Selective Lithium Ion Transport through Hollow-Fiber Membrane Containing Easily-Dissociable 14-Crown-4 Derivative

Hidefumi Sakamoto, Keiichi Kimura, Minoru Tanaka, and Toshiyuki Shono*
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamada-oka, Suita, Osaka 565
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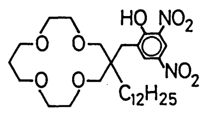
Synopsis. A flow-through transport system was fabricated by using a hollow-fiber impregnated with a 14-crown-4 dinitrophenol solution and was found to allow selective Li^+ transport.

Many attempts to transport alkali metal ions through liquid membranes containing crown ether derivatives as ionophores have been widely made in order to attain an effective separation of a certain metal ion from others. In this kind of liquid membrane system, supported liquid membranes[1–3] containing a crown ether solution using a water-immiscible organic solvent (such as diphenyl ether, *o*-nitrophenyl phenyl ether, and *o*-nitrophenyl octyl ether (NPOE)) may be superior in handling to bulk liquid membranes, and may be employed for industrial applications. In the case of using a hollow-fiber as the support for a liquid membrane,[4] separation of a certain metal ion can be carried out under conditions in which the aqueous solutions of the source and receiving phases flow along either or both sides of the membrane phase. Therefore, such a decrease in the metal ion flux with the ion concentration change in the source phase, as is frequently observed in the conventional membrane transport systems, can be prevented. Since the flux in this flow system is kept constant, a large quantity of the desired cation can be separated from the source phase solution continuously. Alternatively, the transport rate of a certain metal ion may be effectively altered with the ion concentration change in the source phase.

We have synthesized several 14-crown-4 derivatives[5] endowed with a lipophilic chain and a nitrophenol moiety and have employed them as ionophores for proton-driven transport of alkali metal ions using a supported liquid membrane.[2] It was found that Li^+ was transported selectively and enriched in the receiving phase on the proton-driven ion transport. Applications of this Li^+-selective membrane transport system to the corresponding flow-through transport system are useful for effective Li^+ recovery from both spring- and seawater and for the construction of pretreatment systems for selective Li^+ analyses.

In this paper we report on the competitive proton-driven transport of alkali metal ions through a hollow-fiber membrane impregnated with a solution of 14-crown-4 dinitrophenol **1**. The effects of the transport conditions on the ion transportability in this hollow-fiber ion-transport system are also described.

Experimental



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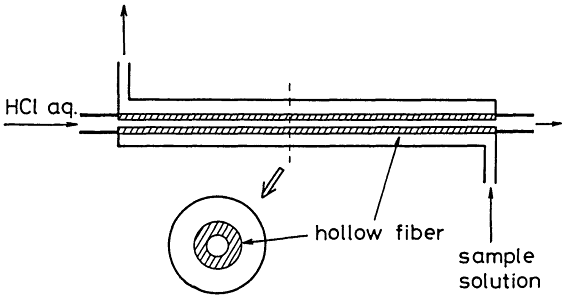

Fig. 1. 14-Crown-4 dinitrophenol **1** and schematic diagram of flow-through transport system.

Competitive transport of alkali metal ions through a hollow-fiber membrane containing 14-crown-4 dinitrophenol **1**, which was prepared according to a previously used procedure,[5] was conducted by using a flow-through transport system (shown schematically in Fig. 1). The inner tube was a hollow fiber (pore size: 0.1 μm, thickness: 0.27 mm, outer diameter: 1.22 mm, inner diameter: 0.68 mm), which was kindly given by Asahi Chemical Industry Co., Ltd. The outer tube was a glass tube (inner diameter: 4.0 mm), both ends of which were joined to the hollow fiber with an epoxy resin adhesive. The hollow fiber was impregnated with a NPOE solution of 14-crown-4 dinitrophenol. Impregnation was performed by slowly flowing a 4×10^{-2} M (1 M=1 mol dm^{-3}) crown ether NPOE solution through the inside of the hollow-fiber membrane. The exposed area in the outer surface of the hollow-fiber membrane was 2.0 cm^2, unless otherwise specified. Aqueous solutions for the source and receiving phases were flowed countercurrently at the inside and outside phases of the hollow-fiber membrane, respectively, at a constant flow rate by using peristaltic pumps. The flow-through transport system was kept at 25 °C by using a thermostated bath during the transport experiment.

