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Facilitated Transport of Naphthalene Derivatives through a Supported Liquid Membrane Containing a Water-Soluble Cyclophane

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ABSTRACT

Cyclophane-mediated transport of two- or three-ring aromatic compounds across aqueous supported liquid membranes (SLMs) was investigated. SLMs containing water-soluble cyclophanes, OCP44 and 66, exhibited facilitated transport for aromatic compounds but not for aliphatic compounds. The flux of 2,6-dimethylnaphthalene was decreased with an increase of membrane thickness, indicating that the rate-determining step of the present cyclophane-mediated transport is the diffusion process of the carrier–solute complex in the membrane. The SLMs showed isomer-selectivity for methylnaphthalenes (MNs), ethylnaphthalenes (ENs), dimethylnaphthalenes (DMNs), and three-ring aromatic compounds. The isomer-selectivity of QCP44 was completely opposite to that of QCP66; the flux order of QCP44 was 2-MN > 1-MN, 2-EN > 1-EN, 2,6-DMN > 1,5-DMN and anthracene > phenanthrene; and that of QCP66 was 1-MN > 2-MN, 1-EN > 2-EN, 1,5-DMN > 2,6-DMN and phenanthrene > anthracene. This difference in flux was discussed in terms of the cyclophane-involved complex formation.

INTRODUCTION

Carrier-mediated transport is one of promising tools for selective separation and has been studied extensively. Armstrong et al. (1) and other researchers (2) reported that cyclodextrin-incorporated aqueous liquid membranes can perform not only facilitated transport but also fine separation for water-insoluble organic compounds.

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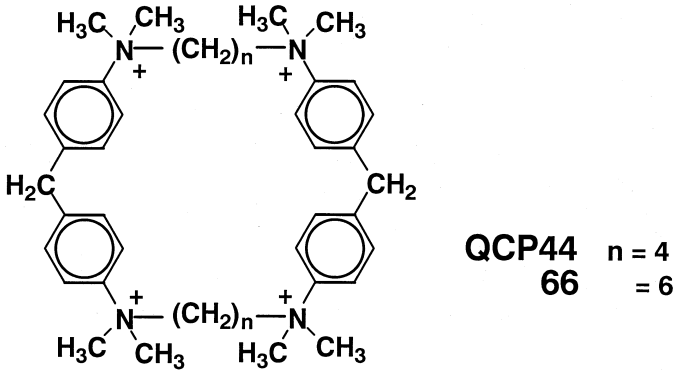

FIG. 1 Structure of QCP44 and 66.

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Water-soluble cyclophanes are another group of hosts bearing nonpolar cavities, and they can form inclusion complexes with hydrophobic guest compounds. In contrast to cyclodextrins, they are fully synthetic hosts, and therefore able to be designed as required for given guest molecules. Although a wide variety of excellent cyclophanes have been synthesized, there are few reports on their utilization as membrane carriers (3).

We report here cyclophane-mediated transport of two- or three-ring aromatic compounds across an aqueous supported liquid membranes (SLM). SLMs containing a water-soluble cyclophane, QCP44 or 66 (Fig. 1)(4), exhibited facilitated transport for aromatic compounds but not for aliphatic compounds. The SLMs also showed isomer selectivity for methylnaphthalenes (MNs), ethylnaphthalenes (ENs), dimethylnaphthalenes (DMNs), and three-ring aromatic compounds.

EXPERIMENTAL

Materials and Reagents

QCP44 and 66 were synthesized according to the method of Odashima et al. (4). Cellulose dialysis membrane was obtained from Asahi Medical Co. (Tokyo, Japan). Naphthalene, 1- and 2-methylnaphthalenes, 1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,8-, and 2,6-dimethylnaphthalenes, anthracene, and phenanthrene were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). 1,7-Dimethylnaphthalene, 1- and 2-ethylnaphthalenes were purchased from Sigma-Aldrich Japan K.K. (Tokyo, Japan). 2,3-Dimethylnaphthalene was purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan).

Measurements

A SLM was prepared by impregnating a cellulose dialysis membrane with a 0.1 M aqueous solution of QCP44 or 66. The transport experiments were

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carried out using the same glass cells as described previously (5). A hexane solution containing 0.1 M aromatic compound (source phase) and pure hexane (receiving phase) were separated by a SLM positioned between two cylindrical half-cells (half-cell volume: 22 mL, membrane area: ca. 7 cm^2). The transport cell was placed in a thermostated water bath (20°C), and both phases were agitated with magnetic stirrers. The increase in the concentration of an aromatic compound in the receiving phase was monitored using gas chromatography (model 380, GL Science, Tokyo, Japan), and the flux was obtained from the slope of the concentration vs time curve.

