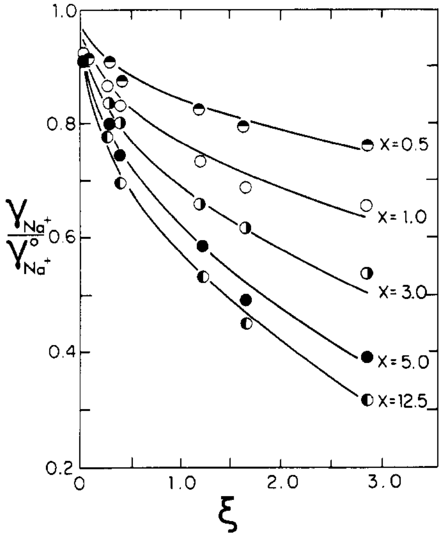

Figure 7. Comparison of experimental values of $\gamma_{Na^+}/\gamma_{Na^+}{}^{\circ}$ for NaPAM-*y* with predictions from additivity eq 11 (solid lines).

where the subscripts have the same meanings as in eq 9 and all other symbols have been previously defined. The first term on the right-hand side of eq 11 is the contribution from the polyelectrolyte; since its value is obtained from measurements in salt-free polyelectrolyte solution, $\gamma_{Na^+}{}^{\circ}$ equals 1. The second term is the simple salt contribution. A comparison of the experimental values with those predicted by additivity eq 11 is made in Figure 7, where again agreement is very good for all values of X, except at the very low charge density of $\xi = 0.02$. Thus from a knowledge of the activity coefficients in salt-free polyelectrolyte solution, the activity coefficients of salt-containing polyelectrolyte solutions can be quite accurately predicted, much more accurately than from either the Manning or Iwasa limiting laws.

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Active Transport and Selective Transport of Alkali Metal Ions through Poly(3-vinyl-1,4-butyrolactone-*co*-acrylonitrile) Membrane

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ABSTRACT: A membrane made of the lactone-containing polymer poly(3-vinyl-1,4-butyrolactone-*co*-acrylonitrile) exhibited active transport and selective transport of alkali metal ions. The active transport of metal ions was promoted by H^+. In the selective transport, the selectivity depended on both the affinity of the carrier fixed to the membrane for alkali metal ions and the hydrophobicity or hydrophilicity of the membrane.

The transport of specific ions is a common function of a biomembrane. It is observed in the active transport of ions through the cell wall, the proton transport in oxidative phosphorylation, and the selective transport of K^+ and Na^+ through the protoplasmic membrane. To develop synthetic membranes having such functions is an important objective of polymer chemistry.

Previously, active transport of metal ions through liquid membranes, such as the transport of alkali metal ions by monensin,[1] transport of Cu^{2+} by β-diketone,[2] and the transport of heavy-metal ions and anions by dithizone or trioctylamine,[2] has been investigated. Selective transport of metal ions through liquid membranes, such as the transport by crown ether[3] and macrocyclic ligands composed of tetrahydrofuran,[4] or through synthetic membranes[5,6] has been studied. With the liquid membrane, there is a membrane stability problem. Active and selective transport through a synthetic membrane carrying a fixed functional group has not been investigated.

We have synthesized several lactone-containing polymers.[7-9] Preliminary experiments showed that, among these polymers, the membrane made of poly(3-vinyl-1,4-butyrolactone-*co*-acrylonitrile) was capable of active and selective transport of metal ions.[10,11] In the present paper,

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Table I
Active Transport of Na$^+$ with Poly(3-vinyl-1,4-butyrolactone-*co*-acrylonitrile) Membrane

expt no.	$[HCl]_{L,0}$/ mol·dm^{-3}	$[NaCl]_{L,0}$/ mol·dm^{-3}	$[NaOH]_{R,0}$/ mol·dm^{-3}	$\overleftarrow{Na^+}^a$	$\overrightarrow{H^+}^a$	$\overrightarrow{Cl^-}$	$\overleftarrow{H_2O}$	concn/%
1	0.5	1.0	1.0	1.0	8.4	7.4	33.0	6.0
2	1.0	1.0	1.0	1.0	5.5	4.5	6.9	14.3
3	2.0	1.0	1.0	1.0	14.2	13.2	53.7	8.4
4	0.2	0.2	0.2	1.0	6.8	5.8	0	2.8
5	0.5	0.5	0.5	1.0	14.1	13.1	0	4.3
6	0	1.0	1.0	0	0	0	0	0

[a] ←, transport from the R side to the L side; →, transport from the L side to the R side.

