

Active Transport Membrane for Anions. III. Effect of Crown Ether and Tautomeric Functional Groups

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Synopsis

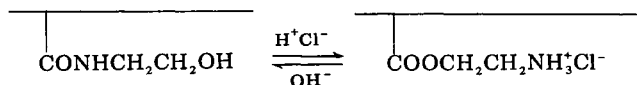
Membranes derived from copolymers having *N*-hydroxyalkyl groups were prepared, and the active transport for anions through the membranes was investigated in the presence of a crown ether which suppresses the diffusion of counter ions. The maximum of the concentrated anions in one side cell was maintained for a long time by the addition of a crown ether in the cell, and a concentration of anions up to 50% was attained. Various *N*-hydroxyalkyl groups of different lengths were incorporated in copolymers with styrene, and the transport for anions was investigated in order to establish the carrier mechanism of the tautomeric functional groups. Longer-length alkyl moieties bearing *N*-hydroxyalkyl groups led to a decrease in the active transport for anions, which supports a carrier mechanism for the membranes.

INTRODUCTION

Many efforts have been made to separate various compounds or ions in an aqueous solution through natural or synthetic membranes. A number of publications dealt with the separation by membranes including reverse osmosis, electro dialysis, or dialysis using concentration gradients of compounds in the solutions. On the other hand, cell membranes of living bodies have a very effective mechanism for the separation of compounds against concentration gradients by active transport.

Ions outside the cell membranes are taken up into the cells by selective capture by a specific functional group as a carrier in the cell membrane resulting in their concentration. Molecular designs for synthetic membranes having an active transport mechanism require a specific functional group in the polymer structure so that the ions may interact specifically and reversibly with the functional group to concentrate the ions from a dilute to a high concentration across the membrane. One of the ways to synthesize an active transport membrane is to introduce a carrier group which has a tautomerism by pH changes in aqueous solution so that ions are carried through membrane.¹

It is known^{2,3} that the *N*-hydroxyethyl amide group exhibits tautomerism between amide and aminoethyl forms and that the transformation between the forms takes place rapidly and is reversible by pH changes in the solution. When a polymer having pendent *N*-hydroxyethyl groups is processed to form a membrane, and the membrane is fixed in a cell as a partition film, for which the solution on one side is adjusted to be acidic and that on the other side to be basic, transport of chloride ion through the membrane is possible due to the tautomerism of *N*-hydroxyethyl groups in acidic and basic solutions^{1,4}:



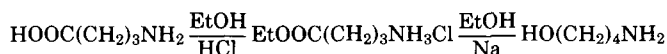
Since proton and hydroxyl ions can diffuse each other through the membranes, neutralization of the solutions takes place on both sides of the membrane. At the final stage the concentrated chloride ions diffuse back again, so that active transport disappears, because the driving force of the active transport is based on the pH differences between the two sides. Diffusion of ions is accompanied by the movement of counter ions such as metal ions, together with the transport of anions. If the diffusion of metal ions were suppressed by lower mobility, active transport would be maintained for a longer period. This expectation led to the idea that metal ions on one side of the cell could be chelated by a crown ether in order to suppress the diffusion of the metal ions through the membrane. This paper deals with the effect of a crown ether on active transport in membranes showing tautomerism.

Polymers having various lengths of *N*-hydroxyalkyl groups were synthesized in order to establish the carrier mechanism caused by changing the functional group in the membrane tautomerically. The effects due to chemical structure of the membrane are also discussed in this paper.

EXPERIMENTAL

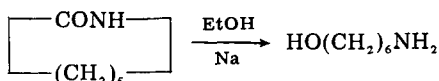
Syntheses of Aminoalcohols

Commercially available monoethanolamine (EA) and *n*-propanolamine (PA) were purified before use by vacuum distillation. *n*-Butanolamine (BA) was synthesized by the following route:



The crude *n*-butanolamine was purified by vacuum distillation (bp 100°C/15 mm Hg).

n-Hexanolamine (HA) was synthesized by the catalytic reduction of ϵ -caprolactam with sodium metal in dry ethanol and purified by vacuum distillation (bp 128°C/17 mm Hg).

