行政院國家科學委員會專題研究計畫成果報告

塑化劑對 Polysulfone 薄膜滲透蒸發特性與溶解與擴散行為之影響

Effect of plasticizer additive on pervaporation characteristics and solution-diffusion behavior of polysulfone membranes

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Abstract

The separation performance of plasticizer additive polysulfone membrane was prepared. The additive plasticizer enhanced the polymer chain mobility of polysulfone membrane and enhancement of polymer chain mobility improved the permeate diffusion in pervaporation process. The separation performance of water and ethanol are shown to be strongly dependent on diffusion selectivity of permeates. On the other hand, the solubility selectivity of water to ethanol showed a slight change with the increase in the plasticizer composition in PSF/plasticizer membrane. This investigation shows that the plasticizer content in PSF/plasticizer membrane enhances the polymer chain mobility and improves the separation performance. It was found that the polymer chain mobility increases with the increase in the plasticizer content in PSF membranes. The dominant factor of mass transport through membrane was the permeate diffusion rate which was strongly affected by the addition of plasticizer in the matrix of PSF membrane. This study reveals that the high ethanol concentration in feed shows a superior performance than the low ethanol concentration feed. This study proves that the polymer chain mobility strongly influences the permeation properties of PSF membrane by adding the plasticizer in polymer membrane.

Keywords: membrane, plasticizer, pervaporation, polysulfone

Introduction

For dehydration of organic azotropic mixture, the mass transfer barrier of permeates should be considered in the period of permeate transport through polymer membrane. The solution-diffusion mechanism was generally applied to describe the transport behavior of permeate in pervaporation membrane. Based on the concept of solution-diffusion model, the permeate dissolves into membrane surface and then diffuses through the polymer membrane. Finally, permeates vaporize and leave the other side of membrane. The separation performance of polymer membrane was determined by the competition between solution and diffusion of permeates when it was passed through the membrane. In general, a high solubility membrane also led to a high diffusivity [1]. It was proposed that the barrier of mass transfer in membrane is affected by the solution and diffusion step in the period of

pervaporation and the vaporization of permeate was proposed as a non-selective step. In many cases, the resistance of diffusion of downstream layer and sorption of upstream determined the high permselectivity membrane [2].

However, for most of the glassy polymer membranes, the permeation rate of pervaporation is determined mainly by the diffusion contribution [3]. Most of the permeate diffusion behavior in pervaporation membrane was explained by free volume model [1]. The theory described that the permeate diffusion behavior can be affected by the relative size of permeate to diffusion path and the polymer chain mobility in membranes.

Many investigators have reported [4-7]_that the improvement of permeation flux could be achieved by increasing the polymer chain mobility, such as blending or grafting hydrophilic polymer for improving the polymer chain mobility in pervaporation process. In those works, the low glassy transition temperature polymer was used to modify the glassy polymer and separation performance is significantly enhanced in pervaporation process. Recently, many investigations [8-11] explored the relationship between polymer chain packing efficiency of plasticizer additive membrane and separation performance of membrane. It was found that the separation performance of polymer membrane was strongly affected by the added plasticizer. On the other hand, there are many studies, which show that the plasticizer additive also significantly affects polymer chain mobility and separation performance of gas separation membrane [12-15]. For the purpose of clearing the plasticizer additive effect on the change of properties of pervaporation membrane, this study aimed at preparing polyslufone/plasticizer composite membrane to separate water from a water/ethanol mixture. These polymers were applied to enhance polymer chain mobility of pervaporation membrane. In order to understand the effect of enhancement of polymer chain mobility on pervaporation performance of polysulfonate membrane, we measured the swelling properties of various amounts and different molecular weights of polyethylene glycol content in polysulfone membrane and analyzed the sorption amount in PSF/plasticizer membrane. The permeation rate and degree of swelling was measured independently. Glass transition temperature (Tg) measurements analyses were used to characterize the morphology change in the modified membrane. The relationship between microstructure change of PSF/plasticizer membranes and pervaporation properties is also discussed in this study. The effect of feed composition was also studied by measuring the pervaporation properties.

Experimental

Materials

Udel ® Polysulfone (PSF) P-3500 and chloroform was obtained from Amoco Performance Products and Merck Chemical Co. Bayer Co supplied the polymer plasticizer (ULTRAMOLL

TGN). The density of polymer plasticizer (ULTRAMOLL TGN) was 1.095 g/cm^3 and the viscosity is 2250 mPa at 20℃.

