# Pervaporation of Chlorinated Hydrocarbon–Acetone Mixtures Through Poly(ethylene-co-Vinyl Acetate) Membranes

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## SYNOPSIS

Crosslinked and uncrosslinked ethylene–vinyl acetate copolymer membranes were prepared. The permeation characteristics in the pervaporation process were examined using carbon tetrachloride–acetone mixtures. Modified membranes exhibit carbon tetrachloride permselectivity, but unmodified membranes did not display the permselectivity of crosslinked polymer. Furthermore, membranes modified with dicumyl peroxide (DCP) showed a higher flux and selectivity than those of benzoyl peroxide (BP) modified ones. The effects of feed concentration, molecular size, and polarity of the permeating species on pervaporation were analyzed. The influence of crosslinking density of the membranes on pervaporation was also analyzed. The maximum separation and flux were found to be associated with an optimum amount of crosslinking agent in the membrane. A mixture of chloroform and acetone having a composition near the azeotropic region was also separated by the pervaporation technique. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Pervaporation is an energy-efficient membrane separation process.[1,2] Membrane separation processes are gaining importance because of their low cost, easy maintenance, and stability in hostile environments. In some cases pervaporation can replace energy-intensive processes like distillation. Pervaporation can be used to separate any liquid mixture in all concentration ranges.[3–7] This method is applicable for:

1. Separation of azeotropic mixtures which are difficult to separate by distillation,[8]
2. extraction of aromatic compounds from dilute solutions,[9]
3. separation of close boiling liquids,[10,11]
4. recovery of dissolved substances.[12]

Pervaporation is defined as the selective evaporation of a component from a liquid mixture through a membrane. In pervaporation, the liquid mixture to be treated is in direct contact with a membrane on one side and the permeated product is removed as vapor from the other side by applying a low pressure. Pervaporation differs from other membrane separation processes in that the material transported undergoes a phase change. This separation is basically a solution–diffusion process. The overall transport can be divided into:

1. sorption into the membrane at the upstream side,
2. diffusion through the membrane,
3. desorption and vaporization at the downstream side.

The sorption and diffusion are considered as the rate-determining step of the mass transfer.

Many workers reported on the separation of binary liquid mixtures by this technique. Huang and Lin[13] studied the separation of binary liquid mix-

## Table I   Details of Materials Used

| Materials | Properties | | Source |
|---|---|---|---|
| Poly(ethylene-co-vinyl acetate) pilene 1802 | Melt flow index (g/10 min) | 2.000 | PIL, Madras |
|  | Density (g/cm$^3$) | 0.937 |  |
|  | Vicat softening point (°C) | 9.000 |  |
|  | Vinyl acetate (wt %) | 18.000 |  |
|  | Intrinsic viscosity (dL/g) Solvent: chloroform Temperature: 28°C | 0.170 |  |
|  | $T_g$ | −10°C |  |

tures of aqueous alcohol solution. They further established some of the characteristics of permeation. Carter and Swamy[14] reported the separation of benzene–alcohol, ethyl acetate–carbon tetrachloride by polyethylene and found that selectivity is related to swelling. Sweeny and Rose[15] followed the influence of size and chemical nature of permeating species on pervaporation. They established the relation of selective permeation to the polarities of the liquid and the polymer. Dinh et al.[16] examined sorption and transport of ethanol–water through EVA membranes. For a 37% vinyl acetate membrane, ethanol permeability was found to increase with ethanol activity in the membrane, whereas water permeability is decreased with water activity. Lee and coworkers[17] followed the transport of steroids through membranes of poly(ethylene-vinyl acetate) and poly(ether urethane).

In this article we report on the pervaporation of chlorinated hydrocarbon–acetone mixtures through poly(ethylene-co-vinyl acetate) membranes. This membrane was selected because of the close solubility parameter of chlorinated hydrocarbon and poly(ethylene-co-vinyl acetate), easy preparation of the membranes, and good mechanical properties. To determine the solubility parameter of the copolymer, swelling coefficients in a series of solvents were determined. The swelling coefficient of EVA was found to be maximum in $CCl_4$ and therefore the solubility parameter of copolymer was taken as equal to that of $CCl_4$ [8.6 $(cal/cm^3)^{1/2}$]. This sort of methodology has been adopted by Aminabhavi and coworkers.[18]

## EXPERIMENTAL

### Materials

Poly(ethylene-co-vinyl acetate), EVA (Pilene, 1802), used was supplied by Polyolefin Industries Limited, Madras, India. The basic characteristics of copolymer are given in Table I. The crosslinking agents selected were dicumyl peroxide (DCP) (40% activated) and benzoyl peroxide (BP). The solvents, carbon tetrachloride, chloroform, dichloromethane, and acetone used in the present study were distilled twice before use.

