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Preparation and pervaporation performance of poly(3-alkylthiophene) membrane

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Abstract

The separation of aqueous alcohol mixtures was carried out using a series of poly(3-alkylthiophene) membranes. The poly(3-alkylthiophene) polymers were prepared by oxidative polymerization in the presence of anhydrous $FeCl_3$ in dry chloroform. The effect of the alkyl group structure of the poly(3-alkylthiophene) membrane on the thermal properties and the pervaporation performances were investigated. The solubility of ethanol in the poly(3-alkylthiophene) membrane is higher than that of water, however, the diffusivity of water through the membrane is higher than that of ethanol. In addition, the effects of the feed composition and the degree of swelling on the pervaporation performances of the poly(3-alkylthiophene) membranes were also studied. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(3-alkylthiophene); Pervaporation; Solubility

1. Introduction

Membrane separation offers an interesting and low-cost alternative to the more traditional separation processes. The mixture can be separated based on differences in molecular size, solubility or charge. The pervaporation process has been widely considered as an alternative conventional separation process if suitable membrane can be fabricated. Recently, the separation of azeotropes, close-boiling mixtures, and aromatic C_8-isomers by pervaporation techniques using polymer membranes has been given much attention [1–5]. To fabricate a good membrane for pervaporation a number of methods of membrane modification have been reported; grafting a selective species onto an inert film [6], blending and crosslinking [7,8], copolymerization [9], and surface modification [10]. However, the efficiency of the pervaporation process depends mainly on the intrinsic properties of the polymers used to prepare the membrane. Therefore, designing membranes with high permeation rate and suitable separation factor are an important issue. Several investigations utilizing conducting polymers as membranes to separate other liquid or ion mixtures have been reported recently [11]. For example, the substituted polypyrrole membrane for separating acetone/water, 2-butanol/water, and 2-butanol/heptane mixtures has been reported by Feldheim et al. [12]. In addition, Liang et al. [13] reported the electronically conductive polymers such as polypyrrole, poly(*N*-methylpyrrole), and polyaniline, as chemically selective layers for membrane separation. In this study, three types of electroactive poly(3-alkylthiophene) polymers were prepared by oxidative polymerization in the presence of anhydrous $FeCl_3$ in dry chloroform. The effects of the alkyl group structure of the alkylthiophene monomers such as hexyl, octyl, and dodecyl, on the membrane properties were investigated. In addition, the effects of feed composition, degree of swelling, and the size of alcohols on the pervaporation performances of the poly(3-alkylthiophene) membranes were studied.

2. Experimental

2.1. Materials

The 3-alkylthiophene membranes, i.e. 3-hexylthiophene, 3-octylthiophene, and 3-dodecylthiophene, were purchased from Tokyo Kasei Co. All reagent-grade chemicals were used directly without further purification. Water was deionized and distilled.

