Pervaporation of Organic Solvents by Poly[bis(2,2,2-trifluoroethoxy) phosphazene] Membrane

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Synopsis

The permeation and pervaporation behavior of water and several organic solvents through poly[bis(2,2,2-trifluoroethoxy)phosphazene] (PBFP) membrane have been investigated in the temperature range from 42 to 80°C. The steady-state permeation fluxes of the solvents increased in the following order: methanol > ethanol > benzene > water > cyclohexane. An Arrhenius plot of permeation flux of water suddenly changed in its gradient at about 66–70°C, which corresponds closely to the $T(1)$ transition temperature (75°C) of PBFP studied. Interestingly, in the pervaporation of water-methanol mixtures, methanol permeated more rapidly through the membrane than did water; however, the pervaporation of water-ethanol mixtures showed poor permselectivities. In the case of an athermal mixture of methanol and ethanol, the fluxes of methanol and ethanol indicated convex and concave curves, respectively, to the axis of methanol concentration; thus the separation characteristics of this system were slightly better than those of a simple distillation technique. The pervaporation of benzene-cyclohexane mixtures showed excellent permselectivity enrichment in benzene resulting in a separation factor of 12.

INTRODUCTION

Poly[bis(2,2,2-trifluoroethoxy)phosphazene] (PBFP) is composed of inorganic main chains, —N=P—, and carries hydrophobic organic side groups of —OCH$_2$CF$_3$. This crystallizable polymer shows a particular first-order transition through which the three-dimensional orders of the polymer chains reduce to the two-dimensional arrays of a mesophase structure.[1] The transition is located between its glass transition temperature and true melting point of PBFP. Recently, Kojima and Magill[2,3] have investigated the morphology of its single crystals and the fine structural changes observed in the crystallizable polymer film. They have showed that crystal modification clearly occurs when the polymer is annealed at the temperature above the $T(1)$ transition.

Although there have been several communications on the physical properties of PBFP, such as mechanical,[4] thermal,[5,6] dielectric behavior,[7,8] and nuclear magnetic resonance (NMR) relaxation,[9] investigations on diffusion or permeation of small molecules through the PBFP films have until now not been reported. Thus we have attempted to examine the temperature dependence of permeation of water through a PBFP membrane in the vicinity of the $T(1)$ transition.
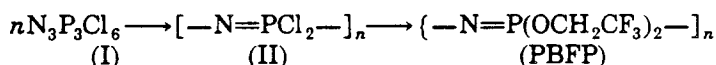
Alternatively, Kimura and Nomura[10] recently reported that silicone rubber, composed of inorganic main chains, —Si—O—, shows particular separation characteristics for water-alcohol mixtures. As the PBFP polymer is also

composed of inorganic main chains like a silicone rubber, we thus investigated the separation behavior of several liquid mixture systems through the PBFP membrane by a pervaporation technique.

EXPERIMENTALS

Sample Preparation

Polydichlorophosphazene was prepared through solution polymerization[11] of hexachlorocyclotriphosphazene (I), kindly supplied by Shin-Nisso Kako Co., and PBFP was then obtained via successive substitution of chlorine atoms in polydichlorophosphazene (II) by trifluoroethoxy groups using a well-known polymer reaction method.[12] These procedures were carried out according to the scheme

$$n N_3 P_3 Cl_6 \longrightarrow [-N{=}PCl_2-]_n \longrightarrow \{-N{=}P(OCH_2CF_3)_2-\}_n$$
$$\text{(I)} \qquad\qquad \text{(II)} \qquad\qquad\qquad \text{(PBFP)}$$

The values of $\overline{M}_n$ and $\overline{M}_w$ of PBFP obtained were measured by a GPC method and estimated as 9.6×10^4 and 15.3×10^4, respectively. These values were determined by comparison with the average molecular weights of standard polystyrenes. A membrane of PBFP was cast from a 10 wt% methyl ethyl ketone (MEK) solution of the polymer, followed by a drying procedure at 35°C for 3 days. The thickness of the membrane used in permeation experiments was 131×10^{-4} cm. The $T(1)$ transition temperature of the as-cast film was measured as 75°C by a Shimadzu DSC-30 at a heating rate of 20°C/min.

Apparatus

The permeation apparatus used has been shown in detail elsewhere.[13] The permeation cell was joined with the carrier gas stream line to a gas chromatograph. The correlation curves of the permeation flux versus the gas chromatographic peak area were obtained by measuring the amount of permeates trapped in unit time.

