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THE COOPERATIVE CARRIERS COMPOSED OF ALKANOIC ACID AND CROWN ETHER EXHIBITING EXCELLENTLY SELECTIVE Na^+ OR K^+ TRANSPORT

Seiichi INOKUMA, Kazuya YABUSA, and Tsunehiko KUWAMURA*
Department of Chemistry, Faculty of Technology, Gunma University,
Kiryu, Gunma 376

In the presence of higher alkanoic acids, 15-membered crown ethers actively transported Na^+ over Li^+ and K^+ with high selectivity and 18-membered ones exclusively transported K^+ in the chloroform membrane system. The transport ability and ion-selectivity are well corresponding to lipophilicity of the cooperative carrier and the cavity size of the crown ether used, respectively.

Recently, a variety of synthetic ionophores, crown ethers,$^{1)}$ and non-cyclic polyethers$^{2)}$ have been used as liquid membrane transport carriers for cations. The influence of the structure of the crown ether on the transport rate and selectivity was detailedly reported for the passive transport of cation across the chloroform membrane.$^{3)}$ On the other hand, multicarrier containing both an electron carrier and a cation carrier was used in the redox-driven transport of cations.$^{4)}$ But, a previous system of much simpler proton-driven cooperative carrier has not yet been so successful,$^{5)}$ and no synthetic carrier being able to transport exclusively Na^+ or K^+ has been found.

We report here simple systems which perform exceedingly selective and efficient transport of Na^+ or K^+ across a liquid membrane containing cooperative carrier composed of higher alkanoic acid and crown ether.

Reagent grade alkanoic acids and crown ethers were used without further purification. Active transport of alkali metal cation was carried out by using the U-tube apparatus similar to that described by Hiratani,$^{6)}$ at 30 °C under the initial transport conditions shown in Fig. 1. The results are summerized in Table 1.

Active transport of cations with octadecanoic acid has previously been

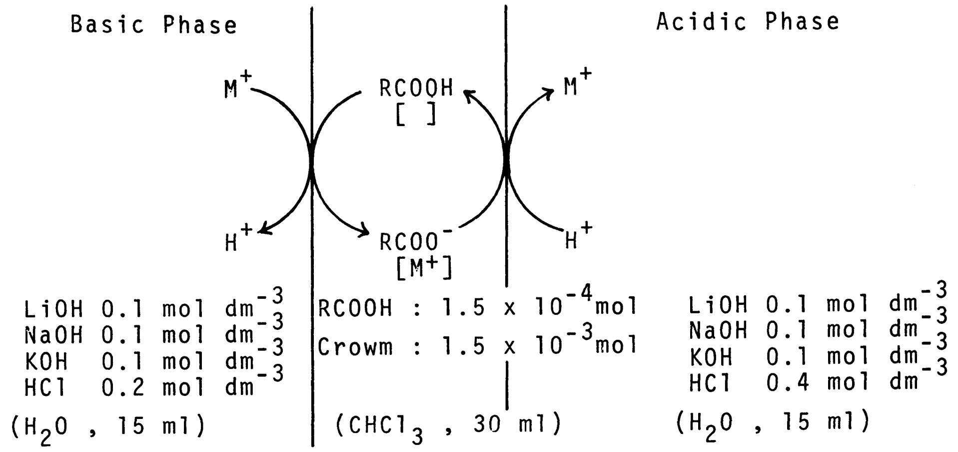

Fig. 1. Liquid membrane system for cation-transport with cooperative carrier. [ ] and $[M^+]$ are crown ether and its M^+-complex.

observed in the pentanol system,$^{7)}$ but, no cation was transported in our chloroform membrane system containing only higher alkanoic acid (Table 1, runs 1 and 2) because of less solubility of its alkali metal salt in chloroform. In addition, dicyclohexano-18-crown-6 also did not transport any cation in the present system (Table 1, run 3), despite this crown ether is well-known to transport actively anion$^{8)}$ and cation$^{4)}$ in some systems different from proton pump. On the other hand, it has been found that the mixtures of higher alkanoic acid and crown ether except for 12-crown-4 transport actively Na^+ and/or K^+ in this proton-driven system. These cooperative carriers exhibited complete exclusion of Li^+ in the competitive transport. Benzo-15-crown-5 and 15-crown-5 with higher alkanoic acid showed Na^+-selectivity over K^+ (Table 1, runs 5-7), and all of the 18-membered crown ethers used with higher alkanoic acid transported K^+ exclusively (Table 1, runs 11-18 and 20-28). These cation-selectivities are in good accord with the fitness of cavity size of the crown ether for incorporating cation.

