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Effects of the Addition of Calixarene to Microphase-Separated Membranes for the Removal of Volatile Organic Compounds from Dilute Aqueous Solutions

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ABSTRACT: This paper describes the removal of benzene from an aqueous solution of dilute benzene using the poly(methyl methacrylate)-graft-poly(dimethylsiloxane) (PMMA-*g*-PDMS) membranes containing *tert*-butylcalix[4]arene (CA) (CA/PMMA-*g*-PDMS) by pervaporation. When an aqueous solution of 0.05 wt % benzene was permeated through the CA/PMMA-*g*-PDMS membranes, they showed strong benzene permselectivity. Both the permeability and the benzene permselectivity of the CA/PMMA-*g*-PDMS membranes were enhanced by increasing the CA content because the affinity of the CA/PMMA-*g*-PDMS membranes for benzene was increased by introducing CA into the membranes. Transmission electron microscope observations revealed that the CA/PMMA-*g*-PDMS membranes had a microphase- separated structure consisting of a PMMA phase and a PDMS phase containing CA. An examination of the permeation mechanism led us to the conclusion that the CA in the microphase-separated structure plays an important role as a carrier to selectively partition benzene from the aqueous solution.

Introduction

Recently, it has been pointed out that the removal of volatile organic compounds (VOCs) from wastewater and the source of tap water is very important for our standard of living.[1−3] There are a variety of separation techniques to remove VOCs from water. In these techniques, the membrane removal technique has great advantages in terms of potential savings in energy costs. The permeation and separation of organic liquid mixtures through a variety of polymer membranes by pervaporation have therefore been studied by many workers.[4−13]

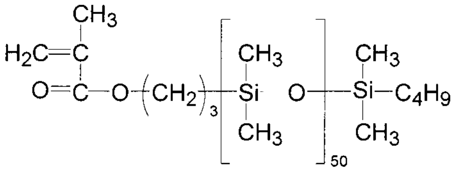
In previous reports,[14−20] we have studied the relationship between the structure of multicomponent polymer membranes containing poly(dimethylsiloxane) (PDMS) and their permselectivity for aqueous ethanol solutions in pervaporation. We demonstrated that the permselectivity of the multicomponent polymer membranes was dependent on the morphology of their microphase separation. In further studies,[21] we made it clear that the microphase separation of graft copolymer membranes between poly(methyl methacrylate) (PMMA) and PDMS significantly influenced their permeability and permselectivity for the removal of VOCs from an aqueous solution of dilute VOCs and that a continuous PDMS phase in the microphase separation plays an important role in the selective removal of VOCs.

Calixarene is a cyclic oligomer that is made up of phenol units linked to alkylidene groups and has a cavity for including a variety of organic compounds, which is similar to cycrodextrins, crown ethers, and so on.[22,23] In particular, *tert*-butylcalix[4]arene (CA) can selectively partition benzene and its derivatives by inclusion in the cavity of CA.[22]

In this study, we tried to introduce CA as a transport carrier for VOCs into multicomponent polymer membranes consisting of PMMA and PDMS to improve their permselectivity. We also discussed the relationship between the benzene permselectivity and the microphase-separated structure of membranes containing CA.

Experimental Section

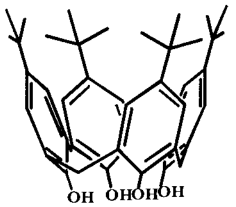
Materials. A poly(dimethylsiloxane) (PDMS) macromonomer (**1**) consisting of 51 units of PDMS was supplied by Toray Dow Corning Silicone Co., Ltd.



$H_2C{=}C(CH_3)-C(=O)-O-(CH_2)_3-[Si(CH_3)_2-O]_{50}-Si(CH_3)_2-C_4H_9$

PDMS macromonomer (1)

Methyl methacrylate (MMA) was purified by distillation under reduced pressure. 2,2′-Azobisisobutyronitrile (AIBN) recrystallized from methanol solution was used as an initiator. *tert*-Butylcalix[4]arene (CA) (**2**) was obtained from Aldrich Chem. Co., Ltd.



