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Characteristics of permeation and separation of dimethyl acrylamide-methyl methacrylate random and graft copolymer membranes for a benzene/cyclohexane mixture

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Summary

When a benzene/cyclohexane mixture was permeated through poly (dimethyl acrylamide-random-methyl methacrylate) (DMAA-r-MMA) and poly (dimethyl acrylamide)-graft-poly (methyl methacrylate) (DMAA-g-MMA) membranes by pervaporation, the benzene-permselectivity of the DMAA-r-MMA membrane changed from the diffusivity selectivity to the solubility selectivity with increasing DMAA content but DMAA-g-MMA membranes with a high DMAA content had the higher apparent diffusivity selectivity than the apparent solubility selectivity. Furthermore, the apparent solubility selectivity for a benzene/cyclohexane mixture between the DMAA-r-MMA membrane and the DMAA-g-MMA membrane with a high DMAA content was remarkably different. These results were attributed to the difference of structure between the copolymers.

Introduction

Recently, much attention has been paid to one of the membrane separation techniques, pervaporation (PV), for the separation and concentration of close-boiling point and azeotropic mixtures such as benzene/cyclohexane mixtures. Based on the solution-diffusion theory, the separation of liquid mixtures in PV is dependent on the difference in the solubility of permeants into polymer membranes and in the diffusivity of permeants in polymer membranes (1). Therefore, the physical and chemical structures of membranes are very important for the membrane function.

In the separation and concentration of the benzene/cyclohexane mixtures in PV, since the swelling of polymer membrane by the feed solution lowers the permselectivity of polymer membranes, the control of swelling of the membrane is very important. Therefore, hydrophilic

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polymers, which have low affinity for hydrocarbons, as a membrane material to depress the swelling of membrane have being applied (2-6). Though hydrophilic polymer membranes are a low permeability for the benzene/cyclohexane mixtures, the benzene-permselectivity, particularly the apparent solubility selectivity, is expected to be enhanced by hydrophilic polymers which have a high polarity (2).

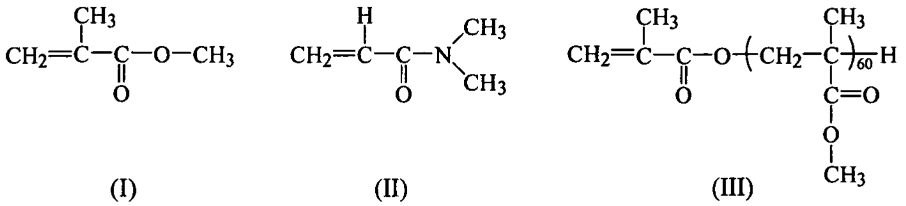
Previously, we have reported that poly (methyl methacrylate) (PMMA) membranes cross-linked with ethylene glycol dimethacrylate have a good benzene-permselectivity but those membranes were little permeability for the benzene/cyclohexane mixtures of low benzene concentration as the effect of the cross-linking was too strong (7).

It is known that the copolymerization of dimethyl acrylamide (DMAA), which has high hydrophilicity, with methyl methacrylate (MMA) leads to the poly (dimethyl acrylamide-random-methyl methacrylate) (DMAA-r-MMA) (8). In this study, in order to enhance the permeability and permselectivity of the PMMA membrane for the benzene/cyclohexane mixtures of low benzene concentration, the DMAA-r-MMA membrane was prepared. Furthermore, the poly (dimethyl acrylamide)-graft-poly (methyl methacrylate) (DMAA-g-MMA), which was made by the copolymerization of DMAA with MMA macromonomer, was also prepared and the effect of the structure of the DMAA-r-MMA and DMAA-g-MMA membranes on the characteristics of permeation and separation for a benzene/ cyclohexane mixture through these membranes by PV is investigated.

