

Uphill and Selective Transport of Alkali and Alkali Earth Metal Ions through 2,3-Epithiopropyl Methacrylate–2-Acrylamide-2-Methyl Propane Sulfonic Acid Copolymer Membranes

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Synopsis

Cationic exchange membranes were prepared with 2,3-epithiopropyl methacrylate (ETMA)–2-acrylamide-2-methyl propane sulfonic acid (AMPS) copolymers. Transport of alkali and alkali earth metal ions against their concentration gradient through the membranes was investigated by using the system, where one side (L side) of the membrane in a diaphragm cell was acidic and the other (R side) alkaline or neutral, under various conditions. The ETMA–AMPS copolymer membranes transported rapidly alkali and alkali earth metal ions against their concentration gradient even from their neutral salt solution. The transport rate and transport fraction of metal ions were greatly affected by the composition of the copolymer membranes and H^+ concentration in the L side. The transport selectivity between alkali metal ions was affected by the composition of the copolymers and the selectivity between alkali and alkali earth metal ions was affected by initial H^+ concentration in the L side.

INTRODUCTION

In the previous articles^{1–3} we have reported that alkali metal ions could be transported against their concentration gradient through the membranes made of 2,3-epithiopropyl methacrylate (ETMA)–methacrylic acid (MAc) or ETMA–methacryloyloxy ethyl phosphoric acid (MP) copolymer and the irradiation of UV light onto these membranes have not only increased the mechanical strength of membranes but also have greatly affected the transport ability of the membranes for alkali metal ions. This is attributed to the fact that poly (ETMA) was easily crosslinked by UV irradiation. The transport of alkali metal ions through the membranes with sulfonic acid groups have been reported.^{4,5} However, the copolymer membranes containing 2-acrylamide-2-methyl propane sulfonic acid (AMPS) have not been reported.

In this article, the synthesis of ETMA–AMPS copolymer membranes and the uphill and selective transport of alkali and alkali earth metal ions through the membranes, and effect of UV irradiation of the membranes on the transport of metal ions were investigated.

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EXPERIMENTAL

Synthesis of ETMA-AMPS Copolymers

ETMA was prepared by the method reported earlier.⁶ AMPS was provided by Nitto Riken Kogyo Ltd. and it was used without further purification. ETMA-AMPS copolymers with various AMPS contents were prepared by a solution polymerization in *N,N*-dimethylformamide (DMF) using azobisisobutyronitrile as an initiator at 50°C for 16 h. The composition of ETMA-AMPS copolymers was calculated from the nitrogen content of the dried polymers by elemental analysis.

Preparation Method of Membranes

The membranes were made by pouring 4 mL of 5% ETMA-AMPS copolymer DMF solution into a flat laboratory dish (4.8 cm diameter) immediately after polymerization and the solvent was allowed to evaporate at 50°C for the desired time, because the ETMA-AMPS copolymers became insoluble in any organic solvent when it was precipitated in organic solvent and dried once. The membranes prepared were removed from the dish in water. The thickness of dried membranes was about 60 μm . In the case of studying the effect of UV irradiation of the membranes on the transport of Li^+ , the membranes were irradiated as follows: After drying the membrane in the dark, the membranes were placed parallel to the lamp and irradiated at a distance of 10 cm from UV light (< 300 nm) at room temperature for the desired time in air. The 6-W low pressure mercury lamp (270 \times 15 mm ϕ) (Ushio OLO 6AB6) was used as a light source for the photocrosslinking of the copolymers.

Apparatus and Measurement

Transport experiment was carried out at 30°C under magnetic stirring, using a diaphragm glass cell (22 cm³) consisting of two detachable parts. The membrane was set in the middle of the two parts of the cell, which was clamped and sealed tightly with silicon rubber packing. The effective membrane area in the cell was 3.14 cm². The concentration of metal ions in both left and right cells was determined by flame emission spectroscopy. The pH of the solution was measured with a pH meter (Model HM-20, TOA Electronics Ltd.). The electronic potential difference between the right side and left side of the membrane in a diaphragm cell was measured by an electrometer HE-104 (Hokuto Denko Ltd.) with two reference electrodes HS-907 (TOA Electronics Ltd.).

The maximum transport fraction and initial transport rate were defined as follows:

$$\text{the maximum transport fraction (\%)} = \frac{C_{\text{max}} - C_{\text{L0}}}{C_{\text{R0}}} \quad (1)$$

where C_{max} , C_{L0} , and C_{R0} are the maximum concentration of alkali metal ion in the L side, the initial concentration of metal ion in the L side, and the initial ion concentration in the R side, respectively;

$$\text{transport rate (mmol h}^{-1} \text{ cm}^{-2}) = \frac{m_t - m_0}{t \times s} \quad (2)$$

where m_t , m_0 , t , and s are the amount (mmol) of metal ion in the L side after t hours at the initial stage, initial amount of metal ion in the L side, the transport time (h), and the effective membrane area (cm^2), respectively.

Measurement of Cation Exchange Capacity of the Membranes

The dried copolymer membrane (0.25 g) was placed in a 100 cm^3 glass stoppered Erlenmeyer flask. Then 50 cm^3 of $0.1 \text{ mol dm}^{-3} \text{ NaOH}$ – $1 \text{ mol dm}^{-3} \text{ NaCl}$ solution was poured in the flask. The mixture was shaken at 30°C for 48 h. The cation exchange capacity was determined by titrating the concentration of NaOH in the supernatant with a $0.1 \text{ mol dm}^{-3} \text{ HCl}$ solution.

Measurement of Water Content and the Swelling Ratio of the Membrane

Water content of the membrane was calculated by use of the following equation:

water content (%)

$$= \frac{\text{wt wet membrane (g)} - \text{wt dry membrane (g)}}{\text{wt dry membrane (g)}} \times 100 \quad (3)$$

The wet membrane was prepared by immersing dry membrane into deionized water for 24 h at room temperature, followed by wiping water on the surface of the membrane with filter paper and then the membrane was weighed.