***tert*-butylcalix [4] arene (2)**

All other solvents and reagents were of analytical grade and were obtained from commercial sources and used without further purification.

Synthesis of Graft Copolymer Consisting of PMMA and PDMS. A graft copolymer consisting of PMMA and PDMS (PMMA-*g*-PDMS) was synthesized by the copolymerization of the PDMS macromonomer with MMA, based on the methods described in previous reports.[14,16,19−21]

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The average molecular weight of the resultant PMMA-*g*-PDMS was determined by gel permeation chromatography (GPC) (Waters Associate Inc.; R-400) with a TSK-GEL column (Tosoh Co. Ltd.; G2000HXL, G3000HXL, G5000HXL) and ultraviolet spectrophotometry (Shimadzu Co. Ltd.; SPD-2A). Tetrahydrofuran was used as an eluant, and the calibration was performed with polystyrene standards. The number-average molecular weight (M_n) of PMMA-*g*-PDMS was about 76 000 g/mol. The ratio of the weight-average molecular weight (M_w) to the M_n (M_w/M_n) was 1.8.

The composition of the PMMA-*g*-PDMS (dissolved in chloroform-*d*) was determined by its 270-MHz ^{1}H nuclear magnetic resonance (^{1}H NMR) (JEOL; GSX-270) spectra, obtained by measuring the integrals of the peaks assigned to the methyl protons (3.5 ppm) of PMMA and the dimethylsiloxane protons (0 ppm) of PDMS. In this study, PMMA-*g*-PDMS with a DMS content of 74 mol % was used as the matrix polymer for preparing the membranes because these membranes showed the highest permeability and permselectivity for an aqueous solution of dilute benzene of PMMA-*g*-PDMS membranes with various DMS contents. This high permeability and permselectivity were due to the fact that membranes with a DMS content of 74 mol % had a microphase separation consisting of a continuous PDMS phase to preferentially permeate benzene.[21]

Preparation of PMMA-*g*-PDMS Membranes Containing CA. After the PMMA-*g*-PDMS was dissolved in benzene at 25 °C to a concentration of 4 wt %, the prescribed amount of CA was added into this benzene solution for the preparation of the casting solution. The PMMA-*g*-PDMS containing CA (CA/PMMA-*g*-PDMS) membranes were prepared by pouring the casting solutions onto rimmed glass plates and then allowing the solvent to evaporate completely at 25 °C. The thickness of the resultant membranes was about 160 μm.

Permeation Measurements. The pervaporation was performed using the apparatus described in previous studies[14−21] under the following conditions: permeation temperature, 40 °C; pressure on the permeate side, 1×10^{-2} Torr. The effective membrane area was 13.8 cm^2. In all pervaporation experiments in this study, the air-side surface of the CA/PMMA-*g*-PDMS membranes faced the feed side of the permeation cell. An aqueous solution of 0.05 wt % benzene was used as the feed solution. The feed flow rate was 300 mL/min. The feed solution was circulated between the pervaporation cell and the feed tank to keep a constant concentration of feed solution in the pervaporation cell. After the feed and permeate containing benzene and water were dissolved in a specific amount of ethanol, the compositions of the feed solution and the permeate were determined by a gas chromatograph (Shimadzu GC-14A) equipped with a flame ionization detector (FID) and a capillary column (Shimadzu Co. Ltd.; PorapacQ) heated to 180 °C. The permeation rate for the aqueous benzene solution during pervaporation was determined from the weight of the permeate collected in a cold trap, the permeation time, and the effective membrane area. The results of the permeation of an aqueous benzene solution by pervaporation were reproducible, and the errors inherent in these permeation measurements were in the range of a few percent for the permeation rates through the membranes.