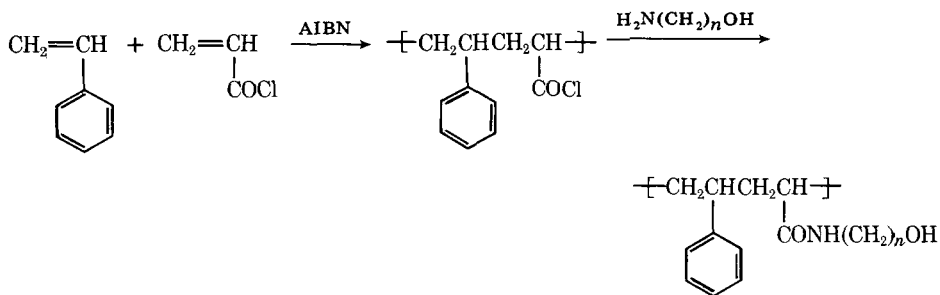


Preparation of Copolymers

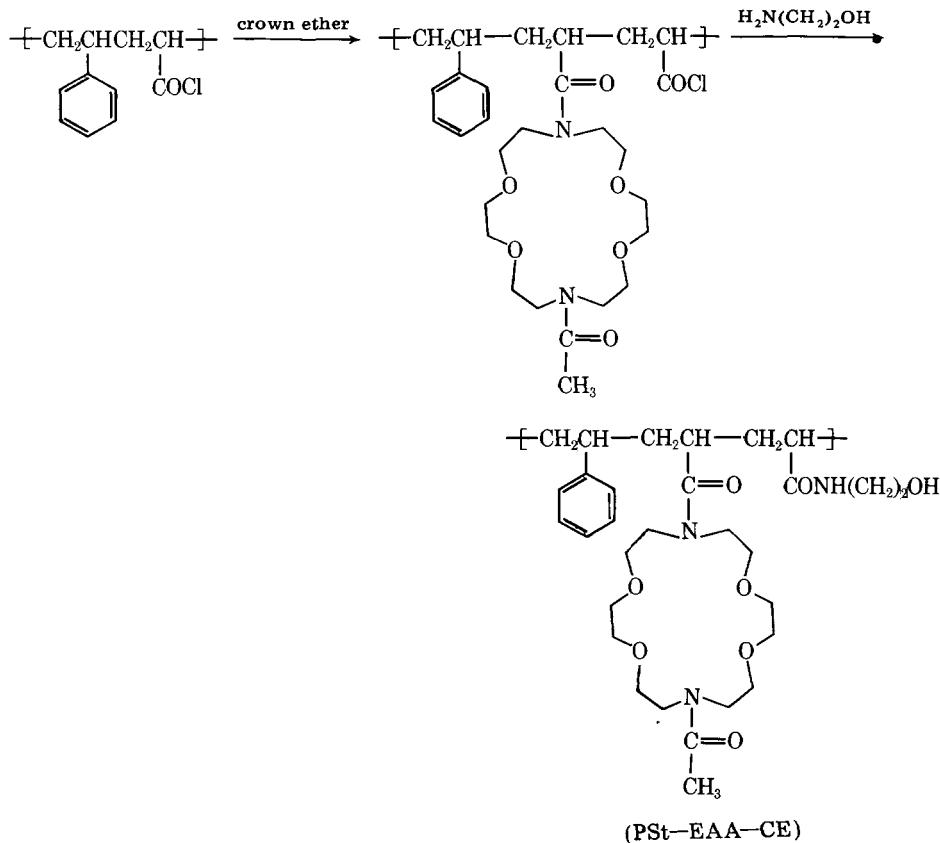
Acryloyl chloride was copolymerized with styrene (St) in benzene in the presence of azobisisobutyronitrile (AIBN) as a radical initiator. After the copolymerization was completed at 60°C for 20 h under a nitrogen atmosphere, the copolymer solution was allowed to mix with an aqueous solution containing an excess amount of an aminoalcohol such as EA, PA, BA, or HA, and agitation of the solution was continued for 5 min in order to transform acryloyl chloride units in the copolymer to *N*-hydroxyalkyl amide units.

Upon reaction with aminoalcohol copolymer started to precipitate out of the solution, and the precipitated copolymer was filtered, washed with water, and

dried in vacuo:



Copolymer containing a crown ether in a membrane structure was also prepared. Copoly(styrene-acryloyl chloride) was dissolved in chloroform, and then half-acetylated diamino-18-crown-6 ether was added in an amount of half-molar to acryloyl chloride unit in the copolymer. After stirring the solution for 5 min, the reaction mixture was allowed to mix with an excess aqueous solution of EA. A precipitated copolymer was filtered, washed with water, and dried. Results of the copolymerization are summarized in Table I.