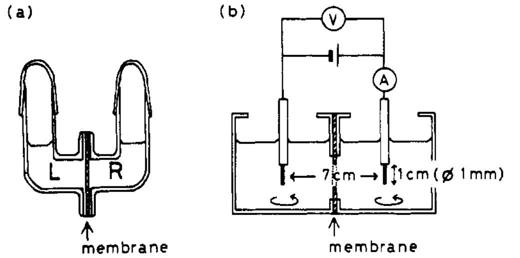

Figure 1. Rough sketches of cells. (a) Active and selective transports: volume 15.0 cm^3; effective membrane area 2.54 cm^2. (b) Electrodialysis: volume 40.0 cm^3; effective membrane area 3.0 cm^2.

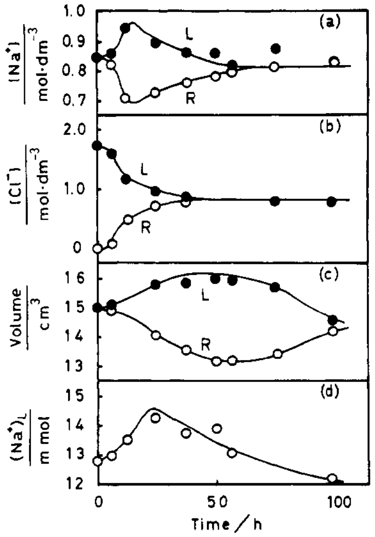

Figure 2. Time–transport curves of Na$^+$, Cl$^+$, and H_2O of the active transport (experiment no. 2 in Table I).

we present a study of these phenomena.

Experimental Section

Materials. Poly(3-vinyl-1,4-butyrolactone-*co*-acrylonitrile) was synthesized as previously described.[8] In the present paper, the lactone content of the polymers was 16.2 and 18.5 mol %.

Preparation of Poly(3-vinyl-1,4-butyrolactone-*co*-acrylonitrile) Membrane. The membrane was cast from *N,N*-dimethylformamide solution (150–180 g·dm^{-3}). The solution was poured onto a glass plate with an applicator, allowing the solvent to evaporate at 40–45 °C for about 3 h. The membrane was removed from the glass plate with a blade. The thickness of the membrane was 30–40 μm.

Apparatus. A glass cell consisting of two chambers was used to study active and selective transport. The membrane, having an area of 2.54 cm^2, was fixed tightly with rubber and Parafilm between two chambers of the cell. Electrodialysis was carried out in a poly(methyl methacrylate) cell. The effective membrane area of the cell was 3.0 cm^2. Sketches of these two cells are shown in Figure 1.

Active Transport. Active-transport experiments were carried out at 40 °C. Initially, the Na$^+$ concentration in the left chamber was the same as in the right chamber. The left chamber also contained HCl, while the right chamber contained NaOH.

Selective Transport. Selective-transport experiments were carried out at 40 °C. The initial concentration was 15.0 cm^3 of an equimolar mixture of alkali metal hydroxides on the R side and 15.0 cm^3 of hydrochloric acid on the L side. At appropriate time intervals, aliquots of 0.1 cm^3 were withdrawn from the both sides and analyzed.

Electrodialysis. Equimolar mixtures of potassium and sodium hydroxides were placed in the chambers of the cell. The fraction of opened lactone in the membrane was estimated by IR. After the degree of lactone opening had reached equilibrium, electrodialysis was carried out with an applied voltage of 10.0 or 1.0 V between platinum rods (diameter 1.0 mm, length 1.0 cm) at 40 °C with magnetic stirring. The selectivity in alkali metal ions transferred was analzyed after passing a current equivalent to 10% of the metal ions.

Analyses. The aliquots were diluted and the concentrations of alkali metal ions were measured with Jarrell-Ash AA780 and AA8200 atomic absorption spectrophotometers. Chloride was determined by the mercuric nitrate method.