RESULTS AND DISCUSSION

Diffusivity of Various Solvents

A permeation flux versus time relation of the water-PBFP system is shown in Figure 1, indicating a typically sigmoidal curve. Table 1 shows the permeation data of t_a and $t_{1/2}$, together with those of other solvent-PBFP systems, where t_a is the time when the permeate appears in the secondary side cell of the apparatus and $t_{1/2}$ is the time that the flux change requires to reach the half-value of the steady-state permeation. Although the value of t_a appeared in pure water or ethanol under these experimental conditions, it was not observed in the case of pure methanol or benzene. With water and ethanol, the values of observed $t_{1/2}$, which are considered to be reciprocally proportional to diffusivity, as suggested by Ziegel et al.,[14] are larger than those of
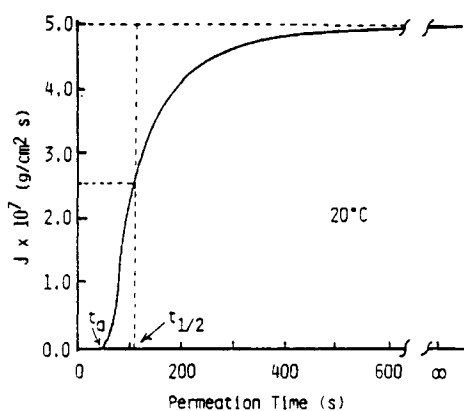
Fig. 1. Typical permeation curve.

TABLE I
t_a and $t_{1/2}$ Values of Permeation Curves of Water, Methanol, Ethanol, and Benezene (at 20°C)

	H_2O	CH_3OH	C_2H_5OH	C_6H_6
t_a (s)	58	$\doteq 0$	6	$\doteq 0$
$t_{1/2}$ (s)	112	60	105	30

TABLE II
Diffusion Data Obtained from Vapor Permeation Experiments[a]

Penetrant	a (g/g)	$D_0 \times 10^8$ (cm^2/s)
H_2O	1290	0.55
CH_3OH	690	2.02
C_2H_5OH	1725	0.45
C_6H_6	155	6.46

[a]D_0, diffusion coefficient at zero penetrant concentration; a, plasticizing coefficient $D = D_0(1 + aC)$; C, penetrant concentration in polymer (g/g).

methanol and benzene. Furthermore, diffusion data from vapor permeation experiments analyzed by Meares's equation[15] are listed in Table II. This result is similar to that obtained from liquid permeation mentioned above; that is, the diffusivity of water is observed to be smaller than that of methanol and benzene, which have a definitely larger molecular volume compared with that of water. This finding is unusual.

Temperature Dependence of Permeation

A temperature dependence of the permeation flux of water through PBFP membrane was measured in the temperature range from 42 to 82°C. An Arrhenius plot of the permeation is shown in Figure 2, indicating a partially linear relationship between the logarithm of flux and the reciprocal absolute temperature below 66°C. The flux increases suddenly at 66°C, and this change
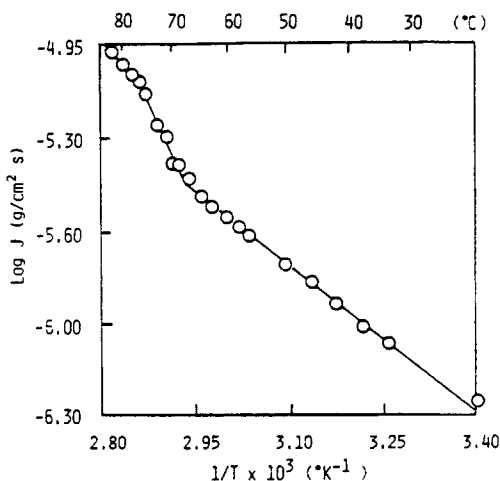
Fig. 2.   Arrhenius plot of permeation flux of water through PBFP membrane.

in flux is related to the $T(1)$ transition of the polymer. This permeability increment is probably based on enhancement of the diffusivity of water due to an increase in the fractional free volume of PBFP associated with the formation of a less loosened structure of the mesomorphic state above the $T(1)$ transition. This enhancement of permeation flux above 66°C is slightly lower than the $T(1)$ transition temperature of the polymer measured by a differential scanning calorimetric (DSC) method. The difference may be based on the plasticizing effect of sorbed water to the PBFP chains.