Half-acetylated diamino-18-crown-6 ether was synthesized by condensation between diamino-18-crown-6 ether and acetyl chloride in excess amount of

TABLE I
Copolymers of Styrene (St) and *N*-Hydroxyalkyl Acrylamide^a

Copolymer ^b		
Composition ^a	$\eta(\text{sp}/C)$	Abbreviation ^a
St/EAA = 5/5	10.5 ^c	PSt—EAA
St/PAA = 5/5	2.40 ^d	PSt—PAA
St/BAA = 5/5	2.65 ^d	PSt—BAA
St/HAA = 5/5	2.26 ^d	PSt—HAA

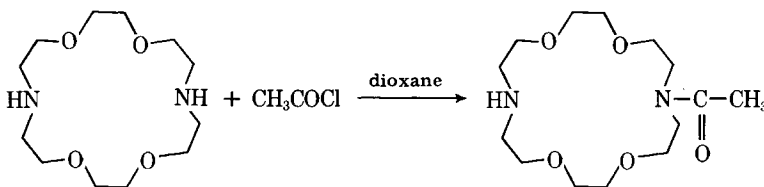
^a $\text{[CH}_2\text{CH(CONH(CH}_2\text{)}_n\text{OH)]}$ $n = 2$, *N*-hydroxyethylacrylamide (EAA); $n = 3$, *N*-hydroxypropylacrylamide (PAA); $n = 4$, *N*-hydroxybutylacrylamide (BAA); $n = 6$, *N*-hydroxyhexylacrylamide (HAA).

^b Copolymerization was carried out in benzene with acryloyl chloride and styrene at 60°C for 20 h.

^c Measured in benzene at 30°C.

^d Measured in benzene-methanol (3:1) at 30°C.

dioxane.



Structure was confirmed by IR spectrum and elemental analysis.

Active Transport of Anions

Membranes were formed by casting solutions of these copolymers in a mixed solvent of benzene and methanol. A uniform and transparent film was obtained on a glass plate or a Teflon sheet by casting the solution either at room temperature or in a heated condition. The film obtained was fixed in a glass cell as a partition, as shown in Figure 1. The left-side (L-side) cell was filled with 0.1 M HCl aqueous solution. The right-side (R-side) cell was filled with 0.1 M NaOH aqueous solution containing 0.1 M of NaCl, which was added in order to adjust the concentration of chloride anion to the same level in both side cells. 15-Crown-5 ether or 18-crown-6 ether was added either in both cells or the R-side cell to form the clathrate of metal ions such as Na^+ or K^+ , respectively.

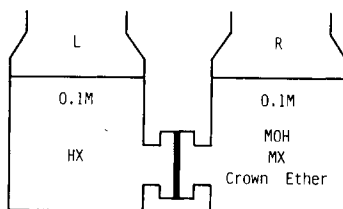


Fig. 1. Separation cell for active transport of anions: X: Cl, Br; M: Na, K; Crown ether: 15 crown-5 ether for Na^+ ; 18 crown-6 ether for K^+ .

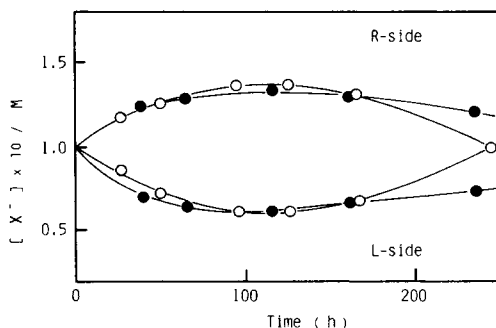


Fig. 2. Transport of chloride anions and bromide anions through PSt—EAA (5/5) membrane at 30°C. (○) KCl; (●) KBr.

The concentration of the anion, such as chloride or bromide, in both cells was determined by a chelatometric titration, and that of the cation, such as sodium or potassium, in both cells by an atomizer–burner method.