Experimental

Copolymerization and preparation of membrane

DMAA and MMA or MMA macromonomer (supplied by Toa Gosei Kagaku Co., Ltd.) (See Scheme 1) with 2,2'-azoisobutyronitorile (0.5 wt% relative to the monomers) as an initiator were dissolved in benzene to make 40 wt % solution. After the mixture was transferred in to a glass tube, the copolymerization was carried out for 6 hr at 60 °C under nitrogen atmosphere. PMMA or PDMAA was produced by the homopolymerization of MMA or DMAA under same condition. The copolymers were reprecipitated from benzene solution into the diethyl ether and dried *in vacuo*. The composition of the copolymers was determined from ^{1}H-NMR (JEOL, EX-270) spectra by the integrals of the peaks assigned



$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_3$ (I)

$CH_2{=}CH{-}C({=}O){-}N(CH_3)_2$ (II)

$CH_2{=}C(CH_3){-}C({=}O){-}O{-}\left(CH_2{-}C(CH_3)(C{=}O{-}O{-}CH_3)\right)_{60}{-}H$ (III)

Scheme 1 (I) Methyl methacrylate (MMA), (II) dimethyl acrylamide (DMAA) and (III) MMA macromonomer

Table 1 DMAA content in the feed solution and copolymer

Copolymer	DMMA content in feed (mol%)	DMMA content in copolymer (mol%)
DMAA-r-MMA	30	26
	50	50
	70	73
DMAA-g-MMA	30	38
	50	60
	70	77

to protons (δ=3.0 ppm) on *N*-methyl group of DMAA and to protons (δ=3.6 ppm) of methyl group of MMA (Table 1).

The DMAA-r-MMA, DMAA-g-MMA, PMMA and PDMAA membranes were prepared by casting a benzene solution of 1.5 wt% polymer on a tetrafluoroethylene plate and evaporating the solvent completely at room temperature. The thicknesses of those membranes were about 50 μm.

Degree of swelling of membrane and solubility selectivity

The PMMA membrane dissolved in the benzene/cyclohexane mixtures with benzene concentration of more than about 40 wt% and indicated little permeability for benzene/ cyclohexane mixtures with benzene concentration of less than about 20 wt% in PV. Therefore, a benzene/cyclohexane mixture of 30 wt% benzene as a feed solution was used in this study. A sample membrane, which reached a sorption equilibrium in a benzene/cyclohexane mixture of 30 wt% benzene at 40 °C was taken out of the vessel, wiped quickly with filter paper and weighed. The degree of swelling (DS) of the membrane was calculated from eq. (1),

$$DS=W_s/W_d \qquad (1)$$

where W_s and W_d are the weights of the membrane swollen in a benzene/cyclohexane mixture and of the dried membrane, respectively.

Furthermore, a sample membrane which reached a sorption equilibrium was put on a boat of pyrolyzer. The composition of benzene/cyclohexane sorbed in the membrane was determined by measuring the vaporized mixtures on a boat of pyrolyzer with gas chromatograph (Shimadzu, GC-14A) (9). The apparent solubility selectivity ($\alpha_{sol,B/C}$) was calculated from eq. (2),

$$\alpha_{sol,B/C}=(M_B/M_C)/(F_B/F_C) \qquad (2)$$

where F_B and F_C are the weight fractions of benzene and cyclohexane in the feed solution and M_B and M_C are those in the membrane, respectively.

PV measurements

PV apparatus has been described in a previous paper (10). The effective membrane area was 13.8 cm^2. The pressure at the downstream side was maintained at 1.33 Pa (0.01 Torr). A benzene/cyclohexane mixture of 30 wt% benzene as the feed solution was permeated at 40 °C. The permeate was collected in the U-tube at liquid nitrogen temperature. After the permeation was reached in the steady-state, the weight and composition of the permeate were measured. A specific flux (F_S) was determined from the weight of the permeate (w), the membrane thickness (l), permeation time (t), and effective membrane area (A) as follows:

$$F_S=wl/At \qquad (3)$$

The benzene concentrations in the feed solution and permeate were determined by gas chromatograph. The separation factor ($\alpha_{sep,B/C}$) was calculated from eq. (4).

$$\alpha_{sep,B/C}=(P_B/P_C)/(F_B/F_C) \qquad (4)$$

where F_B and F_C are the weight fractions of benzene and cyclohexane in the feed solution and P_B and P_C are those in the permeate, respectively.

Furthermore, since the permeability coefficient corresponds to the product of the solubility and diffusion coefficients in the solution-diffusion theory (1), the apparent diffusivity selectivity ($\alpha_{dif,B/C}$) is calculated from the $\alpha_{sep,B/C}$ and $\alpha_{sol,B/C}$ (7, 9,11,12).

$$\alpha_{dif,B/C}=\alpha_{sep,B/C}/\alpha_{sol,B/C} \qquad (5)$$

Results and discussion

Copolymer membranes for benzene/cyclohexane mixture

Fig. 1 shows the effect of the DMAA content on the DS of the DMAA-r-MMA and DMAA-g-MMA membranes for a benzene/cyclohexane mixture of 30 wt% benzene. The DS of the DMAA-r-MMA and DMAA-g-MMA membranes decreased with increasing DMAA content. These results suggest that the introduction of the DMAA which has high hydrophilicity is effective to control the swelling of the PMMA membrane in the benzene/cyclohexane mixture. The DS of the DMAA-g-MMA membranes for a benzene/cyclohexane mixture exhibited slightly higher than that of the DMAA-r-MMA membranes.