Membrane Density. The density of the CA/PMMA-*g*-PDMS membranes was determined by measuring their weights in air and water with an electric specific weight measure (Mirage Boeki; SD-120L) at 25 °C.

Glass Transition Temperature (T_g) Measurements. The glass transition temperatures (T_g's) of the CA/PMMA-*g*-PDMS membranes were determined by differential scanning calorimetry (DSC) (Rigaku: TAS-200). The specimens were heated from about −150 to 130 °C at a heating rate of 20 °C/min.

Transmission Electron Microscopy (TEM). The CA/PMMA-*g*-PDMS membranes were vapor-stained with an aqueous solution of 0.5 wt % RuO_4 in glass-covered dishes.[24] The stained membranes were then embedded in epoxy resin and cut into thin films (thickness ≈60 nm) with a microtome (Leica; Reichert Ultracut E). The morphological features that were highlighted by our staining procedure were observed by transmission electron microscopy (TEM) (JEOL JEM-1210) at an accelerating voltage of 120 kV.

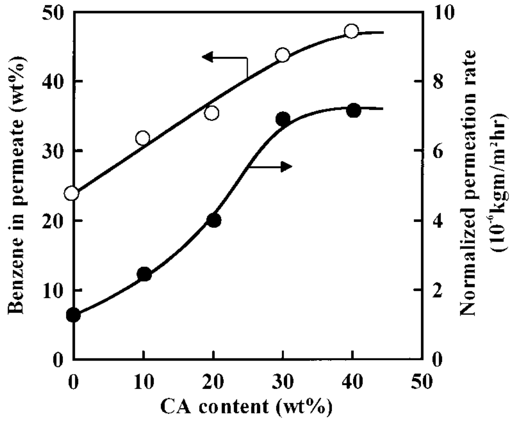

Figure 1. Effects of the calixarene content on the benzene concentration in the permeate (○) and the normalized permeation rate (●) for an aqueous solution of 0.05 wt % benzene through CA/PMMA-*g*-PDMS membranes in pervaporation (40 °C).

Degree of Swelling and Composition of the Solution Absorbed into the Membranes. The CA/PMMA-*g*-PDMS membranes were completely dried under reduced pressure at room temperature and weighed. The dried membranes were immersed into an aqueous solution of 0.05 wt % benzene in a sealed vessel at 40 °C until equilibrium was reached. The membranes were then taken out of the vessel, wiped quickly with filter paper, and weighed. The degree of swelling (DS) of the membranes was determined from eq 1,

$$D_S = W_s/W_d \tag{1}$$

where W_s is the weight of the membrane swollen in an aqueous solution of 0.05 wt % benzene and W_d is the weight of the dried membrane.

In addition, the solution absorbed in the swollen membranes was completely desorbed under reduced pressure and was collected in a cold trap. The composition of the solution in the membrane was determined by measuring the benzene concentration in the collected solution by gas chromatography (Shimazu GC-14A).

Results and Discussion

Permselectivity of Calixarene-Containing Membranes. Figure 1 shows the effect of the CA content on the normalized permeation rate and the benzene concentration in the permeate for an aqueous solution of 0.05 wt % benzene partitioned through a CA/PMMA-*g*-PDMS membrane by pervaporation. The normalized permeation rate in Figure 1 is the product of the permeation rate and the membrane thickness. The fact that the benzene concentration in the permeate was much higher than that in the feed concentration suggests that all of the CA/PMMA-*g*-PDMS membranes were benzene permselective. Both the benzene concentration in the permeate and the normalized permeation rate increased gradually with increasing CA content. This indicates that the addition of CA into the PMMA-*g*-PDMS membrane can enhance both permselectivity and permeability. In general, most modifications of pervaporation membranes cannot improve their permselectivity without lowering their permeability. Therefore, it is unusual that the addition of CA enables the membrane selectivity to increase without lowering the permeability.