The membrane was immersed in a deionized water for 24 h and the swelling ratio of the membrane was calculated as follows:

$$\text{swelling ratio} = v'/v \quad (4)$$

where v and v' are the volume of dry and wet membrane, respectively.

RESULTS AND DISCUSSION

Synthesis of ETMA–AMPS Copolymers with Various AMPS Contents

The synthesized ETMA–AMPS copolymers with various AMPS contents are listed in Table I. The former and latter numbers in the abbreviation of the membrane such as E8A2 and E7A3 in Table I represent the weight ratio of ETMA and AMPS in the feed before copolymerization, respectively.

All these copolymers became insoluble in any organic solvent after they were once dried. The properties of the ETMA–AMPS copolymer membranes are also shown in Table I. The cation exchange capacity, water content, and swelling ratio increased with increasing content of AMPS in the copolymer membranes.

TABLE I
Characterization of (ETMA-AMPS) Copolymer Membranes with Various AMPS Contents

Abbreviation of copolymer	Feed				ETMA/AMPS in copolymer (mol ratio)	Cation exchange capacity (meq/g)	Water ^a content (%)	Swelling ^b ratio
	ETMA (g)	AMPS (g)	ETMA/AMPS (mol ratio)	DMF (cm ³)				
E8A2	1.6	0.4	84/16	20	85/15	1.1	11	1.0
E7.5A2.5	1.5	0.5	80/20	20	79/21	1.7	12	1.2
E7A3	1.4	0.6	75/75	20	74/26	1.8	20	1.2
E6.5A3.5	1.3	0.7	71/29	20	66/34	2.3	24	1.4
E6A4	1.2	0.8	66/34	20	58/42	2.5	36	1.5
E5.5A4.5	1.1	0.9	62/38	20	52/48	3.1	62	2.1

^a {[wt wet membrane (g)] - [wt dry membrane (g)]} / wt dry membrane (g) × 100.

^b [vol wet membrane (cm³)] / [vol dry membrane (cm³)].

Uphill Transport of Li⁺

The transport of Li⁺ through the copolymer membranes with various AMPS contents was carried out by use of the system having 0.05 mol dm⁻³ HCl (L side) and 0.05 mol dm⁻³ LiOH (R side) (Fig. 1).

In all membranes studied Li⁺ was transported against its concentration gradient through the membranes. We call this phenomenon uphill transport of Li⁺.

As shown in Figure 1, E8A2 membrane transported Li⁺ very slowly and the initial transport rate and maximum transport fraction of Li⁺ increased with increasing AMPS content in the membranes up to E7A3 membrane. In the case of E6.5A3.5, E6A4, and E5.5A4.5 membranes with above 34 mol % of AMPS, Li⁺ concentration in the L side began to decrease after 3 or 8 h. In the case of the E6A4 and E5.5A4.5 membranes, the maximum Li⁺ concentration

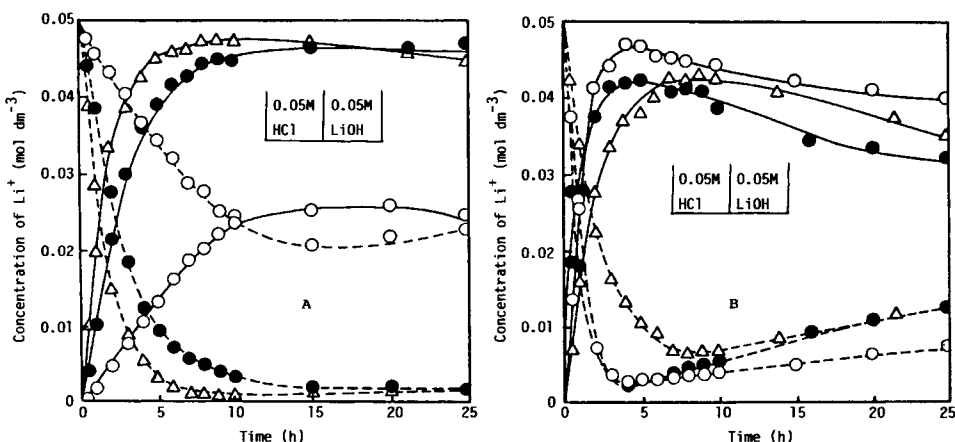


Fig. 1. Transport of Li⁺ through the membranes consisting of various compositions. Membrane in (A): (○) E8A2; (●) E7.5A2.5; (△) E7A3. Membrane in (B): (○) E6.5A3.5; (●) E6A4; (△) E5.5A4.5; (—) L side; (---) R side.

in the L side did not exceed $0.043 \text{ mol dm}^{-3}$ and the transport rate decreased with increasing AMPS content in the membranes. This is due to the reverse diffusion of transported Li^+ from the L side to R side caused by the concentration gradient of Li^+ owing to the high swelling of the membranes. Thus it was found that the composition of the membranes greatly affected the transport of Li^+ through the membranes.

The transport of Li^+ through the ETMA-AMPS copolymer membranes with various compositions was also studied by using the system containing $0.025 \text{ mol dm}^{-3}$ HCl and $0.025 \text{ mol dm}^{-3}$ LiCl (L side) and $0.025 \text{ mol dm}^{-3}$ LiOH (R side) (Fig. 2). Figure 2 also shows the change in concentration of Cl^- , H^+ , and electric potential difference. The E7A3 membranes transported Li^+ most rapidly and the maximum transport fraction was obtained by using the membrane. In all membranes, the Li^+ concentration in the L side decreased gradually after it reached the maximum. Especially, in the case of E6.5T3.5 membrane, the Li^+ concentration in the L side decreased most rapidly after 4 h. It is considered that this phenomenon was brought about by the reverse diffusion of transported Li^+ from the L side to R side caused by the concentration gradient owing to the high swelling of the membrane. The order of transport rate of Cl^- is inversely proportional to that of Li^+ [Fig. 2(B)]. The pH of the R side decreased most rapidly when the E6.5A3.5 membrane was used. This indicates

