Pertraction of Hydrophobic Organic Solutes with a Hydrophobic Membrane

Manabu Igawa,* Toshiyuki Abe, and Hiroshi Okochi
Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686

(Received February 27, 1998; CL-980149)

Pertracion of hydrophobic organic solutes with a hydrophobic membrane is a continuous separation process, which can be used as a substitute of activated carbon. The permeability was affected by the hydrophobicity of the solute and the dissociation in the receiving phase. The pertraction of a hydrophobic solute against its concentration gradient is also possible under a concentration gradient of hydroxide ion.

Activated 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 its usage. If we can replace the activated carbon column to a membrane through which the absorbed solutes are permeated, the 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 as a process of pertraction.[4] However, the solutes distributed highly to the membrane were not enriched because the diffusion coefficient was low for their strong attractive interaction with the membrane.

There have been reported many studies dealing with the active transport and the enrichment of a specific solute mediated by a carrier.[5-7] In this paper, however, we used a hydrophobic organic solvent without a carrier as the membrane to realize nonspecific separation and the enrichment of hydrophobic organic solutes which can be dissociated in alkaline solution.

Pertraction experiment was carried out with a flow type cell composed of three compartments, that is, feed solution, liquid membrane, and receiving phase compartments, which were partitioned to each other by a hydrophilic regenerated cellulose membrane of Visking dialysis membrane (Viskase Sales Corp.) or a hydrophobic Teflon membrane filter (0.1 μm pore size) of Fluoropore (Sumitomo Electric Inc., Ltd.). Each solution was circulated from each reservoir to the compartment by a tubing pump and the thickness of each compartment was 3 mm. The detail of this experiment was the same as that described earlier.[8] The liquid membrane used in this experiment was a hydrophobic solvent of *n*-hexane and the membrane area was 4.2 cm^2. In the dialysis experiment, the solution of the receiving phase was collected in a definite interval. The distribution coefficient of a solute from the aqueous solution to *n*-hexane was obtained by an experiment of batch extraction. The hydrophobic solute used in this study was thymol (2-isopropyl-5-methylphenol) and the concentration was 1 mM unless otherwise stated. The concentrations of the solutes were determined by an HPLC with a C-18 column, the eluent containing 50% acetonitrile and 50% phosphate buffer solution (pH 7), and an ultraviolet spectrophotometer as a detector.

Figure 1 shows the transport behaviors of thymol across liquid membrane. When each phase was partitioned by Fluoropore and the receiving phase solution was alkaline solution, the solute flux was large. The membrane pores in Fluoropore were filled with *n*-hexane, while those in Visking dialysis membrane were filled with water. Then, thymol was rejected by the hydrophilic Visking dialysis membrane and it was more permeable in the liquid membrane partitioned by Fluoropore. The dissociation constant of thymol was about 10.9 which was obtained by the UV absorption as the function of the solution pH. Therefore, thymol was dissociated in the receiving phase and was back-extracted effectively to the phase, when the receiving phase was 1 M NaOH aqueous solution. In the experiments, the dissolution of *n*-hexane to the aqueous phases was negligible small.

Figure 2 shows the relationship between the distribution coefficient and the permeation coefficient. The permeation coefficient was defined by the solute flux divided by the source phase concentration. The distribution coefficient shown here was the concentration of the solute in *n*-hexane divided by that of the solute dissolved in pure water obtained by a batch ex-

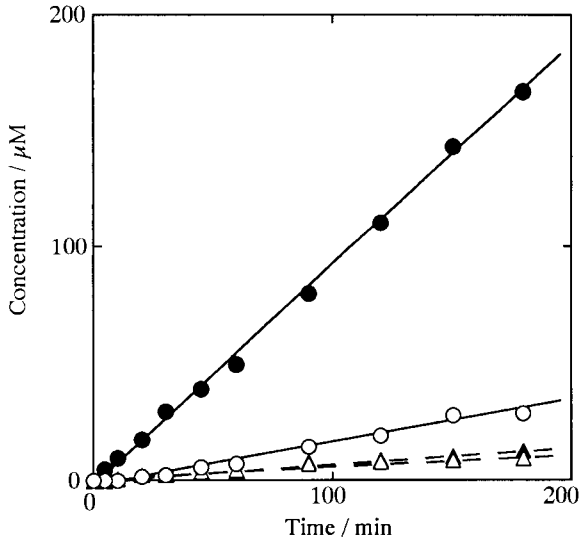

Figure1. Transport of thymol across liquid membrane. The filters partitioning between aqueous phase and the membrane phase were Fluoropore (○, ●) and Visking dialysis membrane (△, ▲). The receiving phase was pure water (○, △) or 1 M NaOH aqueous solution (●, ▲).