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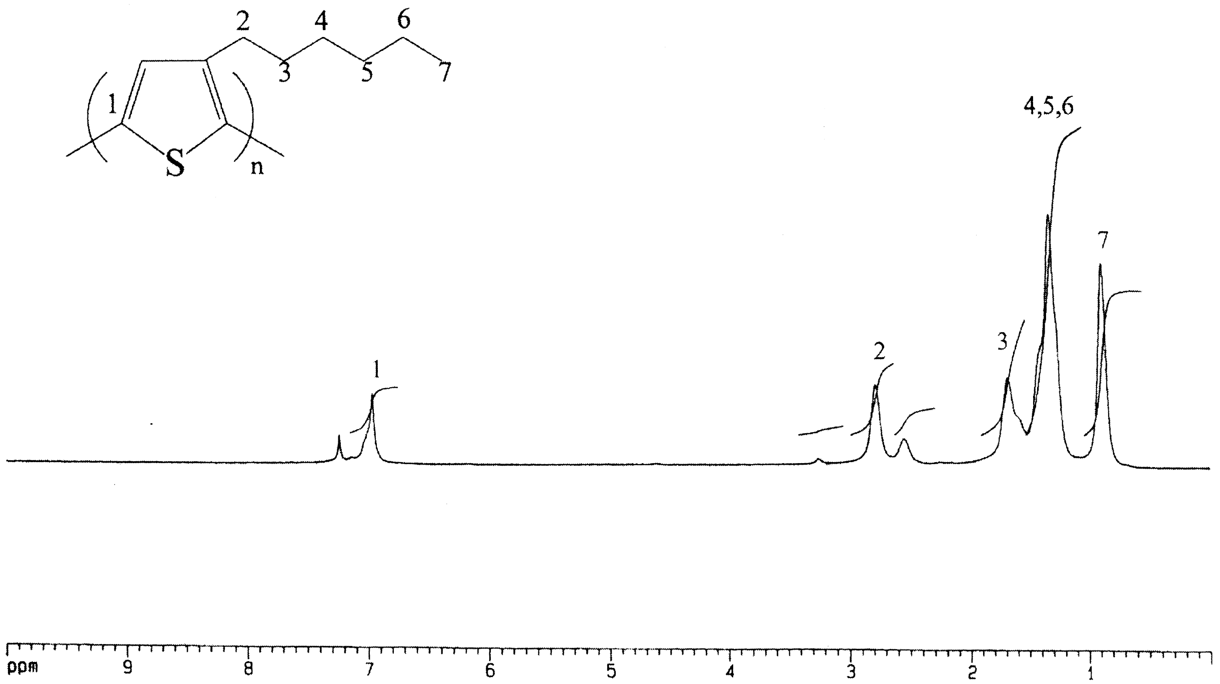

Fig. 1. ^{1}H-NMR spectrum of poly(3-hexylthiophene). Use $CDCl_3$ as solvent.

2.2. Polymer synthesis

The poly(3-alkylthiophene) polymers were synthesized by the oxidative polymerization in the presence of anhydrous $FeCl_3$ in dry $CHCl_3$, according to the method of Hotta et al. and Kang et al. [14,15]. A mixture of $FeCl_3$ (oxidant; 0.06 mol) and dry chloroform (200 ml) in the reaction flask under a dry nitrogen atmosphere, thiophene monomer (0.02 mol) was then added dropwise into the oxidant solution with stirring. The reaction mixture was then poured into a large excess of methanol to precipitate the thiophene polymer.

2.3. Measurement

^{1}H- and ^{13}C-NMR spectra were measured at 30°C on a NMR spectrometer (JEOL EX-400). X-ray diffractograms were recorded with an X-ray diffractometer (Philips Model PW1710). The $\bar{M}_n$ (number-average molecular weight), $\bar{M}_w$ (weight-average molecular weight) were measured by size-exclusion chromatography (GPC) in THF at 30°C. Fourier transform infrared (FTIR) spectroscopy was used obtained at 1 cm^{-1} resolution using a Shimadzu model FTIR-8201 PC.

2.4. Membrane preparation

The poly(3-alkylthiophene) membranes were prepared from a casting solution containing 10 wt.% polymer in $CHCl_3$. The membrane was formed by casting the solution on a glass plate to a predetermined thickness. The glass plate was then heated at 70°C for 40 min. The average thickness of the membranes was about 30–35 μm.

2.5. Pervaporation experiments

A traditional pervaporation apparatus was used in this study [16]. The effective membrane area was 10.17 m^2. A vacuum pump maintained the downstream pressure at 3–5 mmHg. The permeation rate was determined by measuring the weight of the permeate. The compositions of the feed solutions, permeates, and solutions absorbed in the membrane were measured by gas chromatography (GC; China Chromatography 8700). The separation factor was calculated from

$$\alpha_{\mathrm{H_2O/EtOH}} = \frac{\dfrac{Y_{\mathrm{H_2O}}}{Y_{\mathrm{EtOH}}}}{\dfrac{X_{\mathrm{H_2O}}}{X_{\mathrm{EtOH}}}}$$

where $Y_{\mathrm{H_2}}\mathrm{O}$, Y_{EtOH} and $X_{\mathrm{H_2}}\mathrm{O}$, X_{EtOH} are the weight fraction of water and ethanol in the permeate and feed, respectively.