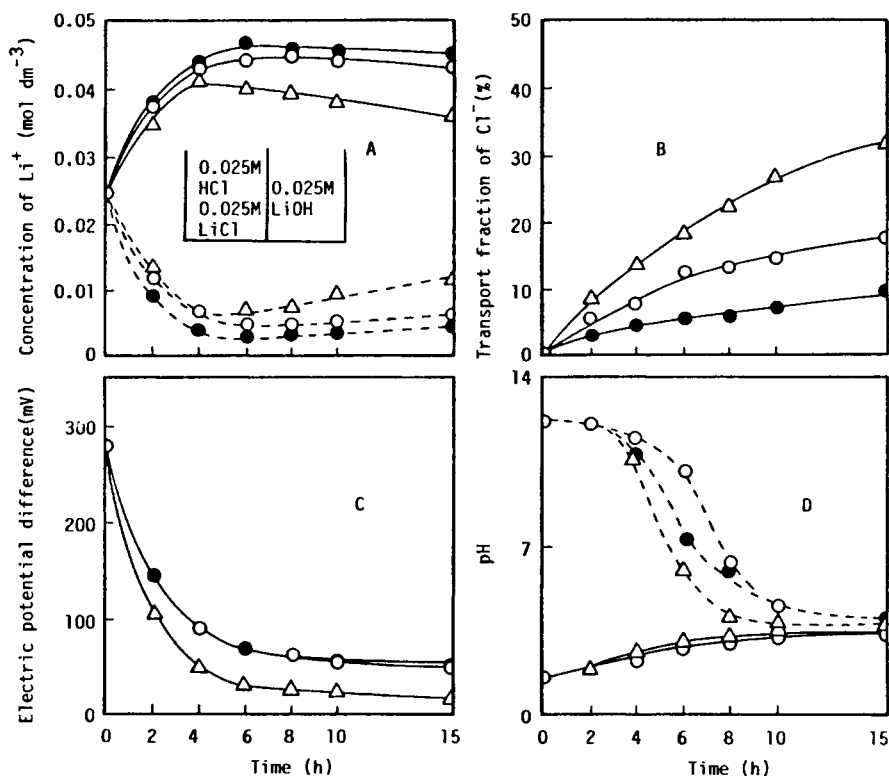


Fig. 2. Change in concentration of Li^+ , Cl^- , H^+ , and in electric potential difference through the membranes: (O) E7.5A2.5; (●) E7A3; (Δ) E6.5A3.5. In (A) and (B): (—) L side; (---) R side.

that H^+ and Cl^- diffuse more easily across the E6.5A3.5 membrane than other membranes because of higher swelling of the membranes. The electric potential difference in Fig. 2(C) was expressed in electric potential of the R side to that of the L side. That is, the positive value indicates that the electric potential in the R side is higher than that in the L side. Li^+ can be transported from the R side with higher electric potential to the L side with lower electric potential and the electric potential difference decreased rapidly as Li^+ in the R side was transported to the L side. Furthermore, it was found that the reverse diffusion of Li^+ transported occurred after the electric potential difference became small.

Effect of H^+ Concentration in the L Side on the Transport of Li^+

The transport of Li^+ through the E7A3 membrane was measured by varying the H^+ concentration in the L side [Fig. 3(A)]. The initial concentration of

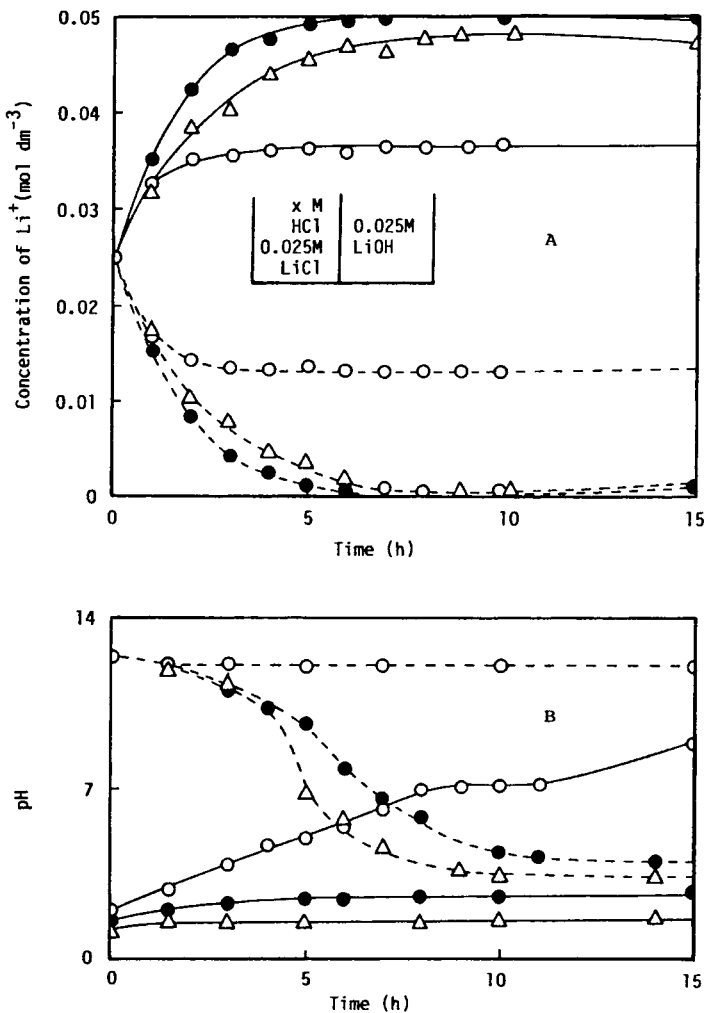


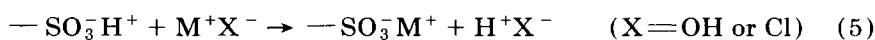
Fig. 3. Change in concentration of Li^+ and in pH on both sides. Membrane, E7A3; H^+ concentration (mol dm^{-3}): (O) 0.01; (●) 0.025; (Δ) 0.05; (—) L side; (---) R side.

