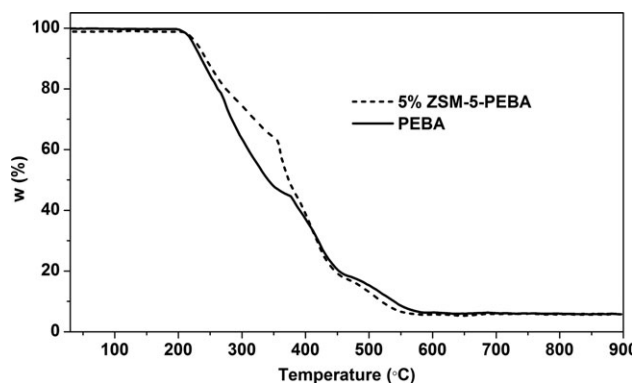


Figure 4. TG curves of PEBA and 5% ZSM-5-PEBA.

factor and permeation flux for 2.5 wt % *n*-butanol aqueous solution. The separation factors of PEBA, 2% ZSM-5-PEBA, 5% ZSM-5-PEBA, and 10% ZSM-5-PEBA membranes all increase with increasing feed temperature. Because the adsorption–desorption rate of *n*-butanol and water molecule is reinforced in the polymer chain and both diffuse more quickly at higher temperature. The relationship between the permeation flux and temperature is determined to follow Arrhenius formula<sup>33</sup>:

$$J_i = J_0 e^{-E_a/RT} \quad (4)$$

where  $J_i$  is the permeation flux of component  $i$ ,  $\text{kg m}^{-2} \text{h}$ ;  $J_0$  is the pre-exponential factor,  $\text{kg m}^{-2} \text{h}$ ;  $E_a$  is the activation energy associated to permeation process,  $\text{kJ mol}^{-1}$ ,  $R$  is the gas constant,  $\text{kJ mol}^{-1} \text{K}$  and  $T$  is the absolute temperature,  $\text{K}$ . The logarithmic plots of *n*-butanol and water fluxes versus reciprocal of absolute temperature for PEBA and 5% ZSM-5-PEBA are showed in Figure 10 and the  $E_a$  values are listed in Table I.

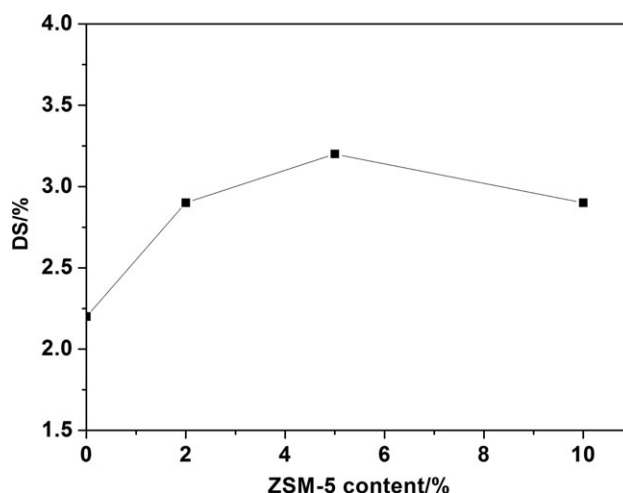


Figure 5. Effect of ZSM-5 content on DS (2.5 wt % *n*-butanol, 35°C).

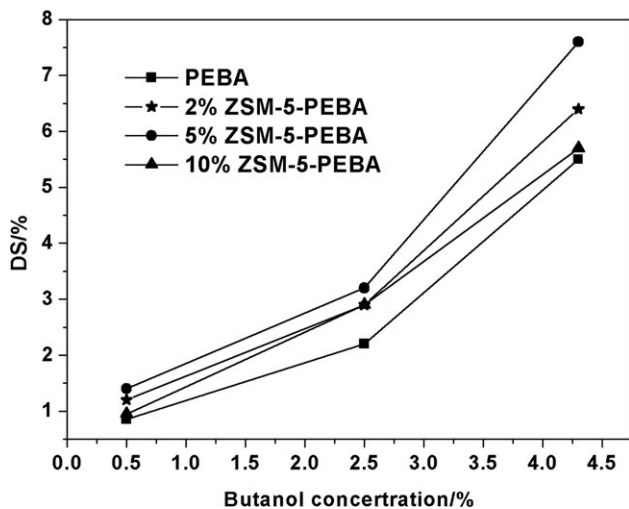


Figure 6. Effect of *n*-butanol concentration on DS (35°C).