2.6. Sorption measurement

A membrane was immersed in ethanol–water mixtures for 24 h. It was subsequently blotted between tissue paper to remove adherent solvent and placed in the left container of a twin tube setup. The system was evacuated while the left container with the swollen membrane was heated to evaporate completely the liquid absorbed in the membrane. The evaporated vapor was trapped in the right container by

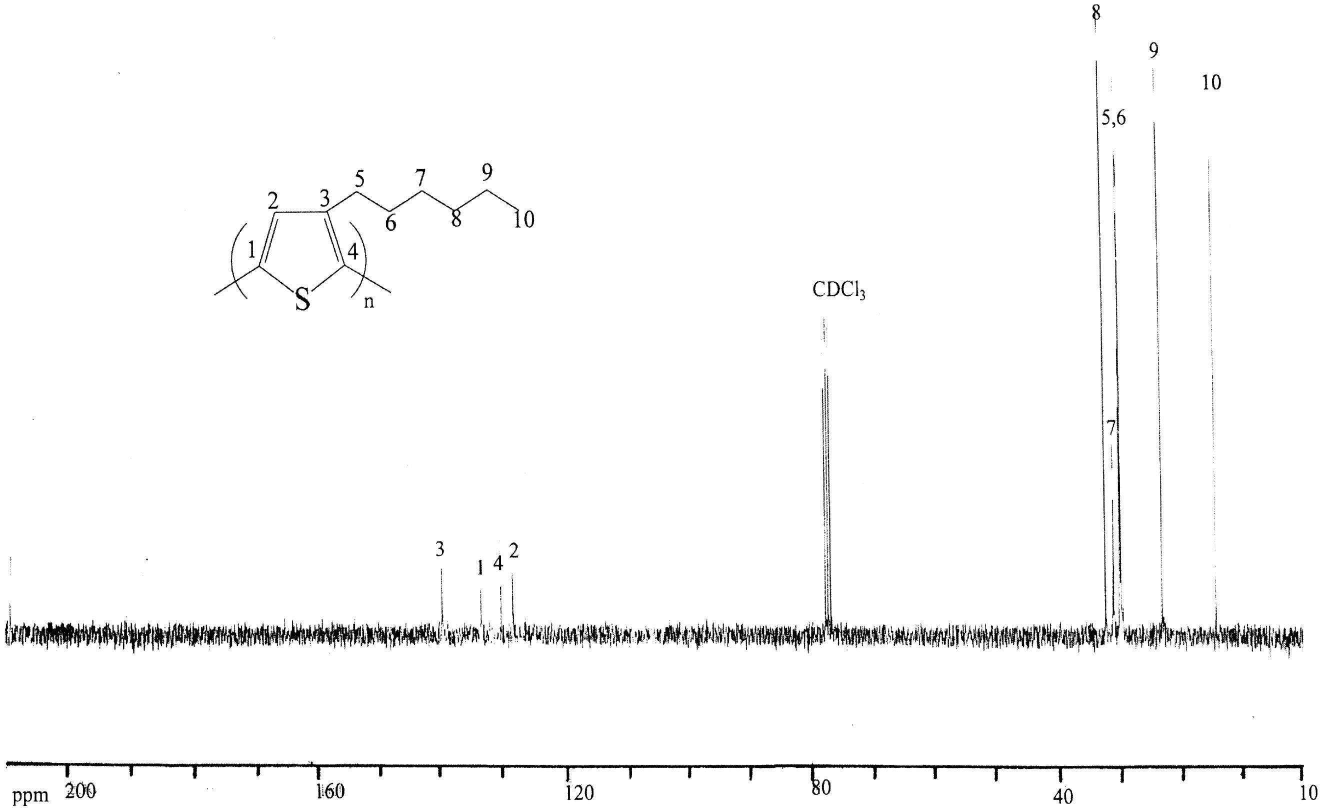

Fig. 2. ^{13}C-NMR spectrum of poly(3-hexylthiophene). Use $CDCl_3$ as solvent.

cooling with liquid nitrogen. The composition of condensed liquid in the right tube was determined by GC.