RESULTS AND DISCUSSION

Effect of Ion Species on Active Transport

It was confirmed in a previous paper¹ that the chloride anion could be transported through the membrane of the copolymer prepared from styrene (St) and *N*-hydroxyethyl acrylamide (EAA). Therefore, the active transport of another anion, namely, bromide, was carried out in order to compare the results with that of the chloride anion. Figure 2 indicates results of the transport of bromide anion in comparison with that of the chloride anion, using the membrane derived from styrene and *N*-hydroxyethyl acrylamide copolymer (PSt—EAA: St/EAA = 5/5). The same active transport of the bromide anion through the membrane was observed, and a maximum, which reached ca. 40% of the anion concentration, appeared after contact of 100 h in the cell. However, the change in concentration of the bromide anion was much slower than that of the chloride anion after the maximum in concentration was reached. This phenomenon can be ascribed to the radius of the bromide anion being larger than that of the chloride anion, leading to a slower diffusion through the membrane.

In order to investigate the effect of the size of the radius of counter ions, the active transport of the chloride anion was carried out through a membrane of PSt—EAA copolymer with sodium or potassium chloride used as a substrate. The results are shown in Figure 3, where it is seen that the same active transport took place for both NaCl and KCl. The total time to reach the original concentration was shorter, however, in KCl than NaCl. The reason can be ascribed to a strong hydration of the sodium cation, which may retard the diffusion of the cation, although the ion radius of potassium is larger than that of sodium.

Since the diffusion of the counter cation through the membrane is an important factor for the active transport of anions, it was expected that the maximum concentration of the transported anion would be maintained if the suppression of the diffusion of cations occurred by means of a clathrate of the cation with a crown ether. Therefore, crown ethers were added into the cell in order to restrict the movement of the cation.

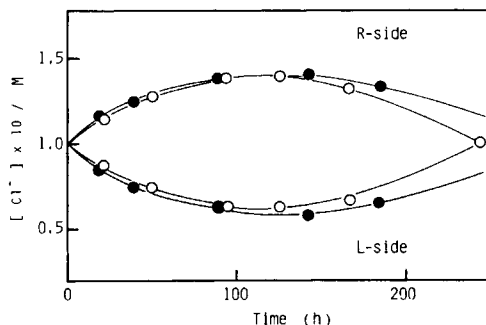


Fig. 3. Effect of the radius of cations on active transport through PST—EAA (5/5) membrane at 30°C. (○) KCl; (●) NaCl.

Figure 4 indicates the concentration changes of the chloride anion in the presence or absence of a crown ether in the R-side cell. The maximum concentration of the transported chloride anion became bigger by the addition of a crown ether, and it was maintained for a longer period of contact time. Presumably, the suppression of the diffusion of potassium cation might occur owing to the clathrate of potassium cation by a crown ether, which might lead to the much slower change of pH, resulting in the slow change of the concentration of the transported chloride anion after the maximum.

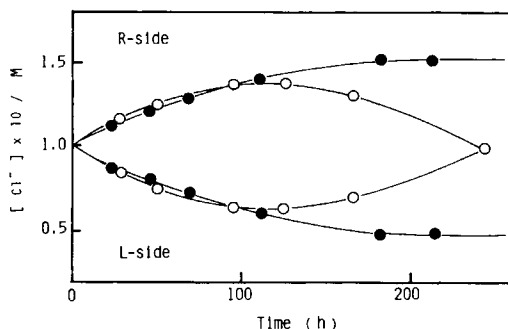


Fig. 4. Change in the concentration of chloride anions passing through PST—EAA (5/5) membrane in the presence or absence of 18-crown-6 ether at 30°C. (●) KCl in the presence of a crown ether; (○) KCl in the absence of a crown ether.

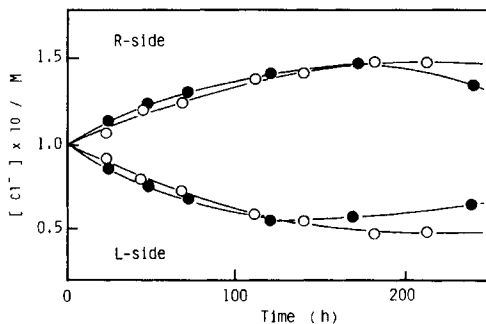


Fig. 5. Change in the concentration of chloride anions passing through PST—EAA (5/5) membrane in the presence of a crown ether at 30°C. (○) KCl in the presence of 18-crown-6 ether; (●) NaCl in the presence of 15-crown-5 ether.