RESULTS AND DISCUSSION

Figure 2 displays a typical result of dimethylnaphthalene transport across a QCP44-containing SLM, together with a result obtained with a SLM containing no QCP44. The concentration of 2,6-dimethylnaphthalene (2,6-DMN) in the receiving phase increased linearly with time, whereas in the absence of QCP44 little permeation was observed. The transport rate of the QCP44-containing SLM was about two orders higher than that of the SLM containing no QCP44. Similar results were obtained for other aromatic compounds. The transport of aromatic compounds was accelerated in the presence of QCP44. This system performed no permeation of aliphatic compounds: Decane and decahydronaphthalene were not transported even in the presence of QCP44. These results indicate that QCP44 acted as a carrier for aromatic compounds and that facilitated transport of aromatic compounds occurred in this system.

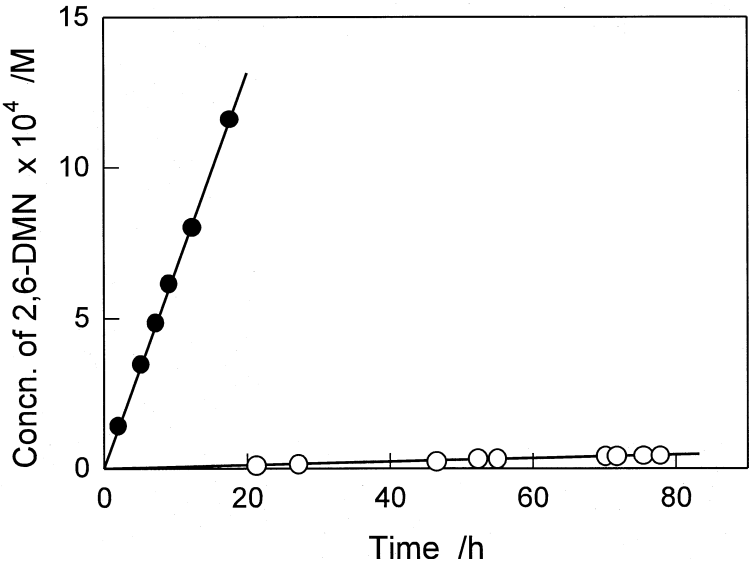

FIG. 2 Time course of the concentration of 2,6-DMN in the receiving phase. (●) SLM containing QCP44, (○) SLM containing no carrier.

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QCP44 has a hydrophobic rectangular cavity of about 3.5 Å (width) × 7.9 Å (length) × 6.5Å (depth) (6). This width is about the same size as the thickness of an aromatic ring, but much narrower than that of hydrocarbon chains of aliphatic compounds. Only aromatic compounds can form inclusion complexes with QCP44. This is why QCP44 acted as a carrier only for aromatic compounds. Table 1 shows some flux data of two- or three-ring aromatic compounds; the results obtained with QCP66 are also given. QCP66 has a cavity whose size is the same in width and depth, but it is two methylene units larger in length than QCP44. The results in Table 1 indicate that irrespective of carrier size, there was a tendency for the flux to decrease with an increase in the carbon number of the solute: naphthalene > MNs > ENs ≒ DMNs > phenanthrene and anthracene. Table 1 also shows that for the fluxes of isomers, the two QCPs gave different flux orders. In the case of QCP44; 2-MN > 1-MN, 2-EN > 1-EN, 2,6-DMN > 1,5-DMN and anthracene > phenanthrene; and in the case of QCP66; 1-MN > 2-MN, 1-EN > 2-EN, 1,5-DMN > 2,6-DMN and phenanthrene > anthracene. It is noteworthy that the order for QCP66 is completely opposite to that for QCP44.

In order to examine the selectivity for isomers in more detail, the ratio of the flux of each dimethylnaphthalene isomer (*i*, *j*-DMN) to that of 2,6-DMN

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TABLE 1
Transport Rates of Several Aromatics across QCP-Containing Aqueous SLM

	Flux × 10^7 (mol·cm^{-2}·h^{-1})	
Aromatics[a]	QCP44	QCP66
Naphthalene	2.6	3.0
1-MN	0.69	1.6
2-MN	1.5	0.92
1-EN	0.24	0.73
2-EN	0.59	0.34
1,5-DMN	0.21	0.91
2,6-DMN	0.63	0.31
Anthracene[b]	0.19	0.043
Phenanthrene[b]	0.140	0.11

[a]MN, EN and DMN stand for methylnaphthalene, ethylnaphthalene, and dimethylnaphthalene respectively.

[b]The initial concentration was 0.05 M (not 0.1 M) due to low solubility.

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TABLE 2
Selectivity of QCP-Containing Membranes for Dimethylnaphthalene Isomers

	Flux ratio ($J_{ij}/J_{2,6\text{-DMN}}$)	
Dimethylnaphthalene[a]	QCP44	QCP66
1,4-DMN (α,α)	0.25	3.0
1,5-DMN (α,α)	0.33	2.9
1,8-DMN (α,α)	0.21	3.5
1,2-DMN (α,β)	0.54	2.1
1,3-DMN (α,β)	0.42	2.1
1,6-DMN (α,β)	0.52	1.7
1,7-DMN (α,β)	0.31	1.9
2,3-DMN (β,β)	1.9	1.3
2,6-DMN (β,β)	1.0	1.0

[a]DMN stands for dimethylnaphthalene.