### Preparation of Membranes

Unmodified poly(ethylene-co-vinyl acetate) was sheeted out on a two-roll mixing mill having a friction ratio 1 : 1.4. The sheeted out stock (about 3 g) was placed between two thin aluminium sheets and pressed on a hydraulic press at 170°C and under a pressure of 25 tonnes to obtain unmodified membranes. Modified membranes were prepared by using DCP and BP. The compositions of mixes are given in Table II. The mixing was done on a two-roll mixing mill as before. The vulcanization behavior of the samples was studied by a Goettfert rheometer. The temperature of the rheometer was 170°C for DCP mixes and 120°C for the BP mix. The rheographs of the DCP mixes and BP mix are given in Figures 1(a) and 1(b), respectively. The films were pressed for their optimum cure times as obtained from the rheographs. Dicumyl peroxide modified membranes

## Table II   Composition of the Mixes

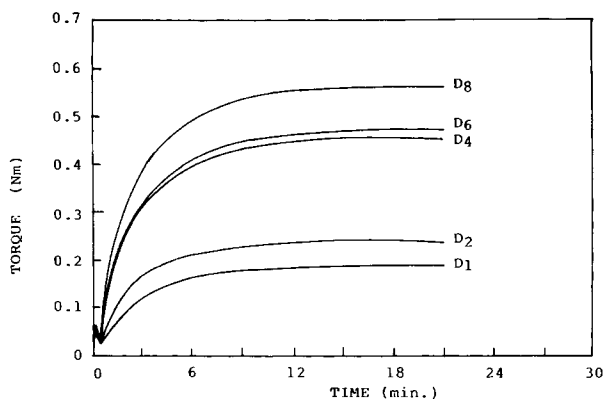| Amount of Polymer (g) | No. of Moles of Peroxide in the Membrane | Representation of Membranes |
|---|---|---|
| 100 | 0.0015, DCP | $D_1$ |
| 100 | 0.0030, DCP | $D_2$ |
| 100 | 0.0060, DCP | $D_4$ |
| 100 | 0.0090, DCP | $D_6$ |
| 100 | 0.0120, DCP | $D_8$ |
| 100 | 0.0165, BP | B |

**Figure 1a**   Rheograph of the DCP crosslinked mixes.

were prepared by curing the samples on a hydraulic press at 170°C and under a pressure of 25 tonnes (Membranes modified with DCP are represented as $D$.) Membranes modified with benzoyl peroxide were prepared by curing samples at 120°C and under a pressure of 25 tonnes. Membranes modified with BP contain 0.0165 mol of BP per 100 g of the polymer (represented as $B$). Thickness of the membranes used was ~ 120 μm.

## Pervaporation

A schematic representation of the pervaporation apparatus is presented in Figure 2. The permeation cell was assembled from two half cells of column couplers made of glass, fastened together by bolted clamps. The capacity of each half cell was about 100 mL and the effective surface area of the membrane is 19.4 cm². The membrane was supported on a finely porous stainless-steel plate with holes (3 mm) drilled in it. Vacuum at the downstream side was maintained by using a Hindhivac (Ed-6). A pressure of 3.5-4 mm was applied. Downstream pressure was measured with a vacuum gauge (Mcleod, Tilting). The membrane was soaked in the mixture for 24 h and then kept in the pervaporation cell for about 2 h in each run to reach equilibrium conditions before collecting the permeate. The permeated vapors were completely condensed in a trap placed in a Dewar Flask cooled to −77°C using dry ice-acetone mixture. Complete condensation was effected by placing two traps in series. The experiments were carried out at room temperature. The permeate and feed compositions were analyzed by a gas liquid chromatograph.

Performance of a membrane in pervaporation is characterized by permeation rate or flux ($J$) and selectivity ($\alpha_{i,j}$).