Figure 5 shows results of the clathrate effect of counter ions on sodium and potassium cations, where 18-crown-6 ether was used for KCl and 15-crown-5 ether for NaCl. In both cases, the clathrate effects were observed to maintain the maximum of the concentration of the transported chloride anion in the R-side cell. However, the clathrate effect of a crown ether in the case of NaCl is smaller than in the case of KCl, presumably because the complex formation constant of 15-crown-5 ether with sodium cation is smaller than that of 18-crown-6 ether with potassium cation.

Figure 6 indicates the relationship among pH changes and concentration changes of K^+ and Cl^- in the cells, in the presence or absence of 18-crown-6 ether. It is clearly seen in Figure 6 that both pH changes and the diffusion of K^+ are suppressed by the addition of the crown ether, which keeps the maximum of the transported concentration of the chloride anion for longer than 200 h. When the crown ether existed in both side cells, the active transport was furthermore enhanced and the maximum of the concentration of the transported chloride anion was maintained for 350 h.

These results suggest that the incorporation of a crown ether in the copolymer could be a good way to keep the maximum of the transported anion through PSt—EAA membrane for a prolonged period. Therefore, a membrane containing *N*-hydroxyethyl group and a crown ether was prepared and the transportation of chloride anion was investigated as shown in Figure 7. PSt—EAA membrane which contains a crown ether could concentrate the transported chloride anion much more than PSt—EAA membrane. Since these two mem-

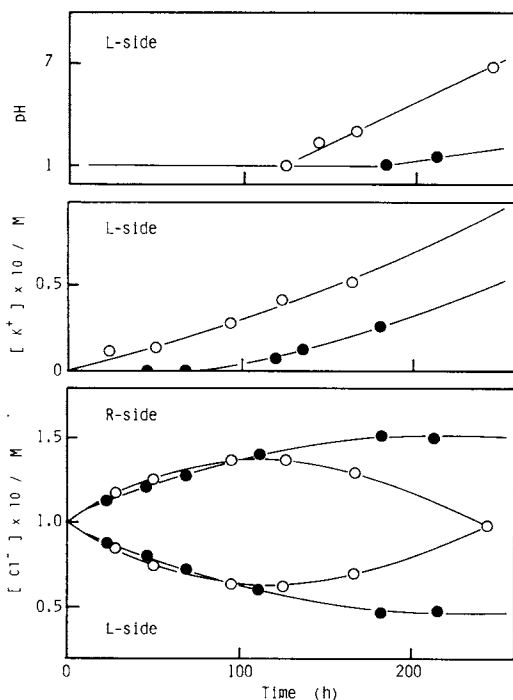


Fig. 6. Relationship among pH changes and concentration changes of potassium cations and chloride anions in the cell at 30°C. (O) KCl in the absence of 18-crown-6 ether; (●) KCl in the presence of 18-crown-6 ether.

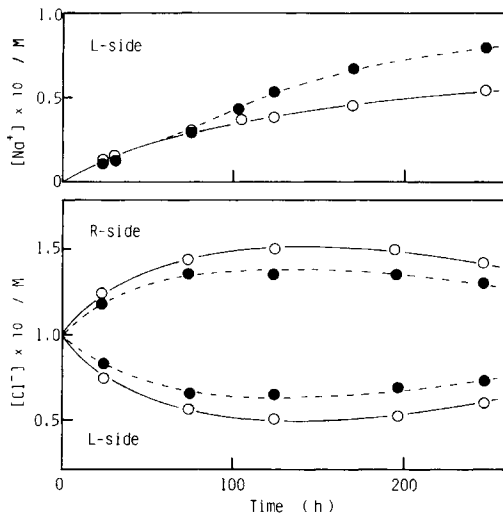


Fig. 7. Change in the concentration of chloride anion through PSt—EAA—CE and PSt—EAA membrane at 30°C. (○) PSt—EAA—CE; (●) PSt—EAA.

branes contained the same contents of styrene in the copolymers, the crown ether incorporated in the membrane was effective for the active transport of anions. Presumably, the movement of sodium cation might suppress considerably owing to the clathration of sodium cation by a crown ether.

It is known that diffusion of transported ions is affected by temperatures. Therefore, temperature effect on the active transport of anions was investigated. As shown in Figure 8, diffusion rate of anion as well as that of cation was fast at high temperature at the initial stage. However, the cation diffused so fast at high temperature that the maximum of the transported anion could not be maintained for a long period.