Spectroscopy. The working membrane was washed once with distilled water, wiped with filter paper to remove external water, and clamped with KRS cells. ATR IR spectra were recorded on JASCO-ATR7 and DS-403G instruments. IR absorption spectra were recorded on a Hitachi EPI-G2 spectrophotometer.

Kinetics of the Reaction of 1,4-Butyrolactone with Alkali Metal Hydroxide and the Reaction of Alkali Metal 4-Hydroxybutanoate with Hydrochloric Acid. The rate of the reaction of 1,4-butyrolactone with alkali metal hydroxide and that of the reaction of alkali metal 4-hydroxybutanoate with hydrochloric acid were measured by modified potentiometric[12] and conductometric methods.

In the potentiometric method, the reaction of 1,4-butyrolactone with alkali metal hydroxide was monitored as follows. A 1.0×10^{-3} mol·dm^{-3} solution in 1,4-butyrolactone was made up to 500 cm^3 with distilled water. With stirring, 0.5 cm^3 of 1.0×10^{-1} mol·dm^{-3} alkali metal hydroxide solution was added to the aqueous solution of 1,4-butyrolactone, and the pH change was recorded at 40 °C. A tenfold excess of substrate over alkali was allowed in this experiment. Under these conditions, the rate of the reaction of 1,4-butyrolactone with alkali metal hydroxide follows pseudo-first-order kinetics:

$$-d[OH^-]/dt = k_2[OH^-][1,4\text{-butyrolactone}] \simeq k_1[OH^-]$$

Alternatively, 1.0 cm^3 of 1.0×10^{-1} mol·dm^{-3} 1,4-butyrolactone was added to 100.0 cm^3 of 2.0×10^{-3} mol·dm^{-3} alkali metal hydroxide, and the reaction was followed by the conductivity changes.

The rate of the reaction of alkali metal 4-hydroxybutanoate with hydrochloric acid was measured in the same manner as above.

Results and Discussion

Time Course of Active Transport. Table I shows the active transport of Na$^+$.

An example of the time course of active transport is shown in Figure 2. Time–transport curves of Na$^+$ and Cl$^-$, time–volume change curves, and the extent of Na$^+$ change on the L side are shown. After the induction period, the Na$^+$ concentration on the L side increased with time; in contrast, that on the R side decreased. After the Na$^+$ concentration on the L side reached a maximum, the Na$^+$

concentration on the L side decreased and that on the R side increased. A back-transfer of the concentrated Na^+ was due to the decrease of the H^+ concentration on the L side.

Meanwhile, Cl^- was transferred after an induction period (in this case 6 h) as shown in Figure 2b. The transfer followed eq 1 and was proportional to the difference in the concentration between the L side and the R side

$$d[Cl^-]_{R,t}/dt = P([Cl^-]_{L,0} - 2[Cl^-]_{R,t}) \qquad (1)$$

where $[Cl^-]_{L,0}$ is the initial Cl^- concentration on the L side, $[Cl^-]_{R,t}$ is the Cl^- concentration at time t on the R side, and P is the permeability coefficient. The permeation of Cl^- is not measurable during the induction period.

H_2O is transferred through the membrane (Figure 2c). The time when the volume of the solution on the L side reached a maximum was different from the time when the transferred Na^+ reached a maximum. The total solution volume decreased with time because of the withdrawal of aliquots for analysis.

The amount of Na^+ on the L side was calculated from the Na^+ concentration and the volume and is shown in Figure 2d. Figures 2a and 2d show that the Na^+ was transported from the R side to the L side across the membrane against its concentration gradient.

In the transport, the balance of the transfer of ions through the membrane was given by eq 2. As the transfer

$$\overleftarrow{Na^+} + \overrightarrow{Cl^-} = \overrightarrow{H^+} + \overleftarrow{OH^-} \qquad (2)$$

of Cl^- from the L side to the R side followed eq 1, which means a simple diffusion mechanism, it is difficult to consider the exchange of Cl^- and OH^-. Consequently, we conclude that Cl^- is transferred from the L side to the R side accompanied by H^+. The transfer of Cl^- accompanied by H^+ leads to a decrease of the efficiency of transfer. Therefore, the amount of transferred H^+ can be expressed by eq 3.

$$\text{amt of transferred } H^+ = \overleftarrow{Na^+} + \overrightarrow{Cl^-} \qquad (3)$$

The time course of the active transport was divided into three periods: the induction period, the transport period, and the diffusion period.