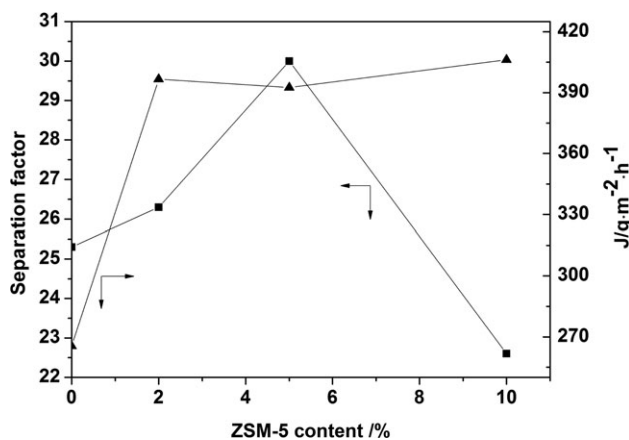


Figure 7. Effect of ZSM-5 content on separation factor and permeation flux (2.5 wt % *n*-butanol, 35°C, 50 L h<sup>-1</sup>).

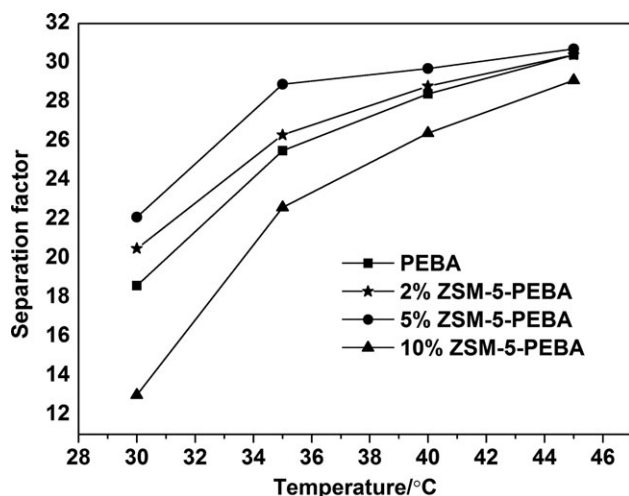


Figure 8. Effect of feed temperature on separation factor (2.5 wt % *n*-butanol, 50 L h<sup>-1</sup>).

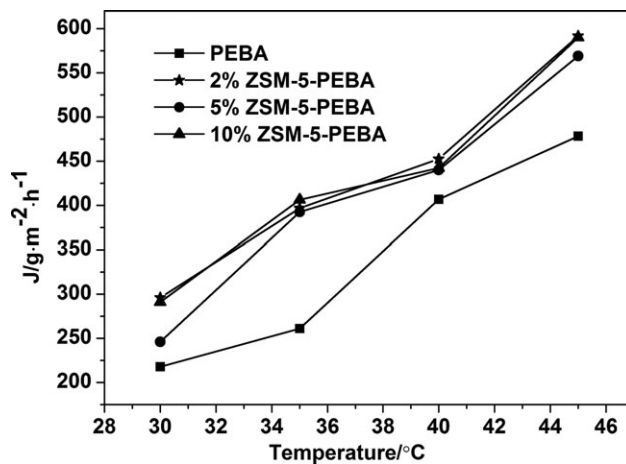


Figure 9. Effect of feed temperature on permeation flux (2.5 wt % *n*-butanol, 50 L h<sup>-1</sup>).

