NOTES *Bull. Chem. Soc. Jpn.*, **56**, *2541—2542 (1983)*

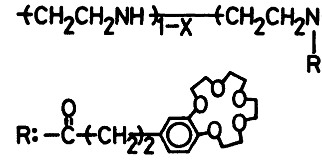
Cation Transport through Liquid Membranes Facilitated by Crown Ether-modified Poly(iminoethylene)s

Jun-ichi Anzai, Yoko Sakata, Yasuhiro Suzuki, Akihiko Ueno, and Tetsuo Osa*
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980

(Received February 24, 1983)

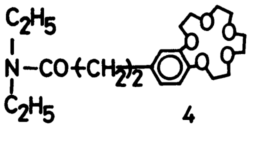
Synopsis. Poly(iminoethylene)s containing benzo-15-crown-5 moieties as pendant groups can transport Rb^+ cation more effectively than the other alkali cations through an organic liquid membrane. The transport selectivities of the polymers diminish drastically with decreasing crown ether content in the polymer chain.

Much effort has been invested in effecting selective transport of alkali cations through artificial liquid membranes using crown-type synthetic carriers.[1—3] A desirable characteristic of crown ethers as cation carriers is their high degree of selectivity. In this connection, it may be interesting to employ polymeric crown ethers as carriers since they are endowed with high selectivities in cation binding.[4] Hence we have prepared crown ether-modified poly(iminoethylene)s (PEI-CR's **1**—**3**) and their monomer model **4** and have recently reported their cation binding properties.[5,6] The purpose of this note is to elucidate their cation transporting properties in liquid membrane systems containing a single cation species in the source aqueous phase. The results are discussed in relation to the crown ether contents in the polymer chain.



$-(CH_2CH_2NH)_{1-X}-(CH_2CH_2\underset{R}{N})_X$

PEI-CR 1 (X=0.68)
PEI-CR 2 (X=0.36)
PEI-CR 3 (X=0.21)



4

Experimental

Materials. The synthetic procedure of **1**—**4** was described previously.[5,6] A commercially available poly(iminoethylene) (PEI) with a molecular weight of 40000—50000 (from Tokyo Kasei) was used. The PEI has a highly branched structure and the ratio of primary, secondary, and tertiary amino groups is about 1 : 2 : 1.

Cation Transport. The transport of alkali cations was performed within a U-shaped glass tube with 17 mm diameter at 23 °C. A 20 ml of dichloromethane (CH_2Cl_2) dissolving one of the carrier compounds was put into the tube as a liquid membrane. A 5 ml of picrate solution was placed in the left arm of the tuve (source phase) and the right arm was filled with the equal volume of water (receiving phase). All three phases were stirred at a constant rate. The amount of metal picrate transported across the membrane was monitored by UV spectroscopy at 354 nm. The plots of the amount of the picrate transported *vs.* time gave good straight lines, from which the transport rates were determined. The amount of cation leakage, estimated from blank experiments, was always less than 1.25×10^{-7} mol dm^{-3} h^{-1}. At the end of the measurement the concentration of alkali picrate in the membrane was determined.

Liquid-Liqud Extraction. Liquid-liquid extractions were carried out employing a H_2O–CH_2Cl_2 system. After good agitation of two layers for 5 min at 23 °C, equilibrium was attained. The detailed procedure of extraction and subsequent analysis has been described elsewhere.[5,6]

Results and Discussion

In order to evaluate the cation binding efficiency and selectivity of **1**—**4**, liquid-liquid extractions were performed. The results are expressed as percentages of extracted picrate salts (Table 1). It is obvious that the polymers **1**—**3** extract the metal picrates more effectively than the monomer model **4**, especially in the cases of K^+ and Rb^+ cations. The selectivity sequence in extracting picrate salts with **1**—**3** is $K^+ > Rb^+ > Cs^+ > Na^+$, while with **4** the sequence is $K^+ > Na^+ > Rb^+ > Cs^+$. These characteristics of polymers in cation binding are believed to arise from the complex formation based on a 1 : 2 cation to crown stoichiometry intramolecularly.[4,6]

The transport rates of alkali cations through CH_2Cl_2 membranes facilitated by **1**—**4** are listed in Table 2

Table 1. Liquid-liquid extraction of alkali cations

Crown ether	Extracted picrate salts (%)			
	Na	K	Rb	Cs
1	30	90	78	39
2	38	88	82	46
3	35	77	76	38
4	8.5	13	4.3	2.1

Aqueous phase: [Picrate salt] = 5×10^{-4} mol dm^{-3}, [Metal hydroxide] = 1×10^{-2} mol dm^{-3}; CH_2Cl_2 phase: [Crown ether] = 1×10^{-3} mol dm^{-3}.

Table 2. Ion transport through CH_2Cl_2 membrane

Crown ether	Transport rate of alkali cations/10^{-6} mol dm^{-3} h^{-1}			
	Na	K	Rb	Cs
1	2.7	11	23	9.4
2	3.9	8.8	19	13
3	9.5	12	18	9.8
4	4.3	7.8	3.2	2.7

Source phase: 2.5×10^{-3} mol dm^{-3} of metal picrate in 5 ml of water; Receiving phase: 5 ml of water; Membrane: 1.25×10^{-4} mol dm^{-3} of crown ether in 20 ml of CH_2Cl_2.

