Pervaporation Separation of MeOH/MTBE through CTA Membrane

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ABSTRACT: In the present work, the pervaporation (PV) separation of a MeOH/MTBE mixture system was studied using a CTA dense membrane. The PV performances were characterized by changing the operating conditions, such as the feed composition and permeation temperature. The results show that the CTA membrane favors MeOH permeation and exhibits specificity during the PV separation process for the MeOH/MTBE system due to the existence of the plasticization effect from the MeOH component. Furthermore, the swelling sorption measurements reaffirm that the plasticization effect has a dominant effect on the transport of the penetrants through the membrane and substantially determines the PV permeation properties. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 377–386, 1999

Key words: pervaporation; cellulose triacetate; plasticization effect; swelling sorption

INTRODUCTION

With the problem of air pollution from the lead in gasoline becoming more serious, more and more attention is being paid to the substitutes for octane boosters, such as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ethers (TAME),[1] wherein MTBE has been extensively tested and proved to be an effective octane enhancer.[2] As an oxygenated fuel additive needed to reformulate gasoline, which meets the requirements of the Clean Air Amendments of the U. S. Government, MTBE was the fastest-growing chemical of the top 50 species in the 1980s.[3] According to the legislation, MTBE, with a gasoline component of up to 9 wt % and even more, it will likely maintain its growth.

MTBE is produced by the reaction of methanol (MeOH) with isobutylene in the liquid phase through a strongly acidic ion-exchange resin catalyst.[4] Since the reaction is an equilibrium one, an excessive quantity of methanol of even up to 20% of a stoichiometric amount is used to achieve the high conversion of isobutylene. The excessive methanol should be removed from the final products, but methanol can form azeotropes with MTBE at a composition of 14.3 wt % methanol. In industrial processes, the reaction mixtures are washed by a large amount of water and distillated to methanol separation.[5] This conventional process is very cost- and energy-intensive. ETBE is produced by the reaction of ethanol and isobutylene by a similar method as with MTBE and also can form azeotropes with ethanol at a composition of 20 wt % ethanol.[1]

Pervaporation (PV) is an attractive alternative technique to conventional processes for the separation of liquid mixtures, particularly in close-boiling-point or azeotropic mixtures. In 1988, the Air Products & Chemicals Co.[6] proposed a hybrid distillation–PV process to separate methanol from MTBE using cellulose acetate (CA) membranes. Since then, Nafion,[7] a silicalilte membrane,[8] PVA/PAA

blend membranes,[9] polysulfone,[10] a polyelectrolyte complex of surfactants,[11] and a plasma graft membrane,[1] among others, were tested to separate this mixture system, wherein most studies have been concerned with the appraisal of new membrane materials. Meanwhile, cellulose ester-based polymer-blend membranes,[12] that is, CAB/CAP blending membranes,[13] have been used to separate ethanol/ETBE mixtures. Jonquieres et al.[14] studied PV transport modeling in the ETBE/EtOH/polyurethaneimide ternary system. Their results gave some references for the PV separation of the MeOH/MTBE system.

To fully investigate the PV separation properties and the mechanism for the MeOH/MTBE system, we chose cellulose triacetate to explore the PV characteristics, whose lower cost, availability in a wide variety of viscosity grades, outstanding tractability, and reasonable resistance to oxidation will guarantee its continued utility for the foreseeable future. Additionally, the acetyl groups, which are smaller than the acyl groups in the CAP and CAB, have little influence on the internal plasticizers of the membrane matrix.[15]

This article reports the PV–separation properties of MeOH/MTBE through CTA dense membranes, wherein including the effect of feed composition, permeation temperature on the PV properties, and the swelling sorption results thus elucidates the PV separation mechanism of this mixture with the CTA dense membranes.

EXPERIMENTAL

Membrane Preparation

Cellulose triacetate (CTA) was from Herculs Ltd., England, type TH 22, with a 43.4% acetylation degree. To obtain the desired membranes, a dioxane solution of 2.0 wt % CTA was cast onto a glass plate after being filtered and degassed and then was dried at room temperature for 48 h. The membrane thickness was 25 μm.