Induction Period. The induction period is defined as the period from the start to the time when the transfer of Cl^- from the L side began to follow eq 1. The induction period was inversely proportional to the initial NaOH concentration on the R side. The transfer of Na^+ and H_2O to the L side could barely be observed in this induction period. In this period, it is considered that the fraction of opened lactone in the membrane came to equilibrium.

Transport Period. The transport period of Na^+ was achieved by formation of the salt consisting of the permeated Na^+ and the carboxylate of the ring-opened lactone moiety in the membrane, as reported previously.[10,11] The liberation of Na^+ was achieved on the L side by the reaction of the carboxylate with H^+. Therefore, the transport rate of Na^+ was expressed as the product of the H^+ concentration and the concentration of the carrier (the ring-opened lactone) available to form a salt with Na^+.

Considering that the fraction of opened lactone is proportional to the NaOH concentration and inversely proportional to the HCl concentration, the fraction of opened lactone, the carrier, may be expressed by the ratio of the initial NaOH concentration on the R side to the initial HCl concentration on the L side. The initial transport rate per carrier was plotted against the initial HCl concentration on the L side, as shown in Figure 3. The initial transport rate per carrier was proportional to the initial HCl concentration. Accordingly, the driving force for transport is considered to be the H^+ concentration gradient. The active transport of Na^+ is achieved by proton transfer. In addition, experiments 1 and 5, which had the same initial HCl concentrations, showed nearly similar transport rates per opened lactone despite a difference in Na^+ concentrations.

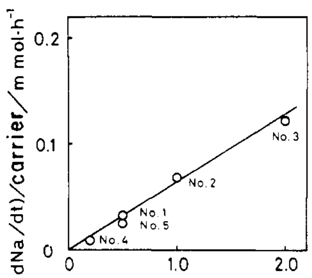

Figure 3. Relationship between active transport rate of Na^+ per carrier and initial HCl concentration.

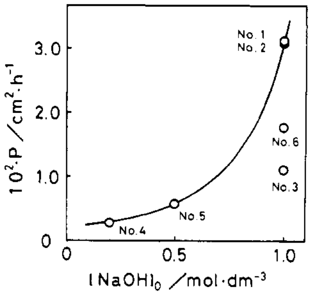

Figure 4. Relationship between permeability coefficient of Cl^- and initial NaOH concentration.

The amounts of H^+ and Cl^- transferred from the L side to the R side and the amount of H_2O transferred from the R side to the L side, per transported Na^+ from the R side to the L side during the transport period, are also shown in Table I. The result that the amount of transferred H^+ was higher than unity shows that the H^+ diffused from the L side to the R side as HCl. This means that the amount of transferred H^+ is larger than that of transferred Na^+. The rate of permeation of water from the R side to the L side was higher than that of the ions. The permeation of water is not directly dependent on the transport of ions but is due to an osmotic pressure effect. In experiments 4 and 5 transfer of H_2O was scarcely observable. This is due to the small difference in ion concentration between the L side and the R side.

It appears that Cl^- permeates the membrane accompanied by H^+, i.e., as HCl. The transfer of Cl^- was not influenced by the transport of other ions and water and followed eq 1. The permeability coefficient obtained from eq 1 is plotted as a function of the initial NaOH concentration on the R side in Figure 4. The higher the initial NaOH concentration, the higher the permeability coefficient observed. It is believed that the higher the swelling of the membrane, the higher the permeability. In experiment 3, where the initial H^+ concentration on the L side was higher than the initial OH^- concentration on the R side, the effect of OH^- decreased substantially and the permeability coefficient, P, was small. In experiment 6, where there was no HCl on the L side, transport of Na^+ did not occur and only the transport of Cl^- was observed. In this case, the permeability coefficient became small, 1.78×10^{-2} $cm^2 \cdot h^{-1}$, despite the fact that the NaOH concentration was the same as in the other experiments. We explain this as being due to the large fraction of lactone

