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Novel Cation Transport Behavior of N-Octadecylmonoazacrown Ethers Cooperated with 2,6-Di(t-butyl)-4-nitrophenol

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A new 'double-cycle' mechanism is presented for the N-octadecylmonoazacrown ether mediated cation transport to an acidic receiving phase cooperated with 2,6-di(t-butyl)-4-nitrophenol. The occurrence of the novel process may be attributable to the lower acidity of the phenol and aggregation behavior of the protonated monoazacrown ethers in the membrane phase.

In the past decade much attention has been paid for the study of the structural effect of crown ethers on the cation-transport rate in liquid membrane systems.$^{1)}$ These studies, using inorganic metal salts or metal picrates, were mainly based on the analysis of the cation transported into the receiving phase.$^{2)}$ We previously showed that trisubstituted phenols having two bulky groups at 2,6-positions and pKa value around 6 are good cooperative carriers in the crown ether mediated liquid membrane transport of alkali-metal cations.$^{3)}$ In this paper we report that N-octadecylmonoazacrown ethers cooperated with 2,6-di(t-butyl)-4-nitrophenol can transport cations by a new mechanism, 'double-cycle' mechanism.

The phenol and crown ether compounds were prepared by the published methods.$^{3,4)}$ Their abbreviated names are as follows: 4-nitro-2,6-di(t-butyl)phenol, **HA**; N-octadecylmonoaza-18-crown-6, **C_{18}A18C6**; octadecyloxymethyl-18-crown-6, **C_{18}18C6**; dot'•' means complexation and dash'-' means protonation. Liquid membrane experiments were performed in a double wall vessel with water jacket under the conditions given in Fig. 1 at 25 °C(400 rpm).$^{5)}$ The cation concentration in the receiving phase was determined by atomic absorption spectrometry at 30 min intervals, and the changes of [**HA**] and [$\mathbf{A}^-$] in the membrane phase were followed by UV spectrometric measurements for 3 h.$^{6)}$

As shown in Fig. 2, when neutral water is used as the receiving phase the concentrations of 2,6-di(t-butyl)-4-nitrophenol([**HA**]) and its anionic form([$\mathbf{A}^-$]) reach to a steady state after about 60 min and hereafter the ratio of [$\mathbf{A}^-$]/[**HA**] is nearly constant during the process. The sum of them is almost equal to the initial concentration([**HA**]$_0$), indicating that cations are transported in a proton-coupled process.$^{7)}$ However, when the receiving phase is replaced by 0.01 M HCl **HA** exists in bulk membrane as major component in place of the anion($\mathbf{A}^-$),

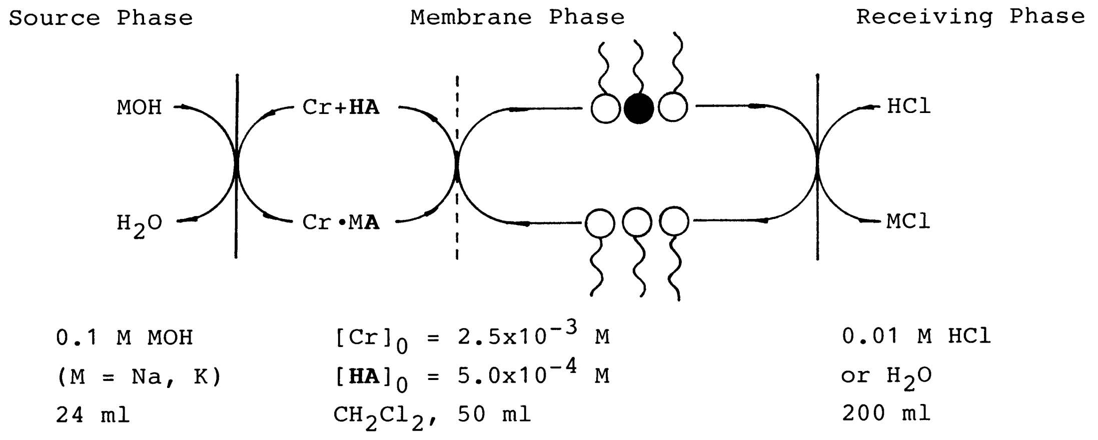

Fig. 1. Liquid membrane system for the 'double-cycle' cation transport, Cr: **C_{18}A18C6**, ○∿∿ : **C_{18}A18C6**-HCl, ●∿∿ : **C_{18}A18C6**·MCl.

