

# Active Transport Membrane for Chlorine Ion

NAOYA OGATA, KOHEI SANUI, and HIDEO FUJIMURA, *Department of Chemistry, Sophia University, Chiyoda-Ku, Tokyo 102, Japan*

## Synopsis

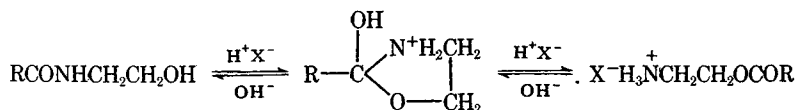
A specific functional group that could interact with ions was introduced in a synthetic membrane to achieve an active transport of ions. One way to synthesize the active transport membrane was to introduce a functional group which had a tautomerism upon pH changes in an aqueous solution. A polymer having pendent *N*-hydroxyethyl amide groups was synthesized to form a membrane, and the membrane was fixed in a cell as a partition film, in which one side of the solution was adjusted to be acidic and the other side basic. It was then possible to transport chlorine ion through the membrane owing to the carrier functions caused by tautomerism of the *N*-hydroxyethyl amide group from the acidic to the basic sides. The transport of the chlorine ion was not dependent on diffusion control.

## INTRODUCTION

A variety of membrane applications in terms of separation of various substrates in aqueous solution, such as desalination of seawater by reverse osmosis, has been reported. The separation of substrates using membranes such as cellulose acetate is, in principle, based on selective filtration of substrates through the membrane. Substrates are moved from a higher concentration side to a lower concentration side through the membrane by diffusion control. However, the membrane in living bodies in many cases functions in a system of antidiffusion control through cell membranes by active transport.

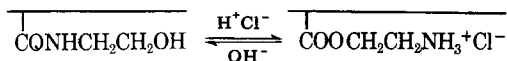
Ions outside of the cells in dilute solution are transported into the cells to concentrate the ions. This is accomplished by selective capture of the ions because of a specific functional group in the cell membrane. Therefore, a specific functional group that can interact with ions was introduced into a synthetic membrane. For example, when a lactone ring, such as phenolphthalein, which can be opened reversibly by pH changes, is introduced into a membrane, it is possible to transport sodium ions through the membrane.<sup>1,2</sup>

*N*-Hydroxyethyl amide group exhibits tautomerism and transforms very rapidly into aminoethyl ester in an acidic solution, which can transform reversibly to the previous amide in a basic solution<sup>3,4</sup>:



When a polymer membrane having pendent *N*-hydroxyethyl amide groups is prepared and fixed in a cell as a partition film, and an acidic solution in one side and a basic solution in the other side is poured into the cell, it is expected

that a chlorine ion may be carried through the membrane owing to the tautomerism:



This article describes the synthesis of an active transport membrane for chlorine ion.

## EXPERIMENTAL

### Synthesis of Copolymer

Acryloyl chloride was copolymerized with methyl methacrylate (MMA), styrene (St), or  $\alpha$ -methylstyrene (MSt) in benzene in the presence of azobisisobutyronitrile (AIBN) as a radical initiator in various feed ratios of copolymers. After the copolymerization was completed at 60°C for 20 hr under nitrogen atmosphere, the copolymer solution was mixed with an aqueous solution containing an excess of monoethanolamine for 5 min with vigorous stirring in order to transform acryloyl chloride units in the copolymer into *N*-hydroxyethyl acrylamide (EAA) units.

Copolymers from styrene and  $\alpha$ -methylstyrene precipitated out of the solution by reaction with monoethanolamine. The precipitated copolymers were filtered and washed repeatedly with water and dried *in vacuo*. Copolymers from methyl methacrylate were obtained as a milky suspension and dialyzed in a cellulose acetate tube with running water. After the dialysis, the aqueous suspension was evaporated under reduced pressure to obtain a solid copolymer. Results of the copolymerization are summarized in Table I.

### Membrane Application

Copolymers reacted with monoethanolamine were dissolved in a mixed solvent of benzene/methanol = 9:1. A uniform and transparent film was obtained on a glass plate by evaporating the solvent. The film was fixed in a cell as a partition film where 1M HCl aqueous solution was put into the left side of the cell and 1M NaOH and NaCl were put into the right side of the cell. The cell was immersed

TABLE I  
Copolymers From *N*-Hydroxyethylacrylamide (EAA) and Methyl Methacrylate (MMA), Styrene (St), or  $\alpha$ -Methylstyrene (MSt)<sup>a</sup>

Polymerization		Yield, %	Copolymer	
Temp., °C	Time, hr		Composition	$\eta_{sp}/C^b$
60	44	100	MMA/EAA = 5:5	1.9
60	20	100	St/EAA = 7:3	0.93
60	20	100	St/EAA = 5:5	10.5
60	20	100	St/EAA = 3:7	0.80
60	20	100	MSt/EAA = 5:5	0.96

<sup>a</sup> Copolymerization was carried out in benzene with various feed ratios of acryloyl chloride and MMA, St, or MSt.