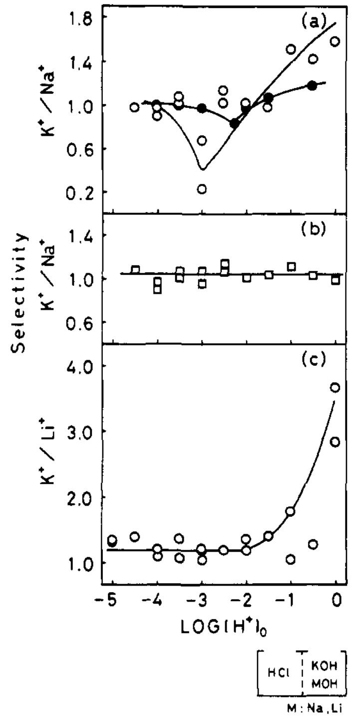

Figure 5. Effect of H^+ concentration on selectivities in transport of alkali metal ions. (a) K^+–Na^+ binary system through the present membrane: (○) $[KOH]_0 = [NaOH]_0 = 5.0 \times 10^{-2}$ mol·dm^{-3}; (●) $[KOH]_0 = [NaOH]_0 = 1.0 \times 10^{-1}$ mol·dm^{-3}. (b) K^+–Na^+ binary system through the cellulose membrane: $[KOH]_0 = [NaOH]_0 = 5.0 \times 10^{-2}$ mol·dm^{-3}. (c) K^+–Li^+ binary system through the present membrane: $[KOH]_0 = [LiOH]_0 = 5.0 \times 10^{-2}$ mol·dm^{-3}.

moieties in the membrane which have opened and formed carboxylate anions, which repel Cl^- and OH^-.

Diffusion Period. In the diffusion period, the concentrated Na^+ and the transferred H_2O on the L side diffused inversely from the L side to the R side to equalize the concentration and the water level on both sides. In experiment 3, where the HCl concentration on the L side exceeded the OH^- concentration on the R side, the lactone moieties were not opened in the diffusion period, and the membrane became hydrophobic. The transfer of H_2O from the L side to the R side was inhibited. In this case the characteristic IR absorptions[8] at 1570 and 1400 cm^{-1}, which were assigned to carboxylate, were not observed, and it was therefore concluded that all lactone rings were closed.

Selective Transportability in the K^+–Na^+ Binary System. Selective transport from the R side to the L side through the membrane was observed under the initial concentrations of potassium hydroxide and sodium hydroxide on the R side and hydrochloric acid on the L side. The ratios of transported ions were calculated from the equation

$$\text{selectivity} = ([K^+]_{L,t}/[K^+]_{R,0})/([Na^+]_{L,t}/[Na^+]_{R,0})$$

where L,t is the concentration on the L side at time t and R,0 is the initial concentration on the R side. The profiles of the selectivities after a 9-h period of transport became similar. Figure 5a shows the selectivity of the transport after 18 h. The ratio of the permeated K^+ to the permeated Na^+ changed with changes of the H^+ concentration. Under the condition that the initial H^+ concentration was low, the selectivity was close to unity; that is, the permeated K^+ was equal to the permeated Na^+. In this region, the permeation rates are expressed by the simple diffusion equation

$$d[M^+]_{L,t}/dt = C([M^+]_{R,0} - 2[M^+]_{L,t}) \qquad (4)$$

where C is the permeability coefficient. Upon integration this becomes

$$[M^+]_{L,t} = ([M^+]_{R,0}/2)[1 - \exp(-2Ct)] \qquad (5)$$

That is, in the region where $[H^+]_0$ was low, each metal ion diffused simply without specific interaction with the membrane.

In the region where $[H^+]_0$ was relatively high, 3.2×10^{-4}–3.2×10^{-3} mol·dm^{-3}, the selectivity became less than unity, and Na^+ permeated faster than K^+. In the region where $[H^+]_0$ was high, $>1.0 \times 10^{-1}$ mol·dm^{-3}, more K^+ permeated than Na^+. At these concentrations, the permeation rates did not coincide with eq 4. This suggests that there is a considerable interaction between the metal ions and the membrane. On the other hand, the cellulose membrane (Visking 27/32) does not show such a profile (Figure 5b). The selectivity and its changes with $[H^+]_0$ in the transport of K^+ and Na^+ were not observed. In this case, the permeation rates coincided with eq 4.