The selectivity is given by

$$\alpha_{ij} = (Y_i/Y_j)/(X_i/X_j) \tag{1}$$

where $Y_i$ and $Y_j$ represent the weight fraction of chlorinated hydrocarbon and acetone in the permeate $X_i$ and $X_j$ those of chlorinated hydrocarbon and acetone in the feed, respectively.

The permeation rate or flux was obtained taking the ratio of the weight of permeate collected to effective area of the membrane and time of collection in g/m² h.

## RESULTS AND DISCUSSION

### Swelling Characteristics

Initially a piece of the dry membrane was weighed and swollen in the solution mixture of known composition for 24 h at 30°C. The swollen membrane was taken out and wiped with tissue paper to remove adherent solvent and then weighed. Difference between weights gave the amount of solvent absorbed by the polymer. The swelling ratio was calculated using the equation

$$S = \frac{W_s - W_d}{W_d} \tag{2}$$

where $W_d$ denotes weight of dry membrane, $W_s$ denotes weight of solvent swollen membrane.

The degree of swelling of unmodified poly-(ethylene-co-vinyl acetate) membrane, DCP modified membrane ($D_4$), and BP modified membranes in the binary mixtures of carbon tetrachloride acetone used in this study are represented in Figure 3. DCP modified membranes exhibited a higher swelling and unmodified membranes exhibited a lower
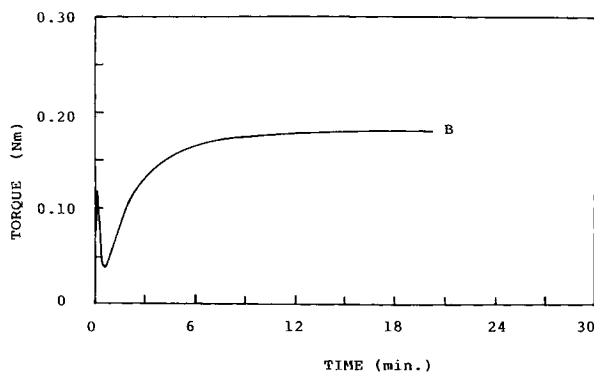


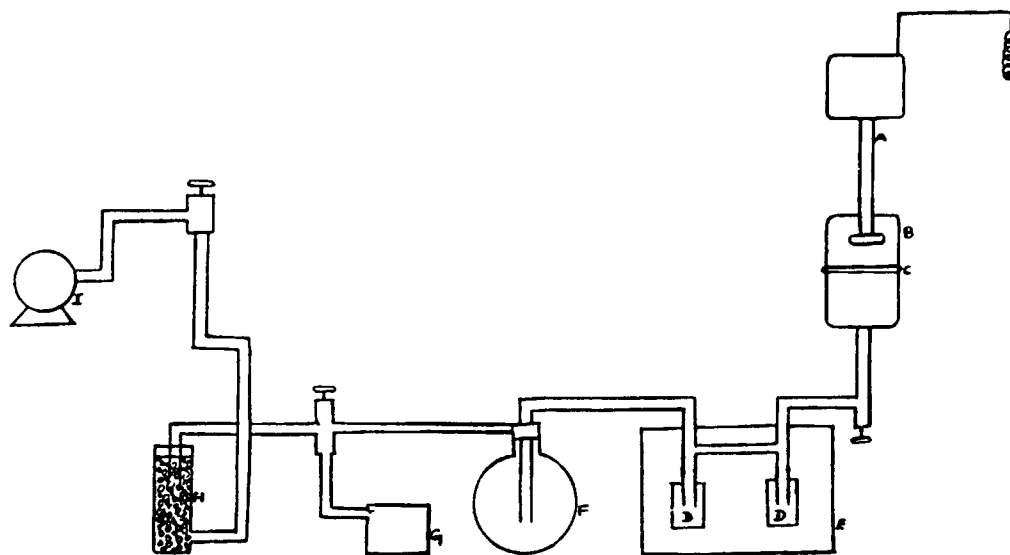**Figure 1b**   Rheograph of the BP crosslinked mix.

**Figure 2**    Schematic diagram of pervaporation apparatus: (A) stirrer, (B) permeation cell, (C) membrane, (D) collection traps, (E) Dewar flask, (F) R. B. flask, (G) pressure gauge, (H) moisture trap, (I) vacuum pump.

swelling. This is due to the crystalline nature of un-modified membranes. The crystalline nature was evident from the X-ray diffraction patterns given in Figure 4. In all cases, as the concentration of carbon tetrachloride in a mixture increased, swelling ratio also increased.