Membrane preparation

The polysulfone/polyethylene glycol membranes were prepared from blend method by adding various amounts of different molecular weights of polyethylene glycol. The polysulfone/TGN membranes were prepared from a casting solution in chloroform. The casting solution was casted onto a glass plate to a predetermined thickness of 350 μm using a Gardner Knife. The membrane was dried at room temperature for 30 minutes, then peeled off and immersed in distilled water for 12 hours, and finally put into vacuum oven for 24 hours before sorption and pervaporation measurements.

Pervaporation experiment

A traditional pervaporation process was used [16]. The pervaporation apparatus is shown in Figure 1. In pervaporation, the feed solution of 90 wt% ethanol solution was in direct contact with the membrane and was kept at 25℃. The effective membrane area was 10.2 cm^2. The down stream pressure was maintained at about 5-8 Torr. The permeation rate was determined by measuring the weights of permeate. The compositions of the feed solution permeate and solution adsorbed in the membranes was measured by gas chromatography (GC, China Chromatography). The separation factor, $\alpha_{A/B}$, was calculated by the formula:

$$\alpha_{A/B} = (Y_A/Y_B)/(X_A/X_B)$$

where, X_A, X_B and Y_A, Y_B are the weight fractions of A and B in the feed and permeate, respectively (A being the more permeative species).

Sorption measurements

The membranes were immersed in the ethanol-water mixture for 24 hours at 25℃. They were subsequently blotted between tissue paper to remove the excess solvent and were then placed in the left half of a twin tube set-up. The system was evacuated while the tube was heated with hot water for 30 minutes and the right tube was cooled in liquid nitrogen. The composition of the condensed liquid in the right tube was determined by G.C. The separation factor of sorption was calculated by:

$$\alpha_{sorp}=(Yw/Ye)/(Xw/Xe)$$

where, Xe, Xw and Ye, Yw are the weight fractions of ethanol and water in the feed and membranes, respectively.

Results and Discussion

Effect of polymer plasticizer (TGN) additive on separation performance of PSF membrane

In this study, the polymer plasticizer (TNG) was added to polysulfone membrane for improving the separation performance. The effect of polymer plasticizer content in membrane on separation performance of TGN/PSF composite membranes is shown in Figure 2. It was found that the polymer plasticizer content in composite membrane significantly affected the

separation factor. However, the TGN content was only slightly affected by the permeation rate of composite membrane. It was found that the permeation flux was almost independent of the TGN content in membrane. However, the separation factor increased with the increase in the TGN content in composite membrane and the separation factor increased up to 6.25 wt % of TGN content in membrane and then decreased with the increase in the TGN composition in composite membranes. Generally, it can be expected that TGN additive enhances the flexibility of polymer chain in composite membrane and it would lead to an increase in permeation flux and a decrease in diffusion selectivity. However, the additive of TGN in polysulfone membrane is against this expectation. The possible reasons that explain this phenomenon is that the polymer chain flexibility and packing density of polymer chain in membrane increased with the increase in the TGN content in TGN/PSF membranes at low TGN content. The higher polymer packing density can be expected to decrease the permeation rate and enhance the diffusion selectivity of modified membranes. As figure 2 shows, the decrease in permeation rate and the increase in separation factor were found while the TGN content was higher than 6.25%. When the higher TGN content was added in composite membrane, the higher polymer chains flexibility could be achieved in PSF membrane. The flexible polymer chain of additive membrane induced a higher permeation rate and low diffusion selectivity. To further prove the above viewpoint, the Tg and swelling properties was measured to clarify the relationship of flexibility of polymer chain and TGN content in membranes.

Effect of TGN content on polymer chain flexibility

The effect of TGN content on glassy transition temperature (Tg) of TGN/PSF membranes is shown in Figure 3. It can be seen that the glassy transition temperature of TGN additive membrane decreases with the increase in the TGN content, it was indicated that more flexible polymer chain can be achieved by adding TGN into PSF membrane. It was proved that the more flexible polymer chain could be obtained by adding TGN in PSF membrane. Generally, flexible polymer chains in membrane lead to an increase in permeation flux and a decrease in diffusion selectivity. For the purpose of understanding the diffusion behavior of TGN/PSF membrane in 90% ethanol solution, swelling tests were made at the same feed solution. Figure 4 shows the effect of TGN additive on the degree of swelling of TGN/PSF membrane for a 90-wt% ethanol solution. It can be seen that the degree of swelling showed a strong dependence on the amount of TGN content in composite membranes. The degree of swelling slightly increased with the increase in the TGN content in TGN/PSF membrane. This result indicates that the flexibility of polymer chain in the composite membrane would be increased by plasticization effect in

90-wt% ethanol solution. Based on the result of Tg and swelling properties, it can be concluded that the polymer chain flexibility would be improved by adding TGN into polymer matrix no matter the composite membrane was at dry state or immersing in 90 wt% ethanol solution.