The dependence of the selectivity in K^+ and Na^+ transport upon proton concentration depended also upon NaOH concentrations. The optimum H^+ concentration, giving the lowest K^+/Na^+ selectivity, was 1.0×10^{-3} mol·dm^{-3} with initial concentrations of KOH and NaOH of 5.0×10^{-2} mol·dm^{-3}. On the other hand, the optimum corresponding H^+ concentration was 3.0×10^{-3} mol·dm^{-3} with initial KOH and NaOH concentrations of 1.0×10^{-1} mol·dm^{-3}. These results suggested that contributing factors in the selectivity in K^+–Na^+ transport are the H^+ and OH^- concentrations. The observation that the higher the OH^- concentrations, the higher the H^+ concentration necessary to give optimum selectivity for Na^+ transport leads to the conclusion that for Na^+ transport the membrane should have an appropriate degree of hydrophilicity.

Selective Transportability in the K^+–Li^+ Binary System. Under initial conditions of potassium hydroxide and lithium hydroxide on the R side and hydrochloric acid on the L side, the transport of K^+ and Li^+ from the R side to the L side was carried out. In Figure 5c, the ratios of transported metal ions, which were calculated from eq 6 at 18 h, were plotted against the initial H^+ concentration

$$\text{selectivity} = ([K^+]_{L,18}/[K^+]_{R,0})/([Li^+]_{L,18}/[Li^+]_{R,0}) \qquad (6)$$

on the L side. In the K^+–Li^+ binary system, the selectivity was always larger than unity; that is, K^+ permeated more readily than Li^+. With this membrane, the selectivity reached about 4.0 at the high H^+ concentration. This suggests the possibility of Li^+ separation from K^+.

Transport Mechanism of Alkali Metal Ions. Under the present conditions, the conclusion that the lactone ring was closed on the acid side and opened on the alkali side was drawn from IR specta.[8,10,11] The ATR IR spectra of both surfaces of the working membrane are shown in Figure 6. The ATR IR spectrum was similar to the IR spectrum. On the alkaline side, the characteristic absorption at 1770 cm^{-1} (lactone) had largely disappeared and new absorptions at 1550 and 1400 cm^{-1}, assigned to carboxylate, appeared. From these ATR IR spectra it was concluded that the lactone moiety was opened on the alkaline side and closed on the acid side. Using the 1,4-butyrolactone as a model compound, we investigated the reaction with alkali metal hydroxide, the ring-opening process, and the reaction of alkali metal 4-hydroxybutanoate with hydrochloric acid. The rate constants of the ring opening of the lactone with alkali metal hydroxide are summarized in Table II. The rates of the ring opening were almost constant with varied kinds of alkali metal. The rate of the reaction of alkali metal 4-hydroxybutanoate with hydrochloric acid was too high to be measured. The

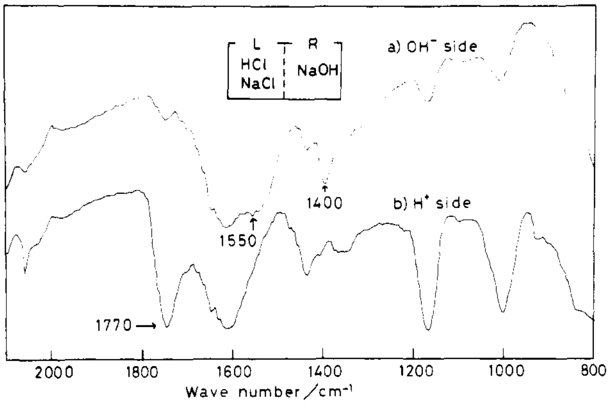

Figure 6. ATR IR spectra of working poly(3-vinyl-1,4-butyrolactone-*co*-acrylonitrile) membrane.

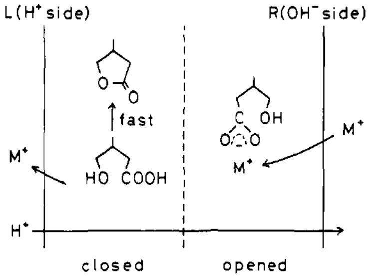

Figure 7. Tentative mechanism of the transport of metal ions.

