Specific Permeation of Hydrophobic Solutes across a Hydrophobic Polymer Membrane

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A hydrophobic solute, thymol, was separated from a hydrophilic solute, glucose, with a separation factor of over 230 across a hydrophobic FEP membrane. Hydrophobic solutes are highly partitioned to the membrane, diffused, and back-extracted to the alkaline receiving phase solution by their dissociation, while hydrophilic solutes are rejected by the membrane.

Active carbon is widely used for the treatment of wastewater containing dissolved toxic hydrophobic solutes by the selective sorption of them, but the active carbon should be regenerated after the solutes are saturated on the active sites. Membrane separation is a continuous process and a hydrophobic membrane process may be substituted for the active carbon.[1] The hydrophobic water structure formed in the water surrounded by a hydrophobic material has unique properties, and the selective permeation of potassium ions is caused by the water structure in the biological membrane.[2] We have examined the hydrophobic membrane for the separation of metal ions and the selective permeation of hydrophobic solutes.[3–6] The hydrophobic solutes were enriched across the hydrophobic membrane by the selective partition and up-hill transport under the gradient of sodium hydroxide concentration.[1,7] The separation for the dissolved solutes between thymol (2-isopropyl-5-methylphenol) and phenol was carried out by using poly(tetrafluoroethene-*co*-hexafluoropropene) (FEP) membrane, but was not effective because the difference of the hydrophobicities between these two solutes was too small.[1] The octanol–water partition coefficient, P_{ow}, is the index of hydrophobicity; $\log P_{\text{ow}}$ is 3.30 and 1.48 for thymol and phenol, respectively.[1] In this research, we tried to apply this method to separate hydrophobic thymol from hydrophilic glucose, whose $\log P_{\text{ow}}$ is -3.3, and we obtained an extremely selective permeation between them. We also obtained the results of the changing permeabilities of solutes, thymol and phenol, depending on their hydrophobicities as controlled by their dissociation across a hydrophobic membrane under an alkaline gradient.

A dense and thin membrane was obtained by coating FEP on a Teflon membrane filter as follows: (1) Teflon membrane filter, Fluoropore, with a 0.1 μm pore diameter (Sumitomo Electric Inc., Ltd. FP-010) is heated at 255 °C for 10 min; (2) the dispersion of poly(tetrafluoroethene-*co*-hexafluoropropene) (Dupont-Mitsui Fluorochemical Co., Ltd., FEP 120-J) was diluted 3–8 times and sprayed on the surface of the Fluoropore; (3) the coating membrane was heated at 85 °C for about 5 min to dry; (4) spraying and drying were repeated several times; (5) the membrane was heated at 300 °C for 30 min at the end. This method is about the same as that reported previously,[6] and the heating temperature at the final step is important. The FEP used in this study was a standard type poly(tetrafluoroethene-*co*-hexafluoropropene), whose hexafluoropropene content was reported to be 10 to 15 wt %.[8]

The permeation experiment was carried out by using an aqueous solution containing organic solutes and an alkali solution; the two solutions were divided by the membrane as described in the previous paper.[1] The sample solutions collected in the experiment were analyzed with a high-performance liquid chromatograph (Shimadzu Co., LC-10AD) equipped with a C-18 column (GL Sciences Inc.) and an ultraviolet spectrophotometer (Shimadzu Co., SPD-6AV) as a detector at 270 nm for thymol and phenol. Glucose concentration was measured with an ion chromatograph (Dionex BIO-LC), to which a CarboPac PA-1 column is attached. Sodium ion in the source phase was measured with an atomic absorption spectrophotometer (Shimadzu AA-6700F).

Figure 1 shows the result of the separation between glucose and thymol. A hydrophobic solute, thymol, was highly partitioned to the membrane, diffused, and back-extracted to the receiving phase of alkaline solution by its dissociation. On the other hand, a hydrophilic solute, glucose, was rejected by the hydrophobic membrane, and the glucose could not be detected in the receiving phase. We can obtain the upper limit of its flux by using the value of the detection limit concentration at the end of the permeation experiment, that is, 0.069 μM. We can evaluate the selectivity by a separation factor, $T^{\text{A}}{}_{\text{B}}$, which is defined by the following equation:[5]

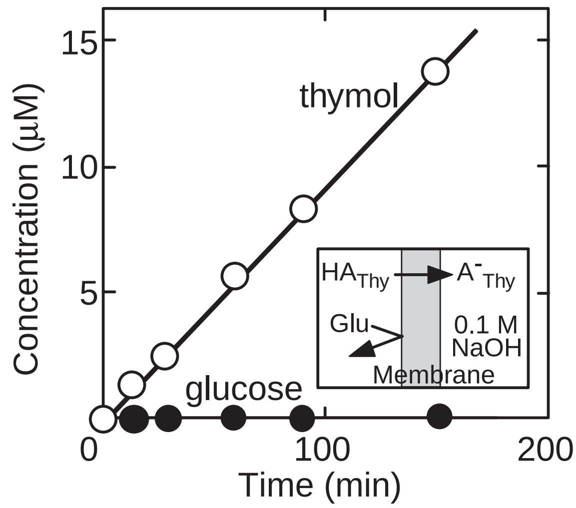

Fig. 1. Permeabilities of thymol (Thy) and glucose (Glu); source phase, 100 mL of 1 mM mixed solution; receiving phase, 100 mL of 0.1 M NaOH solution; membrane, 4.2 cm^2 of FEP coating Fluoropore membrane.