lithium hydroxide in the R side kept constant at $0.025 \text{ mol dm}^{-3}$ and that of hydrochloric acid in the L side was changed from 0.01 to 0.05 mol dm^{-3} . The pH change in both sides was also measured [Fig. 3(B)]. The maximum transport rate and transport fraction were obtained by using $0.025 \text{ mol dm}^{-3}$ HCl. In this case, almost 100% of Li^+ in the R side was transported to the L side against its concentration gradient. When $0.050 \text{ mol dm}^{-3}$ HCl was used, the transport rate and transport fraction became lower than those in the case of using $0.025 \text{ mol dm}^{-3}$ HCl. This decrease in transport rate is attributed to the diffusion of H^+ from the L side to the R side owing to the high H^+ concentration gradient. This was confirmed by a rapid decrease in pH in the R side [Fig. 3(B)]. The pH of the both side became below 7 after about 7 h, when the same concentration of acid as that of alkali was used. This indicates that pH of both sides depends on not only the initial concentration of HCl and NaOH in the L and R side but also the amount of sulfonic acid groups in the membrane which contact an aqueous solution. When 0.01 mol dm^{-3} HCl was used, the low transport fraction was obtained, and the pH in the L side became more than 7 after 8 h. This indicates that OH^- diffused across the membrane owing to its concentration gradient because the initial H^+ concentration is smaller than that of OH^- in the R side.

In the previous article,¹ we have reported that Li^+ could not be transported through the ETMA-MAc copolymer membranes from a neutral solution containing LiCl. So the transport of Li^+ from a neutral solution containing LiCl through the E6.5A3.5 membrane with strong acid groups was investigated by using the system containing various concentrations of $x \text{ mol dm}^{-3}$ HCl (L side) and 0.05 mol dm^{-3} LiCl (R side). The concentration of H^+ in the L side was changed from 0.05 to 0.50 mol dm^{-3} . The results on the system by using 0.5 and 0.05 mol dm^{-3} HCl are shown in Figure 4. The transport rate and transport fraction increased with increasing H^+ concentration. When above 0.1 mol dm^{-3} HCl was used, Li^+ was transported from the R side to L side against its concentration gradient. Thus, it was found that the ETMA-AMPS membranes having sulfonic acid groups were able to transport Li^+ from the R side to the L side even from the neutral LiCl solution. This is attributed to the fact that the sulfonic acid groups of the membranes can ion-exchange even in a neutral salt solution.

The electric potential differences were also shown in Figure 4. In these systems, the electric potential of the R side is higher than that in the L side, the electric potential difference in the system by using 0.5 mol dm^{-3} HCl is higher than that in the system by using 0.05 mol dm^{-3} HCl, the electric potential difference decreased with time, and they became about 20 mV and almost 0 mV after 10 h in the respective system.

From the above results, tentative mechanism of the transport of alkali metal ion (M^+) through the membrane in the system when one side was acid (L side) and the other side alkaline or neutral (R side) is shown in Figure 5. On the alkaline or neutral side metal ions were incorporated into the membrane by the ion exchange reaction



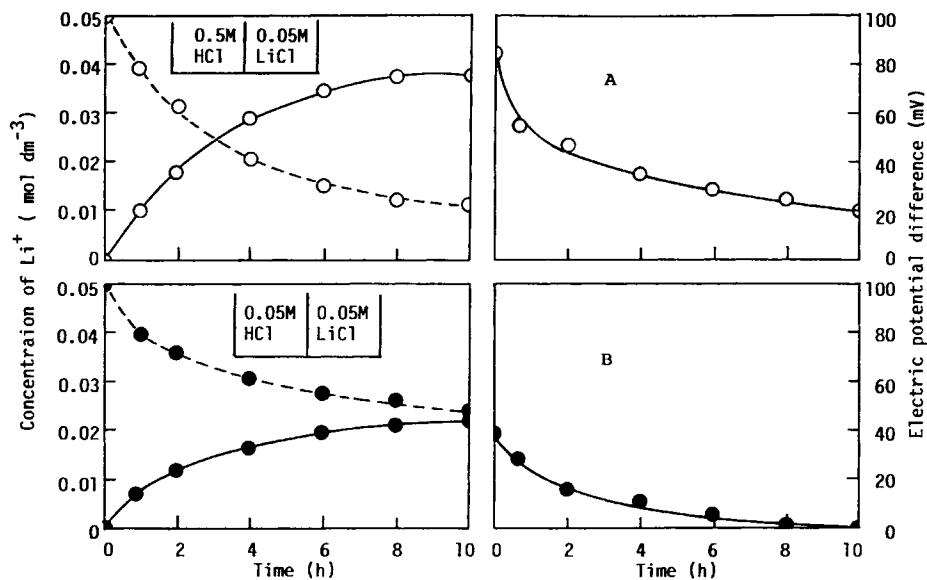


Fig. 4. Change in concentration of Li^+ on the two sides of the membranes and electric potential difference between the L side and R side. Membrane E6.5A3.5. Left: change in concentration of Li^+ , (—) L side; (---) R side. Right: electric potential difference, initial H^+ concentration in the L side (mol dm^{-3}): (A) 0.50; (B) 0.05.

On the other hand, H^+ ions could be transported through the membrane from the L side to the R side by a proton-jump mechanism.⁷ Uragami et al. have reported that H^+ ion was migrated very fast through the membranes by a proton-jump mechanism when alkali metal ions were transported through water-insoluble poly(styrene sulfonic acid) membrane in the system when one side was acid and other side alkaline.⁴

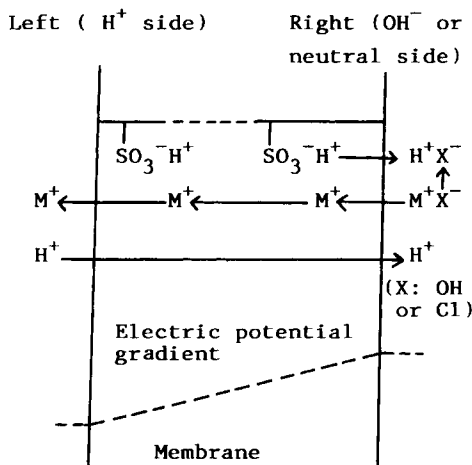
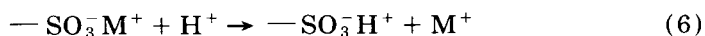


Fig. 5. Tentative mechanism of the transport of alkali metal ions through the ETMA AMPS copolymer membrane.