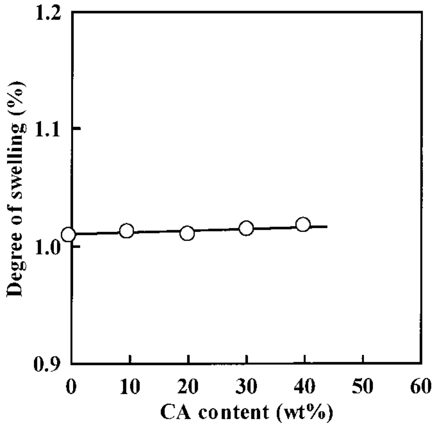

Figure 2. Effects of the calixarene content on the degree of swelling of the CA/PMMA-*g*-PDMS membranes immersed in an aqueous solution of 0.05 wt % benzene at 40 °C.

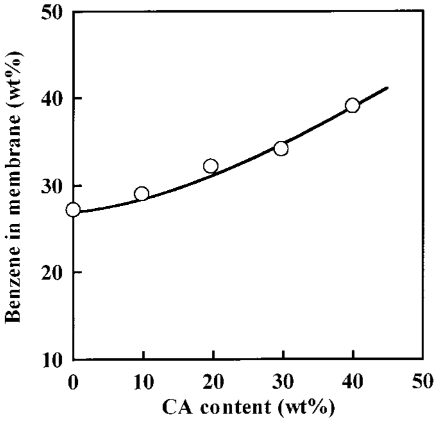

Figure 3. Relationship between the calixarene content and the benzene concentration in the CA/PMMA-*g*-PDMS membranes immersed in an aqueous solution of 0.05 wt % benzene at 40 °C.

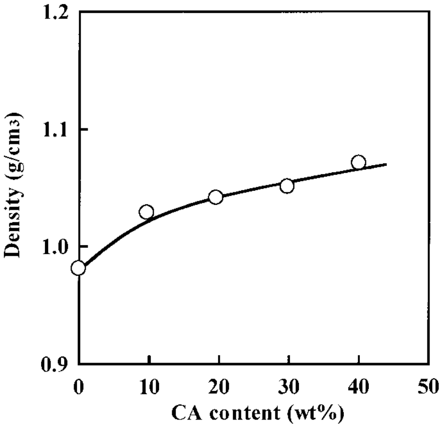

Figure 4. Relationship between the CA content and the density of the CA/PMMA-*g*-PDMS membranes.

To clarify the effects of CA on the permeation and separation characteristics of CA/PMMA-*g*-PDMS membranes, the degree of swelling of the membranes in an aqueous solution of 0.05 wt % benzene was examined. Figure 2 shows that the degree of swelling of the CA/PMMA-*g*-PDMS membranes hardly changed with an increase in the CA content. This stands in contrast to the dramatic increase in the normalized permeation rate and the benzene permselectivity upon increasing the CA content, as shown in Figure 1. Therefore, the enhanced benzene permselectivity created by the addition of CA cannot be explained by a change in the physical structure, like the degree of swelling.

The benzene concentration in the CA/PMMA-*g*-PDMS membranes was examined to discuss the affinity of benzene for the membranes. Figure 3 shows the benzene concentration of the CA/PMMA-*g*-PDMS membranes immersed in an aqueous solution of 0.05 wt % benzene as a function of the CA content. The benzene concentration in the CA/PMMA-*g*-PDMS membranes increased upon increasing the CA content. This indicates that the addition of CA into the PMMA-*g*-PDMS membrane can enhance the preferential absorption of benzene into the membranes. It is well-known that CA can form a complex with benzene.[22] Thus, the enhancement of the benzene concentration in the membranes may be due to the specific interaction between the benzene and the CA in the membranes. As a result, the benzene concentration in a CA/PMMA-*g*-PDMS membrane with a CA content of 40 wt % was 3 times higher than that in a PMMA-*g*-PDMS membrane. The preferential absorption of benzene following the addition of CA is an important factor for the high benzene permselectivity of the CA/PMMA-*g*-PDMS membranes.

