

Pervaporation of Benzene/Cyclohexane and Benzene/*n*-Hexane Mixtures Through PVA Membranes

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Received 19 June 1996; accepted 25 September 1996

ABSTRACT: Poly(vinyl alcohol) (PVA) membranes (both homogeneous and asymmetric) were studied for the pervaporation separation of benzene/*n*-hexane and benzene/cyclohexane mixtures. The asymmetric PVA membrane with skin and porous layers was prepared through the phase inversion technique. Both asymmetric and homogeneous membranes were benzene-selective for all the feed compositions. The benzene separation factor of homogeneous PVA membrane was smaller than three, and the total permeation flux was several g/m²/h. The benzene selectivity of the asymmetric PVA membrane was much higher than that of the homogeneous membrane; weight fraction of benzene in the permeate side was larger than 90% for all the feed compositions. On the other hand, the total flux was almost unchanged compared with that of the homogeneous membrane. These results indicate that the density of the skin layer of the asymmetric membrane should be much higher than that of the homogeneous membrane. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1061–1065, 1997

INTRODUCTION

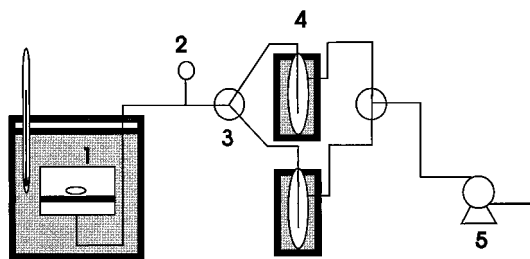
Separation of organic–organic mixtures is one of the most important processes in chemical industry. Distillation is commonly used for the separation at the present stage. However, the distillation process is energy-consuming, and the selectivity would be limited by the vapor–liquid equilibrium. If the process can be replaced by the membrane separation, these problems might be conquered. Membrane separation of organic–organic mixtures have been studied in laboratory scale since the 1960s.^{1–17} Hydrophobic polymers such as polypropylene,^{4,6,7} and polyethylene^{2,4,5,7,13} were used mainly as membrane materials. These hydrophobic materials did not show high selectivity for organic mixtures because they have very small differences in the interaction with one component from the other component in the mixture: either solubility or diffusivity. Recently, higher selective membranes prepared from materials with large

difference in the solubility for one component have been reported by several authors.^{11,13–17}

Separation of aromatic hydrocarbon from aliphatic is a most important target in the membrane separation process of organic–organic mixtures. Specifically, the mixture of benzene and cyclohexane is difficult to separate because they have close boiling points and molecular sizes. The diffusion coefficients might not be so different between benzene and cyclohexane because of similar molecular size and shape. Therefore, the solubility difference should be a key to obtain higher selectivity. Some efforts have been made to search membrane materials based on solubility parameter.¹⁴ Since benzene molecule has π -electron clouds, it is supposed that the interaction to polar molecule of benzene should be larger than that of cyclohexane, which results in larger solubility of benzene in polar or hydrophilic polymeric materials. In fact, the solubility of benzene in water is one order of magnitude larger than that of cyclohexane.¹⁸ Therefore, it should be possible to improve benzene selectivity by using hydrophilic membrane. Another advantage of using hydro-

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1. Permeation Cell 2. Pressure Gauge 3. Three-way Valve
4. Cold Trap 5. Vacuum Pump

Figure 1 Schematic diagram for the pervaporation experimental apparatus.

philic materials might be the stronger resistance to organic solvent. In this study, poly(vinyl alcohol) (PVA), a typical hydrophilic material, was tested for the separation of benzene/cyclohexane and benzene/*n*-hexane mixtures. Two types of PVA membranes, homogeneous and asymmetric, were studied.

EXPERIMENTAL

Membrane Preparation

PVA was kindly supplied by Kuraray Co. (#117H). The degree of polymerization was 1700, and that of saponification was more than 99%. Dimethyl sulfoxide (DMSO) was used as a solvent. Solution of 10% PVA in DMSO was cast onto a glass plate by using a casting knife with a thickness of 200 μm . Then the cast film was immersed in 1-hexanol bath. The membrane solidified after several minutes in the bath. The membrane was removed from the glass plate, washed with *n*-hexane, and dried in a desiccator. The obtained membrane was homogeneous and transparent, with a thickness of 30–40 μm . Membranes with asymmetric cross-sectional structure were obtained when the solvent was partially evaporated in an oven for 5 min at 80°C before the immersion process. The membrane solidified and became opaque after 1–2 min during the immersion process; phase inversion takes place in this process. Then the membrane was washed in *n*-hexane and dried in a desiccator. It was confirmed by an elemental analysis that no DMSO remained in the membrane after drying.