PV Measurement

The PV test unit is illustrated in Figure 1. A membrane sample with a 25-cm^2 permeation area was placed on a porous metal-supporting plate in the permeation cell and sealed with a rubber O-ring. At the downstream side, a vacuum pump was used to remove the permeate, maintaining a pressure less than 200 Pa. The permeate vapor

Figure 1 Schematic diagram of PV apparatus: (1) permeate cell; (2) stirrer; (3) heater; (4) thermometer; (5) permeate collector; (6) vacuometer; (7) tube for safety; (8) cold trap; (9) vacuum pump.

was collected in a trap cooled with liquid nitrogen and the composition was analyzed using a GC-8810 gas chromatograph (Kechuan Instruments Ltd.) with an FID detector. The permeation selectivity is defined as

$$\alpha_{\text{psep}} = \frac{P_{\text{MeOH}}/P_{\text{MTBE}}}{F_{\text{MeOH}}/F_{\text{MTBE}}}$$

where P and F are the weight fraction of each component in the permeate and the feed, respectively. The PV was performed with every feed for 7 h. After that, the used membrane was maintained in the membrane cell with the permeate side vented to the atmosphere overnight and then the same PV experiment was carried out again the next day.

Swelling Experiments and Sorption Measurement

Dry CTA membrane samples of a known weight were immersed in different MeOH/MTBE mixtures to reach the swelling equilibrium. The swollen samples were taken out from the mixtures, and the solution was rapidly wiped onto the surface with tissue paper and then quickly weighted. The swelling degree S is defined as

$$S = \frac{W_s - W_d}{W_d} \times 100$$

where W_d and W_s indicate the weight of the dry and the swollen samples, respectively.

After being weighted, the swollen membranes were placed into a dry flask which was connected to a cold trap and a vacuum pump. With the flask heated by boiling water, the absorbed components

Figure 2 Total flux and selectivity factor as a function of feed composition.

were extracted from the membranes and then collected in the cold trap for 2 h under a vacuum condition. The composition of the collected solution was analyzed with a gas chromatograph. The sorption selectivity is defined as

$$\alpha_{\text{ssorp}} = \frac{A_{\text{MeOH}}/A_{\text{MTBE}}}{F_{\text{MeOH}}/F_{\text{MTBE}}}$$

where A and F are the weight fractions of each component in the absorbed mixtures and feeds, respectively.

RESULTS AND DISCUSSION

Effect of Feed Composition on PV Properties

The effect of the feed composition on the PV characteristics was determined over a range of 2–40 wt % MeOH in the feed at 50°C and the results are shown in Figure 2. The total flux increased monotonously with the MeOH content in the feed, while at the initial time, the permeate selectivity decreased with increasing MeOH content in the feed; then, there was a light resilience above 20 wt % MeOH in the feed. Furthermore, the partial flux and permeate concentration of MeOH and MTBE at 40 and 50°C are also shown in Figures 3 and 4. In the permeate, the MeOH concentration has a minimum value at 19.41 wt % MeOH in the feed and the flux always increases; on the other hand, both the concentration and flux of MTBE have maximum values. The higher the operation temperature, the more significant the change. This is a coupling phenomenon and can

be explained in terms of the plasticization effects of the permeants and the interaction between the permeants and the polymer.[16] A strong interaction can be found at low temperature for this azeotropic mixture and it reduces the plasticization effect. However, as temperature increases, the interaction becomes weaker and the plasticization effect can be recovered. The interacted molecules can cause the immobilization of the permeant molecules and reduce the plasticization effect, so a smaller flux at lower temperature is obtained.

For insight into the permeation behavior in the MeOH–MTBE–CTA system, a deviation coefficient, ε, was introduced, which is a measure of the deviation of the actual molar permeation flux (J) from the ideal molar flux (J^0) to describe the interactions between the polymer and the permeants.[17] For ideal binary liquid permeation, the component molar flux in the mixture can be expressed in terms of the pure component molar permeation flux as follows:

$$J_i^I = x_i J_i^0$$

$$J_j^I = x_j J_j^0$$

where i and j denote the individual components in the mixture, χ is the molar fraction in the feed, the superscript denotes the ideal permeation, and J^0 is the pure component molar permeation flux (the J^0 of MeOH is 811.94 mol m^{-2} h^{-1} and the J^0 of MTBE is 0.162 mol m^{-2} h^{-1}). To determine the deviation of the actual permeation from the ideal situation, the phenomenological deviation coefficients ε_i and ε_j are used as defined below:

$$\varepsilon_i = \frac{J_i}{J_i^I}$$

$$\varepsilon_j = \frac{J_j}{J_j^I}$$

The deviation coefficients $\varepsilon_{\text{MeOH}}$ and $\varepsilon_{\text{MTBE}}$ for each component are described in Figure 5. The values of both $\varepsilon_{\text{MeOH}}$ and $\varepsilon_{\text{MTBE}}$ over the range of feed composition are well above unity. This positive deviation indicates that a plasticization effect from MeOH and MTBE existed in the system. The value of $\varepsilon_{\text{MTBE}}$ is much higher than that of $\varepsilon_{\text{MeOH}}$. This means that the plasticization effect of MeOH is much more intensive than that of MTBE, and

Figure 3 MeOH content in the permeant (a) and partial flux (b) as a function of feed composition at 50 and 40°C, respectively.