2.7. Specific volume measurements

The specific volume was measured by using a micromeritrics Accupyc 1330 Pycnometer. This instrument measures the volume of the solid by the gas displacement method.

2.8. Contact angle measurement

The contact angle of water was measured by a FACE contact angle meter (CA-D type, Kyowa Interface Science Co. Ltd) at 25°C and 60% relative humidity. Water droplets (sessile drops volume ca. 1.8×10^{-3} cm^3) were placed on the membrane covered with a fixing knob. After 10 s the dimensions of the droplets were measured. The droplets were small enough to be approximated as spheres. The contact angle was then calculated by the following equation:

$$\text{contact angle} = 2\tan^{-1}(h/r)$$

where h and r are the height and the radius of the spherical segment, respectively.

2.9. Degree of swelling

The clean and dried membranes with known weights were immersed in ethanol feed concentration at 25°C for 24 h to reach equilibrium swelling. These pieces were rapidly removed from the surface solvent, and placed on a weighing scale. The first reading was taken at 40 s interval. The weight of the solvent swollen membrane was obtained by extrapolating the initial potion of the experimental curve to zero line. The degree of swelling of the membrane was defined by the following equation:

$$\text{Degree of swelling} = (W_w - W_d)/W_d \times 100\%$$

where W_d and W_w denote the weight of dry and swollen membranes, respectively.

3. Results and discussion

3.1. Properties

Three types of poly(3-alkylthiophene) polymers were prepared by oxidative polymerization in the presence of anhydrous $FeCl_3$ in dry chloroform. The ^{1}H-NMR and ^{13}C-NMR spectra of the poly(3-hexylthiophene) are shown in Figs. 1 and 2, respectively. Each signal can be assigned as shown in the figure. The methyl protons ($-CH_3$) and carbon atom ($-CH_3$) of the hexyl group appeared at 0.89 and 14.1 ppm, respectively. The FTIR spectra of the poly(3-alkylthiophene) polymers were similar. For instance, poly(3-hexylthiophene) exhibited absorption at 2960 cm^{-1} ($-CH_3$), 2922 cm^{-1} ($-CH_2$), 1460 cm^{-1} (C=C, ring),

Table 1
Synthesis of poly(3-alkylthiophene) polymers

Polymer	Yield (%)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
Poly(3-dodecylthiophene)	86	5.61	3.06	1.83
Poly(3-octylthiophene)	88	5.43	2.77	1.95
Poly(3-hexylthiophene)	85	5.98	2.81	2.1

830 cm^{-1} (–CH), and 710 cm^{-1} (=C–S). On the basis of the results mentioned above, the poly(3-hexykthiophene) was successfully synthesized. In addition, the results of polymerization are shown in Tables 1 and 2. The weight average molar masses ($\bar{M}_w$) are in the range of $5.4–5.9 \times 10^4$ with a molar mass distribution 1.8–2.1. The specific volume of the poly(3-alkylthiophene) polymers ranks in the following order: poly(3-dodecylthiophene)(poly(3-octylthiophene)-(poly(3-hexylthiophene). From the viewpoint of molecular structure, the polymer with a larger substituted group gives a higher barrier to chain rotation than that with a smaller one. The higher barrier to rotation in the poly(3-alkylthiophene) membranes may also inhibit local segmental motion. Thus, the polymer packing density is lower when a larger pendant group is introduced onto polymer backbone. In addition, X-ray diffraction measurements of the poly(3-alkylthiophene) polymers indicated that all polymers are essentially amorphous, as shown in Fig. 3. The larger pendant group in polymer backbone seems to result in a relaxation structure of the poly(3-alkylthiophene) polymers.