The activation energy of permeation is an important parameter to indicate the effect of temperature on the permeation flux. The activation energy of *n*-butanol is always higher than that of

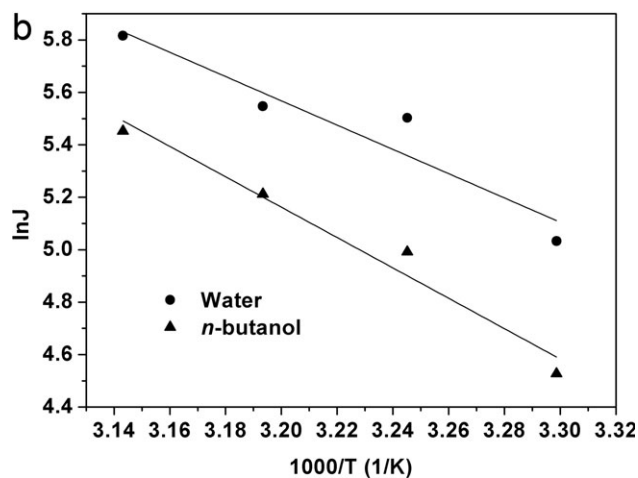
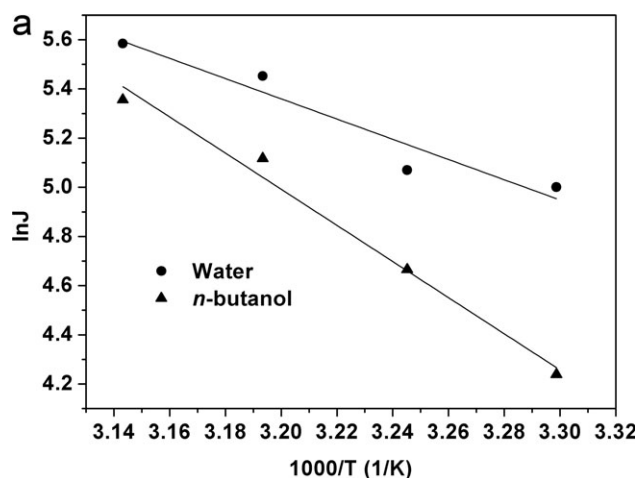


Figure 10. Logarithmic plots of *n*-butanol and water fluxes versus reciprocal of absolute temperature for (a) PEBA and (b) 5% ZSM-5-PEBA membrane.

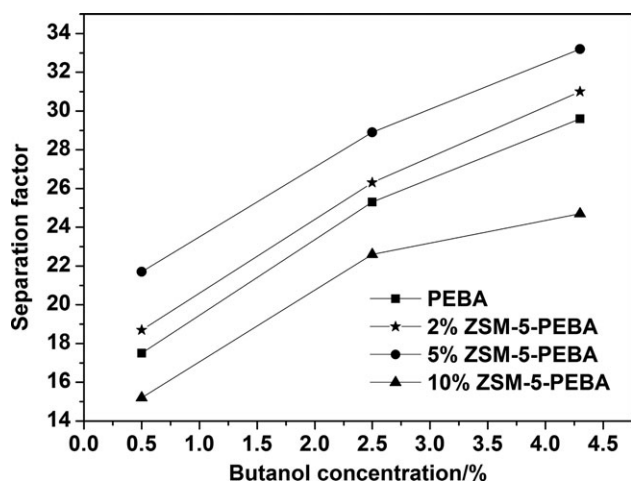
**Table I.** Activation Energy ( $E_a$ ) of *n*-Butanol and Water Fluxes for PEBA and 5% ZSM-5-PEBA Membrane

Membrane	$E_a$ (kJ/mol)	
	<i>n</i> -Butanol	Water
PEBA	61.1	34.2
5% ZSM-5-PEBA	48.2	38.5

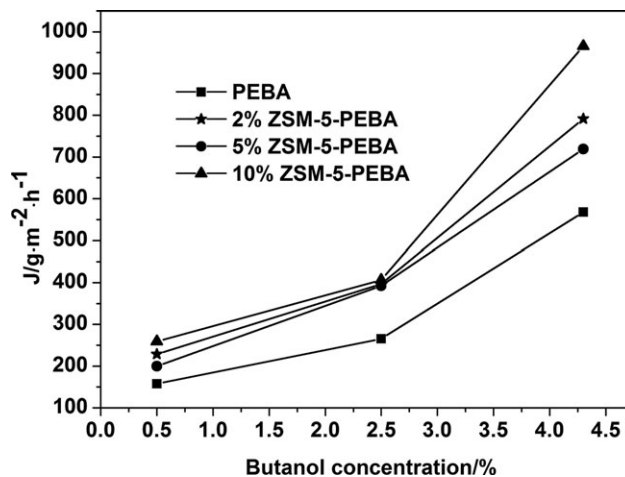
water whatever in PEBA or 5% ZSM-5-PEBA membrane. That means the permeation of *n*-butanol through the membrane is more temperature-sensitive than water. With the increasing temperature, the permeation flux of *n*-butanol increases much more than water. As a result, the separation factor increases. The highest separation factor is 30.7 and the permeation flux is 569  $\text{g m}^{-2} \text{ h}$  at 45°C for 5% ZSM-5-PEBA membrane.