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$$T^{A}{}_{B} = \text{flux to source phase concentration ratio of solute A/flux to source phase concentration ratio of solute B.} \quad (1)$$

Then, the separation factor of hydrophobic thymol to hydrophilic glucose is over 230. Such a high selectivity for organic materials has never been reported for artificial polymer membranes, although the high selectivity values have been reported for biological lipid membranes.[9] Both of the solutes were not dissociated in the source phase solution and mostly dissociated in the receiving phase, because each pK_a value is 12.46 for glucose[10] and 10.9 for thymol,[1] and the source phase solution was pH 6.1. Therefore, the hydrophobicity of each solute is the most dominating factor of this separation, while the hydroxide ion concentration difference enhances the permeabilities.[1] The enhanced transport of hydrophobic solutes is limited for the organics which are dissociated in alkaline solution, but many organic solutes are dissociated in the alkaline solution with a high pH.

Figure 2 shows the pH dependencies of the fluxes of thymol and phenol. The pH of the source phase solution was adjusted by using Sørensen buffer solution.[11] The permeabilities of these solutes decreased rapidly with the increase of pH because these solutes become hydrophilic in the high pH regions due to their dissociation. These solutes could not be detected in the receiving phase when the pH was larger than each pK_a value, 9.99 for phenol[10] and 10.9 for thymol.[1] The effects of changing hydrophobicities of the solutes on their permeabilities are larger than expected from the previous work.[1] That is, the effect of receiving phase solution pH on their permeabilities was already examined, but the effect was not so large as the effect of the source phase solution pH. In the system, the sodium ions transported into the source phase were not detected and sodium hydroxide ions in the receiving phases were practically not transferred across the membrane. Hydrophilic solutes are very unlikely to be permeated across the hydrophobic membrane, as shown in Figs. 1 and 2.

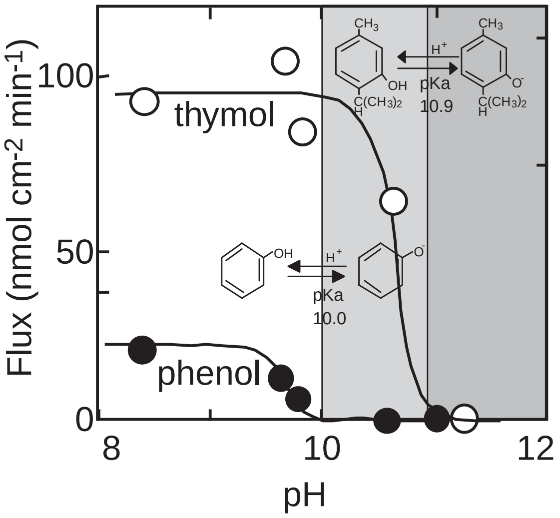

Fig. 2. pH dependence of thymol and phenol fluxes; source phase, 100 mL of 1 mM mixed solution; receiving phase, 100 mL of 0.1 M NaOH solution; membrane, 4.2 cm^2 of FEP coating Fluoropore membrane.

Teflon is a hydrophobic material, but little irreversible adsorption occurred on the surface. Therefore, this membrane system will be useful as the continuous wastewater treatment process for dissolved hydrophobic and toxic materials.

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References

1 M. Igawa and S. Nemoto, *Bull. Chem. Soc. Jpn.*, **77**, 1939 (2004).

2 Y. Zhou and R. MacKinnon, *Biochemistry*, **43**, 4978 (2004).

3 M. Igawa, M. Seno, H. Takahashi, and T. Yamabe, *J. Membr. Sci.*, **2**, 263 (1977).

4 M. Igawa, A. Saito, N. Sasamura, M. Tanaka, and M. Seno, *J. Membr. Sci.*, **14**, 59 (1983).

5 M. Igawa, Y. Nakamura, K. Takahashi, M. Tanaka, and M. Seno, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 165 (1982).

6 M. Igawa, R. Nishiura, N. Mashiyama, and Y. Usuda, *Bull. Chem. Soc. Jpn.*, **65**, 1871 (1992).

7 M. Igawa, T. Abe, and H. Okochi, *Chem. Lett.*, **1998**, 597.

8 T. Satokawa, "Handbook of Fluorocarbon Resin (Japanese)," The Nikkan Kogyo Shimbun, Ltd. (1990), p. 219.

9 A. Walter and J. Gutknecht, *J. Membr. Biol.*, **90**, 207 (1986).

10 "Bunseki Kagaku Binran (Handbook of Analytical Chemistry)," 5th ed, ed by The Japan Society of Analytical Chemistry, Maruzen, Tokyo (2001), p. 642.

11 "Handbook of Chemistry and Physics," 84th ed, ed by D. R. Lide, CRC Press, Boca Raton (2003), pp. 8-48–8-58.