Effect of TGN content on sorption and diffusion behavior of composite membrane

In order to clarify the factors that influence the separation performance of TGN/PSF membrane, the effect of TGN/PSF composition in membrane on water or ethanol content in TGN/PSF membrane was investigated. The effect of TGN composition on ethanol and water content in membrane are shown in Figure 5. It can be seen that the water content decreased with the increase in the TGN composition in membrane. On the other hand, the ethanol content increased with the increase in the TGN content in membranes. It was found that the additive of TGN in polysulfone membrane preferred ethanol rather than water. Based on the viewpoint of solubility difference (17), the solubility difference between ethanol and membrane was smaller than the solubility difference between water and membrane. Therefore, the higher TGN content in the membrane, the more the ethanol content was expected in membrane. As shown in Figure 6, the solubility selectivity was calculated by the ratio of water content to ethanol content in membrane. It indicates that the solubility selectivity decreased with the increase in the TGN content in membrane. As the permeate content analysis shows, it may be noted that the decrease of solubility selectivity was contributed by the increase of ethanol composition in membrane. However, as shown in Figure 2, the separation factor first increased with the increase in the TGN content in composite membrane and then decreased with higher TGN composition. Therefor, the decrease of separation factor in higher TGN content may be duet to the decrease of diffusion selectivity while the permeate transport through the composite membranes. Based on the concept of the solution-diffusion mechanism, influential separation factors can be considered to be both the permeate sorption and permeate diffusion properties of TGN/PSF membrane. Therefore, both the sorption and diffusion properties should be discussed relative to the TGN content of TGN/PSF membranes. The diffusion selectivity (α^d) can be defined as the ratio of permeation selectivity (α^p) and sorption selectivity (α^s):

$$\alpha^p = \alpha^d \alpha^s, \quad (1)$$

Figure 7 shows the relationship between diffusion selectivity and TGN content in composite membranes. It can be seen that the sorption selectivity decreased with increasing TGN content in composite membranes. On the other hand, the diffusivity selectivity first increased and then decreased with higher TGN content in composite membrane. It also can be seen that the diffusion selectivity first increased up to a TGN content of 12.5% and then decreased

with the further increase in the TGN content in membranes. This result implies that a flexible polymer chain of TGN additive membrane was formed. It was also found that the too flexible polymer chain appeared to achieved a good separation properties of composite membrane when the TGN content was more than 12.5% and then the permeate diffusion selectivity was lost due to the high polymer chain flexibility. It is worth noting that the effect of TGN content on separation factor and the effect of TGN content on diffusivity selectivity in composite membrane showed similar behavior. It indicates that the dominant separation factor might be diffusion selectivity and not solubility selectivity. It can be concluded that the TGN additive in PSF membrane enhanced the polymer chain mobility. However, the low content TGN in membrane increased the polymer chain flexibility but higher flexible polymer chain in composite membranes lost the diffusion selectivity when the TGN content was more than 12.5% in membranes.

Effect of feed concentration on pervaporation properties

The effect of ethanol composition in feed on permeation flux and separation factor of PEG/PSF membranes with TGN content 12.5-wt% is shown in Figure 8. It can be seen that the permeation flux slightly changed with the increase in ethanol in feed and then decreased with the increase in the ethanol composition in feed. The separation factor increased with the increase in the ethanol composition in feed solution. It indicates that permeate concentration was not a strong factor of influence on permeation rate. It is worth noting that the significant increase in separation factor can be observed at high ethanol composition. It can be seen that the permeation rate was almost constant in all the concentration range of feed solution. The permeation behavior can be explained by the swelling properties at various concentrations of feed solution. Figure 9 shows the effect of feed ethanol concentration on the degree of swelling of TGN/PSF membrane, which contains 12.5 % TGN. Based on the swelling test in all ranges of feed solution, it can be concluded that the permeation rate was almost independent of the feed ethanol concentration. This phenomenon may be due to the low degree of swelling in all ranges of feed solution. However, the feed concentration showed a significant influence on the separation factor of composite membranes. To further distinguish the factors of influence on separation factor, the sorption and diffusion properties were made.

