

The Pertraction of Hydrophobic Organic Solutes across a Hydrophobic Membrane

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The pertraction of hydrophobic organic solutes across a hydrophobic membrane is a continuous separation process, which can be used as a substitute to active carbon. The permeabilities of hydrophobic organic solutes were examined in a two compartment cell partitioned by a hydrophobic membrane. The permeability was dominated by the hydrophobicity of the solute and the dissociation in the receiving phase. The permeability of the hydrophobic solutes increased with increasing pH of the receiving phase solution for the Teflon membrane filter Fluoropore. The preferential permeability of a hydrophobic solute was obtained, and the pertraction of a hydrophobic solute against its concentration gradient was also possible under a concentration gradient of hydroxide ion. Solute permeability changes were observed by coating the surface of Fluoropore to cover its pores with tetrafluoroethene–hexafluoropropene copolymer, FEP, and a highly selective permeability was obtained between phenol and 2-isopropyl-5-methylphenol (thymol) by suppressing the phenol permeability by coating the FEP membrane.

Active carbon has been frequently used in the treatment of wastewater to separate dissolved hydrophobic organic solutes,[1] but its regeneration is necessary after a definite period of use. If we can replace the active carbon column with a membrane through which the adsorbed solutes are permeated, regeneration will be unnecessary and the separation process becomes a continuous process.

Igawa et al. have already reported the enrichment of hydrophobic organic solutes and chelates through hydrophobic membranes under a pressure gradient,[2,3] which can be called a process of pertraction.[4] However, the highly distributed solutes in the membrane were not enriched because the diffusion coefficient was low for their strong attractive interaction with the membrane.

Many studies have reported dealing with active transport and the enrichment of a specific solute mediated by a carrier in a liquid membrane.[5–7] Pertraction with a liquid emulsion membrane was reported by Li at first,[8] and has also been reported by many authors.[9] The liquid emulsion membrane was used for wastewater containing a high concentration of phenol, and the concentration was reduced to less than 1 ppm by this treatment.[10] The membrane area is large when the emulsion is used, an efficient selective transport is possible, but not only the organic membrane solvent but also the carrier or the surfactant leak to the treated wastewater solution. We reported the pertraction of hydrophobic solutes across an *n*-hexane membrane without a carrier to realize nonspecific separation and the enrichment of hydrophobic organic solutes, which can dissociate in alkaline solution.[11] Hydrophobic solutes can be selectively transported across the membrane, and will be able to be used as a wastewater treatment. However, the solvent was also dissolved into the aqueous solution. Therefore, the authors attempted to use hydrophobic polymer membranes for the pertraction, although the permeability of the polymer membrane is lower in general than that of the liquid membrane.

In this report, the Teflon membrane filter Fluoropore and an FEP membrane coated on Fluoropore were used in a continuous pertraction process. These membrane materials are hydrophobic, although the adsorption properties of hydrophobic solutes regarding the materials are not strong. The permeability of various organic solutes and the influences of the solute concentration, the receiving phase pH, and the flow rate on the permeabilities were examined to clarify the permeation characteristics of the hydrophobic membranes.

Experimental

The pertraction experiment was carried out with a flow type cell composed of two compartments, that is, source phase and receiving phase compartments, which were partitioned from each other by a hydrophobic membrane with a membrane area of 4.2 cm^2, as reported earlier.[12] Each solution was circulated from a reservoir to the compartment by a tubing pump at a rate of 16 mL/min. The thickness of each compartment was 3 mm. The volumes of the source phase and receiving phase solutions were 500 mL and 100 mL, respectively, and the concentration of the source phase solution was 1 mM unless otherwise stated. Ethanol at first and then pure water were circulated to rinse the system after the permeation experiment because the solutes were adsorbed by the system. The partition coefficient of the organic solutes from the aqueous solution of pure water or 0.1 mol/L sodium hydroxide solution to *n*-hexane was obtained by a batch extraction experiment to characterize the hydrophobic–hydrophilic properties of the solutes.

