Selective Transport of Benzene Derivatives through a Poly(vinyl Chloride) Membrane based on Cyclodextrin Complexation

Jun-ichi Anzai, Yutaka Kobayashi, Akihiko Ueno, and Tetsuo Osa*

Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan

Regio-isomers of nitrophenol, nitroaniline, and iodophenol are transported with high selectivity through a plasticized poly(vinyl chloride) membrane by the use of selective complexation of α-cyclodextrin and the substrate in solution.

Many kinds of cyclodextrin (CD) polymer gels as well as CD-bound silica gels have been developed and used as a stationary phase in liquid chromatography in order to separate and purify aromatic compounds.[1—3] CDs have been used in the mobile phase also.[4] The preparation of CD–immobilized membranes has also been reported.[5,6] In this connection the effect of CD on substrate transport through membranes has been studied by us for *p*-nitroaniline[7] and by Siegel *et al.* for potassium *p*-nitrophenolate.[8] This communication describes some preliminary data on the effective membrane separation of regio-isomers of disubstituted benzenes by use of α-CD complexation in aqueous solution.

A liquid–liquid dialysis method was adopted to study the membrane permeability of substrates at 23 °C using a U-shaped glass cell divided into two compartments by a membrane, the effective membrane area being 2.54 cm^2. A poly(vinyl chloride) (PVC) membrane plasticized with di-isodecyl phthalate (*ca.* 0.1 mm thick) was used.† The substrate and α-CD in H_2O (20 ml) was placed in one arm of the cell (source phase) and the other arm was filled with an equal volume of water (receiving phase). Both compartments of the cell were magnetically stirred at a constant rate. The amount of substrate transported across the membrane was monitored by h.p.l.c.

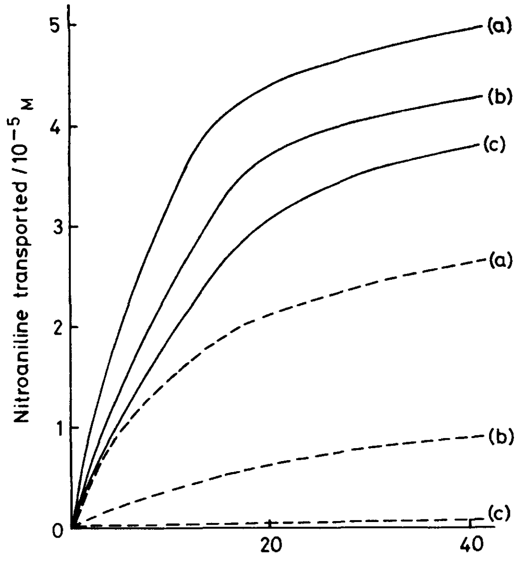

Figure 1. Permeation of *o*, *m*, and *p*-NA, (a), (b), and (c) respectively, through a PVC membrane in the presence (----) and absence (———) of 5×10^{-2} M α-CD. Source phase: [*o*-NA] = [*m*-NA] = [*p*-NA] = 1×10^{-4} M in 20 ml water. Receiving phase: 20 ml water.

Figure 1 shows the permeation of *o*-, *m*-, and *p*-nitroaniline (*o*-, *m*, and *p*-NA) through the membrane in the presence and absence of α-CD. It can be seen that, in the absence of α-CD, NA isomers permeate through the membrane according to their concentration gradient. Permselectivity among the isomers was low, the concentration ratio of *o*-NA : *m*-NA : *p*-NA in the receiving phase being 1.4 : 1.2 : 1.0 after 23 h. In contrast, the *o*-NA : *m*-NA : *p*-NA ratio in the receiving phase after 23 h was 44 : 14 : 1.0 in the presence of 5×10^{-2} M α-CD in the source phase. An important feature in the permeation of NA isomers in the presence of α-CD is the severely suppressed permeation of *p*-NA. Although α-CD addition reduced the permeation efficiency of *o*-NA and *m*-NA also, the effects were rather small. These observations suggest that the selective permeation of NA isomers in the presence of α-CD originates from selective complex formation between α-CD and substrate in the source aqueous phase. It seems reasonable that CD-bound NA and CD itself can not dissolve into the hydrophobic membrane phase because of their hydrophilic nature. In fact, based on sulphuric acid–phenol colorimetry,[9] we can detect no CD in the receiving phase at the end of the permeability measurements. In other words NA isomers permeate through the membrane only when they are in the uncomplexed form. These considerations are consistent with the fact that the complex formation constants of α-CD for the NA isomers lie in the order *p*-NA>*m*-NA>*o*-NA.[10]

Table 1 lists the results obtained with *o*-, *m*-, and *p*-isomers of nitrophenol (NP), iodophenol (IP), as well as with NA. Permeation behaviour of NP isomers in the presence of α-CD resembles that of NA. More noticeable is the highly selective permeation of *o*-IP over the *m*- and *p*-isomers. This means that one can separate *o*-IP in a reasonably pure form from a 1 : 1 mixture of *o*-IP : *m*-IP or *o*-IP : *p*-IP by use of the present α-CD–PVC membrane system. This method may be applic-

Table 1. Selective permeation of nitrophenols, nitroanilines, and iodophenols in the presence of 5×10^{-2} M α-CD.[a]

	10^6[Substrate]/M in the receiving phase after 23 h		
Substrate	*o*-	*m*-	*p*-
NP	23	2.7	0.7
NA	22	7.0	0.5
IP[b]	6.9	<0.3	
IP[b]	7.4		<0.3

[a] Initial conditions of the permeation were the same as those in Figure 1. [b] *o*-IP–*m*-IP and *o*-IP–*p*-IP mixtures were used because of the difficulty in simultaneous determination of *m*-IP and *p*-IP by h.p.l.c.

---

† The membrane contains PVC, di-isodecyl phthalate: 34.5, 65.5 wt%, respectively.

able to the separation and purification of various kinds of regio-isomers.

Received, 2nd April 1985; Com. 446

References

1 M. Tanaka, Y. Mizobuchi, T. Sonoda, and T. Shono, *Anal. Lett., Part A*, 1981, **14**, 281.
2 K. Matsunaga, M. Imanaka, T. Ishida, and T. Oda, *Anal. Chem.*, 1984, **56**, 1980.
3 W. L. Hinze, T. E. Riehl, D. W. Armstrong, W. DeMond, A. Alak, and T. Ward, *Anal. Chem.*, 1985, **57**, 237.
4 W. L. Hinze, *Sep. Purif. Methods*, 1981, **10**, 159.
5 C. H. Lee, *J. Appl. Polym. Sci.*, 1981, **26**, 489.
6 H. Hirai, M. Komiyama, and H. Yamamoto, Extended Abstracts of The 2nd International Symposium on Cyclodextrin, Tokyo, 1984, p. 183.
7 J. Anzai, Y. Kobayashi, A. Ueno, and T. Osa, *Makromol. Chem., Rapid Commun.*, 1984, **5**, 715.
8 B. Siegel, D. Eberlein, D. Rifkin, and K. A. Davis, *J. Am. Chem. Soc.*, 1979, **101**, 775.
9 M. Dubois, K. A. Gilles, J. K. Hamilton, P. A. Rebers, and F. Smith, *Anal. Chem.*, 1956, **28**, 350.
10 Y. Kawaguchi, M. Tanaka, M. Nakae, K. Funazo, and T. Shono, *Anal. Chem.*, 1983, **55**, 1852.