Chromatographic Method

The solubility in the PVA membrane is a key point for separation. However, the sorption amount of

benzene or hexane in PVA was too small to measure. Instead, a chromatographic method was used in this study to evaluate the interaction between PVA and the permeants (benzene, *n*-hexane, and cyclohexane). Particles of PVA meshed with 20–30 μm diameter were packed in a glass column with 2 m length and 3 mm inner diameter. Small amount (several μL) of sorbent was injected into the column with helium carrier, and the outlet response was monitored by a thermal conductivity detector. The column temperature was kept 35°C.

Pervaporation

The schematic diagram for the pervaporation experimental apparatus is shown in Figure 1. The membrane was mounted in a stainless steel cell, of which the temperature was kept constant at 50°C. The downstream pressure was 0.1 Torr. The feed liquid was stirred to avoid the concentration polarization. The permeate was collected by a cold trap cooled by liquid nitrogen. The permeation flux was calculated from the weight change, and the permeate composition was analyzed by gas chromatography.

RESULTS AND DISCUSSION

Chromatographic Measurements

Table I shows the results of the chromatographic measurement for benzene, *n*-hexane, and cyclohexane. Benzene showed the longest retention time, which reflects the largest sorption constant of benzene in PVA. Therefore, it was confirmed that the interaction of benzene with PVA is stronger than those of the other components.

Cross-sectional Structure of PVA Membranes

Figure 2 shows a scanning electron microscopic image of the cross-section of the PVA membrane (homogeneous membrane, hereafter) prepared without solvent evaporation. The cross-section

Table I Retention Time for PVA Column

Component	Retention Time (min)
Benzene	1.35
<i>n</i> -Hexane	0.85
Cyclohexane	0.86

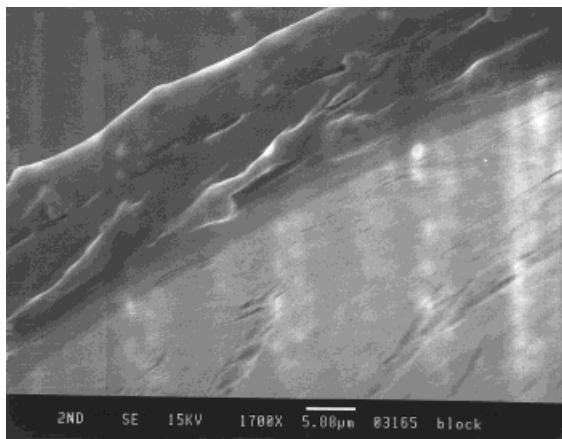


Figure 2 Scanning electron microscopic image for the cross-section of the homogeneous PVA membrane.

was uniform, and no pore was observed. Figure 3 shows the cross-sectional image of the PVA membrane with partial solvent evaporation. The membrane has an asymmetric structure with nonporous skin layer (3–4 μm) and porous support layer (10–15 μm) (asymmetric membrane, hereafter).

Pervaporation Performances of the Homogeneous PVA Membrane

Figure 4 shows the separation diagram for the benzene/*n*-hexane and benzene/cyclohexane mixtures through homogeneous PVA membrane. The PVA membrane was benzene-selective for all the feed composition range presumably because of the larger affinity of benzene to PVA. The separation factors for these systems were not very large

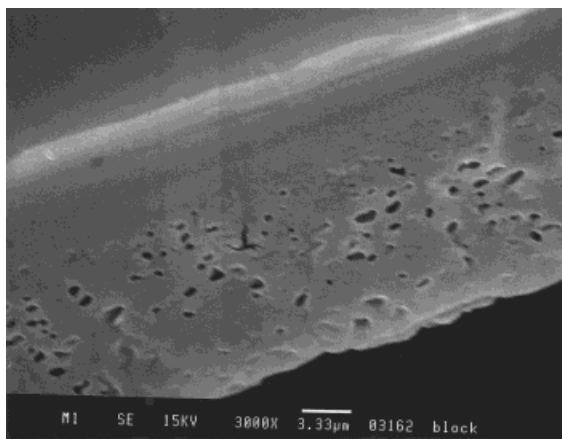


Figure 3 Scanning electron microscopic image for the cross-section of the asymmetric PVA membrane.