<sup>b</sup> Measured in benzene at 30°C.

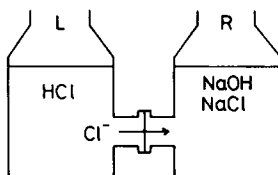


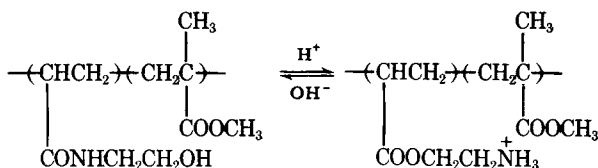
Fig. 1. Separation cell for active transport of  $\text{Cl}^-$  ion.

in a constant-temperature bath set at  $30^\circ\text{C}$ . Figure 1 shows a schematic representation of the cell.

The concentration of chlorine ion,  $\text{Cl}^-$ , in both left and right cells was determined by chelatometric titration and that of sodium ion,  $\text{Na}^+$ , in both cells was determined by atomic absorption.

## RESULTS AND DISCUSSION

Figure 2 indicates infrared spectra of the MMA-EAA film which was immersed in acidic and basic aqueous solution, respectively, and dried. The spectrum of the film immersed in acidic solution exhibits absorption owing to ester carbonyl group at  $1720\text{ cm}^{-1}$  and broad absorption owing to the dissociated amino group in the range of  $2700\text{--}2300\text{ cm}^{-1}$ , while that of the film immersed in basic solution showed absorptions owing to amide group at  $1650$  and  $1550\text{ cm}^{-1}$  and absorption owing to hydroxyl group at  $3300\text{ cm}^{-1}$ . Therefore, it is confirmed that the copolymer from MMA-EAA has the following tautomerism based on pH changes in aqueous solution:



Films obtained from the copolymer of St-EAA, MSt-EAA were prepared with a thickness of  $20\ \mu\text{m}$  and were fixed in the cell. Figure 3 shows the concentration

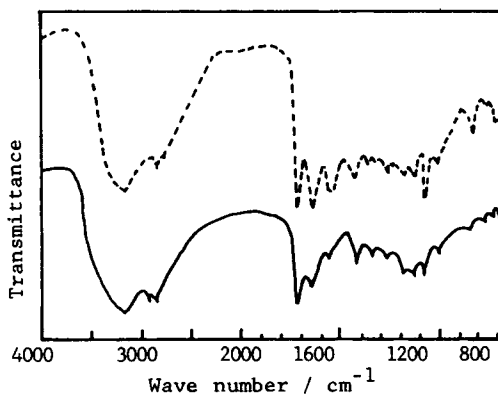


Fig. 2. Infrared spectra of the film from MMA-EAA: (—) in acidic solution; (---) in basic solution.

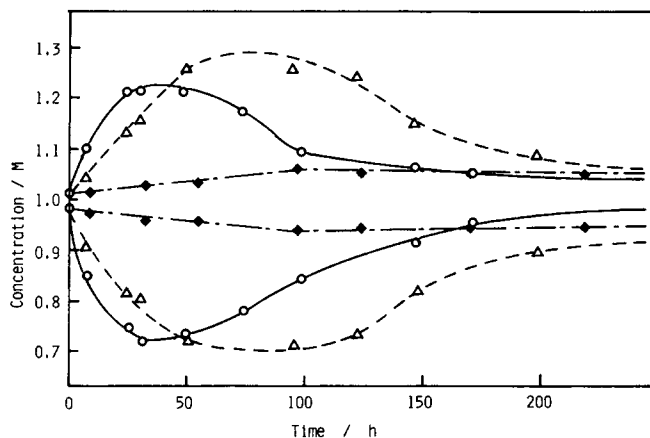


Fig. 3. Change in the concentration of  $\text{Cl}^-$  ion in a separation cell at  $30^\circ\text{C}$ : ( $\Delta$ ) St/EAA = 3:7; ( $\circ$ ) St/EAA = 5:5; ( $\blacklozenge$ ) St/EAA = 7:3.

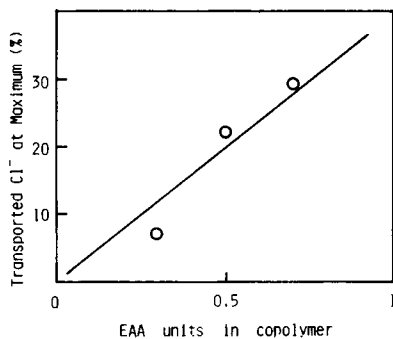


Fig. 4. Maximum amount of transported  $\text{Cl}^-$  ion as a function of EAA units in the copolymer St-EAA.