Structure of Calixarene-Containing Membranes. In general, the permeation and separation of organic liquid mixtures through polymer membranes are dependent on the membrane structure. For example, an increase in membrane density often leads to a lowering of permeability due to decreasing space to permeate the penetrant. This section focuses on the membrane structure to elucidate the effects of CA on their permeability and permselectivity of CA/PMMA-*g*-PDMS membranes.

Figure 4 shows the effects of the CA content on the density of the CA/PMMA-*g*-PDMS membranes. The addition of CA into the CA/PMMA-*g*-PDMS membranes resulted in an increase in the membrane density. Generally, increasing the membrane density often causes a lowering of the permeability due to a lowered diffusivity of the penetrants in the high-density matrix. Although the membrane density increased in the CA/PMMA-*g*-PDMS membranes with increasing CA content, both the permeability and the benzene selectivity were still enhanced. Since the benzene molecule is much larger than the water molecule, an enhancement of the benzene permselectivity following an increase in membrane density cannot be attributed to the physical structure of the CA/PMMA-*g*-PDMS membranes. Therefore, the fact that both the normalized permeation rate and the benzene permselectivity increased in the CA/PMMA-*g*-PDMS membranes suggests that the permeation and separation mechanisms for an aqueous benzene solution through the CA/PMMA-*g*-PDMS membrane is quite different from the usual pervaporation mechanism.

In previous studies,[14−16,19−21] we reported that the morphology of the microphase-separated structure in multicomponent polymer membranes significantly influenced the permeation and separation of organic liquid mixtures in pervaporation. In the selective permeation removal of benzene from water, the continuity of a PDMS phase in their microphase separation of the PMMA-*g*-PDMS membranes played a particularly important role. Therefore, investigating the effects of the CA content on the morphology of the CA/PMMA-*g*-PDMS membranes is of great importance for clarifying the mechanism why the addition of CA into the PMMA-

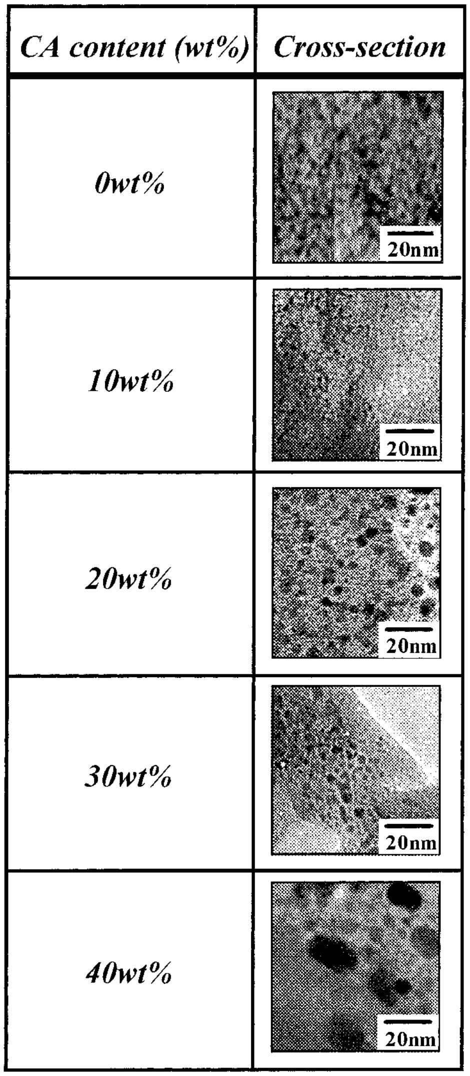

Figure 5. Transmission electron micrographs of cross sections of CA/PMMA-*g*-PDMS membranes with various CA contents. The dark region stained by RuO_4 represents the PDMS component and CA.