When such H^+ ions reached the region where the metal sulfonate was formed, metal ions were released by the ion exchange reaction



The metal ions released were transported to the acidic side by the electric potential gradient through the membrane. As a result, alkali metal ions were transported from the R side to the L side and H^+ ions were oppositely to alkali metal ions. Figures 2 and 4 show that Li^+ transported more rapidly in the system with higher electric potential difference than in that with lower electric potential difference. From these results, it is considered that the main driving force for transport of metal ions is the electric potential difference.

Selective Transport of Alkali Metal Ions through the ETMA-AMPS Copolymer Membranes

In the previous articles,^{1,2} we have reported that the transport selectivity between alkali metal ions could be increased by using UV-irradiated ETMA-MAc copolymer membranes and the selectivity increased with increasing irradiation time up to 2–3 h, although the transport rate of alkali metal ions decreased with increasing time of UV irradiation.

The selective transport of alkali metal ions was investigated by use of the E6.5A3.5 membranes UV-nonirradiated and UV-irradiated for 16 h. The L side was 0.05 mol dm⁻³ HCl solution and the R side was a solution containing two kinds of alkali metal ions of 0.025 mol dm⁻³ each (Fig. 6).

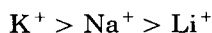
The transport selectivity of metal ions through the membrane was calculated from the following equation:

$$\text{transport selectivity} = \frac{M_{1t}^+/M_{10}^+}{M_{2t}^+/M_{20}^+} \quad (7)$$

where M_{1t}^+ and M_{2t}^+ are the concentration of each metal ion in the L side after t hours and M_{10}^+ and M_{20}^+ are the initial concentration of each metal ion in the R side.

Figure 6 (A) shows the selective transport of Na^+ and Li^+ . In the early stage, Na^+ was transported more rapidly than Li^+ . The selective transport of K^+/Li^+ and K^+/Na^+ was also measured. The selectivities calculated from the concentration of each ion after 1 h were 1.41, 1.23, and 1.19 for K^+/Li^+ , K^+/Na^+ , and Na^+/Li^+ , respectively (Table II).

From these results, it was found that the transport rate of alkali metal ions from the alkali side to the acidic side through the membranes is given in the following order:



It is known that alkali metal ions are hydrated in an aqueous solution and the order of the size of these hydrated ions is as follows:

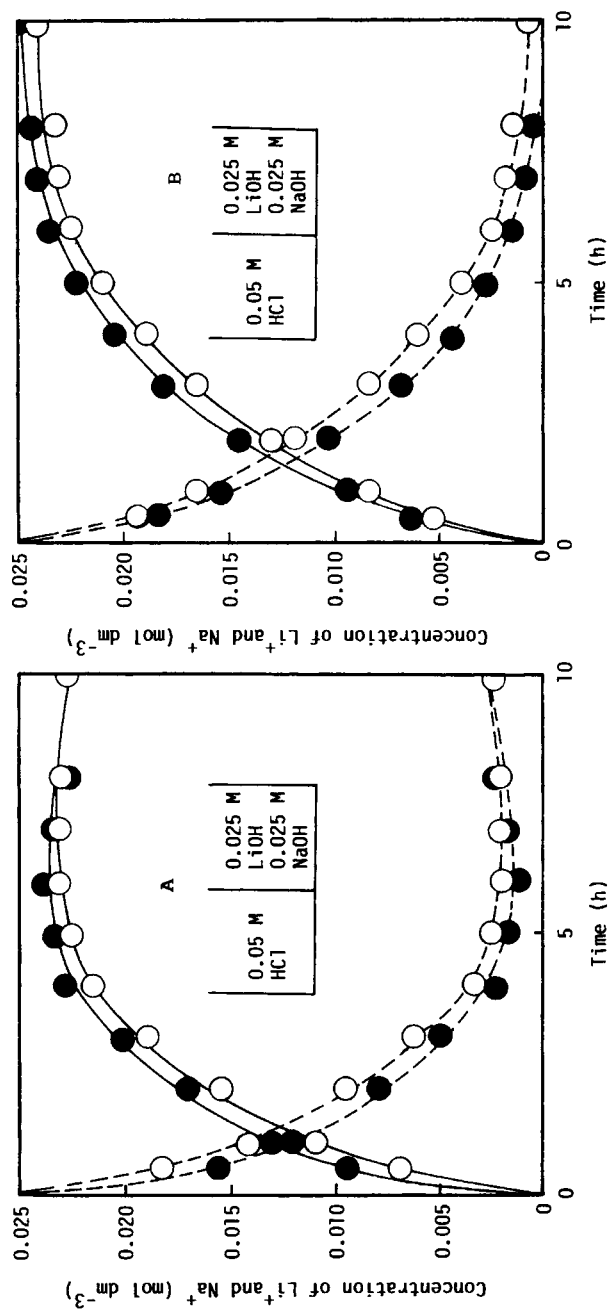


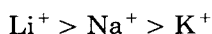
Fig. 6. Change in concentration of Na^+ and Li^+ on the two sides of the membrane. Membrane: (A) E6.5A3.5 nonirradiated; (B) E6.5A3.5 UV-irradiated for 16 h. (●) Na^+ ; (○) Li^+ ; (—) L side; (---) R side.

TABLE II
The Transport Rate, Transport Fraction, and Selectivity of Alkali Metal Ions^a

	Transport rate ($\times 10^2$ mmol h ⁻¹ cm ⁻²)				Transport fraction (%)			Selectivity (M ₁ ⁺ /M ₂ ⁺)	
K ⁺ /Li ⁺	K ⁺	8.41	Li ⁺	6.24	K ⁺	89	Li ⁺	88	1.41
K ⁺ /Na ⁺	K ⁺	8.90	Na ⁺	7.57	K ⁺	88	Na ⁺	88	1.23
Na ⁺ /Li ⁺	Na ⁺	9.04	Li ⁺	7.64	Na ⁺	89	Li ⁺	84	1.19
Na ⁺ /Li ⁺ ^b	Na ⁺	6.66	Li ⁺	5.96	Na ⁺	98	Li ⁺	94	1.22

^a Membrane E6.5A3.5.