Effect of feed ethanol concentration on sorption and diffusion behavior

In order to calculate the solubility of PSF membrane in various ethanols concentrations, the water and ethanol content in membrane were measured and it was showed in Figure 10. It was found that the water content in membrane decreased and ethanol content increased with increasing feed ethanol concentration. The sorption selectivity and diffusion selectivity was calculated by the previous equation. Figures 11,

and 12 show the effect of ethanol concentration in feed on the sorption selectivity and diffusivity selectivity of TGN/PSF membrane with 12.5wt% TGN content, indicating that the sorption selectivity increased with the increase in ethanol concentration in the feed solution. On the other hand, the diffusivity selectivity was calculated by dividing separation factor by solubility selectivity. It can be seen that both sorption selectivity and diffusion selectivity increased with the increase in the ethanol concentration. It implies that the polymer chain enhancer additive improves permeate selectivity whether in sorption behavior or in diffusion behavior. It is interesting to note that both sorption and diffusion selectivity increased in all feed ethanol concentration. Generally, the selectivity of sorption behavior usually showed a different trend than the diffusion behavior when the permeate passes through the membranes. To further distinguish these results, the swelling test and sorption measurements at different ethanol concentrations in feed were made. It showed that the degree of swelling of TGN/PSF membrane slightly increased with the increase in ethanol concentration. The polymer chain flexibility of swelling membrane is usually dependent on the degree of swelling. The significant increase in polymer chain flexibility induced an increase in permeate diffusion path when the permeate transfers through the membranes. Based on the swelling test, it may be concluded that the transport path of permeates was slightly increased with the increase in ethanol concentration in feed. Based on the result of swelling test and diffusion selectivity, it can be concluded that a high selective membrane can be achieved by controlling the optimum swelling condition in composite membranes.

Conclusions

TGN additive successfully improved the pervaporation performance of polysulfone membrane. Tg and swelling measurement proved that the polymer chain flexibility would be improved by the addition of TGN into membrane whether or not the composite membrane was dry or immersing in 90-wt% ethanol solution. The polymer chain flexibility and packing density of polymer chain in membrane increased with the increase in the TGN content in TGN/PSF membranes at low TGN content. However, the higher polymer packing density can be expected to decrease the permeation rate and enhance the diffusion selectivity of modified membranes. Based on the result of this study, it can be concluded that a high selective membrane could be achieved by controlling the optimum swelling condition in TGN additive membranes.

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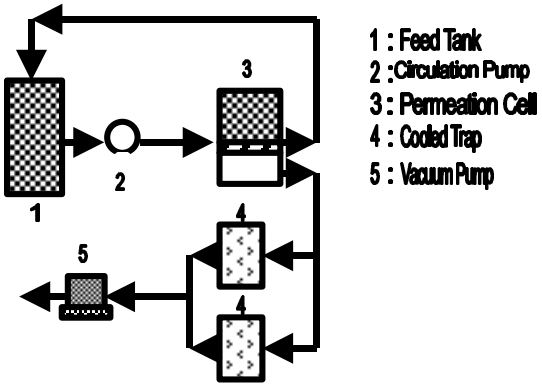

Figure 1. Schematic diagram of pervaporation apparatus.

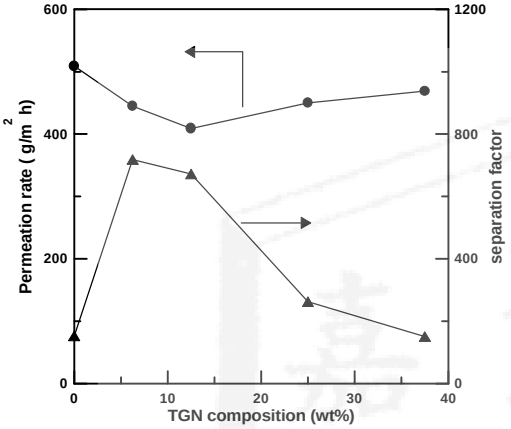

Figure 2. Effect of TGN content (TGN) on pervaporation performance of PSF/TGN membranes for 90w% ethanol solution in feed at 25℃.

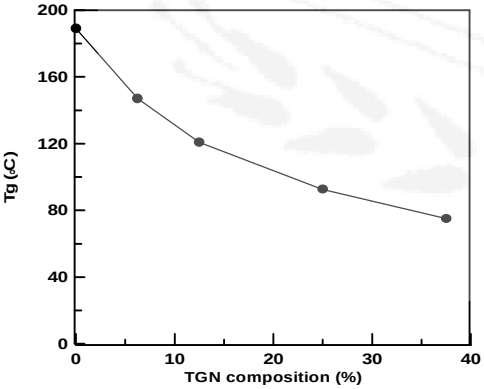

Figure 3. Effect of TGN content (TGN) on glassy transition temperature of PSF/TGN membranes.