## Effect of Feed Composition

The effect of feed composition on the pervaporation of carbon tetrachloride–acetone mixtures through
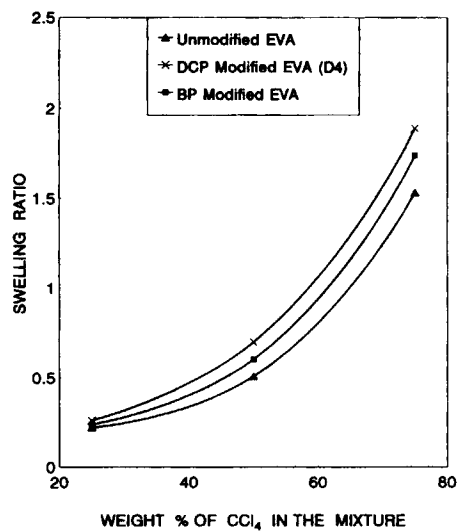
unmodified and modified ($D_4$ and $B$ membranes were used) poly(ethylene-*co*-vinyl acetate) membranes are given in Figure 5. Since the solubility parameters of



**Figure 3**    Dependence of swelling ratio on the amount of carbon tetrachloride in the mixtures of carbon tetra-chloride–acetone for EVA membranes.
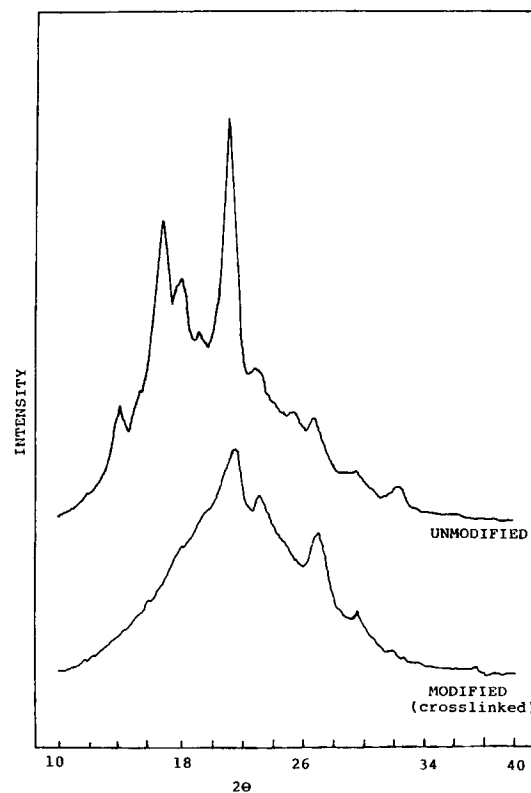


**Figure 4**    X-ray diffraction patterns of unmodified and modified (crosslinked) membranes.
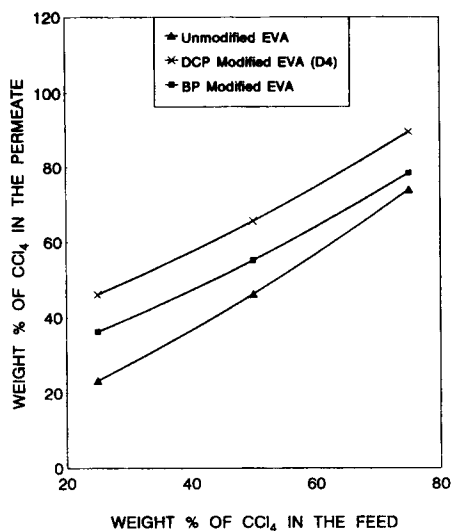
**Figure 5** Effect of feed composition on the pervaporation of carbon tetrachloride–acetone mixtures through unmodified, DCP modified, and BP modified membranes.

carbon tetrachloride and poly(ethylene-co-vinyl acetate) are close, we expected that carbon tetrachloride would preferentially permeate and hence would be more selective toward carbon tetrachloride. However, experiments showed that unmodified membranes do not exhibit any carbon tetrachloride selectivity and the separation factor is close to unity. We believe this is due to long range order persisting in unmodified membranes; even though sorption of carbon tetrachloride in the membrane is high its diffusion is lower than that of acetone. Thus both molecules can permeate with equal probability.