Table II
Rate of Ring Opening of 1,4-Butyrolactone with Alkali

MOH	$k_1{}^a$/min^{-1}	$1/t_{1/2}{}^b$/min^{-1}
LiOH	0.105	0.11
NaOH	0.136	0.13
KOH	0.117	0.11

[a] Potentiometric method; [MOH] = 1.0×10^{-4} mol·dm^{-3}, [1,4-butyrolactone] = 1.0×10^{-3} mol·dm^{-3}. [b] Conductometric method; [MOH] = 2.0×10^{-3} mol·dm^{-3}, [1,4-butyrolactone] = 1.0×10^{-3} mol·dm^{-3}.

IR[8,10,11] and ATR IR spectra showed the final structure of the lactone moiety on the acid side to be the ring-closed form. This result implies that this reaction proceeded independently of the type of alkali metal cation and that alkali metals were released extremely fast from the carrier. The rates of ring opening and release of alkali metal were very much higher than the rate of transport of metal ions. It is concluded that both processes of incorporation and release of alkali metal ions had no influence on the selectivity of their transport.

The tentative transport mechanism deduced from these results is shown in Figure 7. Metal ions bound to the carboxylate group following opening of the lactone on the alkaline side are shown as being taken into the membrane, transferred through the membrane, and released by H$^+$ on the acid side. In this system, H$^+$ plays the roles of driving force and controlling reagent for the properties of the membrane. The carboxylic acid formed by the reaction of the carboxylate with H$^+$ was rapidly transformed into the lactone. That is, metal ions were transported from the alkaline side to the acid side. We speculate that the binding of the metal ions to the carboxylate due to the ring opening of the lactone affects the selectivity.

As mentioned above, under the active-transport system, where one side was acidic and the other alkaline, the driving force of the transport of metal ions is the difference in H$^+$ concentration. In addition, H$^+$ governs the degree of lactone opening in the membrane. In this system, H$^+$ plays the roles of driving force and controlling reagent for the properties of the membrane.

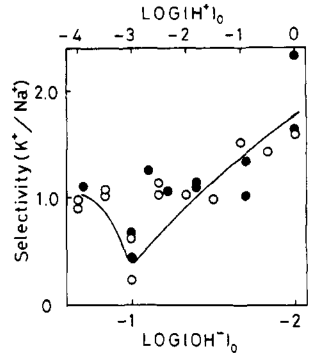

Figure 8. Selectivities in transport of K$^+$ and Na$^+$ by (○) active-transport method and (●) electrodialysis method.

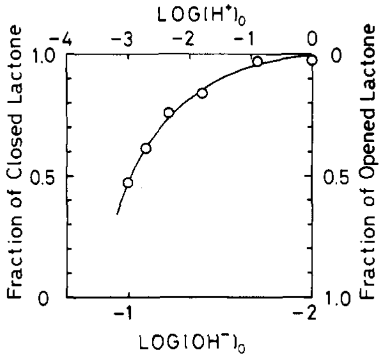

Figure 9. Relationship between fraction of closed and opened lactone and H$^+$ concentration in the active-transport method and OH$^-$ concentration in the electrodialysis method.

Electrodialysis. The electrodialysis method was investigated to clarify directly the effect of the properties of the membrane on selectivity. The profile of selectivity of the K$^+$–Na$^+$ binary system as observed by electrodialysis resembled that measured by the active-transport system, as shown in Figure 5a. The selectivity varied from 2.0 to 0.4. The selectivities observed by electrodialysis are plotted in Figure 8 compared to those measured from the active-transport system.

The contributions of the OH$^-$ and H$^+$ concentrations to the ring opening and the ring closing of the lactone are confirmed in Figure 8. The relationship between the extent of lactone opening and OH$^-$ concentration is shown in Figure 9. The pK_a of the lactone in the membrane was determined to be about 13.0, using the Henderson–Hasselbalch equation. The value of n in this equation was estimated to be about 0.5. It is inferred that the activity coefficient of the carboxylate ion in the membrane due to the ring opening of the lactone was less than unity.