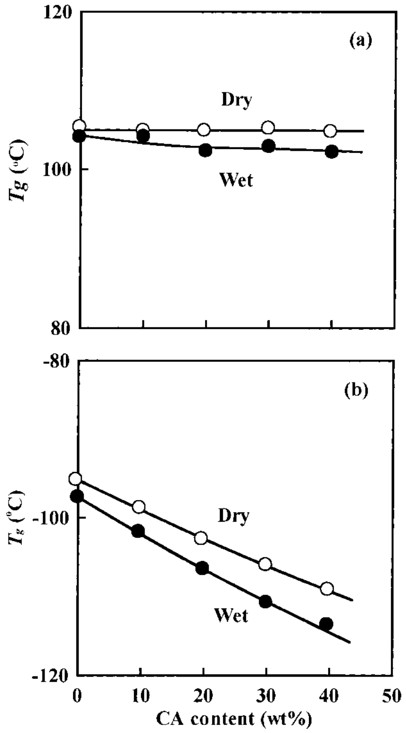

Figure 6. Effects of the CA content on T_g's of the PMMA phase (a) and the PDMS phase (b) in the microphase separation of CA/PMMA-*g*-PDMS membranes: (○) the dried membranes; (●) the membranes immersed in an aqueous solution of 0.05 wt % benzene. Higher and lower T_g's observed in DSC of the CA/PMMA-*g*-PDMS membrane were assigned to the PMMA and PDMS phases.

g-PDMS membrane enhanced both the permeability and the permselectivity.

Transmission electron micrographs of cross sections of CA/PMMA-*g*-PDMS membranes at various CA contents are shown in Figure 5. The PDMS component and the CA were stained by RuO_4, but the PMMA component was not. These micrographs clearly demonstrate that all CA/PMMA-*g*-PDMS membranes had a distinct microphase separation. As reported in previous studies,[14,16,19-21] PMMA-*g*-PDMS membranes with a high DMS content had a distinct microphase separation consisting of a continuous PDMS phase and a discontinuous PMMA phase. In the PMMA-*g*-PDMS membranes, the continuous PDMS phase played an important role in the preferential permeation of benzene from water.[21] The TEM image of PMMA-*g*-PDMS membrane without CA in this study was transferred to a microcomputer and the contrast of the phase separation image was enhanced. It was also confirmed that the PMMA-*g*-PDMS membrane without CA had a microphase separation consisting of a continuous PDMS phase and a discontinuous PMMA phase. Similarly, since the CA/PMMA-*g*-PDMS membranes have microphase separation with a continuous PDMS phase, it is presumed that the benzene was preferentially permeated through the PDMS phase. Some clusters of CA were observed in the TEM images of the CA/PMMA-*g*-PDMS membranes with a CA content of over 20 wt %. These clusters grew gradually upon increasing the CA content. These observations suggest that these clusters were mainly formed by CA.

To investigate the distribution of CA in the microphase separation, the effects of the CA content on the T_g's of the PMMA phase and the PDMS phase were examined by DSC. The DSC measurements demonstrated that the CA/PMMA-*g*-PDMS membranes had two T_g's assigned to the PMMA phase and the PDMS phase, which were around 105 and −100 °C, respectively. Figure 6 shows the effects of the CA content on the T_g's of the PMMA and PDMS phases in dried CA/PMMA-*g*-PDMS membranes and versus membranes immersed in an aqueous solution of 0.05 wt % benzene. When the CA content was increased, the T_g of the PDMS phase in both dried and wet CA/PMMA-*g*-PDMS membranes decreased, but the T_g of the PMMA in them did not change. When CA was added into a PMMA homopolymer, the T_g decreased linearly with the CA content similarly to the T_g of the PDMS phase in the CA/PMMA-*g*-PDMS membranes. Therefore, the lack of change in the T_g of the PMMA phase and the decrease in the T_g of the PDMS phase suggest that the CA in the CA/PMMA-*g*-PDMS membrane was present in the PDMS phase rather than in the PMMA phase. The DSC measurements revealed that the CA was more preferentially distributed in the PDMS phase than in the PMMA phase. In addition, immersing the CA/PMMA-*g*-PDMS membranes in an aqueous solution of 0.05 wt % benzene significantly decreased the T_g of the PDMS