Modified membranes exhibit a selectivity greater than unity for all concentration ranges and were more selective toward $CCl_4$. As a result of crosslinking, there is a reduction in crystallinity and this was evident from X-ray diffraction patterns given in Figure 4. Thus $CCl_4$ can permeate more easily through the modified membranes. DCP modified membranes showed a greater selectivity factor than BP modified membranes.

Permeation rate (flux) for various carbon tetrachloride–acetone mixtures through unmodified, DCP, and BP modified membranes are presented in Figure 6. Unmodified poly(ethylene-co-vinyl acetate) membranes show almost a constant rate up to 50 wt % of carbon tetrachloride followed by a marginal decrease at higher concentration. Membranes modified with DCP ($D_4$) exhibit increasing flux with increasing concentration of carbon tetrachloride in the feed mixture. With increase in carbon tetrachloride concentration, free volume of the membrane in-

creases due to plasticization, and hence rate increases. The high flux values are quite reproducible. Even though BP modified membranes exhibit higher selectivity than unmodified membranes their fluxes are lower than those of the unmodified ones. The low flux rate is due to the large extent of crosslinking produced by BP. Therefore polymer chains become less flexible. This can be understood from swelling ratio values. The swelling ratio values indicate that at the same loading of BP or DCP in EVA, the extent of crosslinking is higher in the case of BP (Fig. 3).

## Effect of Crosslinks on Pervaporation

The influence of the number of moles of DCP used in the membrane on the pervaporation of a 50 wt % of carbon tetrachloride–acetone mixture is presented in Figure 7. With increasing number of moles of DCP in the membrane, concentration of carbon tetrachloride in the permeate and the permeation rate increase, reach a maximum, and then decrease. Therefore, for maximum flux and selectivity an optimum amount of crosslinking agent should be used.

The increased permeation rate and selectivity upon the addition of moderate amounts of DCP are due to the increase in permeability as a result of the disorder induced in the membrane structure. The reduction in crystallinity was analyzed by X-ray diffraction studies (Fig. 4). Increased flux and selectivity are also due to the elasticity of the membranes. With a large amount of crosslinking agent, extent of crosslinks becomes high and hence polymer chains
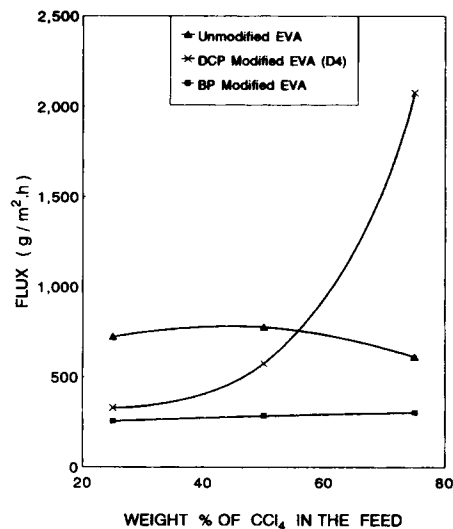


**Figure 6** Effect of feed composition on permeation rate for unmodified, DCP modified, and BP modified membranes.
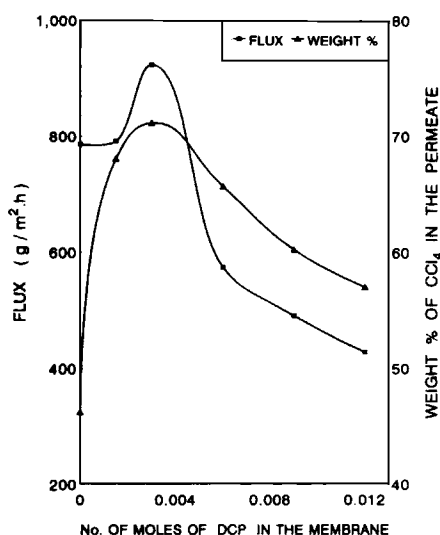
**Figure 7** Effect of the number of moles of DCP in the membrane on the pervaporation of 50 wt % of carbon tetrachloride–acetone mixture.

become less flexible; this prevents migration of both molecules. The reproducibility of these results is also very good. Similar results were reported by Sun and coworkers[4] in the pervaporation of alcohol/water mixtures through block polymers of styrene/butadiene/styrene and styrene/ethylene–butylene/styrene. As the amount of divinyl benzene (DVB) in the membranes was increased, both separation and flux increased, attained a maximum, and then decreased.