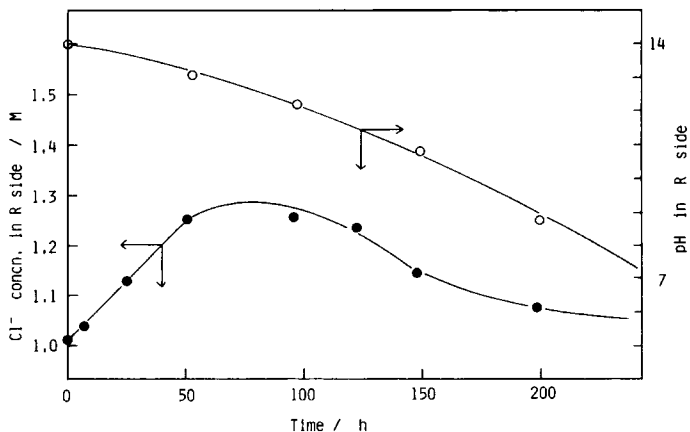


Fig. 5. Relationship between the transported  $\text{Cl}^-$  ion and changes of pH in R side cell (St/EAA = 3:7).

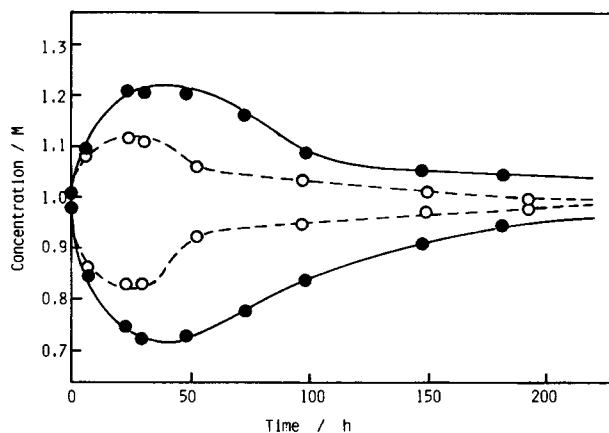


Fig. 6. Change in the concentration of  $\text{Cl}^-$  ion in a separation cell through repeated use of the membrane from St-EAA (St/EAA = 5:5): (●) first use; (○) second use.

change of  $\text{Cl}^-$  ion left and right through the membrane from the copolymers with different compositions of St and EAA. The concentration of  $\text{Cl}^-$  in the right cell, which was basic, increased up to a maximum and then decreased with time, while that in the left cell was just the opposite. The maximum amount of the transported  $\text{Cl}^-$  ion from left to right cells (Fig. 4) was proportional to the content of EAA units in the copolymer. The initial concentration of  $\text{Cl}^-$  ion was the same in both left and right cells, suggesting active transport of  $\text{Cl}^-$  ion through the membrane.

Figure 5 indicates relations between the transported  $\text{Cl}^-$  ion and changes of pH in the right cell. The pH value decreased with time. This pH change is attributed to a transport of  $\text{H}^+$ ,  $\text{OH}^-$ , and  $\text{Na}^+$  ions, as well as  $\text{Cl}^-$  ion, in both side cells. A maximum in the  $\text{Cl}^-$  concentration appeared because of the neutralization of the aqueous solution in both cells. Tautomerism of the *N*-hydroxyethyl amide group did not occur.

Membranes from the copolymers of St-EAA and MSt-EAA were used repeatedly for transport of  $\text{Cl}^-$  ion. Figure 6 shows results of repeated use of

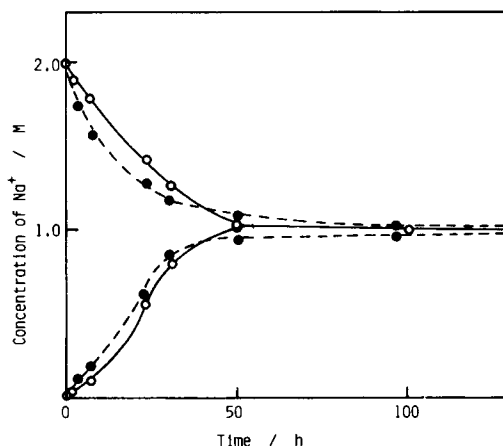


Fig. 7. Change in the diffusion of  $\text{Na}^+$  ion in a separation cell through repeated use of the membrane from St-EAA (St/EAA = 5:5): (○) first use; (●) second use.