The membranes used in this experiment were the Teflon membrane filter Fluoropore with a 0.1 μm pore diameter (Sumitomo Electric Inc, Ltd. FP-010) or the coated FEP membrane. The coating method was as follows; 1) Fluoropore is heated at 300 °C for ten minutes, 2) the dispersion of tetrafluoroethene–hexafluoropropene copolymer (Dupont-Mitsui Fluorochemical Co., Ltd., FEP 120-J) was diluted 3–8 times and sprayed on the surface of the

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Table 1. Partition Coefficient from Pure Water or Sodium Hydroxide Aqueous Solution to *n*-Hexane, $\log P_{ow}$, and pK_a of Organic Solutes

Organic solutes	pK_a[a)]	$\log P_{ow}$[a)]	Partition coefficient	
			Pure water	1 M NaOH
Phenol	9.99	1.48	0.11	0.01
1-Naphthol	9.39	2.84	2.57	0.04
m-*t*-Butylphenol	10.12	3.65	11.7	0.04
Thymol (2-Isopropyl-5-methylphenol)	10.9	3.30	49.0	0.03

a) pK_a and $\log P_{ow}$ values except for thymol are from Ref. 13 and pK_a and $\log P_{ow}$ values of thymol are from Ref. 11 and Ref. 14, respectively.

Fluoropore, 4) the coating membrane was heated at 120 °C for about ten minutes to dry, 5) spraying and drying were repeated several times, 6) the membrane was heated at 350 °C for 30 min at the end. The coating membrane was observed by a scanning electron microscope (Hitachi Ltd., S-4000) and a digital microscope (Sonic Co., BS-D8000 II) to confirm whether the layer was formed uniformly after the operation of the above-mentioned. To observe the cross section of the membrane, the membrane was cut by the fine edge of a razor.

In the permeation experiment, the solution of each phase was collected in a definite interval. The samples collected after the permeation and the partition experiments were analyzed by high-performance liquid chromatography (Shimadzu Co., LC-10AD) with a C-18 column (GL Sciences Inc.). The eluent contained 50% acetonitrile and 50% phosphate buffer solution (pH 7), with an ultraviolet spectrophotometer as a detector (Shimadzu Co., SPD-6AV) at 270 nm.

Results and Discussion

Organic Solute Permeabilities across the Fluoropore Membrane. Four species of organic solutes were used in this experiment and their pK_a, octanol/water partition constant, the log of P_{ow}, and partition coefficient from water to *n*-hexane are shown in Table 1. The hydrophobic–hydrophilic properties of organic solutes have been studied using various indexes, and $\log P_{ow}$ is frequently used as the index of hydrophobicity. However, the partition coefficient from water to *n*-hexane was measured and used as the index of hydrophobicity, because octanol is an amphiphilic solvent and the membrane used in this study is very hydrophobic. The hydrophobicity determined by the partition coefficients to *n*-hexane is as follows: phenol < 1-naphthol < *m*-*t*-butylphenol < thymol (2-isopropyl-5-methylphenol). These solutes dissociate in a high pH solution, and the partition coefficient is decreased by the dissociation. The change in the partition by dissociation is large for a hydrophobic solute. Figure 1 shows the result of the permeation experiment of these organic solutes. The permeability increased with an increase in the hydrophobicity of the solutes, and the solutes dissociated in the receiving phase were back-extracted effectively to the phase, when the receiving phase was 0.1 mol/L sodium hydroxide aqueous solution. The increase in the solute permeability by the dissociation in the receiving phase was large for a hydrophobic solute. The permeability of 1-naphthol was smaller than that of phenol, although the hydrophobicity of 1-naphthol is larger than that of phenol. This may be caused by the small steric hindrance of phenol for the permeation across the polymer membrane,