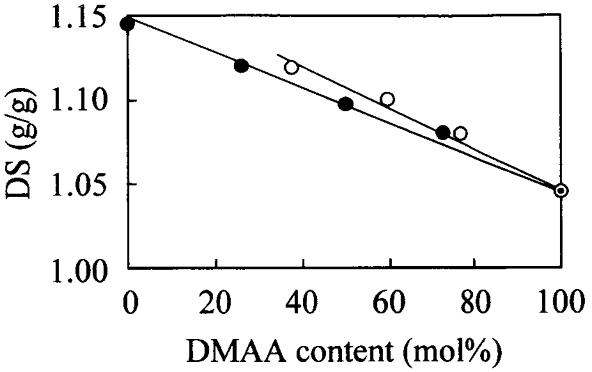


Fig. 1. Effect of the DMAA content on the DS of the DMAA-r-MMA (●) and DMAA-g-MMA (○) membranes for a benzene/cyclohexane mixture of 30 wt% benzene

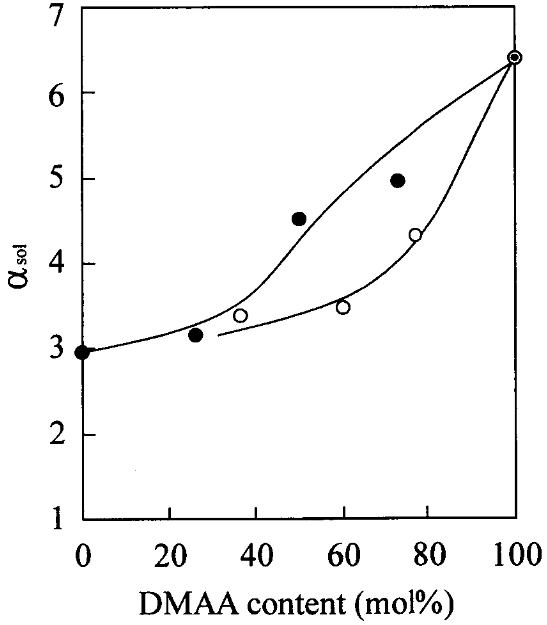


Fig. 2. Effect of the DMAA content on the α_{sol} of the DMAA-r-MMA (●) and DMAA-g-MMA (○) membranes for a benzene/cyclohexane mixture of 30 wt% benzene

Fig. 2 shows the α_{sol} of the DMAA-r-MMA and DMAA-g-MMA membranes for a benzene/cyclohexane mixture of 30 wt% benzene. The α_{sol} increased with an increase in the DMAA content. These increases in the α_{sol} were led by the control of swelling of membrane with an introduction of DMAA. Compared the α_{sol} of the DMAA-r-MMA membrane with the DMAA-g-MMA membrane, in the DMAA content of less than 50 mol%, the former was almost same as the latter but in more than 50 mol%, the former was higher than the latter.

Since the DMAA-g-MMA has the PMMA graft chains, the DMAA-g-MMA membranes may reflect relatively stronger property of PMMA compared with the DMAA-r-MMA membranes. Consequently, the DS and α_{sol} of the DMAA-r-MMA membranes for a benzene/cyclohexane mixture were approximately intermediate between those of the PMMA membrane and of the PDMAA membrane, and those of the DMAA-g-MMA membranes were close to those of the PMMA membrane. From these results, it is suggested that the DS and α_{sol} of the DMAA-r-MMA and DMAA-g-MMA membranes for a benzene/cyclohexane mixture may be depended on the copolymer structure.