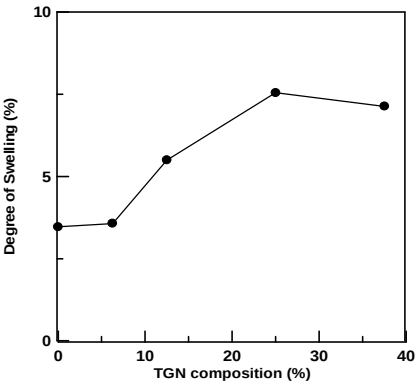

Figure 4. Effect of TGN contenton degree of swelling of

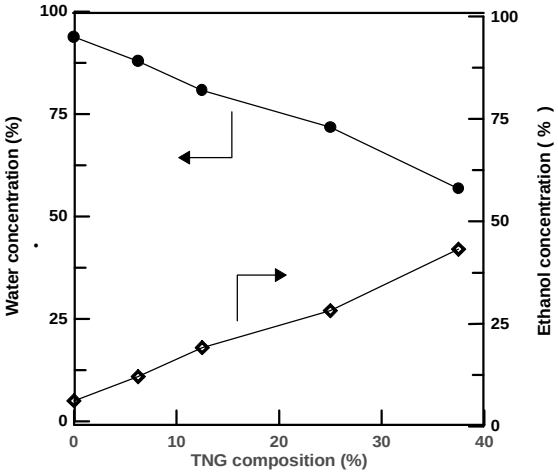

Figure 5. Effect of TGN content (TGN) on permeate content in PSF/TGN membranes for immersing in 90w% ethanol solution at 25℃

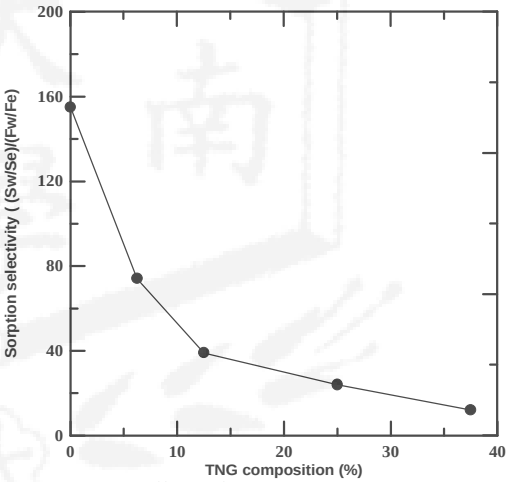

Figure 6. Effect of TGN content (TGN) on sorption selectivity of PSF/TGN membrane for 90-wt% ethanol solution in feed at 25℃.

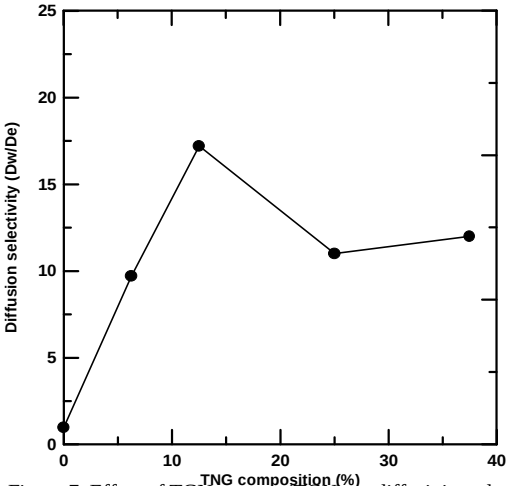

Figure 7. Effect of TGN content (TGN) on diffusivity selectivity of PSF/TGN membrane for 90-wt% ethanol solution in feed at 25℃.

