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Selective Transport of Potassium Ions against Their Concentration Gradient by Pentaethylene Glycol Derivative Containing Both 8-Quinolyl and *o*-Carboxylphenyl Terminal Groups[1)]

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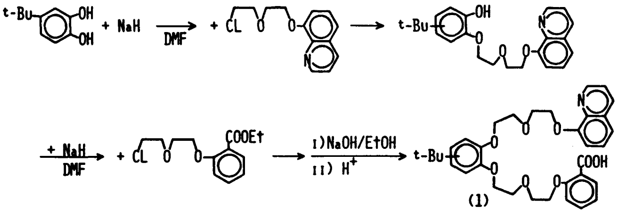
Synopsis. A pentaethylene glycol derivative containing both 8-quinolyl and *o*-carboxylphenyl terminal groups can transport potassium ions selectively against the concentration gradient in liquid membrane systems containing more than one alkali ion species in aqueous solution. Uptake of cations by this synthetic ionophore from the aqueous solution into the organic layer is confirmed to be important for exhibiting this excellent selectivity toward potassium ions.

Some of the noncyclic polyether compounds have been reported to be selective carriers of cations in the liquid membrane system.[2)] The author and coworkers have recently reported that the oligoethylene glycol derivatives containing both basic quinolyl and acidic carboxyl terminal groups exhibit the selective uptake of an alkali ion into chloroform.[3)] They also exhibit the transport of alkali ions against the concentration gradient in the presence of single cation species in the aqueous solution; the properties of complexation and transport are largely dependent on the length of the oxyethylene chain.[4)] In this study the author wishes to report the selective transport of potassium ions in aqueous solutions containing some other alkali ion species through liquid membranes by a synthetic polyether (**1**).

Results and Discussion

The pentaethylene glycol derivative (**1**), in which the 4-*t*-butyl *o*-phenylene group is introduced among the oxyethylene chains, was prepared by the procedure described below. It is a glassy solid (pale yellow): $UV_{max}(CHCl_3)$ 286 nm ($\varepsilon=8300$); IR (neat) 3250 and 2550 (carboxyl OH), 1740—1680 (broad, carboxyl C=O), and 1160—1080 cm^{-1} (ether C–O–C); NMR ($CDCl_3$) $\delta=8.93$ (1H, m, aromatic), 8.15 (1H, m, aromatic), 8.02 (1H, m, aromatic), 7.5—6.8 (10H, m, aromatic), *ca.* 7.5 (1H, broad, COOH), 4.5—3.7 (16H, m, $O-CH_2-CH_2-O$), and 1.28 (9H, s, $C-CH_3$). Found: C, 69.91; H, 6.23; N, 2.54%. Calcd for $C_{34}H_{39}N_1O_8$: C, 69.25; H, 6.67; N, 2.38%.



(1)

Transport of alkali ions across a chloroform liquid membrane by the synthetic ionophore (**1**) was carried out in a previously-described U-type cell[4)] at 25±0.2 °C. The solution was stirred at 200 min^{-1}. The amounts of the metal ion transported from Phase I (an alkaline aqueous solution) to Phase II (an acidic aqueous solution) were determined by atomic absorption analysis for lithium, sodium, and potassium ions, and flame analysis for rubidium and caesium ions.

The experimental results are shown in Figs. 1 and 2. In the control experiment (without ionophore) the ion transport was confirmed to be negligible even after 2 d.[4)] As indicated in Fig. 1,[5)] in the ion transport experiment for the single alkali ion species, the difference of the transport capability of the ionophore (**1**) for each alkali ion seems to be small. Surprisingly, the transport phenomena for the three alkali ion species (Li, Na, and K) existing together, as shown in Fig. 2, are quite different from that in Fig. 1. Under these conditions, potassium ions were selectively transported by **1**, while little transport of lithium ions was detected in Phase II and the amount of sodium ions transported was less than 1/4 of the amount of potassium ions. The ionophore

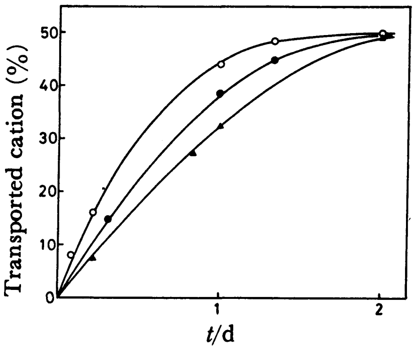


Fig. 1. Ion transport by **1** for single cation species.[5)] Phase I: 15 ml of 0.1 M alkali hydroxide aqueous solution; Phase II: 15 ml of 0.1 M alkali chloride +0.1 M HCl aqueous solution; Phase III: 30 ml of chloroform containing 1.5×10^{-4} mol of **1**.
—○—: K^+, —●—: Na^+, —▲—: Li^+.

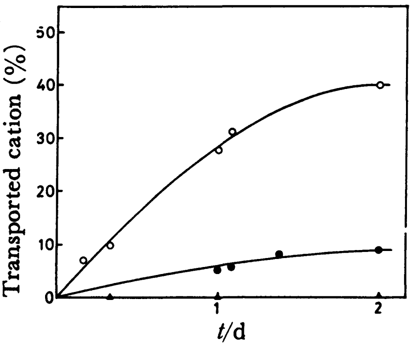


Fig. 2. Ion transport by **1** for lithium, sodium, and potassium ion species existing together. Conditions: see Table 1.
—○—: K^+, —●—: Na^+, —▲—: Li^+.