The rate of K^+-transport depended on two factors, chain length of alkanoic acid and the amount of the crown ether, having an optimum value for the each factor (Table 1, runs 11-16, 20-25, 22, and 26-28). The significance of the soft anion such as picrate, nitrate and thiocyanate anions has been confirmed in both extraction of cation$^{9)}$ and passive$^{3)}$ or active$^{10)}$ cation-transport. The long chain alkanoates also act as a soft and liposoluble counter anion in cation-transport. The lipophilicity increases with increasing alkyl chain length of alkanoate, therefore, the higher acids are favorable to the present active transport. The ternary complexes which formed from cation, alkanoate anion, and crown ether at the basic interface, diffuse across the membrane and release cation at the acidic interface regenerating the carrier (Fig. 1). Thus, the above-mentioned two factors determining the rate of K^+-transport seem to be related hydrophile-lipophile-balance and distribution coefficient of the ternary complexes.

Table 1. Competitive transport of Li^+, Na^+, and K^+

	Cooperative carriers		Transported ions (%)[a]		
Run	Alkanoic acids	Crown ethers	Li^+	Na^+	K^+
1	$C_{11}H_{23}COOH$	-	0	0	0
2	$C_{17}H_{35}COOH$	-	0	0	0
3	-	DC-18-6[b]	0	0	0
4	$C_{11}H_{23}COOH$	12-4[c]	0	0	0
5	$C_{11}H_{23}COOH$	15-5[d]	0	34	11
6	$C_{11}H_{23}COOH$	B-15-5[e]	0	29	4
7	$C_{17}H_{35}COOH$	B-15-5	0	19	6
8	HCOOH	18-6[f]	0	0	0
9	CH_3COOH	18-6	0	0	0
10	C_3H_7COOH	18-6	0	0	0
11	$C_7H_{15}COOH$	18-6	0	0	9
12	$C_9H_{19}COOH$	18-6	0	0	57
13	$C_{11}H_{23}COOH$	18-6	0	0	61
14	$C_{13}H_{27}COOH$	18-6	0	0	61
15	$C_{15}H_{31}COOH$	18-6	0	0	57
16	$C_{17}H_{35}COOH$	18-6	0	0	55
17	$C_{11}H_{23}COOH$	DB-18-6[g]	0	0	67
18	$C_{17}H_{35}COOH$	DB-18-6	0	0	52
19	C_3H_7COOH	DC-18-6	0	0	0
20	$C_7H_{15}COOH$	DC-18-6	0	0	11
21	$C_9H_{19}COOH$	DC-18-6	0	0	48
22	$C_{11}H_{23}COOH$	DC-18-6	0	0	59
23	$C_{13}H_{27}COOH$	DC-18-6	0	0	66
24	$C_{15}H_{31}COOH$	DC-18-6	0	0	49
25	$C_{17}H_{35}COOH$	DC-18-6	0	0	51
26	$C_{11}H_{23}COOH$	DC-18-6[h]	0	0	26
27	$C_{11}H_{23}COOH$	DC-18-6[i]	0	0	54
28	$C_{11}H_{23}COOH$	DC-18-6[j]	0	0	49

a) Atomic absorption and/or flame analyses, after 48 h. Reproducibility, ±10 %. b) Dicyclohexano-18-crown-6. c) 12-Crown-4. d) 15-Crown-5. e) Benzo-15-crown-5. f) 18-Crown-6. g) Dibenzo-18-crown-6. h) Used 1.5×10^{-4} mol. i) Used 7.5×10^{-4} mol. j) Used 3.0×10^{-3} mol.

In conclusion, the present system performed active transport of alkali metal cations with high selectivity and large rate, by use of cooperative carrier composed of commercially available crown ether and higher alkanoic acid.

Further investigation is in progress on synergistic function of the carrier in cation-extraction and on the relationship between the structure of cooperative carrier and selectivity for various cations.

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