Osmotic pressure of ions or compounds in a solution has frequently been found

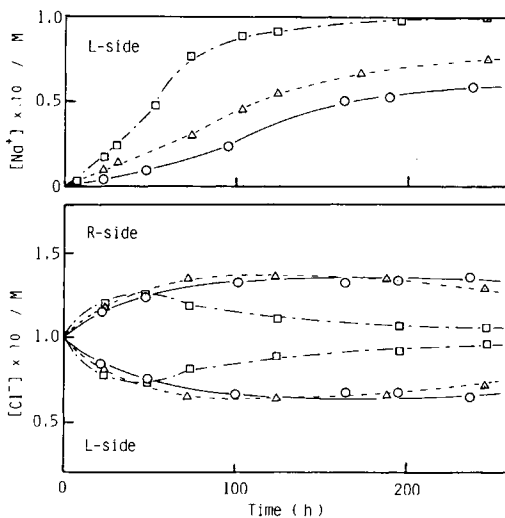


Fig. 8. Temperature effect on the active transport of anions through PSt—EAA (5/5) membrane. (○) 10°C; (△) 30°C; (□) 50°C.

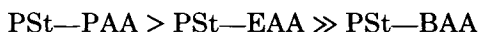
to be important in studies of transport through a membrane. The osmotic pressure across membranes should be considered because the ionic strength in the acidic side is less than that in the basic side. The difference in osmotic pressure in both cells might cause the apparent transport of the chloride anion which was attained by the movement of NaOH and NaCl across the membrane to the acidic side. Therefore, sucrose was added in the acidic side cell to cancel the difference in osmotic pressure at the initial stage. However, no effect of sucrose was observed on the active transport of chloride anion up to the maximum concentration. On the other hand, the addition of sucrose retarded the decrease of chloride anion after the maximum, presumably because of the suppression of the diffusion of counter ions by sucrose.

These results suggest that a double-layer membrane containing both crown ether and tautomeric functional groups could be a good molecular design for the active transport of anions. Work is being carried out to confirm this.

Active Transport of Membranes Having Various *N*-Hydroxyalkyl Groups

Copolymers having various *N*-hydroxyalkyl groups of different lengths were prepared in order to investigate the structural effect of the tautomeric functional groups on the active transport of anions in terms of a carrier function based on the tautomerism. Various *N*-hydroxyalkyl groups were incorporated in the copolymers derived from styrene and acryloyl chloride, and the active transport of the chloride anion through the membranes from the copolymers was investigated.

The tautomerism of *N*-hydroxyalkyl groups was determined by the infrared spectra of the membranes which were immersed in an acidic and basic solutions. Infrared spectra of the membranes derived from PSt—EAA, PSt—PAA, or PSt—BAA exhibited the tautomerism between amide and ester forms, owing to the pH changes of the solution. The tautomeric changes of the *N*-hydroxyalkyl groups took place in the following order:

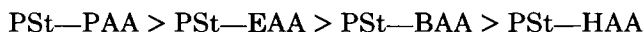


No tautomerism of the functional group was detected in the membrane derived from PSt—HAA.

Figure 9 indicates the active transport of chloride anion through the membranes from PSt—EAA, PSt—PAA, PSt—BAA, and PSt—HAA. The initial increasing rates of the transport of chloride anion could be arranged in the following order:



On the other hand, the maximum amount of the transported chloride anion was in the following order:



The membrane from PSt—PAA could concentrate up to 50% of the chloride anions, while the result for PSt—EAA was 45%. These orders of the active transport were very similar to the degree of tautomeric changes of *N*-hydroxyalkyl groups in the copolymers. A longer alkyl length between amide and hy-

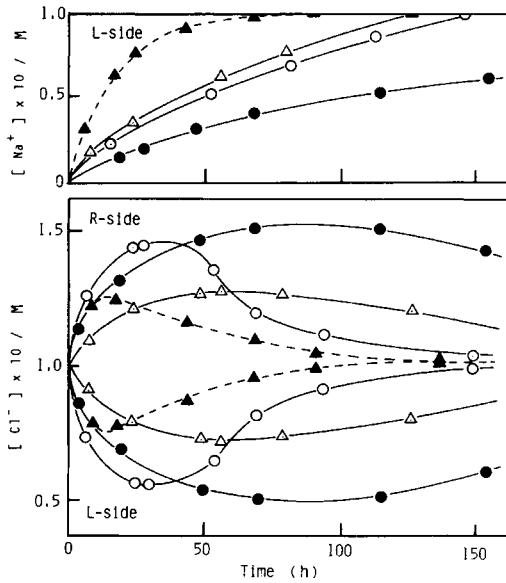


Fig. 9. Active transport of the chloride anion through various membranes. (O) PSt—EAA; (●) PSt—PAA; (Δ) PSt—BAA; (▲) PSt—HAA.