TABLE 1. ION TRANSPORT BY **1** THROUGH CHLOROFORM MEMBRANE

Coexistent cations	Transported cation after 2 d (%)[d] Li (1.32)	Na (1.90)	K (2.66)	Rb (2.98)	Cs (3.38)	Total	Selectivity for K^+
Li/Na/K (1 : 1 : 1)[a]	≈0	9	40	—	—	49	K/Li≫10 K/Na=4.4
Na/K/Ca (1 : 1 : 1)[b]	—	5	36	—	8	49	K/Na=7.2 K/Cs=4.5
K/Rb (1 : 1)[c]	—	—	33	17	—	50	K/Rb=1.9

a) Phase I: 15 ml of 0.1 M LiOH+0.1 M NaCl+0.1 M KCl aqueous solution; Phase II: 15 ml of 0.1 M LiCl+0.1 M NaCl+0.1 M KCl+0.1 M HCl aqueous solution; Phase III: 30 ml of chloroform containing 1.5×10^{-4} mol of **1**. b) Phase I: 15 ml of 0.1 M NaOH+0.1 M KCl+0.1 M CsCl aqueous solution; Phase II: 15 ml of 0.1 M NaCl+0.1 M KCl+0.1 M CsCl+0.1 M HCl aqueous solution; Phase III: 30 ml of chloroform containing 1.5×10^{-4} mol of **1**. c) Phase I: 15 ml of 0.1 M KOH+0.1 M RbCl aqueous solution; Phase II: 15 ml of 0.1 M KCl +0.1 M RbCl+0.1 M HCl aqueous solution; Phase III: 30 ml of chloroform containing 1.5×10^{-4} mol of **1**. d) The values in parentheses are the ionic diameters (Å) of each cation.

(**1**) also exhibits a large selectivity toward potassium ions both for sodium, potassium, and caesium ions existing together and for potassium and rubidium ions existing together; these latter have almost the same ionic diameter, 2.66 and 2.98 Å respectively (see Table 1).

From Table 1, the order of the cation selectivity of **1** is as follows: $K^+ > Rb^+ > Cs^+ \approx Na^+ > Li^+$. And in every case, the total amounts cations transported reach finally about 50% after two days. It is considered that hydrochloric acid not only is consumed to release the cation transported into Phase II from Phase III (an organic layer), but also reacts with alkali hydroxide in Phase I to give the alkali halide, because hydrochloric acid can be carried as the quinolinium salt of **1** in the reverse direction from Phase II to Phase I across Phase III.[4]

In Table 2 are shown the results of uptake of alkali ions into the organic layer from aqueous solution in the presence of the ionophore (**1**). These results correspond to those of the transport experiment (see Table 1). Thus, it is considered that the step of the uptake of the cation into the chloroform layer from Phase I is important for exhibiting the excellent selectivity with 9 toward potassium ions in these transport experiments. The detailed mechanism of the cation selectivity of **1** is now under investigation.

TABLE 2. EXTRACTION OF ALKALI IONS INTO CHLOROFORM LAYER

a) For single ion species.

Alkali ion species	Li	Na	K	Rb	Cs
Decrease of cation in aq solution (%)	39	43	43	41	41

Initial aqueous layer: 1.0 ml of 0.1 M alkali hydroxide; Organic layer: 0.05 mmol of **1** in 2.0 ml of $CHCl_3$.

b) For multiple ion species.

Alkali ion species	Li	Na	K	Na	K	Cs	K	Rb
Decrease of cation in aq solution (%)	3	7	36	5	32	7	32	17
Composition of cation in 1.0 ml of initial aqueous layer	0.1 M LiOH +0.1 M NaCl +0.1 M KCl			0.1 M NaOH +0.1 M KCl +0.1 M CsCl			0.1 M KOH +0.1 M RbCl	
Organic layer	0.05 mmol of **1** in 2.0 ml of $CHCl_3$							

Experimental

General Procedure of Ion Transport. In the cell was placed 30 ml of chloroform containing 1.5×10^{-4} mol of **1**. The two kinds of aqueous solutions used for Phases I and II were subsequently poured into the appropriate side. The cell was placed in a water bath. The transport of alkali ions was initiated by the addition of the aqueous solutions. At each time point, 50-μl of solution was withdrawn from each phase, and the concentration of cation was adjusted by using a measuring flask and determined by atomic absorption or flame analysis.

Extraction of Alkali Ion with 1 into Chloroform. In a 5-ml microvial, which contained a small stirrer, was placed 2.0 ml of chloroform containing 0.5×10^{-4} mol of **1** and 1.0 ml of an aqueous solution containing one or more alkali ions, as described in Table 2. After the solution was stirred at room temperature for 1 d, the concentration of alkali ions in the upper aqueous solution was determined by atomic absorption or flame analysis.

References

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5) In Fig. 2, only the results in the cases of Li, Na, and K ions are depicted because the five curves for the five cations are too close together; the curves for Rb and Cs ions are located between those for K and for Na ions.