For the proton-driven cation transport, the source (outer) phase contained 1.1×10^{-2} M tetramethylammonium hydroxide (TMAOH) and alkali metal ions, and the receiving (inner) phase did 2.0×10^{-3} M hydrochloric acid. The source phase contained alkali metal chlorides (Li^+, Na^+, K^+, Rb^+, Cs^+) of 1.0×10^{-3} M each for competitive transport. Upon examining the dependence of metal ion (Li^+ and Na^+) concentrations on the Li^+ transportability, the source phase contained Li^+ and Na^+ of appropriate concentrations. In competitive cation transport under conditions in which the temperature was changed from 6 to 45 °C, the source phase of the transport system contained Li^+ and Na^+ of 1.0×10^{-3} M each.

The eluted solution of the receiving phase was collected by a fraction collector every fifteen minutes. The alkali metal ions in the receiving aqueous phase were determined by flame photometry. Aliquots (1 ml) of the aqueous phase were occasionally taken; then, ten-fold diluted solutions were subjected to ion determination.

Results and Discussion

Competitive Transport of Alkali Metal Ions. Crown ether **1** is endowed with a 14-crown-4 site, which complexes Li^+ selectively, a dinitrophenol moiety as a proton-dissociable anionic site to counterbalance the positive charge of the complexed cation, and a dodecyl group to have the ionophore stay in the membrane phase. This crown ether, the pK_a of which is 4.92 (in 50% dioxane-H_2O), is able to deprotonate under weakly basic conditions and, thereby, to complex Li^+. It was previously shown that effective Li^+-selective transport was attained by using a U-tube equipped with a supported liquid membrane made from a microporous polypropylene film, which was impregnated with a **1**-NPOE solution. That is to say, at the basic interface the dinitrophenol moiety loses a proton; concurrently the crown ether moiety interacts with a lithium ion and forms an electrically-neutral complex. The crown-Li^+ complex diffuses to the acidic interface through the membrane, where it is forced to release the Li^+ by protonation of the anionic site.

The transport profile of alkali metal ions for a flow-through system with a hollow-fiber membrane containing the crown ether NPOE solution is depicted in Fig. 2. It should be noted that cation transport through the membrane is extremely specific to Li^+ and the Li^+ flux appears to level off within 1 h. The other alkali metal ions, even Na^+ which is quite similar to Li^+ in the chemical property, moved through the membrane only at such low transport rates. The Li^+ concentration in the receiving phase was 4.5×10^{-5} M at a flow rate of 0.19 ml min^{-1} (a linear velocity of 52.3 cm min^{-1} in the inner phase of the hollow fiber). The concentration of metal ion in the receiving phase varied inversely as the flow rate of the receiving phase, while the concentration was independent of the flow rate of the source phase. The metal ion transportability was also proportional to the exposed membrane area and, therefore, the length of hollow fiber.

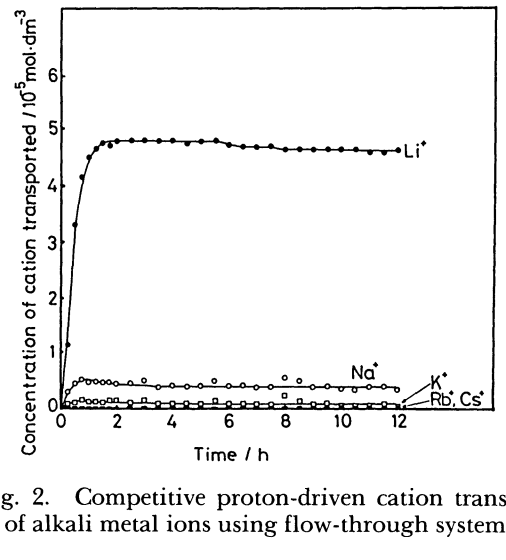

Fig. 2. Competitive proton-driven cation transport of alkali metal ions using flow-through system.