Figure 4 Partial flux of MTBE as a function of feed composition at 50 and 40°C, respectively.

the plasticization effect of MeOH more remarkably enhances the permeation of MTBE than MTBE does to MeOH. This is why there is a minimum value for the separation factor in Figure 2.

In fact, the details in the deviation coefficient greatly correlates with the results indicated in the PV tests. For the PV properties of MTBE in the tested system, below approximately 20 wt % MeOH content in feeds, the plasticization effect of MeOH increases with increasing MeOH content and enhances the diffusion of MTBE compared with the flux of a pure MTBE solvent at 50°C. So, in this range, the flux and concentration of MTBE in the permeate always increases. But above approximately 20 wt % MeOH content, the plasticization effect of MeOH decreases with increasing

Figure 5 Plot of the deviation coefficient of each component versus feed composition.

MeOH content; as a result, the flux and concentration of MTBE in the permeate also decreases.

For the PV properties of MeOH in the tested system, the MeOH content in the permeate is very high even with a high MTBE content in the feed because the membrane performs almost no permeation for the pure MTBE solvent and then decreases because of the permeation of MTBE being enhanced. At high MeOH concentration, the MeOH content in the permeate increases because the membrane is fully swollen so that there is even more MeOH dissolved or absorbed in the membrane compared with the case where MTBE is absent. This will result in that the MeOH molecules occupy many more hydrophilic groups of a membrane polymer and orientation of the dis-

solved molecules creates obstacles for the MTBE so that the flux of the MTBE decreases. All these will be proved in the swelling sorption results in the case of a thermodynamical equilibrium.

Effect of Temperature on PV Properties

The effect of temperature on PV performance was tested at different temperatures in this study. Figure 6 depicts the permeability and separation factor at 40 and 50°C for a MeOH concentration range over 2–40 wt %. It is shown that the flux increased and the separation factor decreased with increasing temperature. Particularly at 50°C, the changes are more intensive than are those at 40°C. The reason is that increasing temperature can enhance the

Figure 6 Total flux and selectivity factor as a function of feed composition at 50 and 40°C, respectively.

polymeric chain, resulting in the enlargement of the occupation volume of the chains and the formation of voids or channels that help the transport in the polymer, but increasing of the voids or channels decreased the selectivity. Empirically, the temperature dependence of the permeation flux often follows an exponential fashion (i.e., an Arrhenius equation), as shown in Figure 7 by semilogarithmic plots for feeds with 13.04, 19.41, and 37.52 wt % MeOH content over the range of 30–50°C, respectively. For both feeds with 19.41 and 37.52 wt % MeOH content, a good linear relationship existed in the plot; for feed with 13.04 wt % MeOH, there is an inflection at 40°C in the whole curve, wherein the part of the curve over 40–50°C almost parallels both of the other curves, but it has a very different condition over 30–40°C. The data of the activation energy for the three contents were calculated from the Arrehenius equation and are listed in Table I. Generally, the activation energy for permeation is regarded as a combination of the enthalpy of the permeant sorption in the membrane and the activation energy of the permeant diffusion through the membrane, so it can reveal some characteristics of the diffusion mechanism. It is known that there are two ways to improve the plasticization effect to result in polymer relaxation: (1) increasing the operation temperature, and (2) increasing the MeOH content in the feeds. But the result of the polymer relaxation is that there may be a morphological alternation and a transport mechanism transition during the permeation processes. By deduction from the results of the apparent activation energy of the PV, the PV separation mechanism for the above three feeds should be in two pathways for the penetrate through the membranes: One is that for

13.04 wt % feeds (over 40–50°C) and 19.41 and 37.52 wt % feeds; the other is that for 13.04 wt % feeds (over 30–40°C). Meanwhile, it was also found that the activation energy of MeOH permeation is much lower than that of MTBE and close to the total activation energy, indicating that the permeation of MeOH molecules through the membranes consumes less energy than that of the MTBE molecules at this concentration and that the energy consumption in the PV lies mainly on the permeation of MeOH molecules for highly MeOH-selective materials.