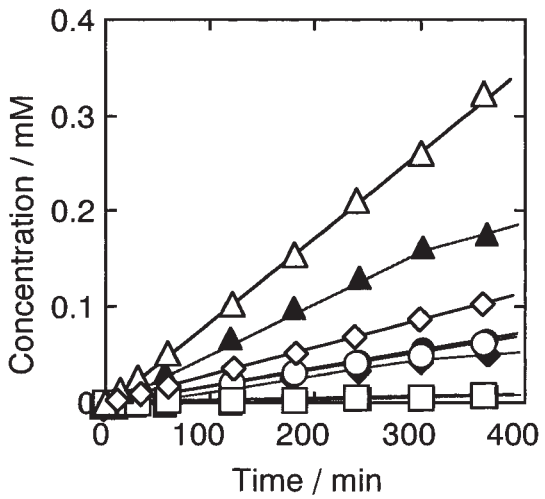

Fig. 1. Permeabilities of organic solutes across Fluoropore; source phase, 0.5 L of 1 mM thymol (△, ▲), *m*-*t*-butylphenol (◇, ◆), 1-naphthol (□, ■), and phenol (○, ●); receiving phase, 0.1 L of pure water (▲, ◆, ■, ●) or 0.1 M NaOH (△, ◇, □, ○).

because the molecular weight of phenol is 65% that of 1-naphthol. In the experiment, the transported amount of sodium hydroxide was negligible, and pH change in the source phase solution was not detected when the receiving phase was 0.1 M sodium hydroxide aqueous solution.

These phenomena can be explained kinetically as reported earlier.[15] The solute flux, J_s, can be described by Eqs. 1 to 3:

$$J_s = k_{1,s}C_s - k_{-1,s}C_{m,s} \quad (1)$$

$$J_m = D/L(C_{m,s} - C_{m,r}) \quad (2)$$

$$J_r = k_{-1,r}C_{m,r} - k_{1,r}C_r. \quad (3)$$

In these equations, k_1 and k_{-1} are the transfer rates from the aqueous phase to the membrane phase and from the membrane phase to the aqueous phase, respectively. C is the solute concentration, and the subscripts, s, r, and m mean the interface of the source phase side, the interface of the receiving phase side, and the membrane phase, respectively. The symbols D and L in Eq. 2 are the diffusion coefficient in the membrane and the membrane thickness, respectively. When k_1 is large and k_{-1} is small, and the partition coefficient, K, which is the ratio of k_1 to k_{-1}, is large, these equations suggest that the solute flux detected in the source phase, J_s, and the membrane phase concentration, C_m, become large values at the beginning of the

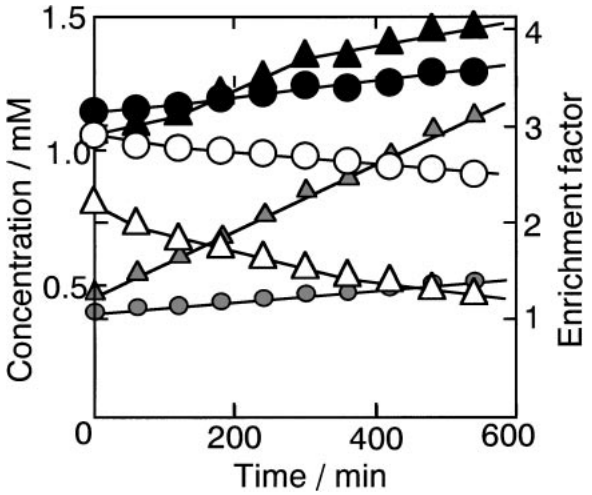

Fig. 2. Enrichment of organic solutes; source phase, 0.1 L of 1 mM thymol (△) and phenol (○); receiving phase, 0.1 L of 0.1 M NaOH and 1 mM thymol (▲) and phenol (●); enrichment factor of thymol (▲) and phenol (●), concentration ratio of receiving phase to source phase.

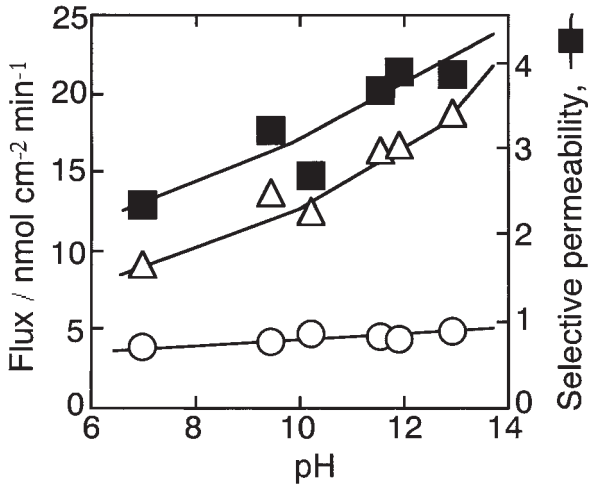

Fig. 3. Effect of receiving phase pH on permeability; source phase, 0.5 L of 1 mM thymol (△) and phenol (○); receiving phase, 0.1 L of NaOH and NaCl (total concentration, 0.1 M); selective permeability, flux ratio of thymol to phenol.