and the rate of cation transport increases markedly both for Na$^+$ and K$^+$ ion (Fig. 2 and Table 1). The transport through $CHCl_3$ membrane proceeded also with disappearance of the anion in the bulk membrane phase, although the rate was smaller than that through CH_2Cl_2, probably because of the low extractability of the $CHCl_3/H_2O$ system for the cation crown complex. Since such unusual phenomena are not observed in the **C_{18}18C6**·K$^+$ system(Table 1, Runs 5 and 6), it seems that the counter anion in the bulk membrane phase is chloride ion Cl$^-$ which comes from the hydrochloride of the monoazacrown ether(**C_{18}A18C6**-HCl) in the process. Furthermore, cation was little transported in the absence of the phenol(Table 1, Run 7). These facts lead us to introduce a new mechanism for these transport systems, 'double-cycle' mechanism. As schematically shown in Fig. 1, the new mechanism contains an extra exchange process within the membrane (dash line in Fig. 1) and is very different from those reported before,[1,7] which concerned only with the exchange processes at the two interfaces (solid line in Fig. 1). In the present process the lipophilic anion **A**$^-$ exists only in a thin layer at the source phase-membrane interface. In fact a thin yellow layer could be observed steadily at the source phase-membrane interface for the **HA/C_{18}A18C6**/HCl systems.

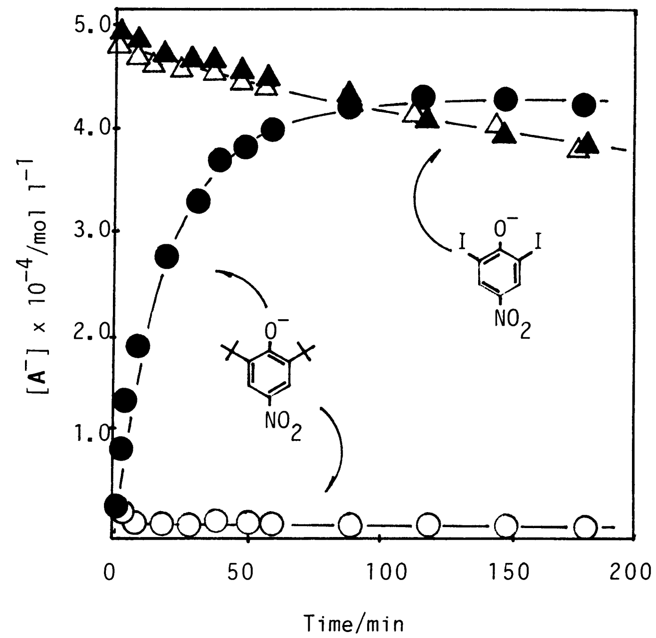

Fig. 2. A time course of [**A**$^-$] in the membrane phase for KOH/**HA**/**C_{18}A18C6** systems. Receiving phase: H_2O ● , ▲ ; 0.01 M HCl ○ , △ .

Table 1. Cation Transport with a Crown Ether/Lipophilic Phenol System

Run	Crown ether	Cation	Receiving phase	$[\mathbf{A}^-]([\mathbf{HA}])$[a]	$[M^+]$[b]	J[c]
1	$\mathbf{C_{18}A18C6}$	Na^+	H_2O	3.5(2.2)	1.9	3.6
2			0.01 M HCl	0.1(4.8)	7.6	15
3		K^+	H_2O	4.2(1.4)	1.5	2.5
4			0.01 M HCl	0.1(4.9)	10	20
5	$\mathbf{C_{18}18C6}$	K^+	H_2O	4.0(1.5)	1.3	2.7
6			0.01 M HCl	4.0(1.7)	2.2	3.8
7[d]	$\mathbf{C_{18}A18C6}$	K^+	0.01 M HCl	-	0.3	0.0
8[e]	$\mathbf{C_{18}A18C6}$	K^+	H_2O	3.7(1.9)	1.1	2.3
9[e]			0.01 M HCl	0.1(4.7)	3.3	5.8
10[f]	$\mathbf{C_{18}A18C6}$	K^+	H_2O	3.8(1.2)	1.1	2.0
11[f]			0.01 M HCl	3.9(1.0)	3.2	6.1