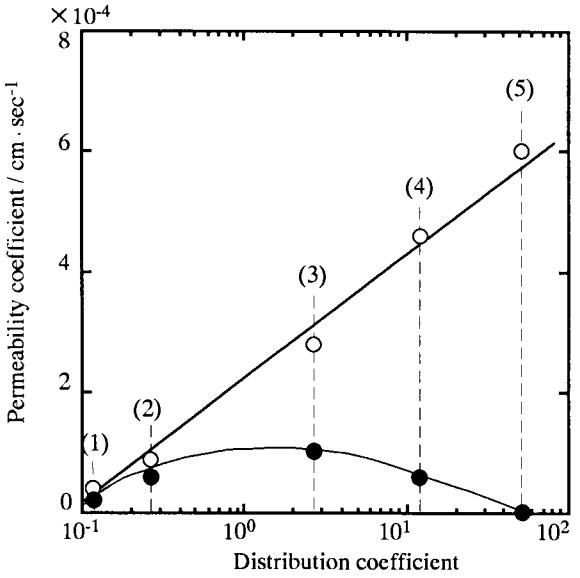

Figure 2. Relationship between distribution coefficient and permeability coefficient. The receiving phase was pure water (●) or 1 M NaOH aqueous solution (○). The solutes were phenol (1), benzyl alcohol (2), 1-naphthol (3), *m-t*-butylphenol (4), and thymol (5).

periment. When the receiving phase was pure water, there was a maximum value, because highly hydrophobic solutes with high distribution coefficients were difficult to be back-extracted. However, the permeation coefficient increased with the increase of the distribution coefficient when the receiving phase was alkaline solution. In the receiving phase solution, the organic solutes used in this study were dissociated and were effectively back-extracted. These phenomena can be explained kinetically.[9] The solute flux, J_s, can be described as eqs. 1 and 2.

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

$$J_r = k_{-1,r}C_{o,r} - k_{1,r}C_r \quad (2)$$

In these equations, k_1 and k_{-1} mean the dissolution rates from aqueous phase to membrane phase and from membrane phase to aqueous phase, respectively, C means the solute concentration, and the subscripts, s, r, and o mean the interface of the source phase side, the interface of the receiving phase side, and the organic phase. When k_1 is large and k_{-1} is small, where the distribution coefficient is large, these equations suggest that the solute flux detected in the source phase, J_s, and the organic phase concentration, C_o, become large values, while the solute flux detected in the receiving phase, J_r, is a small value. When $k_{1,s}$ and $k_{-1,r}$ are large and $k_{-1,s}$ and $k_{1,r}$ are small, where distribution 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 become large values.

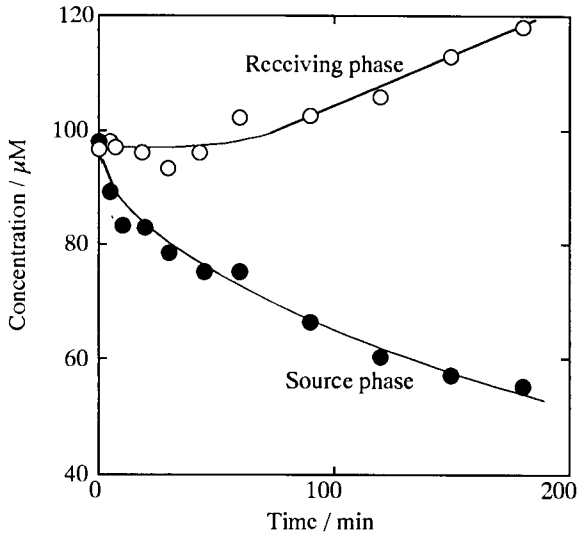

Figure 3. Transport of thymol against its concentration gradient. Source phase was 100 mL of pure water, receiving phase was 100 mL of 1 M NaOH aqueous solution, and the liquid membrane phase was 30 mL of *n*-hexane.

Figure 3 shows the pertraction behavior of thymol, when there was no concentration difference in the initial experimental condition. When the receiving phase solution was 1 M NaOH aqueous solution, the distribution coefficient became very small in the receiving phase and a hydrophobic solute was transported against its concentration gradient after a lag time with the consumption of hydroxide ion in the receiving phase.

Hydrophobic solutes can be enriched by the pertraction under pH gradient, when the solute can be dissociated in the receiving phase. Then, pertraction can be used to remove some hydrophobic solutes dissolved in water.

References

1 M. J. Hammer and M. J. Hammer, Jr. "Water and Wastewater Technology", Englewood Cliffs (1996).
2 M. Igawa, A. Saito, N. Sasamura, M. Tanaka, and M. Seno, *J. Membr. Sci.*, **14**, 59 (1983).
3 M. Igawa, T. Tachibana, K. Yoshida, M. Tanaka, and M. Seno, *Chem. Lett.*, **1984**, 1527.
4 S. Schlosser and E. Kossaczky, *J. Membr. Sci.*, **6**, 83 (1980).
5 E. M. Choy, D. F. Evans, and E. L. Cussler, *J. Amer. Chem. Soc.*, **96**, 7085 (1974).
6 C. A. Koval and T. Spontarelli, *J. Amer. Chem. Soc.*, **110**, 293 (1988).
7 M. Igawa, E. Kobayashi, A. Itakura, K. Kikuchi, and H. Okochi, *J. Phys. Chem.*, **98**, 12447 (1994).
8 M. Igawa, K. Saito, F. Monoe, K. Nishida, M. Tanaka, and M. Seno, *Nippon Kagaku Kaishi (J. Chem. Soc. Jpn.)*, **1985**, 826.
9 W. Stumm and J. J. Morgan, "Aquatic Chemistry (3rd Ed.)", Wiley-Interscience (1996).