Except for the accelerating movement of small molecule, the motion of the polymer segments in the PEBA matrix is also enhanced, which lead to a larger free volume for all the membranes at higher feed temperature. Thus the permeation fluxes of the plain membrane and the composite membrane increase with the increasing temperature. Incorporation of ZSM-5 zeolite can decrease the activation energy of *n*-butanol flux of the composite membrane.

**Effect of Feed Concentration.** The effect of different feed concentrations (0.5, 2.5, and 4.3 wt %) on pervaporation performance is also investigated. Figures 11 and 12 show the separation factor and permeation flux both increase as the feed concentration increase. When the feed concentration is 4.3 wt %, the separation factor and permeation flux are 33.3 and 719.3  $\text{g m}^{-2} \cdot \text{h}$  respectively for 5% ZSM-5-PEBA. On the one hand, the increasing *n*-butanol concentration would enhance the trans-membrane concentration gradient, i.e., the driving force of pervaporation process increases. Then *n*-butanol is easier to transfer across the membrane. On the other hand, according to the swelling studies, the DS of all the membranes increase with increasing *n*-butanol concentration, which means more *n*-buta-



**Figure 11.** Effect of feed concentration on separation factor (35°C, 50 L  $\text{h}^{-1}$ ).



**Figure 12.** Effect of feed concentration on permeation flux (35°C, 50 L  $\text{h}^{-1}$ ).

anol and water, could be adsorbed in the membrane. As PEBA and zeolite-filled membranes all present *n*-butanol preferential adsorption, more adsorption sites could be taken by *n*-butanol at high concentration than at low concentration. In addition, as described above, *n*-butanol molecule could transfer directly through the zeolite channel while water molecule has to move round the zeolite particle. Therefore, the diffusion rate of *n*-butanol is faster than that of water, resulting in the increased separation factor at higher feed concentration.

The permeation flux of PEBA and composite membranes increases significantly with the increasing feed concentration, as Figure 12 shows. This could be explained by the swelling study results too. More *n*-butanol and water are adsorbed at higher *n*-butanol concentration. And the higher DS results in more free volume and less transfer resistance. In addition, the increasing driving force accelerates the diffusion rate. Then higher flux is obtained.

## CONCLUSIONS

A series of ZSM-5 zeolite-filled PEBA membranes were prepared and applied in the pervaporation of *n*-butanol aqueous solution. XRD analysis demonstrated the zeolite particle could distribute well in the PEBA matrix. SEM analysis indicated different distribution condition for the membranes with different zeolite content.

The swelling study results suggested that the DS of zeolite-filled membranes were always higher than the plain PEBA membrane. As the zeolite content increased the DS first increased and then decreased. The reason was that the preferential adsorption capacity of the composite membrane to *n*-butanol was improved for the addition of high organophilic zeolite. On the other hand, the zeolite also had swelling suppression effect on the polymer membrane matrix, which led to a decrease of DS when the zeolite content was higher than 5 wt %.

The effects of zeolite content, temperature, and feed concentration on pervaporation performance were investigated. The separation factor of the composite membrane first increased and then decreased with increasing zeolite content. Because of the

contradictory effect of the preferential adsorption to *n*-butanol and the increasing transport resistance with zeolite content, compared to the plain PEBA membrane and 10 wt % ZSM-5-PEBA membrane, 5 wt % ZSM-5-PEBA membrane presented higher permeation flux and separation factor. The separation factor and permeation flux both increased as the feed temperature and concentration increased. The activation energy of permeation for *n*-butanol was higher than water, which meant *n*-butanol partial flux increased more than water and a higher selectivity could be obtained as the feed temperature increased. After incorporation of ZSM-5 zeolite, the activation energy of *n*-butanol decreased.

#### ACKNOWLEDGMENTS

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