droxyl moieties caused the decrease in the active transport function of the chloride anion through the membranes. Therefore, it is presumed that the carrier mechanism of *N*-hydroxyalkyl groups in the membranes is based on the tautomerism of the functional groups.

In order to confirm the carrier mechanism of the tautomeric groups, the transport of the chloride anion through various membranes without having the tautomeric functional groups was investigated. Membranes were prepared from various polymers, such as a ketalated poly(vinyl alcohol) (PVA—K) or an acetylated cellulose (CA). Figure 10 indicates results of the active transport of the

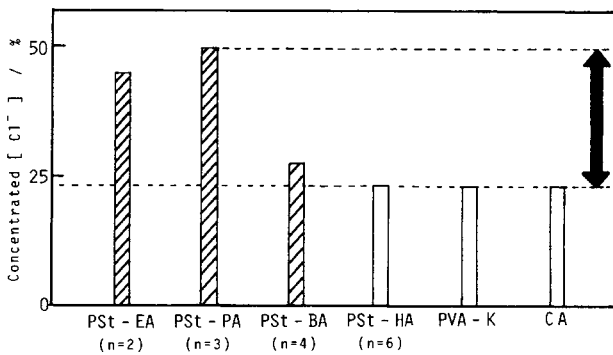
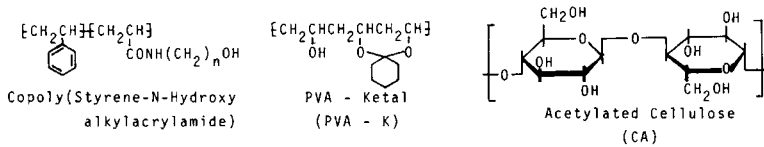


Fig. 10. Relationship between various kinds of membranes and maximum amount of transported chloride anion at 30°C.

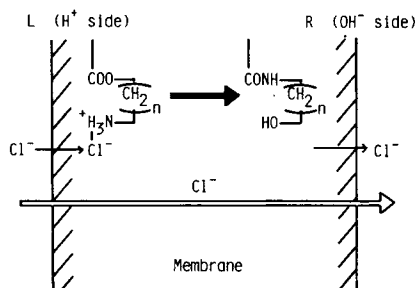


Fig. 11. Postulated mechanism of the active transport through the membrane having tautomeric functional groups.

chloride anion through these membranes. The membranes from PVA—K and CA could concentrate up to 24% of the chloride anions at the maximum concentration; the membrane from PSt—HAA, in which no tautomerism was observed, gave the same maximum value. This active transport phenomenon might be accompanied by the diffusion of the counter ion, namely, sodium cation, through the hydrophilic membrane. Therefore, some chloride anions could be moved from L-side to R-side of the cell through the membrane. However, as shown in Figure 10, the membranes derived from copolymers which have tautomeric groups could concentrate the chloride anion twice as high as the membrane without tautomeric groups.

This result also strongly supports the carrier mechanism of the tautomeric functional groups through the membrane; such a mechanism can stimulate the active transport of anions. The postulated mechanism of the active transport through the membrane is shown in Figure 11; anions combined with the tautomeric functional groups are transported one by one through the membrane from acidic to basic sides, and are eliminated from the surface of the membrane in the basic solution. The L-side surface of the membrane, which is in contact with an acidic solution, has aminoethyl ester groups by virtue of the tautomerism; these form salts with the chloride anion. The chloride anion might move through the membrane by the salt formation with the aminoethyl groups. In a basic medium, the aminoethyl ester form transform into neutral *N*-hydroxyethyl amide form, which might eliminate the combined chloride anions from the membrane. Thus, the chloride anions might be transported from acidic side to basic side. This carrier mechanism could be similar to the active transport of the cell membranes in living bodies. A multilayer membrane having the tautomeric functional groups may be more effective for the active transport of anions. Results of such studies will be published.

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