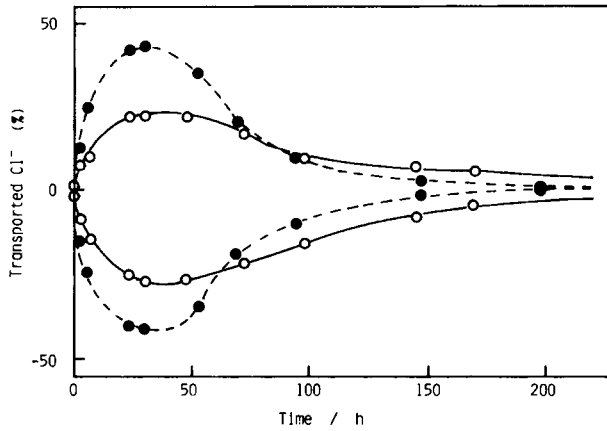


Fig. 8. Relationship between initial concentration of an aqueous solution in both cells and change in the concentration of  $\text{Cl}^-$  ion through the membrane from St-EAA (St/EAA = 5:5): (O)  $[\text{L}]_0 = [\text{R}]_0 = 1.0\text{M}$ ; (●)  $[\text{L}]_0 = [\text{R}]_0 = 0.1\text{M}$ .

membrane from St-EAA. Maximum concentrations of  $\text{Cl}^-$  ion between first use and second use were considerably different, because of some physical change in the membrane, such as morphologic change of crystalline structure. No

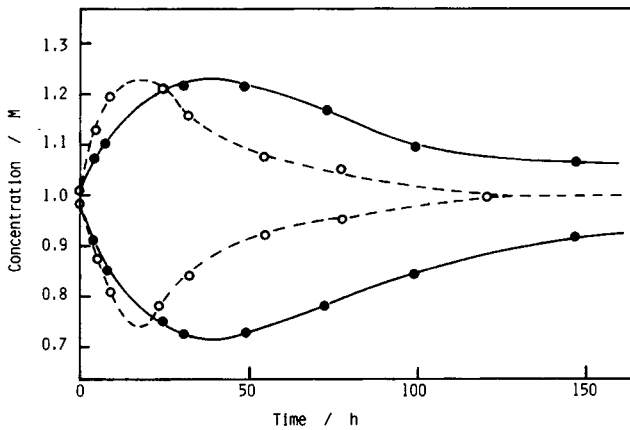


Fig. 9. Change in the concentration of  $\text{Cl}^-$  ion through the membrane from St-EAA and MSt-EAA: (●) St/EAA = 5:5; (O) MSt/EAA = 5:5.

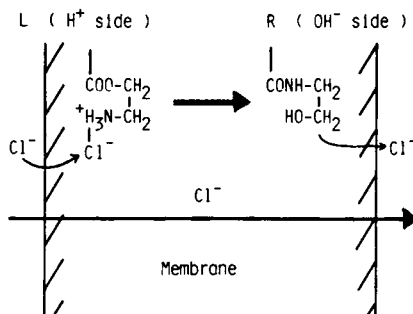


Fig. 10. Tentative mechanism of the transport of  $\text{Cl}^-$  ion through the membrane containing EAA units.

chemical change occurred, since infrared spectra of first and second use of the membrane were identical. Third-use membrane was scarcely different from the second-use membrane.

Figure 7 indicates a diffusion of  $\text{Na}^+$  ion. In view of the rate of diffusion, second use was faster than first, because of a previous difference in maximum amount of the diffusion of  $\text{Na}^+$  ion. Furthermore, the maximum amount of  $\text{Cl}^-$  ion might increase if the diffusion of  $\text{Na}^+$  ion could be prevented.

Figure 8 indicates the concentration change of an aqueous solution in both side cells through membranes obtained from St-EAA. Results indicate that the more dilute the initial concentration on the aqueous solution, the greater the increase in concentration percentage of the  $\text{Cl}^-$  ion.

Figure 9 shows a comparison of transported  $\text{Cl}^-$  ion between the copolymer St-EAA and MSt-EAA. Maximum concentration of  $\text{Cl}^-$  ion was nearly the same, but the concentration of  $\text{Cl}^-$  ion attained to maximum was more rapid in the membrane from MSt-EAA than that from St-EAA. This might be ascribed to the difference of crystallinity in the copolymers.

A tentative mechanism of the transport of  $\text{Cl}^-$  ion is shown in Figure 10. At first, when a specific functional group, ethylamino ester group in copolymers, was in the left side ( $\text{H}^+$  side), the hydrochloride was formed in the presence of hydrochloric acid. Then the hydrochloride moved through the membrane. When the hydrochloride reached the right side ( $\text{OH}^-$  side), ethylamino ester hydrochloride changed to the *N*-hydroxyethylamide group by tautomerism and the  $\text{Cl}^-$  ion was released in the right cell. As the results of this mechanism,  $\text{Cl}^-$  ion was transported from the acidic to the basic side. Since the initial concentration of  $\text{Cl}^-$  ion was originally identical in both cells, the increase of the  $\text{Cl}^-$  concentration in the right cell suggests active transport of  $\text{Cl}^-$  ion through the membrane containing EAA units.

## References

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