The variation in the MeOH content in the permeate can be related to the difference in the activation energy for MeOH and MTBE and is expressed by the Arrhenius-like equation[18] for both MeOH and MTBE:

$$y_{MeOH} = \cfrac{1}{1 + \cfrac{A_{MeOH}}{A_{MTBE}} \exp(-\cfrac{E_{MeOH} - E_{MTBE}}{RT})}$$

where y_{MeOH} is the MeOH content in the permeate. A_{MeOH} and A_{MTBR} are the preexponential factors, and E_{MeOH} and E_{MTBE} are the activation energy for both. The equation suggests that the larger the difference in the activation energy between MeOH and MTBE the sharper is the decrease in the MeOH content in the permeate and the separation factor. This result can correlate with the effect of the feed composition on the PV properties mentioned above.

Solubility–Diffusion Mechanism in the PV Permeation

In the PV process, generally, the penetrant through the membrane is thought to be the solubility–diffusion mechanism. The permeability of a penetrant through a membrane is a function of the solubility and diffusivity in the membrane phase. To investigate the solubility–diffusion mechanism during the PV processes, the swelling sorption results were obtained for the three feeds with 13.04, 19.41, and 37.52 wt % MeOH content and are listed in Table II. Moreover, the sorption kinetics $M_t/M_\infty - t^{1/2}$ were also conducted for the diffusion coefficient with the initial slope[19] in Figure 8, where M_t is the mass of the sorbed mixture at time t and M_∞ is the equilibrium mass of the absorbed mixture during the sorption experiment. Table II shows

Figure 7 (a) Ln total flux, (b) partial flux of MeOH, and (c) partial flux of MTBE versus $1/T$ for three feeds of different contents over 30–50°C.

that there is no substantial difference among the solubility coefficients, and the sorption selectivity has the same changing tendency with the selectivity results. Compared with the solubility coefficient, the diffusion coefficient acts with a decisive character for the PV transport

Table I   Total and Partial Activation Energy of the Three Different Feed Contents

Feeds	E_t	E_{MeOH}	E_{MTBE}	$E_{MTBE} - E_{MeOH}$
13.04%	64.61 (30–40)	38.27 (30–40)	26.58 (30–40)	−11.69
	7.352 (40–50)	6.68 (40–50)	14.88 (40–50)	8.2
19.41%	7.278	6.15	17.57	11.42
37.52%	7.19	5.92	15.58	9.66

Temperature range 30–50°C; unit: kJ/mol.

and correlates with the obtained flux of different feed compositions.

According to the Flory–Huggins equation,[20]

$$\ln a_s = \ln \phi_s + \phi_p + \chi \phi_p^2$$

with χ the polymer–solvent interaction parameter, it can be achieved by the swelling in the pure solvent through

$$\chi = -\left(\frac{\ln(1 - \phi_p) + \phi_p}{\phi_p^2}\right)$$

and then the mean clustering sizes in a given polymer–solvent system can be written as[21]

$$MCS = \left(\frac{1}{1 - 2\chi\phi_s}\right)$$

It is known that during the diffusion process there exists a plasticization effect and clustering behaviors for the solvent molecule penetration through the membrane matrix, wherein the plasticization effect can enhance the transport and

the clustering will hinder the transport. According to the swelling sorption results, the calculated clustering sizes are listed in Table II and did have any large differences for any of the three feeds. In reviewing the results of the effect of the feed composition on the permeability, the results obtained from the swelling sorption reaffirms that it is a plasticization effect that caused the relaxation, increasing the relaxation-deducing sorption fraction and thus substantially determining the permeability.

On the other hand, the sorption kinetics $M_t/M_\infty - t^{1/2}$ showed that for the feed with 13.04 wt % MeOH content the curve is two-staged with a second jump presented after 3 days. For the feeds with 19.41 and 37.52 wt % MeOH content, both curves exhibited one platform after undergoing the beginning increase. Since the absorbed molecules could significantly plasticize the glassy polymer during the sorption process, the polymer chains will undergo the relaxation process, wherein the relaxation time depends mainly on the operation temperature and the amount of the absorbed permeate molecules, particularly the

Figure 8   Sorption kinetics $M_t/M_\infty - t^{1/2}$ for three feed contents at 30°C.

stronger polarity molecules.[22] Under this circumstance, there are two sorption behaviors of the permeate molecules in the glassy membrane: diffusion (Fickian) sorption and relaxation-deducing sorption. As both the permeate concentration and the operation temperature increases, the polymer relaxation is quickly exhibited and the relaxation-deducing sorption quickly occupies the sorption sites. As a result, the ratio of the relaxation-reducing sorption to the Fickian sorption also increases. If the permeate concentration and operation temperature are high enough, the relaxation time will be significantly reduced. The relaxation-deducing sorption will dominate the total sorption and a situation may occur where no Fickian sorption can be observed. The results hold a reverse position for lower permeate concentration and operation temperature.