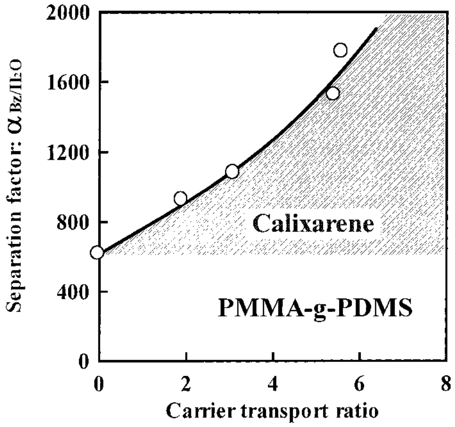

Figure 7. Separation factor for an aqueous solution of 0.05 wt % benzene through CA/PMMA-*g*-PDMS membranes as a function of the carrier transport ratio. The carrier transport ratio is the ratio of the permeation rate through CA/PMMA-*g*-PDMS membranes with and without CA as a carrier.

phase, but the T_g of the PMMA phase changed very little. This decrease in the T_g of the PDMS phase upon immersing the membranes in an aqueous benzene solution can be attributed to the absorption of benzene into the PDMS phase containing the CA. Consequently, since the CA was more preferentially distributed in the PDMS phase than in the PMMA phase, the benzene was preferentially absorbed into the former phase due to the strong interaction between CA and benzene. It is guessed that this preferential absorption of benzene into the PDMS phase containing CA is an important factor to selectively permeate benzene from water.

Permeation Mechanism of Benzene through Calixarene-Containing Membranes. Some researchers have reported the facilitated transport of gas,[25] ion,[26,27] and various solutes through polymer membranes with a carrier.

In this study, to investigate the role of CA as a carrier in the CA/PMMA-*g*-PDMS membrane, the efficiency of the carrier transport for benzene was defined as follows,

$$\text{carrier transport ratio} = \frac{P_{\text{carrier}}}{P_0} \tag{2}$$

where P_{carrier} and P_0 are the permeation rates through the CA/PMMA-*g*-PDMS membranes with and without the carrier, respectively. A carrier transport ratio over 1 means that the transport of benzene by CA as a carrier was more predominant than that in the PMMA-*g*-PDMS matrix. Figure 7 shows the relationship between the carrier transport ratio calculated using eq 2 and the separation factor for an aqueous solution of 0.05 wt % benzene through a CA/PMMA-*g*-PDMS membrane. The separation factor, $\alpha_{\text{benzene/H}_2\text{O}}$, is defined as $\alpha_{\text{benzene/H}_2\text{O}} = (P_{\text{benzene}}/P_{\text{H}_2\text{O}})/(F_{\text{benzene}}/F_{\text{H}_2\text{O}})$ where P_i and F_i are the weight compositions of component *i* in the permeate and in the feed solution, respectively. A separation factor over 1 represents a membrane that is benzene permselective. The region of the oblique line in Figure 7 demonstrates that the benzene from an aqueous benzene solution was preferentially separated by CA as a carrier. As can be seen in Figure 7, the separation factor for benzene permselectivity increased with an increasing carrier transport ratio, and the benzene permselectivity of CA was more predominant than that through the matrix of the PMMA-*g*-PDMS membrane. These findings suggest that the high benzene permselectivity of the CA/PMMA-*g*-PDMS membranes was due to the fact that the transport of benzene was facilitated in the membranes by a specific interaction between the CA and the benzene.