permeation experiment, while the solute flux detected in the receiving phase, J_r, is a small value.

When the transport is in the steady state, J is equal to J_s, J_m, and J_r, and the second term on the right side of Eq. 3 is negligible because of the dissociation in the receiving phase. Based on this, the following equation can be obtained:

$$J = k_{1,s}C_s/\{k_{-1,s}(L/D + 1/k_{-1,r}) + 1\} \quad (4)$$

when $k_{1,s}$ and $k_{-1,r}$ are large, and $k_{-1,s}$ and $k_{1,r}$ are small, such that the partition coefficient is large at the source phase interface and small at the receiving phase interface, these equations suggest that the solute fluxes detected in both phases are large. Thymol and phenol have very different partition coefficients and were used in this experiment for this reason.

The enrichment of the solutes is also possible in this system. Figure 2 shows the results of a permeation experiment where thymol and phenol in both phases were equal in concentration at the beginning of the experiment. In this experiment, the volume of the source phase solution was 100 mL, which was equal to that of the receiving phase. The receiving phase was 0.1 mol/L NaOH solution, and the solutes were transported against the concentration gradient. The enrichment factor is defined as the concentration ratio of the receiving phase to the source phase, as shown in Fig. 2. Thymol was concentrated in the receiving phase and the enrichment factor increased up to three times after 10 h under these experimental conditions. A hydrophilic solute, phenol, was also concentrated, but its enrichment factor is much smaller than that of thymol. Hydrophobic solutes can be enriched by the pertraction under a pH gradient, when the solute is dissociated in the receiving phase and the pertraction will be used to remove some hydrophobic solutes dissolved in water.

The effect of the receiving phase solution pH was examined and the results are shown in Fig. 3. The receiving phase solution contained not only sodium hydroxide but also sodium chloride to maintain a constant ionic strength. The influence of the dissociation on the flux of phenol by dissociation was small because it is a hydrophilic solute not distributed highly to the membrane. However, thymol was not extracted effectively to a low pH solution, but the permeability increased with the increase in pH. Selective permeability between thymol and phenol can be defined as (flux of thymol/source phase concentration of thymol)/(flux of phenol/source phase concentration of phenol), which is the flux ratio of thymol to phenol because of the equal concentration of thymol to phenol, and it increased with the increase in pH.

In general, the pumping rate affects the permeation phenomena, because the unstirred layer on the surface of the membrane influences the permeation phenomenon, and the thickness of the layer decreased with the pumping rate. In the layer, the solute permeability is dominated by the diffusion coefficient in water. It has been reported that the thickness is proportional from -0.6 to -0.8 power of the linear velocity,[16] and, in this case, the best linearity is obtained for the power of -0.60, as shown in Fig. 4. The reciprocal of the diffusion flux is proportional to the diffusion layer thickness in general, and then there was a linear relationship between the reciprocal of the flux and -0.60 power of the linear velocity. The y-intercept in the relationship is the flux when the effect of the unstirred layer on the permeability is negligible, and the selective permeability was about four in that case.

The influence of the source phase concentration on the permeabilities is shown in Fig. 5, and the flux increased with concentration. The concentrations of thymol and phenol in the source phase were equal to each other. The slopes for the solutes were about one for both solutes, although the slope of thymol was slightly higher than that of phenol. The selectivity rises slightly at a high concentration. This may be caused by the formation of a dimmer,[17] for the hydrogen bonding between hydroxy groups of two phenol molecules in the hydrophobic membrane and the steric hindrance increased for phenol at a high concentration.