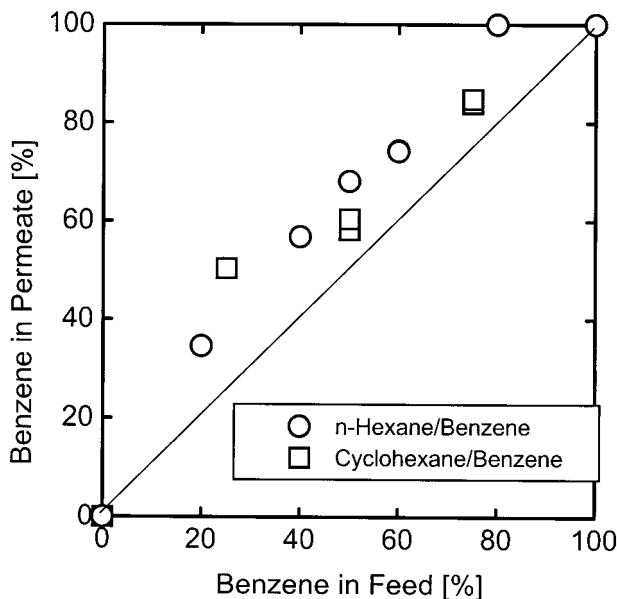


Figure 4 Separation diagram of the homogenous PVA membrane.

(about 1.5 or 3). Figure 5 shows the permeation flux through the homogeneous PVA membranes. The total fluxes were in the order of several $\text{g}/\text{m}^2/\text{h}$ and almost unaffected by the feed composition. These performances of the homogeneous PVA

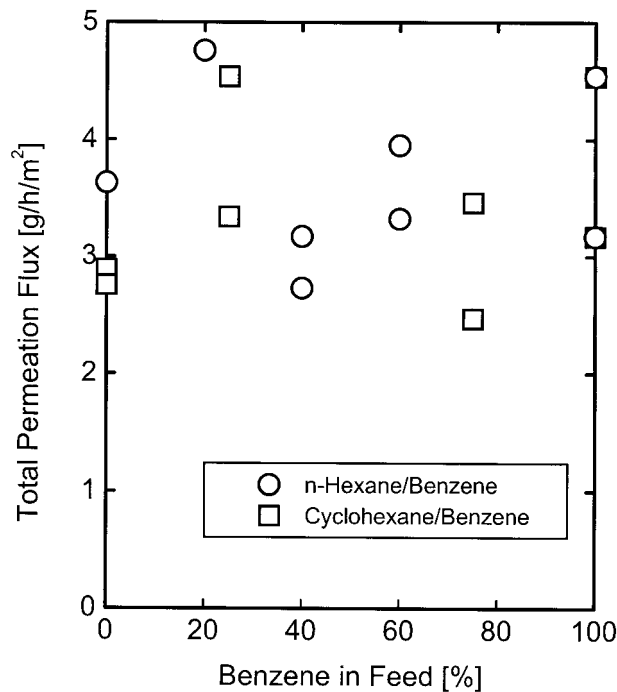


Figure 5 Total permeation flux as a function of feed through the homogenous PVA membrane.

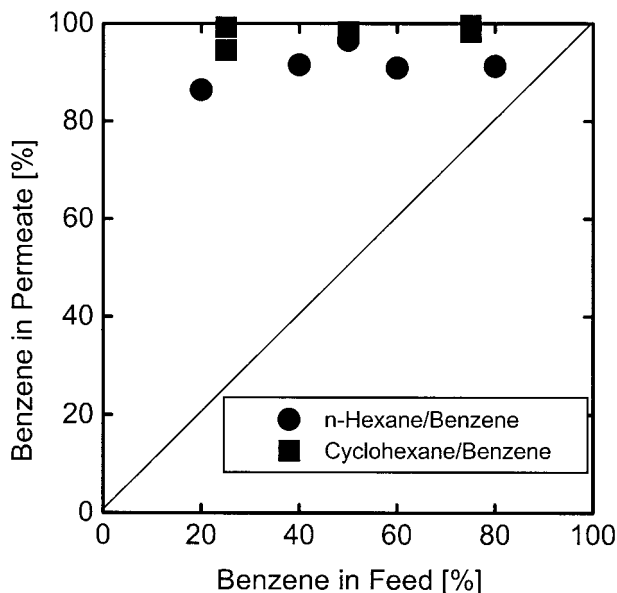


Figure 6 Separation diagram of the asymmetric PVA membrane.

membrane were practically insufficient both in selectivity and flux. A way to increase the permeation flux is by reducing the membrane thickness. When the thickness was decreased, the mechanical strength of the membrane would be also decreased, and sometimes the selectivity should fall down because of more pin-holes in the membrane. An asymmetric membrane might be a way to increase the permeation flux without sacrificing the selectivity. As shown in the cross-sectional structure of PVA membranes Section, an asymmetric structure of PVA membrane can be obtained by a partial solvent evaporation before the solvent exchange process. In the next section, the pervaporation performance of the asymmetric PVA membrane would be reported.