To prevent the electrolysis of water, we performed the electrodialysis at 1.0 V. The alkali concentration of the feed solution was fixed at 1.0×10^{-2} mol·dm^{-3}, and the Na$^+$ concentration was varied from 1.0×10^{-2} to 1.0×10^{-1} mol·dm^{-3} by adding NaCl. The fraction of opened lactone rings, the carrier, in the membrane was about 0.16. In the experiments using this membrane the current was constant (3.7 μA) despite the change in the Na$^+$ concentration. This result supports the conclusion the transport of Na$^+$ is determined by the amount of carrier in the membrane.

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On the Polarity of the Microenvironment of Polymers in Solution. 3. Poly[4(5)-vinylimidazole] in One-Component and Binary Mixtures

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ABSTRACT: Solution properties of poly[4(5)-vinylimidazole] (PVIm) were studied. Polyelectrolyte behavior of PVIm in methylcellosolve and mixtures of ethanol/water and dioxane/water and the suppression of the polyelectrolyte behavior by lithium chloride were studied viscosimetrically. The molecular weight of PVIm was determined by light scattering. Titration behavior of PVIm was measured and the dissociation constant of the solvatochromic compound was determined. For the estimation of the polarity of the microenvironment of PVIm, two differently labeled PVIm's were prepared. On the basis of the shift of the charge-transfer absorption band of the solvatochromic form of the 1-[β-(methacryloyloxy)ethyl]-4-(3-ethoxy-4-hydroxystyryl)pyridinium chloride (MSC) and 1-(δ-bromobutyl)-4-(3-ethoxy-4-hydroxystyryl)pyridinium bromide (BSB) it has been found that the polarity of the microenvironment of the polymer chains of PVIm in binary mixtures of alcohol/water and dioxane/water is lower than that of the solvent. At a low content of water in the mixture, selective sorption of water on the polymer coil yields a detected polarity in the neighborhood of the polymer even higher than that of the solvent used. In PVIm where a solvatochromic label is bound near the polymer chain, a lower polarity of the microenvironment of the polymer has been found than that of the polymer possessing a solvatochromic label farther from the polymer chain. Hydrophobic sorption of the compounds with a long aliphatic chain on the polymer chain of the PVIm in binary mixtures of ethanol/water with a low content of ethanol has been revealed.

Introduction

Polymers carrying imidazole substituents have been studied intensively in view of their catalysis of solvolytic reactions. The catalytic efficiency of polymers possessing pendant imidazole residues on reactions of low molecular weight compounds can be generally influenced[2] by a change of the local concentration of a compound in the neighborhood of the polymer due to electrostatic or hydrophobic forces, by steric factors, and by cooperative effects.

Poly[4(5)-vinylimidazole], the polymer studied most extensively from this point of view, exhibits a number of interesting properties. It possesses a hydrophobic aliphatic backbone and pendant amphiphilic groups. The electrostatic and hydrophobic interactions and the steric and cooperative effects have been studied in detail as to their effect on the catalytic activity of the polymer.[3] The hydrophobic interactions of PVIm with the neutral esters possessing a long aliphatic chain are probably most effective in increasing its catalytic efficiency. It seems reasonable to suppose that, besides the catalytically active hydrophilic part of the polymer, the hydrophobic character of the polymer chain backbone plays an important role.

In mixed solvents with a different affinity of the components of the solvent medium toward the polymer, one component of the mixture may be selectively bound to the polymer chain. The composition of the solvent in the polymer domain where the catalytic reaction occurs can then be considerably different from the bulk composition. This may influence the evaluation of the effect of high molecular character of the catalyst on the activity of imidazole residues in PVIm. For this reason we have tried to obtain by use of a polarity indicator some information concerning the polarity of the microenvironment of PVIm in solution where binding and conversion of the substrate takes place.

The quantitative evaluation of the sorption of compounds possessing long alkyl chains on PVIm from an ethanol/water mixture would also aid the interpretation of the increased solvolysis rate of active esters with similar alkyl groups.

In parts[4] 1 and 2 of this series the method proposed by Kosower[5] for semiempirical determination of the solvent polarity was employed to measure the polarity of the microenvironment of synthetic vinyl polymers. Small concentrations of monomer residues with pyridinium be-

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