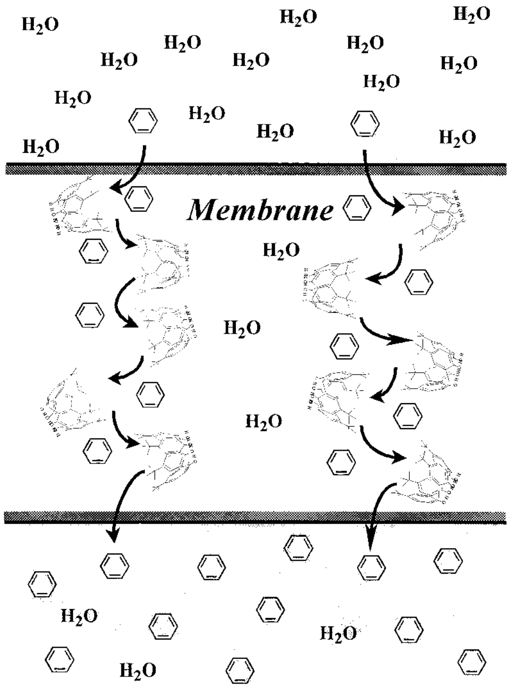

Figure 8. Tentative illustration of the permselective permeation mechanism for benzene in an aqueous solution of dilute benzene through CA/PMMA-*g*-PDMS membranes on the basis of the solution-diffusion model.

In the solution-diffusion model,[28,29] it is well-known that the permeability and permselectivity of the pervaporation membranes are mainly governed by (i) the solubility of the penetrants through the membrane (solution process) and (ii) the diffusivity of the penetrants through the membrane (diffusion process). Based on the solution-diffusion theory, a permselective mechanism for the partitioning of an aqueous solution of dilute benzene through CA/PMMA-*g*-PDMS membranes can be explained by the tentative model shown in Figure 8. As described in the previous section, the CA/PMMA-*g*-PDMS membranes have a stronger affinity for benzene than for water because of the recognition function of CA. In the solution process, therefore, the solubility of benzene in the membranes is enhanced by the addition of CA. On the other hand, the carrier transport mechanism implies that CA as a carrier facilitated the transport of benzene in the CA/PMMA-*g*-PDMS membrane. Thus, in the diffusion process, the benzene absorbed into the CA/PMMA-*g*-PDMS membrane is preferentially transported over water by CA as a carrier due to the specific interaction between the CA and the benzene. The continuous PDMS phase containing the CA in the CA/PMMA-*g*-PDMS membrane might act also as a path to transport the benzene by CA. Thus, the strong enhancement of the benzene permselectivity of the CA/PMMA-*g*-PDMS membranes can be attributed to both CA functioning as a carrier to selectively transport benzene and the continuity of the PDMS phase in the microphase separation.

Conclusions

Calixarene (CA), which can form a complex with benzene, was introduced into a PMMA-*g*-PDMS membrane to improve the benzene permselectivity for the removal of benzene from an aqueous solution of dilute benzene. The benzene permselectivity of CA/PMMA-*g*-PDMS membranes for an aqueous solution of 0.05 wt % benzene was then investigated from the viewpoint of the molecular recognition function of CA and the microphase-separated structure of the membrane. When an aqueous solution of 0.05 wt % benzene was permeated through the CA/PMMA-*g*-PDMS membranes, their permeability and benzene permselectivity were enhanced upon increasing the CA content. The introduction of CA into the PMMA-*g*-PDMS membranes increased the solubility of benzene into the membranes because of the specific interaction between the CA and the benzene. In addition, the TEM observations demonstrated that the CA/PMMA-*g*-PDMS membranes had a microphase separation consisting of a discontinuous PMMA phase plus a continuous PDMS phase, including CA. Therefore, the improvement of both the membrane permeability and the permselectivity by introducing CA was dependent on (i) preferential absorption of benzene into the CA/PMMA-*g*-PDMS membranes and (ii) the high diffusivity of benzene in the continuous PDMS phase with CA. We conclude that introducing molecular recognition devices such as CA into microphase-separated membranes is very effective for improving both the permeability and the permselectivity of pervaporation membranes for removing VOCs from water.

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