PV results

The PV results of the DMAA-r-MMA and DMAA-g-MMA membranes for a benzene/cyclohexane mixture of 30 wt% benzene were shown in Fig. 3. The DMAA-g-MMA with a DMAA content of 77 mol% and PDMAA membranes exhibited little permeability for a benzene/cyclohexane mixture of 30 wt% benzene. The α_{sep} of the DMAA-r-MMA and

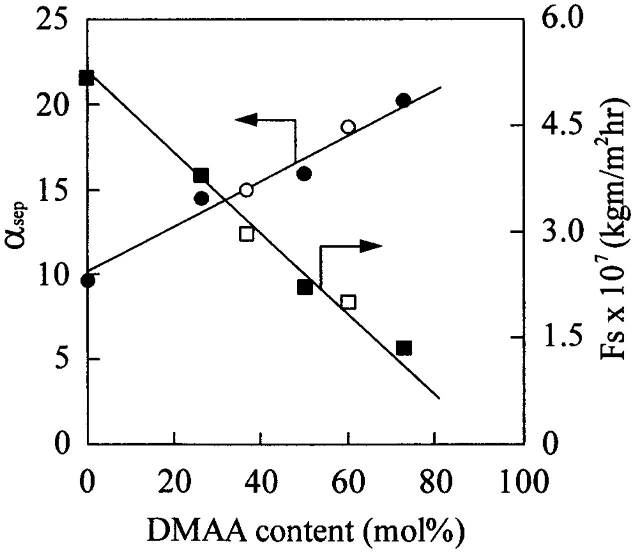


Fig. 3. Effect of the DMAA content on the α_{sep} and NPR for a benzene/cyclohexane mixture of 30 wt% benzene through the DMAA-r-MMA (●, ■) and DMAA-g-MMA (○, □) membranes by PV

DMAA-g-MMA membranes, however increased with increasing DMAA content. This result suggests that the use of DMAA as one component of the membrane material is very effective to enhance the benzene-permselectivity with the PMMA membrane. However, the Fs decreased with an increase of the DMAA content, because the swelling of these membranes was depressed.

The α_{sep}, α_{sol} and α_{dif} for the DMAA-r-MMA and DMAA-g-MMA membranes for a benzene/cyclohexane mixture of 30 wt% benzene are summarized in Table 2. The α_{dif} of the DMAA-r-MMA membrane with a DMAA content of 26 mol% was higher than α_{sol} but the α_{sol} of the membranes with 50 and 73 mol% was higher than α_{dif}. The benzene-permselectivity of the PMMA membrane for benzene/cyclohexane mixture was strongly governed by the α_{dif} (7) and the PDMAA membrane had a high α_{sol}. Therefore, it was presumed that the property of the PMMA strongly appeared in the DMAA-r-MMA membranes with a low DMAA content and the property of the PDMAA was reflected these membranes with an increase in the DMAA content. On the other hand, the benzene-permselectivity of the DMAA-g-MMA membranes with the DMAA contents of 38 and 60 mol% was always governed by the α_{dif} regardless of the DMAA content. These results are due to the fact that a higher property of PMMA on the basis of the MMA graft chains in DMAA-g-MMA membranes as mentioned above influenced not only the DS and α_{sol} for the benzene/cyclohexane mixture but also the characteristics of permeation and separation. Therefore, the DMAA-r-MMA membranes with a high content of DMAA had a high α_{sol} and the DMAA-g-MMA membranes had a high α_{dif}.

From the above results, it was found that the difference of chemical structure between the DMAA-r-MMA and DMAA-g-MMA led to the difference of the characteristics of permeation and separation for a benzene/cyclohexane mixture between these membranes in PV.

Table 2 Relationship among α_{sep}, α_{sol} and α_{dif} for a benzene/cyclohexane mixture of 30 wt% benzene through the DMAA-r-MMA and DMAA-g-MMA membranes by PV.

Membrane	DMMA content in copolymer (mol%)	α_{sep}	α_{sol}	α_{dif}
DMAA-r-MMA	0	9.71	2.95	3.29
	26	13.9	3.15	4.41
	50	16.3	4.51	3.61
	73	20.6	4.96	4.15
	100	-	6.04	-
DMAA-g-MAA	38	15.2	3.36	4.52
	60	18.8	3.46	4.39
	77	-	4.28	-

Conclusion

The benzene-permselectivity of the PMMA membrane for the benzene/cyclohexane mixture were enhanced by the copolymerization of MMA with DMAA which has a high hydrophilicity. These results strongly depended on the depression of swelling of membranes for a benzene/cyclohexane mixture with the introduction of the DMAA component. Furthermore, it was found that though the benzene-permselectivity for the benzene/cyclohexane mixture with the DMAA-r-MMA and DMAA-g-MMA membranes consisted of a similar copolymer composition significantly different, and this difference was attributed to the structure of these membranes.

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