Organic Solute Permeability Across Coating Membrane. As described above, the selectivity of the organic solutes was

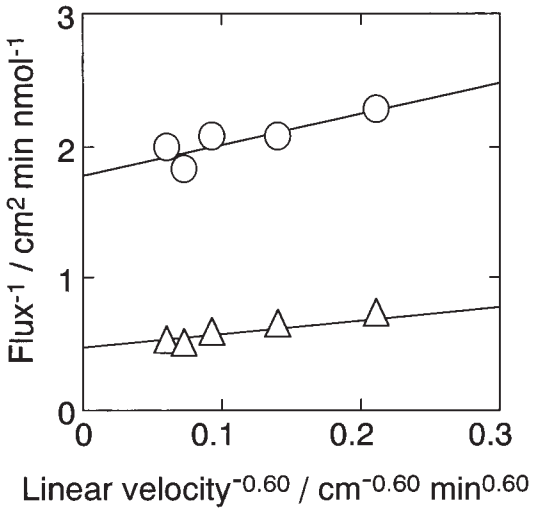

Fig. 4. Effect of linear velocity on permeability; source phase, 0.5 L of 1 mM thymol (△) and phenol (○); receiving phase, 0.1 L of NaOH.

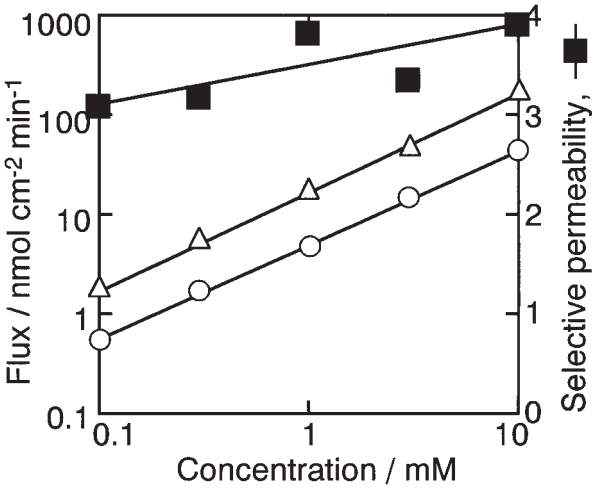

Fig. 5. Effect of concentration on permeability; source phase, 0.5 L of thymol (△) and phenol (○); receiving phase, 0.1 L of 0.1 M NaOH; selective permeability, flux ratio of thymol to phenol.

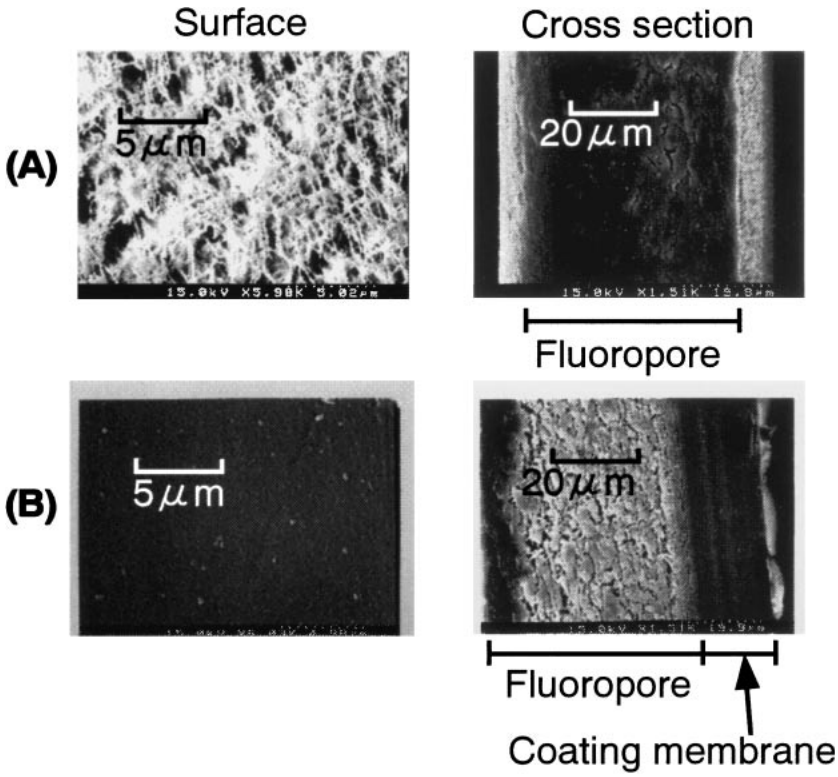

Fig. 6. SEM photographs of Fluoropore (A) and FEP coating membrane on Fluoropore (B).