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was measured. The results are shown in Table 2. The flux ratio was decreased in the following order: for QCP44, 2,3-DMN > 2,6-DMN > 1,2-DMN > 1,6-DMN > 1,3-DMN > 1,5-DMN > 1,7-DMN > 1,4-DMN > 1,8-DMN; and for QCP66, 1,8-DMN > 1,4-DMN > 1,5-DMN > 1,3-DMN ≒ 1,2-DMN > 1,7-DMN > 1,6-DMN > 2,3-DMN > 2,6-DMN. These orders imply that the flux depends on the position of two methyl groups, i.e., for the case of QCP44 the flux order is β,β-DMN > α,β-DMN > α,α-DMN; and for QCP66 it is α,α-DMN > α,β-DMN > β,β-DMN.

On the basis of NMR and structure-modification studies, Odashima et al. (7) proposed that the complex between CP44 (the precursor of QCP44) and naphthalene has a structure where the naphthalene ring is included in the cyclophane cavity with its long axis tilted about 30° ("pseudoaxial" form). According to this "pseudoaxial" structure for the QCP44-involved complex, the distance between the methyl moiety of methylnaphthalene and the cyclophane ring is greater for the β-position than for the α-position, i.e., the steric hindrance of β-methylnaphthalene is lower than that of α-methylnaphthalene. In fact, the stability constants of β-substituted naphthalenes are greater than those of α-substituted naphthalenes (7). On the other hand, in the case of QCP66 the naphthalene ring can be accommodated in the cyclophane cavity with its long axis parallel to the cavity plane because the cavity of QCP66 is longer by two methylene units than that of QCP44. In this complex structure the distance between the methyl group and the cyclophane ring becomes greater for the α-position than for the β-position, and the stability constants of

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α-substituted naphthalenes become greater than those of β-substituted naphthalenes (7).

The orders of transport rates among the isomers of naphthalene derivatives shown in Tables 1 and 2 are in good accordance with those of complex stability, i.e., the isomers forming a more stable complex with the cyclophane gave higher fluxes. This good correlation implies that the complex concentration at the membrane interface determines the transport rate. According to the ordinary carrier-mediated transport mechanism, when the extraction process of a solute via complex formation is fast and rapidly attains its equilibrium state, the transport rate of the solute is proportional to the complex concentration at the membrane interface (diffusion-controlled transport). An easy way to determine whether the transport system is "diffusion-controlled" or "reaction-controlled" is to measure the dependence of the transport rate on membrane thickness. If the plot of the reciprocal of the transport rate is proportional to the membrane thickness, the transport process is determined to be "diffusion-controlled" with considerable certainty (8). As shown in Fig. 3, a plot of the reciprocal of the transport rate of 2,6-DMN against the membrane thickness gave a straight line through the origin, indicating that the rate-determining step in the present transport system is the diffusion process of the carrier–solute complex in the membrane, and the complex formation reaction at the membrane interface is in equilibrium. This is why the transport selectivity was parallel to the complex formation ability.

The results described above demonstrate that water-soluble cyclophanes, QCPs, acted as good carriers for aromatic compounds in an aqueous-sup-

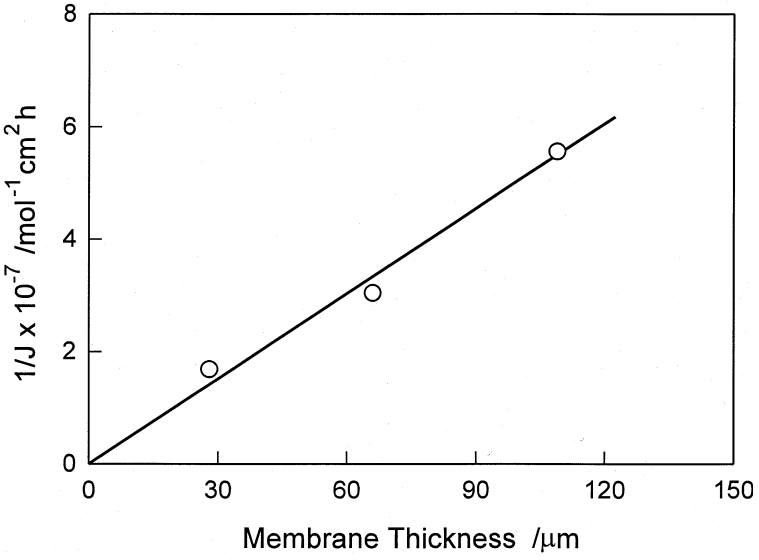

FIG. 3 Plot of the reciprocal of the flux of 2,6-DMN against membrane thickness.

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ported liquid membrane and that selective transport occurs for aromatic isomers. The fact that a slight change in the cavity size of the cyclophanes gave rise to a great change in selectivity provides an attractive possibility for the selective transport of various compounds bearing no functional groups, such as —NH_2 or —COOH, by using a rigorously sized host compound.

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