Effects of Transport Conditions. The flux of metal ion transported was directly proportional to the logarithm of the metal ion concentration under conditions in which the Li^+ and Na^+ concentrations in the source phase were varied from 1.0×10^{-5} M to 1.0×10^{-3} M (Fig. 3). The metal ion flux is generally proportional to the cation concentration in the source phase, in the case of a conventional hollow-fiber membrane systems containing ionophores.$^{6)}$ The difference in the concentration dependence on metal ion flux between this system and conventional hollow-fiber membrane systems has not yet been understood.

The concentration of Na^+ which coexists with Li^+ in the source phase is an important factor governing the Li^+ transportability. Competitive transport of Li^+ and Na^+ through the supported hollow-fiber membrane was carried out by varying the Na^+ concentration in the source phase from 1.0×10^{-3} M to 1.0×10^{-1} M and keeping the Li^+ concentration constant (1.0×10^{-3} M). Increasing the Na^+ concentration enhanced the Na^+ transportability and lowered the Li^+ transportability. It is consequently shown in Table 1 that the selectivity ratio of Li^+ over Na^+ hardly changes.

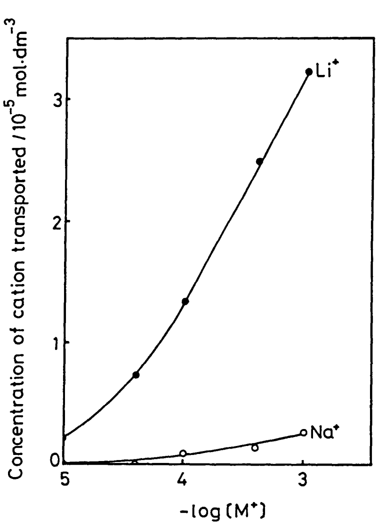

Fig. 3. Effect of cation concentration in source phase on cation transportability.

Table 1. Effect of Na^+ Concentration on Cation Transportability

Cation concentration in source phase (10^{-3}mol dm^{-3})		Concentration of cation transported (10^{-5}mol dm^{-3})		Selectivity ratio
Li^+	Na^+	Li^+	Na^+	Li^+/Na^+
1.0	1.0	3.01	0.10	30
1.0	4.0	2.80	0.32	33
1.0	10.0	2.35	0.83	28
1.0	40.0	1.28	1.98	26
1.0	100.0	0.71	2.62	27

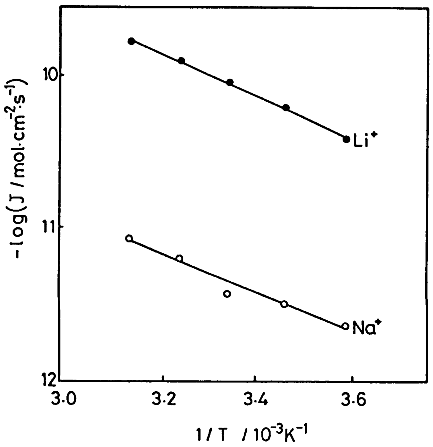

Fig. 4. Arrhenius plots for flux of cation transported.

Permeation coefficients of the metal ions were measured at temperatures ranging from 6 to 45 °C. The Arrhenius plots of Li^+ and Na^+ gave simple straight lines with nearly equal slopes (Fig. 4). If the cation membrane transport were governed only by the cation–crown ether complexation, the transport rates would decrease with a rise in temperature, since the stability of cation–crown ether complexes decreased with temperature.[7,8] It may, therefore, be considered that for a proton-driven cation transport through the hollow-fiber membrane containing **1** the rate-determining step of metal ion transportability is the permeation process of the crown-metal ion complex through the membrane phase.

In conclusion, a hollow-fiber membrane impregnated with a 14-crown-4 dinitrophenol NPOE solution can separate Li^+ efficiently from other alkali metal ions in the flow-through transport system. This supported hollow-fiber membrane was sufficiently stable to permit metal ion transport for 25 h. The present flow-through cation transport system possesses an advantage over a previously-reported batch system in that Li^+ can be separated continuously, although the flow-through system is not superior to the batch system regarding selectivity. Thus, continuity in Li^+ separation seems to allow the present flow-through Li^+ transport system to be applicable to various fields of Li^+ separation and analyses.

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