3.2. Effect of feed ethanol concentration on the pervaporation performances

The effect of feed ethanol concentration on the pervaporation performances of the poly(3-alkylthiophene) membranes are shown in Figs. 4 and 5. The separation factor and permeation rate increased as the feed ethanol concentration increased for all the poly(3-alkylthiophene) membranes. These phenomena might be due to the fact that the poly(3-alkylthiophene) membranes were easily swollen at the high ethanol concentration of the feed solution. For example, the difference of the solubility parameter between the ethanol and the poly(3-hexylthiophene) membrane ($\delta_{\mathrm{EtOH}} - \delta_{\mathrm{membr}} = 8.3\ (\mathrm{MPa})^{1/2}$) is lower than that of the water and the poly(3-hexylthiophene) membrane ($\delta_{\mathrm{H_2O}} - \delta_{\mathrm{membr}} = 30.2\ (\mathrm{MPa})^{1/2}$). Hence, the water molecules can easily diffuse through the poly(3-hexylthiophene) membrane because the interaction between the water and the poly(3-hexylthiophene) membrane is very weak and the molar volume of water is small. Thus, a higher ethanol content results in an increasing separation factor. Moreover, the affinity between the permeates and the poly(3-alkylthiophene) membranes can further illustrate the above phenomenon. The degree of swelling increases as the feed ethanol concentration increases, as shown in Table 3. This can be explained by the fact that the strong affinity between ethanol and poly(3-alkylthiophene) membrane plasticizes the membranes. These results agree with the ones mentioned above. In addition, the effect of poly(3-alkylthiophene)

Table 2
Properties of synthesized poly(3-alkylthiophene) polymers

Polymer	Glass transition temperature (°C)	Specific volume (cm^3/g)	Crystallinity
Poly(3-hexylthiophene)	−11	0.839	Amorphous
Poly(3-octylthiophene)	−9	0.911	Amorphous
Poly(3-dodecylthiophene)	−7	0.931	Amorphous

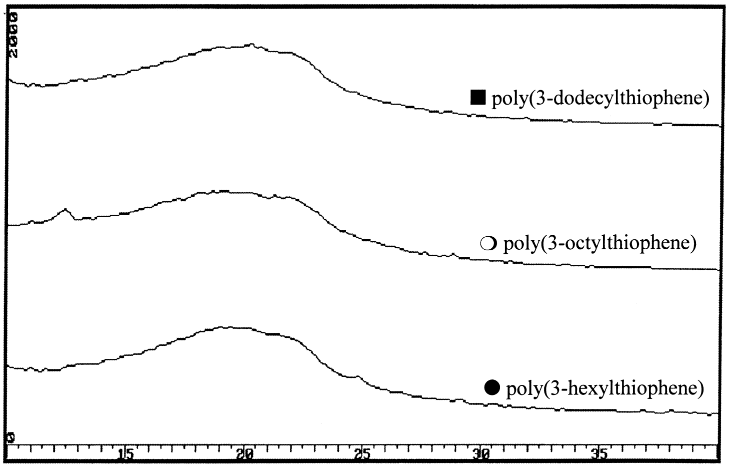

Fig. 3. X-ray diffraction patterns of the poly(3-alkylthiophene) polymers (●) poly(3-hexylthiophene), (○) poly(3-octylthiophene), (■) poly(3-dodecylthiophene).

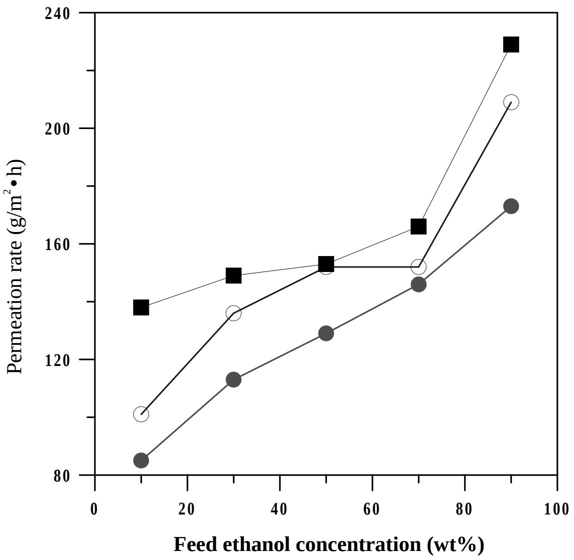

Fig. 4. Effect of feed ethanol concentration on the permeation rate. (●) poly(3-hexylthiophene), (○) poly(3-octylthiophene), (■) poly(3-dodecylthiophene).