The above facts can account here for the sorption behavior. For the sorption of the feed with 13.04 wt % MeOH content, initially, the diffusion sorption occurs first and tend to equilibrium. But since the polymer relaxation-deducing occurs slowly, the relaxation-deducing sorption would be present and, thus, there finally exists a second jump in the curve. According to the extent of the increase, the diffusion sorption is dominant for the total sorption of the feed with 13.04 wt % MeOH content. For the sorption of the feeds with 19.41 and 37.52 wt % MeOH content, the deduced relaxation time will be reduced with respect to a higher MeOH content. According to Figure 8, the relaxation-deducing sorption simultaneously is exhibited with the diffusion sorption at the beginning of the sorption because there is only one platform.

Based on the sorption results, we can also discuss the PV properties. With the increasing permeate concentration, the plasticization effect in-

creases so that the polymer relaxation is fully exhibited. As a result, the flux synchronously increases (Fig. 2). Comprehending the results of the temperature dependence (Fig. 7) and the sorption behavior, for the permeation of feeds with 13.04 wt % MeOH content over 30–40°C, the polymer relaxation occurs slowly with a lower temperature and a lower permeate concentration. So, the diffusion sorption is dominant. But over 40–50°C, the situation is reverse because there is an inflection in the plot of the temperature dependence. It means that there is an alternation in the transport mechanism with the plasticization effect improving over the range of 40–50°C. So, it is thought that the relaxation-deducing sorption is dominant over 40–50°C. For the permeation of feeds with 19.41 and 37.52 wt % MeOH content over 30–50°C, the temperature dependence is similar to that of the feed with 13.04 wt % MeOH content over 40–50°C. It indicates that there is a similar transport mechanism for both. Of course, this result is from the relaxation deduced by the plasticization effect of the permeant molecules based on the higher permeate concentration. So, it is thought that the relaxation-deducing sorption is dominant for the permeation of feeds with 19.41 and 37.52 wt % MeOH content.

CONCLUSIONS

In this article, the PV separation of MeOH/MTBE mixtures by a CTA dense membrane was studied. For the feeds with a range over 2–40 wt % MeOH, the flux always increases and the selectivity factor has a minimum value, wherein the partial flux of MeOH always increases and its concentration in the permeate also has a minimum value, but

Table II Swelling Sorption Results for the Three Different Feed Contents

Feeds	MeOH (wt %)	Absorbed Mixture Inside Membrane			
		Solubility[a]	Selectivity[b]	Clustering Sizes[c]	Diffusion Coefficient[d]
13.04%	70.60	9.02×10^{-2}	16.20 /176.24	1.45 /1.21	2.924×10^{-8}
19.41%	67.87	14.26×10^{-2}	8.77 /23.22	1.81 /1.35	5.428×10^{-8}
37.52%	94.48	10.93×10^{-2}	28.50 /43.34	2.02 /1.04	30.914×10^{-8}

Sorption temperature: 50°C.
[a] Total amount of absorbed mixture g/100 g dry membrane.
[b] The first no. is sorption selectivity; the second no. is PV selectivity.
[c] The first no. is the mean clustering size of MeOH; the second no. is the mean clustering size of MTBE.
[d] The initial slope of the sorption kinetics $M_t/M_\infty - t^{1/2}$; unit: cm²/s.

both of those of MTBE have maximum values. The possible explanation contributes to the difference in the plasticization effect between the permeants and this has been proved in the swelling sorption measurements. In regard to the effect of temperature, the activation energy data prove that the membrane is permselective for MeOH and exposes the different PV separation mechanisms for the different feed compositions through the polymer matrix.

During the swelling sorption experiments, the data of the sorption kinetics $M_t/M_\infty - t^{1/2}$ can well correlate the above results and confirm the existence of the different PV separation mechanisms for the different feed compositions. The analysis results show that it is the plasticization effect that causes the relaxation, increasing the relaxation-deducing sorption fraction and thus substantially deciding the permeability.

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