Pervaporation of Liquid Mixtures

Figure 3 displays changes in permeation fluxes of water-alcohol (methanol or ethanol) mixtures as a function of alcohol concentration. In the case of the water-methanol mixture, the flux of water decreases gradually with decreasing water concentration in the feed. Alternatively, the flux of methanol increases rapidly with increasing methanol concentration; it reflects the concentration dependence of diffusivity in this system. These results imply that the diffusivity of water through the membrane depends slightly on concentration because of its low affinity to PBFP. However, methanol shows a relatively large concentration dependence. In contrast, the flux of water in a water-ethanol mixture shows the maximum value at the ethanol concentration of about 50–60%. This feature probably depends on the amount of water sorbed from the mixture. It is well known in water-alcohol mixtures that the amount of water sorbed from the mixture by polymer shows the maximum value at some concentration of alcohol[16] accompanied by destruction of the hydrogen bonds of water; this maximum value increases with increasing chain lengths of hydrophobic groups of the alcohols. The phenomenon may be explained by the fact that the number of carbon atoms in alcohol increases the heat of mixing.[17] Hence this effect would strongly appear in the water-ethanol mixture compared with the water-methanol mixture.
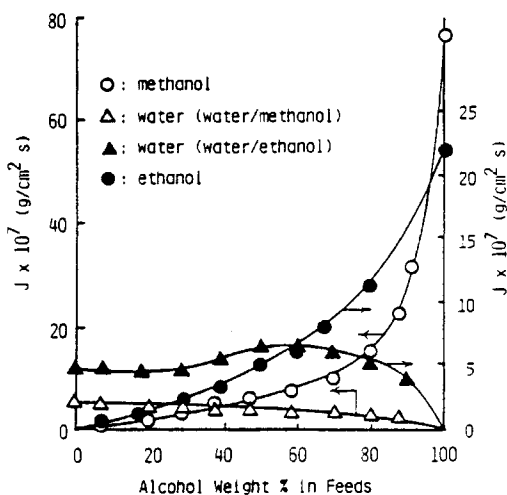
Fig. 3. Permeation flux J versus feed concentration curves. System: water-methanol-PBFP; water-ethanol-PBFP.
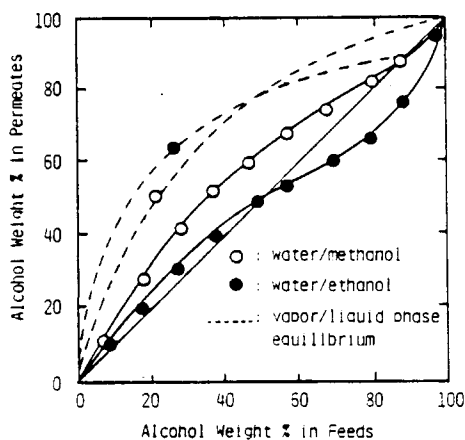

Fig. 4. Separation characteristics of PBFP membrane for water-methanol and water-ethanol mixtures.

Figure 4 shows the separation characteristics of water-methanol and water-ethanol mixtures, indicating that the selective permeation of methanol occurs in the former systems. In general, the permselectivity of water in mixed solvents is expected to occur particularly in a polar polymer membrane, such as a poly(vinyl acetate) film, even though the film has a stronger affinity to methanol than to water.[18] On the other hand, methanol is considered to permeate selectively through a hydrophobic polymer membrane.[19] However, this PBFP membrane shows smaller permselectivity of water than a silicon rubber membrane; thus, in this case, the separation characteristics of the membrane for a water-ethanol mixture were worse than for the water-methanol mixture. In a high water concentration region, the permeation of water is
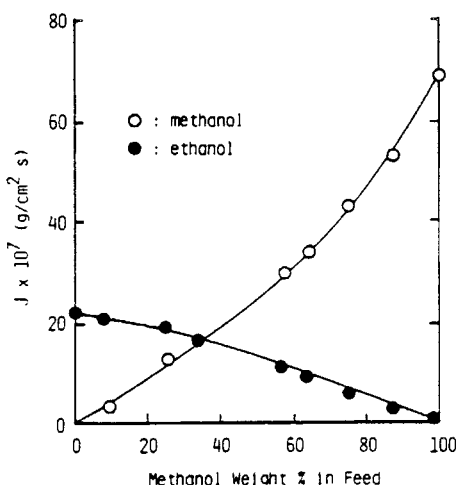
Fig. 5.   Permeation flux J versus feed concentration curves. System: methanol-ethanol-PBFP.

comparatively small and the selective permeation of alcohol occurs to some extent. This phenomenon probably arises from the formation of clusters of water on the hydrophobic chains of the polymer.

