Transport of Neutral Azobenzene Derivatives by Methylated Cyclodextrins

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Methylated β-cyclodextrins and α-cyclodextrin transport neutral azobenzene and its derivatives through an aqueous phase with high efficiency and selectivity.

There have been many reports on the transport of cations through lipophilic membranes mediated by natural or synthetic carriers,[1] but few on the transport of neutral molecules by artificial carriers. Recently, the transport of neutral arenes through an aqueous phase mediated by microemulsion globules[2] and by cationic macrocyclic hosts[3] have been reported.

Cyclodextrins(CD) can be considered as one of the best potential carriers for neutral molecules because they form inclusion complexes with various lipophilic molecules.[4] However, their use has been limited by the fact that most of the inclusion complexes with lipophilic molecules, including organic compounds usually used as solvents, are almost insoluble both in water and in organic solvents. Now we have overcome this difficulty by using methylated cyclodextrins as carrriers and diethyl ether as an organic phase. In this communication we report that heptakis(2,6-di-*O*-methyl)-β-CD (Me_2β-CD), and heptakis(2,3,6-tri-*O*-methyl)-β-CD (Me_3β-CD), can transport azobenzene and its derivatives through an aqueous phase effectively and selectively.

All the experiments were performed in a U-type cell (17 mm in diameter) at 20 °C. Figure 1 indicates the arrangement of the phases. The source phase (I) is a solution of the substrate in diethyl ether (5 ml), phase (II) is a magnetically stirred solution of methylated cyclodextrin or α-CD (0.25 M) in water (20 ml), and the receiving phase (III) is pure diethyl ether (5 ml). The concentration of substrates transported were determined by electronic absorption spectroscopy. The initial transport rates are listed in Table 1.

In the absence of carriers there was little transport of the

Table 1. Relative rates of transport of azobenzenes.[a]

PhN=NC$_6$H$_4$–R-*p*	α-CD (mol h^{-1})	Me_2β-CD (mol h^{-1})	Me_3β-CD (mol h^{-1})
R = H	1.27×10^{-4}	3.16×10^{-4}	8.0×10^{-5}
R = NMe_2	3.5×10^{-6}	3.3×10^{-4}	7.5×10^{-5}
R = NEt_2	[b]	9.9×10^{-5}	2.6×10^{-5}

[a] Transport rate was determined from the rate of appearance of substrate in the receiving phase III; reproducibility, 10% or better. [b] Insoluble inclusion complexes were formed.

substrate. In the case of azobenzene, for example, no detectable amount of substrate is transported through the aqueous phase for at least several hours. However, in the presence of methylated β-CD or α-CD the substrates were transported effectively through the aqueous phase. Under these conditions non-methylated β-CD and γ-CD formed insoluble inclusion complexes with solvents and/or substrates. Methylated β-CDs showed higher transport efficiencies than α-CD. Me_2β-CD was 2.5 times more efficient than α-CD for transport of azobenzene and 94 times more efficient than α-CD for transport of dimethylaminoazobenzene. Me_2β-CD was four times more efficient than Me_3β-CD for transport of both dimethylaminoazobenzene and diethylaminoazobenzene. α-CD showed marked selectivity toward azobenzene over dimethylaminoazobenzene. Me_2β-CD showed similar efficiency for transport of azobenzene and dimethylaminoazobenzene. Me_2β-CD and Me_3β-CD both transported

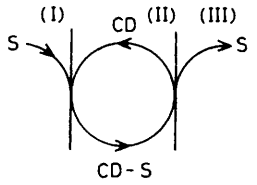

Figure 1. Arrangement of the phases in the liquid membrane system. CD–S: inclusion complex of azobenzene with methylated cyclodextrin.

dimethylaminoazobenzene three times more efficiently than diethylaminoazobenzene. These selectivities are probably caused by differences in the stabilities of the inclusion complexes, which may reflect the sizes and nature of the cavities of the host molecules.

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