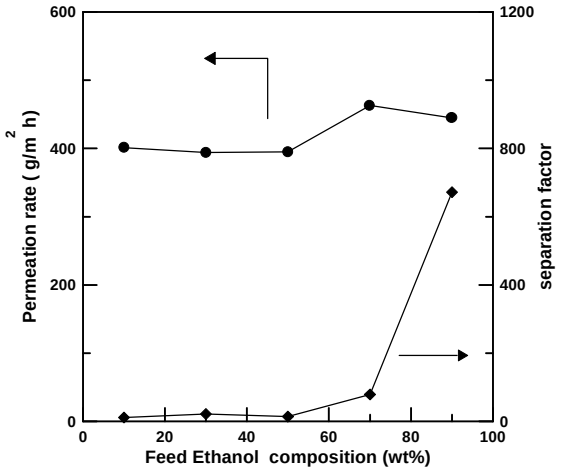

Figure 8. Effect of feed ethanol composition in feed on permeation flux and separation factor of PSF/TGN membrane with 12.5 wt% TGN content, feed solution was at 25℃.

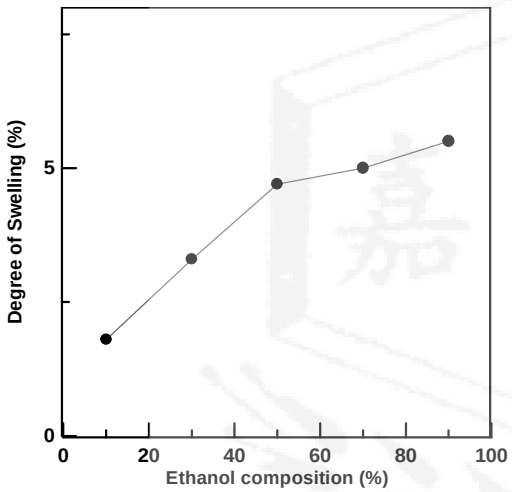

Figure 9. Effect of feed ethanol composition on degree of swelling of PSF/TGN membranes with 12.5 wt% TGN content at 25℃..

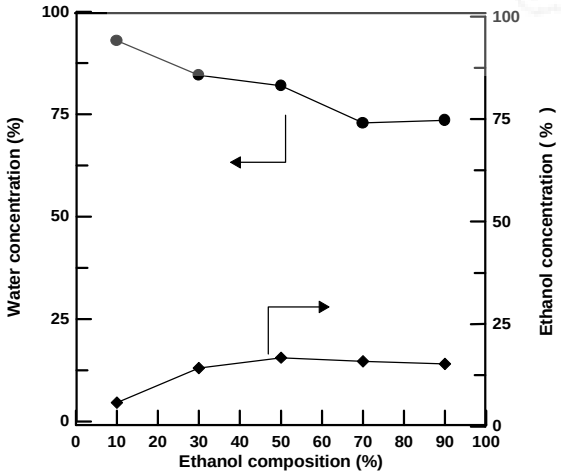

Figure 10. Effect of feed ethanol composition on sorption content in PSF/TGN membranes with 12.5 wt% TGN content at 25℃.

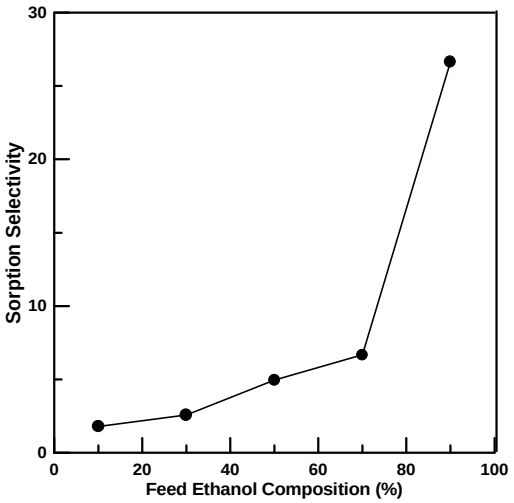

Figure 11. Effect of ethanol concentration in feed on sorption selectivity of PSF/TGN membrane with 12.5wt% GN content at 25℃.

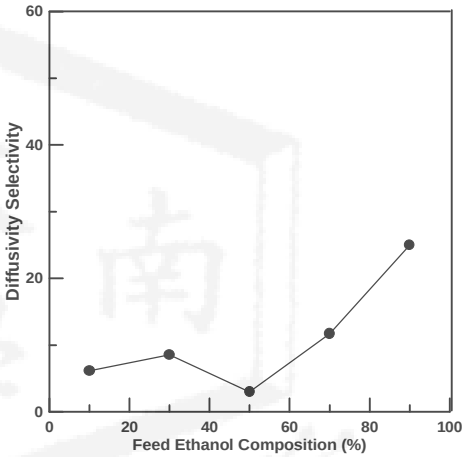

Figure 12. Effect of feed ethanol concentration on diffusion selectivity of PSF/TGN membrane with 12.5wt% TGN content at 25℃.