polymers structure on the contact angle is shown in Table 4. Compared with the poly(3-dodecylthiophene) membrane with a hydrophoblic substituted group (dodecyl) in the polymer backbone, the poly(3-hexylthiophene) membrane with a hexyl group in the polymer backbone has a lower water contact angle, which could be explained by the fact that the introduction of a bulky dodecyl group into the polymer backbone increases the hydrophobicity of the poly(3-dodecylthiophene) membranes. Hence, a higher water permselectivity was obtained through the poly(3-hexylthiophene) membrane. In order to study the effect of solubility and diffusivity on the membrane permselectivity, sorption experiments on the poly(3-hexylthiophene) membranes were performed. The water composition in the membrane and in the permeate are summarized in Table 5. It can be seen that the water composition in the membrane and in the permeate are higher than that in the feed, indicating that the water molecules are selectively dissolved into the membrane and are preferentially permeated through the membrane. Furthermore, the ethanol composition in the membrane is higher than that in the permeate for the ethanol concentrations varying from 10 to 90 wt.%. These phenomena might be due to the fact that the solubility of ethanol (4 g/100 g) in the poly(3-hexylthiophene) membrane is higher than that of the water (1 g/100 g). It can be observed that water has a very low interaction with the membrane and, consequently, a low solubility is found. In addition, once the water molecules are incorporated into the poly(3-hexylthiophene) membrane, they can easily diffuse through the poly(3-hexylthiophene) membrane because the interaction between the water molecules and the poly(3-hexylthiophene) membrane is very weak and also the molecular size of water is smaller than that of ethanol. Consequently, the diffusivity of water is higher than that of ethanol.

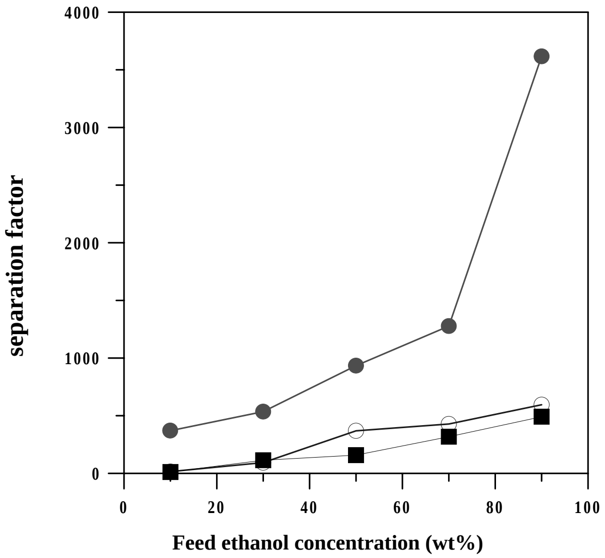

Fig. 5. Effect of feed ethanol concentration on the separation factor. (●) poly(3-hexylthiophene), (○) poly(3-octylthiophene), (■) poly(3-dodecylthiophene).

Table 3
Effect of feed ethanol concentration on the degree of swelling for the poly(3-hexylthiophene) membrane

Feed ethanol concentration (wt.%)	Degree of swelling (wt.%)
0	1.1
10	1.7
30	2.5
50	2.8
70	3.5
90	3.9
100	4.1

3.3. Effect of feed ethanol composition on the sorption and diffusion properties

The effects of feed ethanol composition on the sorption and diffusion properties are discussed in this section. The sorption experiments were performed to determine the separation factor of partition, $\alpha_{\text{partition}}$, for the poly(3-hexylthiophene) membranes. For the pervaporation, the permeability coefficient represents the product of the partition coefficient and the diffusion coefficient. Thus, the separation factor of pervaporation, $\alpha_{\text{pervaporation}}$, is also expressed as the product of $\alpha_{\text{partition}}$ and that of the diffusion, $\alpha_{\text{diffusion}}$, as follows:

$$\alpha_{\text{pervaporation}} = \alpha_{\text{partition}} \times \alpha_{\text{diffusion}}.$$