not high as in the case of the *n*-hexane membrane,[11] which may be caused by the large pore size in Fluoropore. The coating membrane was formed on Fluoropore to narrow the pore size. The cross section and the surface of the membrane were observed by SEM, as shown in Fig. 6. From this observation, the thickness of the coating layer can be obtained. Figure 7 shows the relationship between the thickness of the coating layer and the mass of the coating amount on Fluoropore. When the coating amount was less than 1.2 mg/cm^2, the coating FEP entered into the pore, and the coating layer could not be observed on the surface of Fluoropore. However, the thickness increased linearly with the coating amount when the amount was over 1.2 mg/cm^2.

The permeation experiment was carried out with the FEP coating membrane. The solute flux is proportional to the reciprocal of the membrane thickness, and the limiting step of the transport is the diffusion in the coating membrane described in Eq. 2. Therefore, $L/D \gg 1/k_{-1,s}$, $1/k_{-1,r}$ in Eq. 4, and the following equation can be adopted in this case:

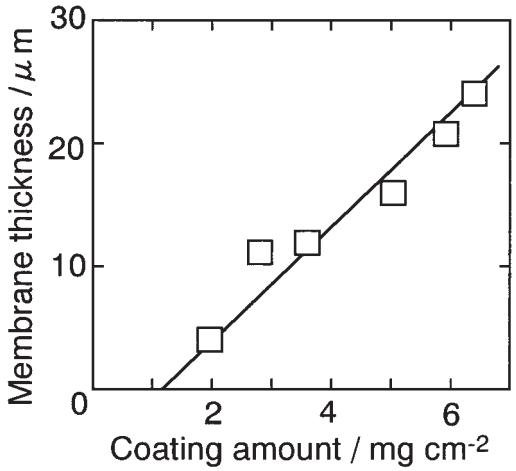

Fig. 7. Relationship between coating membrane thickness and coating amount.

$$J = Dk_{1,s}C_s/(k_{-1,s}L) = DKC_s/L. \quad (5)$$

Figure 8 shows the relationship between the reciprocal of the flux and the coating membrane thickness. There were linear relationships for the two solutes, as estimated by Eq. 5. The separation factor can be increased to about 6 or 7 by coating, which may be caused by the suppressed leakage of a small hydrophilic solute, phenol, through the membrane. This factor varied widely because of the heterogeneous coating which was caused by the uncontrolled factors in the coating process, and the coating process will be improved further in our future work.

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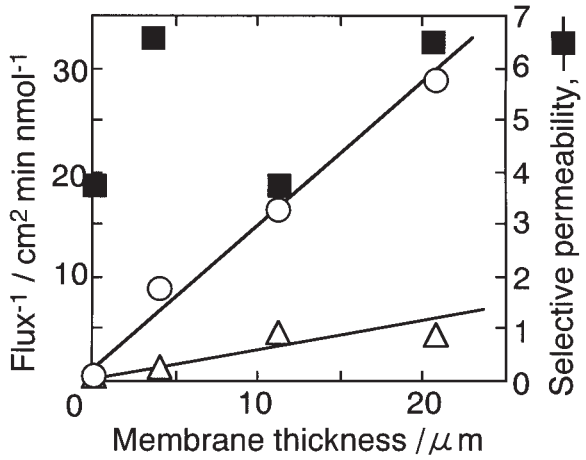

Fig. 8. Effect of coating membrane thickness on permeability; source phase, 0.5 L of 1 mM thymol (△) and phenol (○); receiving phase, 0.1 L of 0.1 M NaOH.

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