Pervaporation Performance of Asymmetric PVA Membranes

Figure 6 shows the pervaporation separation phase diagram for benzene/cyclohexane and benzene/*n*-hexane for asymmetric PVA membranes. The asymmetric PVA membrane, as well as homogeneous PVA membrane, was benzene-selective for all the feed compositions. However, the benzene selectivity of the asymmetric membranes was much larger than that of homogeneous membranes; benzene is enriched to more than 90% in the permeate side for both mixtures for all feed compositions. The selectivity for benzene in ben-

zene/cyclohexane mixture was larger than that of benzene/*n*-hexane mixture. The permeation flux increased with an increasing benzene concentration in feed as shown in Figure 7. The flux through the asymmetric PVA membrane was smaller than that through the homogeneous PVA membranes.

The larger selectivity for the asymmetric PVA membrane can be explained in terms of the density difference in the skin layer and the homogeneous membrane; the polymer packing density of the skin layer should be larger than that of the homogeneous PVA membrane. According to the sorption-diffusion theory,¹⁸ the selectivity of pervaporation is determined by the two types of selectivity, namely sorption selectivity and diffusion selectivity. The sorption selectivity reflects the difference in the affinity of the permeants to the membrane. When the density of the membrane polymer increases, the distance between the permeant molecule and the polymer chain decreases; the absorbed molecules in the membrane should be affected more strongly by the potential field of the polymer chain. Thus, the sorption selectivity becomes more sensitive to the affinity of the permeant molecules to the membrane polymer chain itself. Since benzene has larger affinity to PVA, the benzene selectivity based on sorption increases when the polymer density increases. On

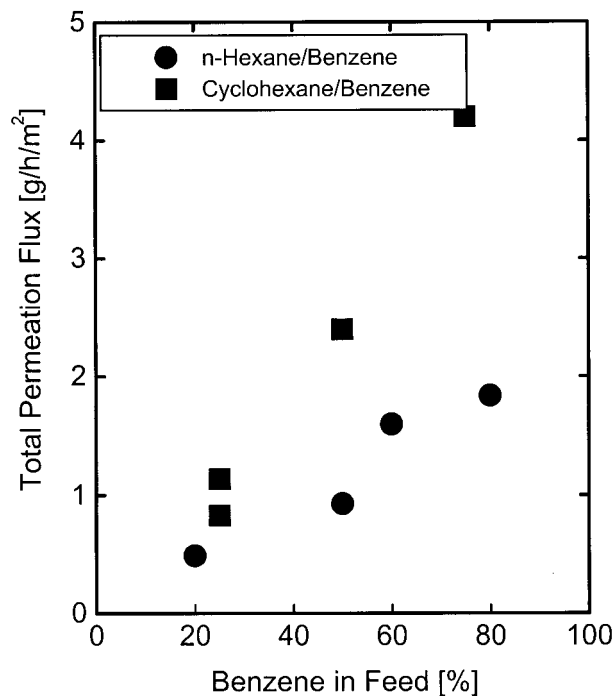


Figure 7 Total permeation flux as a function of feed composition through the asymmetric PVA membrane.

the other hand, the diffusion selectivity should be determined mainly by the shape and size of the permeant molecules. The differences in the molecular shape and size are small for benzene/cyclohexane system; the diffusion selectivity should not be changed when the density of the membrane polymer changed. Since *n*-hexane is a linear molecule, the diffusion coefficient of *n*-hexane would be less affected by the density increase than that of benzene; benzene selectivity based on diffusion should be decreased when the density increased. However, since the pervaporation selectivity should be determined mainly by the sorption selectivity, the overall benzene selectivity for benzene/*n*-hexane, as well as that for benzene/cyclohexane, should increase when the membrane polymer density increases. The benzene selectivity for *n*-hexane/benzene through a denser membrane was smaller than that for cyclohexane/benzene because of the smaller selectivity based on diffusion. The permeation resistance of benzene per unit membrane thickness for the skin layer of the asymmetric membrane is much smaller than that of the homogeneous membrane; this result also indicates that the density of the skin layer in the asymmetric membrane is much higher than that of homogeneous membrane.

The increase in the density of the skin layer should be caused by the solvent evaporation process. In the partial solvent evaporation process, the concentration of the polymer film near the surface was greatly increased; thus, the polymer chain should be reconfigured to become more densely packed. For the process without solvent evaporation, on the other hand, the polymer concentration is not high enough so that the polymer chain should loosely pack.

CONCLUSION

A PVA membrane was used for the pervaporation of benzene/*n*-hexane and benzene/cyclohexane mixtures. The membrane was benzene selective for all the feed compositions. The reason is the interaction of benzene (sorption) with PVA is stronger than that of other components because of stronger interaction between hydroxyl group

in PVA and π -electrons in benzene. The benzene selectivity of homogenous PVA membrane was not larger than three. The benzene selectivity of the asymmetric PVA membrane was more than 10, while the permeation flux was almost unchanged. These results could be interpreted in terms of the polymer packing density of the skin layer in the asymmetric membrane and the homogenous membrane.

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