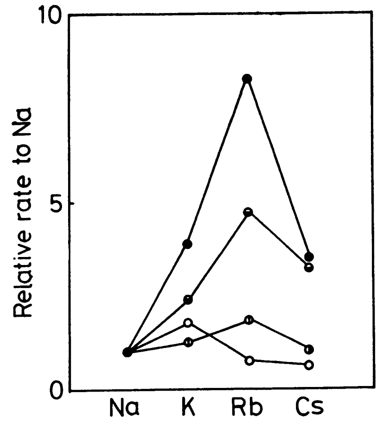


Fig. 1. Transport selectivity of **1**—**4** relative to Na cation.
—●—: **1**, —◒—: **2**, —◐—: **3**, —○—: **4**.

TABLE 3. CATION CONCENTRATION IN MEMBRANE PHASE[a)]

Crown ether	Concentration of alkali cations/10^{-5} mol dm^{-3}			
	Na	K	Rb	Cs
1	2.6	5.0	4.8	3.1
2	3.1	6.7	5.9	5.2
3	5.0	7.2	6.7	5.2
4	0.2	0.4	0.1	<0.1

a) These values were determined at the end of the transport rate measurements reported in Table 2.

and the transport selectivities relative to Na$^+$ cation are illustrated in Fig. 1. Polymers **1**—**3** transport Rb$^+$ cation more effectively than the other cations examined (Rb$^+$>K$^+$$\approx$Cs$^+$>Na$^+$) under our experimental condition. The observed Rb$^+$ selectivity of **1**—**3** in cation transport is apparently incompatible with the data shown in Table 1 suggesting their K$^+$ selectivity. This discrepancy between the transport and extraction selectivities of polymers can interpreted reasonably based on the fact that there is an optimum range in value of the cation–carrier complex stability constant for the maximum cation transport.[7,9] In our case, polymers **1**—**3** can transfer K$^+$ cation more effectively than the other cations from the source phase into the membrane but can not release it rapidly to the receiving phase owing to the high stability of polymer–K$^+$ complexes in the membrane. Alternatively, Rb$^+$ cation, which binds to polymers rather loosely, can be released rapidly at the interface from the membrane to the receiving phase. In the case of **4**, the transport selectivity is in accord with the sequence of the binding selectivity (K$^+$>Na$^+$>Rb$^+$>Cs$^+$). In the case of the relatively low stability complexes such as **4**–cation complexes, the uptake process of cations from the source phase into the membrane seems to determine the overall transport rates. On the contrary, as for the relatively high stability complexes such as the polymer–cation complexes, the overall rates of transport are probably governed by the releasing process. The importance of the rate of release is also suggested from the data of cation concentration in the membrane (Table 3). These data indicate that K$^+$ cation, in all polymer systems, is transported less effectively than Rb$^+$ in spite of higher concentration of K$^+$ in the membrane. As is obvious from the above discussion, a moderately stable complex formation in the membrane is required for the effective transport of cations.

Figure 1 shows that the transport selectivity of **1**—**3** diminishes drastically with decreasing crown ether content in the polymer chains. The Rb$^+$/Na$^+$ selectivities of **1**—**3** are 8.3, 4.7, and 1.8 for **1**, **2**, and **3**, respectively. These remarkable differences in selectivity among the polymers can not be explained only from the extraction data. The unsubstituted amino groups in the polymer backbone, which were shown to bind alkali cations weakly with no selectivity,[6] may participate in the transport process, resulting in the low selectivity of **2** and **3**. Although the reason for the remarkable dependence of the trasport selectivity on the contents of the crown ether moieties in the polymers is not obvious, it should be noted that a high degree of crown ether contents in the polymer chain is an essential requirement for the selective carriers of alkali cations. Thus it appears that PEI-CR's **1**—**3** function as Rb$^+$ selective carriers in liquid membrane systems containing a single cation species in the source aqueous phase.

References

1) C. F. Reusch and E. L. Cussler, *AIChE J.*, **19**, 736 (1973).

2) J. D. Lamb, R. M. Izatt, P. A. Robertson, and J. J. Christensen, *J. Am. Chem. Soc.*, **102**, 2425 (1980).

3) K. Hiratani, *Bull. Chem. Soc. Jpn.*, **55**, 1963 (1982).

4) S. Kopolow, T. W. Hogen Esch, and J. Smid, *Macromolecules*, **4**, 359 (1971).

5) J. Anzai, Y. Sakata, A. Ueno, and T. Osa, *Makromol. Chem. Rapid Commun.*, **3**, 399 (1982).

6) J. Anzai, Y. Sakata, Y. Suzuki, A. Ueno, and T. Osa, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 855 (1983).

7) M. Kirch and J. M. Lehn, *Angew. Chem., Int. Ed. Engl.*, **14**, 555 (1975).

8) Y. Kobuke, K. Hanji, K. Horiguchi, M. Asada, Y. Nakayama, and J. Furukawa, *J. Am. Chem. Soc.*, **98**, 7414 (1976).

9) J. D. Lamb, J. J. Christensen, J. L. Oscarson, J. L. Nielsen, B. W. Asay, and R. M. Izatt, *J. Am. Chem. Soc.*, **102**, 6820 (1980).