In Figure 5, the permeation fluxes of methanol and ethanol for their athermal mixtures are plotted against methanol concentration. The curves for methanol and ethanol show shapes that are convex and concave to the abscissa, respectively. These shapes are typical permeation curves for the athermal mixtures, which were reported in a previous paper.[20] The origin of these shapes can be explained by the fact that the diffusivity of ethanol increases by a large plasticizing effect of methanol on the PBFP chains; in other words, the diffusion of ethanol increases with increasing free volumes formed by methanol sorbed in the membrane.

Figure 6 shows the separation characteristics of the methanol-ethanol mixtures together with their liquid-vapor equilibrium curve. Although the
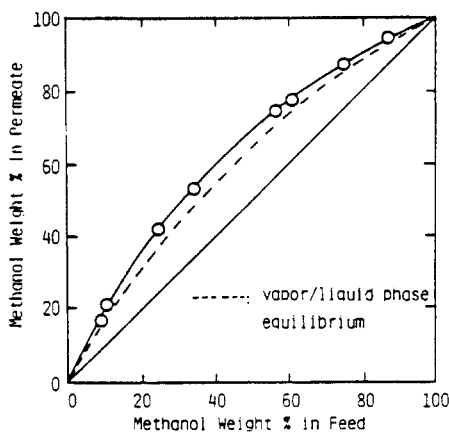

Fig. 6.   Separation characteristics of PBFP membrane for methanol-ethanol athermal mixture.
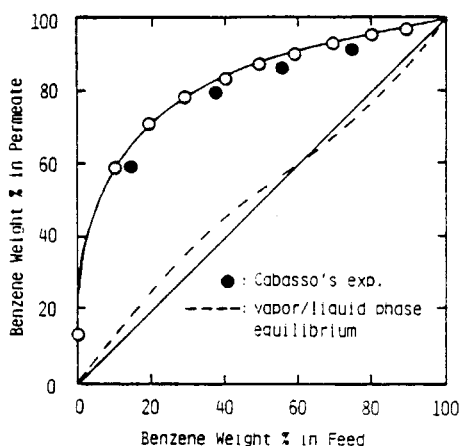
Fig. 7. Separation characteristics of PBFP membrane for benzene-cyclohexane mixture.

separation efficiency of the system is better than that of a distillation procedure, as indicated by the liquid-vapor phase equilibrium line, it is worse than those expected from the permeation data of pure solvents. Since the mixture belongs to an athermal system, the amount of either methanol or ethanol sorbed by the polymer membrane should have a linear relationship to its concentration in the mixture.[21,22] However, as shown in Figure 5, methanol and ethanol permeated with the features of curves that are convex and concave, respectively, to the concentration axis. This permeation behavior has further reduced the separation characteristics. This originates from the enhanced diffusivity of ethanol as the result of coexistence of methanol, which has a larger plasticizing effect than ethanol.[22]

The difference in boiling point between benzene and cyclohexane is only 0.6°C; thus, as illustrated by the dotted line in Figure 7, the liquid-vapor equilibrium of the mixture is considered a kind of close-boiling system. Attempts to separate the mixture by a pervaporation method have been made by several workers.[23,24] For example, Cabasso et al.[23] examined the separation behavior of a polyphosphonate membrane applied to the same mixture and obtained the result of excellent permselectivity, shown by the solid circles in Figure 7. The separation characteristics of the PBFP membrane, indicated in Figure 7 by the open circles, are very similar to Cabasso's result, and the maximum separation factor of this case was calculated as 12. The permeation fluxes of pure benzene and pure cyclohexane were 1.5 and 0.1 μg/cm²-s, respectively. The relation between the fluxes and the concentration of individual liquids in the mixture are similar to that of the methanol-ethanol athermal system, as shown in Figure 6. The benzene-cyclohexane system in particular has the largest separation factors compared with those of the other mixed solvent systems studied here. This result is probably related to the large difference in affinity of PBFP between benzene and cyclohexane.

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