^b UV-irradiated for 16 h.



Accordingly the order of transport rate is inversely proportional to the size of the hydrated ions.

The initial transport rate of Li⁺ and Na⁺ through the membrane UV-irradiated became smaller than that through the membrane UV-nonirradiated as shown in Table II. However, the maximum transport fraction increased by using the UV-irradiated membrane. Figure 6(B) and Table II show the almost 100% of Na⁺ could be transported from the R side to the L side after 10 h.

The transport selectivity of Na⁺/Li⁺ through the UV-irradiated membrane calculated by the above method was 1.22 (Table II). Thus the selectivity was hardly changed by using the UV-irradiated membrane, although the transport rate decreased and the transport fraction increased.

These results indicate that the membranes became dense due to the photocrosslinking by UV irradiation and it became difficult for metal ions to permeate through the irradiated membranes. The increase in the transport fraction is attributed to the fact that alkali metal ions transported can hardly diffuse reversely from L side to the R side due to the concentration gradient because of the dense membrane.

Effect of Composition of the Membrane on the Transport Selectivity of K⁺/Li⁺

The effect of the composition of the membranes on the selective transport of K⁺ and Li⁺ was studied by using the various ETMA-AMPS copolymer membranes with different compositions (Fig. 7). The system contained 0.05 mol dm⁻³ HCl (L side) and 0.025 mol dm⁻³ LiOH-0.025 mol dm⁻³ KOH (R side). The transport selectivity was calculated by eq. (7), where M_{1t}⁺ and M_{2t}⁺ are the concentrations of each alkali metal ion in the L side at the time when the concentration of alkali metal ion which was transported faster became the same on both sides. The transport selectivity of K⁺/Li⁺ through the E8A2, E7.5A2.5, E7A3, and E6.5A3.5 membranes were 1.81, 1.39, 1.28, and 1.30, respectively.

Thus the transport selectivity has a tendency to increase with decreasing AMPS content in the membrane, although the transport rate of alkali metal ion decreased with increasing AMPS content in the membranes. This is at-

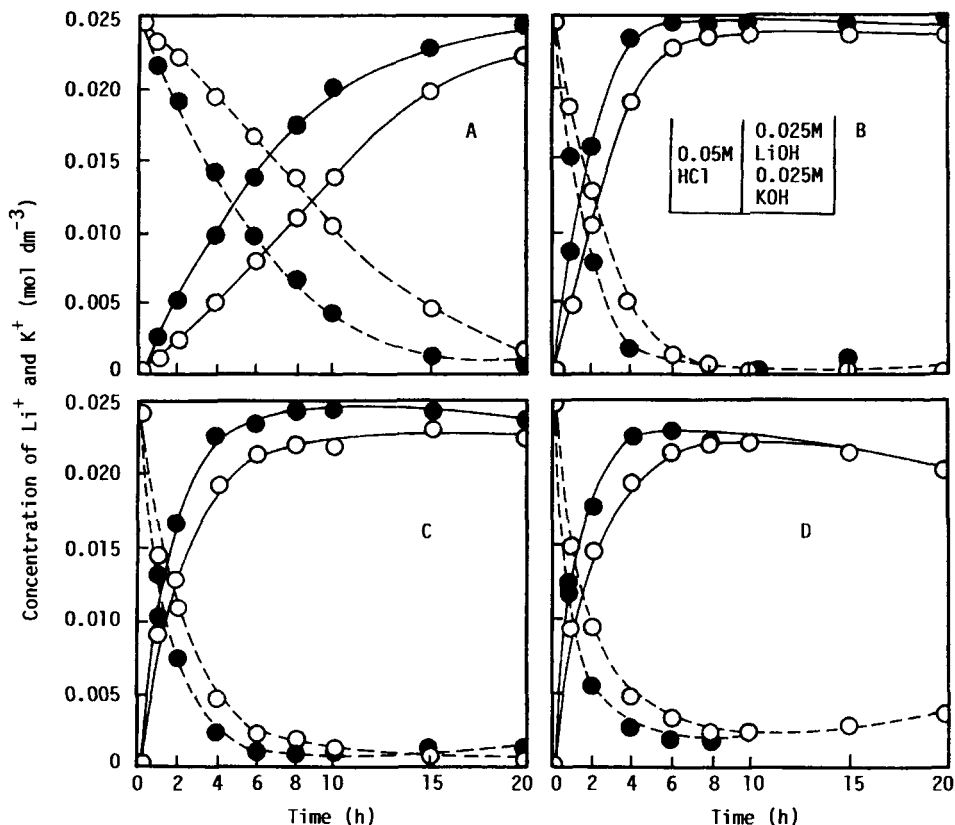


Fig. 7. Change in concentration of Li^+ and K^+ on the two sides of the membranes. Membrane: (A) E8A2; (B) E7.5A2.5; (C) E7A3; (D) E6.5A3.5. (O) Li^+ ; (●) K^+ ; (—) L side; (---) R side.

tributed to the fact that larger hydrated ion becomes more difficult to permeate through the ETMA-AMPS copolymer membranes with lower AMPS content than those with higher AMPS content.

Effect of Initial pH on the Selective Transport of Alkali Metal Ions

The effect of pH on the selective transport of alkali metal ions through the E6.5A3.5 membrane was investigated by using the system containing x mol dm^{-3} HCl (L side) and two kinds of alkali metal neutral salt solution of 0.025 mol dm^{-3} each (R side). The concentration of HCl was changed from 0.01 to 0.50 mol dm^{-3} . The results on K^+/Li^+ system by using 0.01, 0.05, and 0.5 mol dm^{-3} HCl are shown in Figure 8.