## Effect of Molecular Size and Polarity of the Permeating Species

The influence of molecular size and polarity of permeating species on pervaporation is given in Figure 8. The pervaporation of 50 wt % of carbon tetrachloride $(CCl_4)$–acetone, chloroform$(CHCl_3)$–acetone, dichloromethane $(CH_2Cl_2)$–acetone mixtures were followed. It was observed that, as the number of chlorine atoms in the chlorinated hydrocarbon increases, selectivity and permeation rate decrease first and then increase. In fact we expected a low selectivity and permeation rate for carbon tetrachloride–acetone mixture, due to the large molecular size of the permeating species. However a reverse trend was noticed, that is, high rate and selectivity were observed. The selectivity and permeation rate for dichloromethane–acetone mixture are higher than for the chloroform–acetone mixture but less than those of the carbon tetrachloride–acetone mixture. EVA membranes are substantially polar due

to pendant acetate groups in the polymer chain. Therefore, there may be dipole interaction with the permeating species. Due to its symmetrical structure, carbon tetrachloride is nonpolar (zero dipole moment) and hence it diffuses more easily through the membrane. Even though chloroform is less polar (1.01 D) than dichloromethane (1.57 D) the observed decrease in permeation rate and selectivity of chloroform as compared to dichloromethane is due to the effect of increased molecular size of the permeating species. Thus in pervaporation of different mixtures with polar and nonpolar species, polarity determines the permeation rate and selectivity. Among the polar permeating molecules, molecular size is the deciding factor. A polar permeating species with large molecular size exhibits lower selectivity and permeation rate than low molecular weight counterparts.

## Separation of Azeotropic Mixture

Chloroform and acetone form a high boiling azeotrope at 78.5 wt % of chloroform. The modified EVA membranes showed a chloroform selectivity from chloroform–acetone mixtures. A composition of chloroform and acetone near the azeotropic region was examined by pervaporation. A high selectivity and a higher flux were observed. The results are given in Table III. Thus the modified membranes are effective for the separation of azeotropic mixtures.
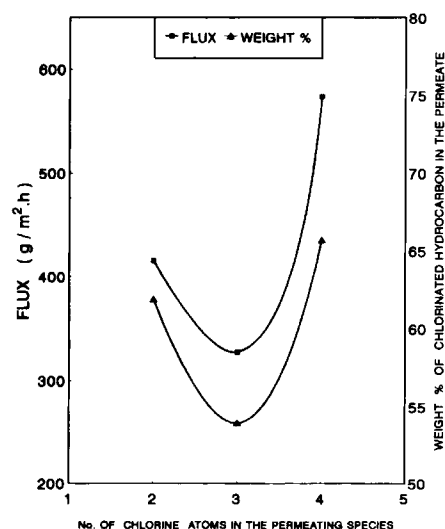


**Figure 8** Effect of polarity and molecular size of the chlorinated hydrocarbons on pervaporation of 50 wt % of chlorinated hydrocarbons–acetone mixtures through DCP modified membranes.

**Table III  Separation of Chloroform–Acetone Mixture**

| Wt % of $CHCl_3$ in the Feed | Wt % of $CHCl_3$ in the Permeate | Selectivity $(\alpha_{ij})$ | Permeation Rate $(g/m^2\ h)$ |
|---|---|---|---|
| 81.2 | 97.6 | 9.42 | 8469.07 |

## CONCLUSION

Poly(ethylene-co-vinyl acetate) membranes exhibit carbon tetrachloride selectivity from carbon tetrachloride–acetone mixtures only after the membranes are modified with either benzoyl peroxide or dicumyl peroxide. For maximum flux and selectivity, there should be an optimum amount of the crosslinking agent. As the amount of carbon tetrachloride in the feed composition increases, both rate and selectivity increase. In different mixtures with polar and nonpolar species, permeation rate and selectivity are influenced by polarity. For mixtures with polar permeating species, the permeation rate and selectivity are influenced by molecular size of the permeating species. Polar species with high molecular weight have low permeation rate and selectivity. Pervaporation of chloroform–acetone mixture having composition near the azeotropic region showed high flux and separation factor.

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