a) $[\mathbf{A}^-]$ and $[\mathbf{HA}]$ in membrane phase at the steady state, 10^{-4} M. b) $[M^+]$ in receiving phase after 3 h, 10^{-4} M. c) Cation flux calculated from the linear increase of $[M^+]$ in receiving phase, 10^{-8} mol cm^{-2} min^{-1}. d) No lipophilic phenol was used. e) $CHCl_3$ was used in membrane phase. f) 2,6-Diiodo-4-nitrophenol was used as the cooperative carrier.

The exchanges at the two interfaces(solid line in Fig. 1) are similar with those in the proton-coupled transport,[7,8] while the exchange within the membrane phase(dotted line) was unexpected and is interesting. The driving force for such a process could be understood as follows. In the presence of excess $\mathbf{C_{18}A18C6}$, HCl in receiving phase can easily enter into the CH_2Cl_2 membrane phase as the hydrochloride and the cation-uptake from the source phase would become the rate determining step in the process. Once the complex $\mathbf{C_{18}A18C6 \cdot MA}$ forms in the membrane phase the counter anion can be neutralized by a stronger acid, $\mathbf{C_{18}A18C6}$-HCl, to give $\mathbf{C_{18}A18C6}\cdot$MCl, since the acidity of **HA**, pKa = 6.6 in 20% aq. dioxane(w/w), is much weaker than that of the hydrochloride, and in fact the phenol **HA** could not protonate the monoazacrown ether in CH_2Cl_2. The explanation is supported by the fact that such an exchange of the anion could not be observed when a stronger acid, 2,6-diiodo-4-nitrophenol whose acidity and lipophilicity are very close to picric acid,[9] was used as the cooperative carrier(see Fig. 1 and Table 1, Runs 10 and 11). In the latter the increase in transport rate could be explained by the proton-driven process at the cation-release step as reported by Okahara et al.[10] The exchange within the membrane can be written as $\mathbf{C_{18}A18C6 \cdot MA}$ + $\mathbf{C_{18}A18C6}$-HCl $\longrightarrow$ $\mathbf{C_{18}A18C6}\cdot$MCl + $\mathbf{C_{18}A18C6}$ + **HA**. So that for the 'double-cycle' process the monoazacrown ether acts as a free form and/or its **HA** complex in the cation-uptake step in place of its protonated form for the ordinary proton-driven process. The change of the working specie and the existence of the facile exchange would lead to the large increase in the rate of cation transport observed here.

Another factor may also favor the exchange and the existence of $\mathbf{C_{18}A18C6}\cdot$MCl in CH_2Cl_2 membrane phase. We think that there is a reversed-micelle like aggregate of **C_{18}A18C6**-HCl and **C_{18}A18C6**·MCl in the process since the exchange did not occur when N-heptylmonoazacrown ethers are used, although the crown leaked heavily into the aqueous phase. This assumption is also supported by the effect of acid in the receiving phase on the transport. For the **HA/C_{18}A18C6**/HCl systems the organic membrane phase turned cloudy soon after stirring began. However, when HNO_3 was used the membrane phase was transparent, while the membrane phase became emulsified completely when H_2SO_4 was used. The transport rates for both systems are lower than that of the **HA/C_{18}A18C6**/HCl system. It is very difficult to reproduce the membrane phase under the transport conditions in other measurements, but for a simple system, **C_{18}A18C6**-HCl in $CDCl_3$, a preliminary ^1H NMR study showed evidence which suggests the formation of the aggregate,$^{11)}$ and further studies about the novel transport behavior are now in progress.

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