The transport rate of each alkali metal ion increased with increasing HCl concentration. In all cases, K^+ was transported more rapidly than Li^+ . The selective transport of Na^+/Li^+ and K^+/Na^+ was also investigated by use of the similar system as that of K^+/Li^+ . All the transport selectivities of Na^+/Li^+ , K^+/Na^+ , and K^+/Li^+ vs. initial pH were plotted in Figure 9. The selectivities were calculated by using the concentration of each alkali metal ion after 4 h. The selectivities were hardly changed by pH, and all the values were more

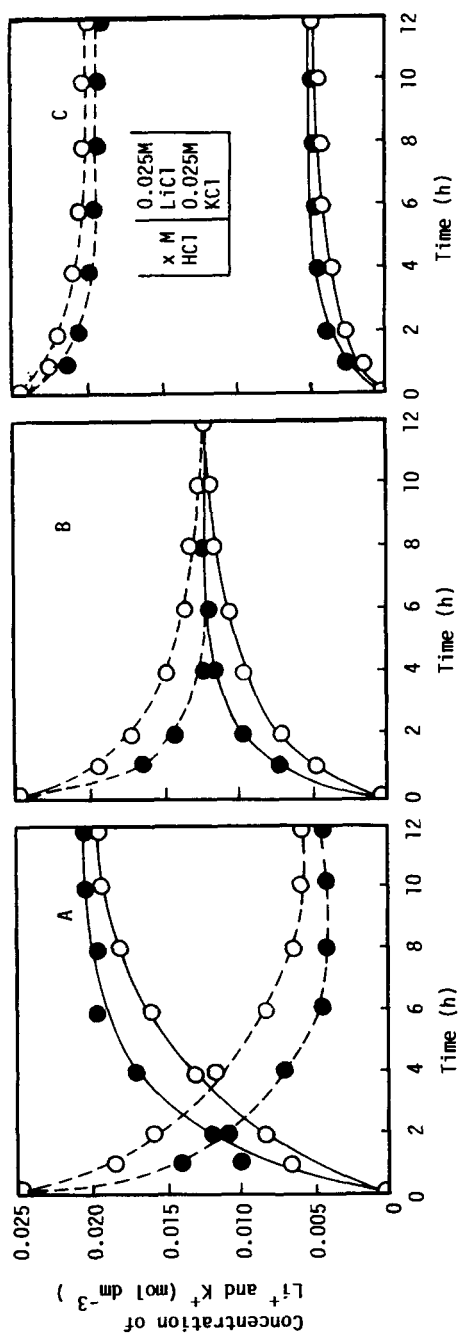


Fig. 8. Change in concentration of Li^+ and K^+ on the two sides of the membranes. Membrane E6.5A.3.5. Initial H^+ concentration in the L side (mol dm^{-3}): (A) 0.05; (B) 0.01; (C) 0.01. (O) Li^+ ; (●) K^+ ; (—) L side; (---) R side.

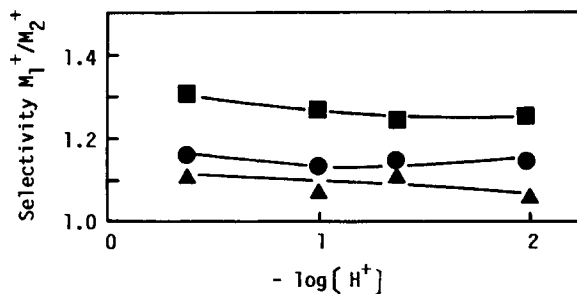
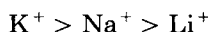


Fig. 9. Effect of initial H^+ concentration in the L side on the selectivity of alkali metal ions. Membrane E6.5A3.5. System: $x \text{ mol dm}^{-3} \text{ HCl}$ (L side)– $0.025 \text{ mol dm}^{-3} \text{ M}_1\text{Cl}$ – $0.025 \text{ mol dm}^{-3} \text{ M}_2\text{Cl}$ (R side). Selectivity: (●) Na^+/Li^+ ; (▲) K^+/Na^+ ; (■) K^+/Li^+ .

than unity. The results indicate that the transport rate of alkali metal ions from the neutral side to acidic side through the membrane is also given in the following order as the same as that in the previous system containing alkali hydroxide:



Effect of Initial pH on the Selective Transport of Na^+ and Ca^{2+}

The selective transport between Na^+ and Ca^{2+} through the E6.5A3.5 membrane was investigated by using the system containing $x \text{ mol dm}^{-3} \text{ HCl}$ (L side) and $0.025 \text{ mol dm}^{-3} \text{ NaCl}$ – $0.025 \text{ mol dm}^{-3} \text{ CaCl}_2$ (R side). The HCl concentration was changed from 0.01 to 0.50 mol dm^{-2} . The results on the systems using 0.01, 0.05, and $0.5 \text{ mol dm}^{-3} \text{ HCl}$ are shown in Figure 10. Ca^{2+} and Li^+ were transported from the R side to the L side against their concentration gradient, when $0.50 \text{ mol dm}^{-3} \text{ HCl}$ was used. Ca^{2+} was transported more rapidly than Na^+ when above $0.05 \text{ mol dm}^{-3} \text{ HCl}$ was used, whereas Na^+ was transported faster than Ca^{2+} when $0.01 \text{ mol dm}^{-3} \text{ HCl}$ was used. In the latter case, the transport rate of alkali and alkali earth metal ion is very low.

The same phenomenon was observed in the selective transport of Na^+/Ca^{2+} by using the system containing $x \text{ mol dm}^{-3} \text{ HCl}$ (L side) and $0.025 \text{ mol dm}^{-3} \text{ NaOH}$ – $0.025 \text{ mol dm}^{-3} \text{ CaCl}_2$ (R side). In this system, both Na^+ and Ca^{2+} were transported slightly faster than those in the system containing no NaOH.