The results of the separation factor of partition and the separation factor of diffusion are shown in Fig. 6. It shows that the separation factor of partition increases with

Table 4
Contact angle of poly(3-alkylthiophene) membranes

Membrane	Water contact angle (°)	Ethanol contact angle (°)
Poly(3-dodecylthiophene)	101	18
Poly(3-octylthiophene)	98	22
Poly(3-hexylthiophene)	94	24

Table 5
Effect of feed composition of aqueous ethanol solutions on the composition of the solution adsorbed and permeated with poly(3-hexylthiophene) membranes

Feed ethanol composition (%)	Ethanol in permeate (%)	Ethanol in membrane (%)
10	0.03	0.9
30	0.08	3.2
50	0.106	6.0
70	0.156	8.1
90	0.178	9.3

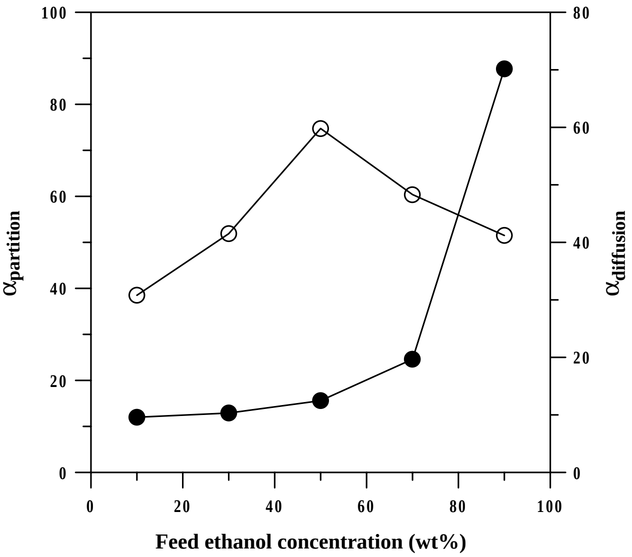

Fig. 6. Effect of feed ethanol concentration on the separation factor of partition and diffusion for the poly(3-hexylthiophene) membranes. (●) separation factor of partition, (○) separation factor of diffusion.

increasing the feed ethanol concentration. These phenomena might be due to the fact that the high affinity between the ethanol molecules and the poly(3-hexylthiophene) membrane results in the membrane structure that is more swollen. Hence, the water molecules can easily dissolve into the membrane, which results in an increase in the separation factor of partition. The separation factor of diffusion first increases but then decrease with an increase in the feed ethanol concentration (feed ethanol concentration(50 wt.%). In general, the separation factor of diffusion strongly related to the membrane structure: a denser membrane structure results in a higher separation factor of diffusion. These phenomena might be due to the fact that the excessive swelling due to the ethanol molecules can easily diffuse through the poly(3-hexylthiophene) membrane as the feed ethanol concentration is higher than 50 wt.%. Consequently, the effect of the solution dominates the behavior of pervaporation because the separation factors of pervaporation follow the same trend as the separation factor of partition, but not the trend of the separation factor of diffusion.

4. Conclusion

A series of poly(3-alkylthiophene) polymers were successfully prepared in this article. The specific volume of the poly(3-alkylthiophene) polymers ranks in the following order: poly(3-dodecylthiophene)(poly(3-octylthiophene)(poly(3-hexylthiophene). The poly(3-hexylthiophene) membrane has good pervaporation performance: the separation factor is 3617 and the permeation rate is 173 g/m^2 h. All poly(3-alkylthiophene) membranes were absorptive and permselective towards water. The effect of the degree of swelling on the partition of feed solution on the membrane plays an important role in the pervaporation separation process.

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