The selectivities were calculated by using the concentration of metal ions after 4 h and they were plotted vs. initial pH in the L side (Fig. 11). The transport selectivities were affected by initial pH in the L side. The maximum transport selectivities were obtained when 0.05 and $0.1 \text{ mol dm}^{-3} \text{ HCl}$ were used in the system containing NaOH and NaCl in the R side, respectively.

It is known that cation exchange resins have a higher affinity for Ca^{2+} than Na^+ because of its higher valence. So ETMA–AMPS copolymer membranes are considered to absorb more rapidly Ca^{2+} than Na^+ . The metal ions released by ion exchange with H^+ were transported to the acidic side by the electric potential gradient. Consequently, Ca^{2+} was transported more rapidly than Na^+ from the R side to the L side when sufficient amount of H^+ existed in the L side. That is the case when above $0.05 \text{ mol dm}^{-3} \text{ HCl}$ solution was used. On

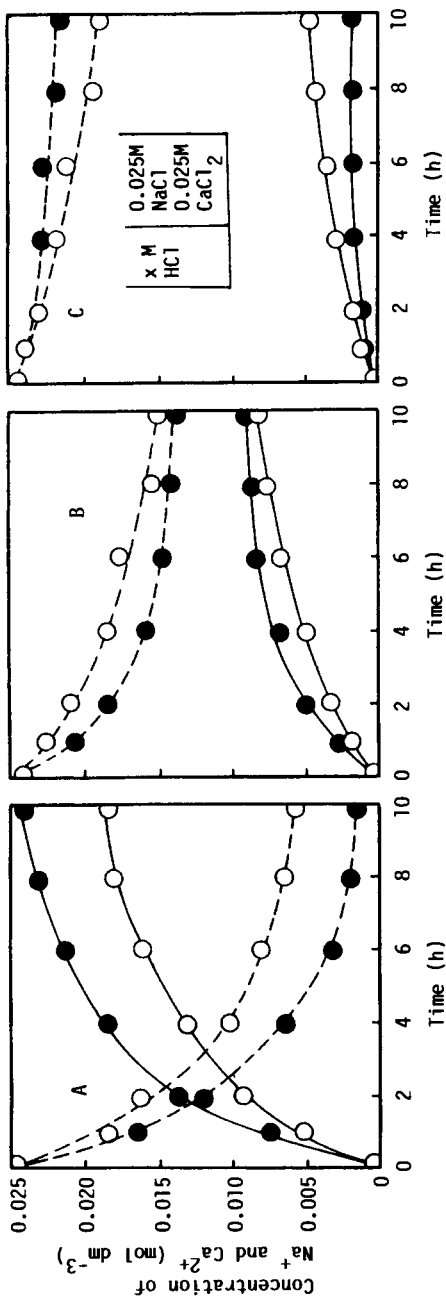


Fig. 10. Change in concentration of Na⁺ and Ca²⁺ on the two sides of the membranes. Membrane EG.5A3.5. Initial H⁺ concentration in the L side (mol dm⁻³): (A) 0.5; (B) 0.05; (C) 0.01. (○) Na⁺; (●) Ca²⁺; (—) L side; (---) R side.

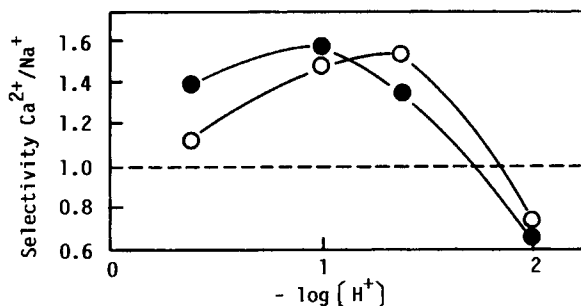


Fig. 11. Effect of initial H^+ concentration in the L side on the selectivity of Ca^{2+}/Na^+ . Membrane E6.5A3.5. System: (○) $x \text{ mol dm}^{-3}$ HCl (L side)– $0.025 \text{ mol dm}^{-3}$ NaOH– $0.025 \text{ mol dm}^{-3}$ $CaCl_2$ (R side); (●) $x \text{ mol dm}^{-3}$ HCl (L side)– $0.025 \text{ mol dm}^{-3}$ NaCl– $0.025 \text{ mol dm}^{-3}$ $CaCl_2$ (R side).

the other hand, as shown in Figure 10, Na^+ was transported more rapidly than Ca^{2+} when 0.01 mol dm^{-3} HCl was used, although their transport rates were very small. In the use of 0.01 mol dm^{-3} HCl, Ca^{2+} became more difficult to be released with HCl than Na^+ , because HCl concentration is low and the ETMA–AMPS copolymer membranes have a higher affinity for Ca^{2+} than Na^+ . These are the reasons for the fact that the selectivity of Ca^{2+}/Na^+ became less than unity when 0.01 mol dm^{-3} HCl was used (Fig. 11).

CONCLUSION

ETMA–AMPS copolymer membranes were prepared by evaporation of solvent from the DMF solution at 50°C . ETMA–AMPS copolymer membranes transported rapidly alkali and alkali earth metal ion against their concentration gradient even from neutral salt solution. Transport of metal ions through the membranes were greatly affected by the composition of the copolymer membranes and initial H^+ concentration in the L side. Transport selectivity of alkali metal ions were affected by the composition of the copolymer membranes, and the selectivity between alkali and alkali earth metal ion was affected by initial H^+ concentration in the L side.

References

1. T. Nonaka, H. Maeda, M. Nakayama, and H. Egawa, *J. Appl. Polym. Sci.*, **34**, 1025 (1987).
2. T. Nonaka, H. Maeda, M. Nakayama, and H. Egawa, *J. Appl. Polym. Sci.*, **37**, 241 (1989).
3. T. Nonaka and H. Egawa, *J. Appl. Polym. Sci.*, **40**, 769 (1990).
4. T. Uragami, R. Nakamura, and M. Sugihara, *Polymer*, **24**, 559 (1983).
5. T. Wada, T. Uragami, and M. Sigihara, *Polym. Bull.*, **14**, 219 (1985).
6. H. Egawa and T. Nonaka, *Kobunshi Ronbunshu*, **35**, 21 (1978).
7. J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

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