Studies of Synthesis and Permeabilities of Special Polymer Membranes. LI. Active Transport of Halogen Ions through Chitosan Membranes

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Synopsis

Anion exchange membranes containing amino groups, insoluble in acidic and alkaline aqueous solutions, were prepared from chitosan, poly(vinyl alcohol), and glutaraldehyde. Using the membrane in a diaphragm cell, one side being adjusted to be acidic and the other alkaline, it was possible to transport actively halogen ions through the membrane from the acidic side to the alkaline side against the concentration gradient between both sides of the membrane. The active transport of halogen ions through the membrane was significantly influenced by the pH difference and electric potential difference between both sides of the membrane.

INTRODUCTION

In previous papers, active and selective transports of metal ions[1–5] and organic ions[6] through synthetic polymeric membranes having a specific functional group have been reported. Also, Ogata et al.[7] have reported that chlorine ion could be actively transported through polymeric membranes having pendant *N*-hydroxyethyl amide groups, which could transform reversibly by tautomerism with pH changes, from an acidic side to an alkaline side. In order to transport actively metal ions, organic ions, and chlorine ions, it was required that the specific functional groups fixed to the membrane, such as the lactone ring, *N*-hydroxyethyl amide group, carboxyl group, and sulfonic acid group, etc., could be changed reversibly and rapidly by pH changes. From this viewpoint, it is expected that an anion exchange membrane containing amino groups would transport actively various anions. The present paper is concerned with active transport of halogen ions such as Cl^-, Br^-, and I^- through an anion exchange membrane containing amino groups, prepared by chitosan, poly(vinyl alcohol), and glutaraldehyde, which is fixed in a diaphragm cell, one side being alkaline and the other acidic.

EXPERIMENTAL

Materials

Chitosan, prepared from chitin powder (Shigma Chemical Co.) by the method of Fujita,[8] and with free amino groups of 92%, and poly(vinyl alcohol) (PVA) produced by Kurary Co., Ltd. were employed as the membrane substance. All reagents used here were of best grade from commercial sources.

Preparation of Membranes

Casting solutions were prepared from a desired mixture of 2.5 wt % chitosan solution in 2 vol % acetic acid, 5.0 wt % PVA, and 5.0 wt % glutaraldehyde aqueous solutions. Membranes were prepared by pouring onto a rimmed glass plate and allowing the water to evaporate at 40°C for 5 h in an oven. After immersing the membranes in $1N$ NaOH for 3 days, they were washed repeatedly with water and kept in pure water (25°C). The thickness of the membranes used in this work were $100 \pm 10 \ \mu$m.

Apparatus and Measurements

Transport experiments were carried out at 25°C under magnetic stirring, using a diaphragm cell consisting of two detachable parts made of poly(methyl methacrylate). The membrane was fixed in the middle of the two parts of the cell, which were clamped and sealed tight with silicon rubber packings. The effective membrane area in the cell was 4.0 cm^2.

Water flux through the membranes under pressure was determined by using a reverse osmosis cell as described in an earlier paper.[9]

The concentration of Na$^+$ ion, in both the left and right part of the cell, was determined by atomic absorption photometry. The accuracy of the determination by this method was of the order of ppm. The concentration of halogen ions X$^-$, such as Cl$^-$, Br$^-$, and I$^-$, in both cells was determined indirectly by measuring the amount of Ag$^+$ ion by means of atomic absorption photometry. That is, a given sample solution was added to a known concentration of AgNO$_3$ aqueous solution (A mol/L), a precipitate of AgX was removed completely by the filtration, and residual amount of Ag$^+$ ion in the filtrate (B mol/L) was determined:

$$\text{concn of X}^- \text{ (mol/L)} = A - B$$

The determination of the halogen ion concentration caused by this method contained an error of about 1–2%. In the transport of ions through the membrane, the concentrations of halogen ions and Na$^+$ ion must be corrected by amount of water transported osmotically.[10] In this work, the changes of the volume in both the left side and the right side with time were determined by means of a measuring microscope. However, we could not observe any volume change in both sides of the membrane caused by an osmotic transport of water. This phenomenon may be attributed to an open membrane structure.

The electric potential difference between the left side and the right side across the membrane in a diaphragm cell was measured by a potentiometer (Hitachi-Horiba F-7SSII type).

Membrane Character

The ion exchange capacity per unit weight of dry membrane was determined by the usual method given as follows:

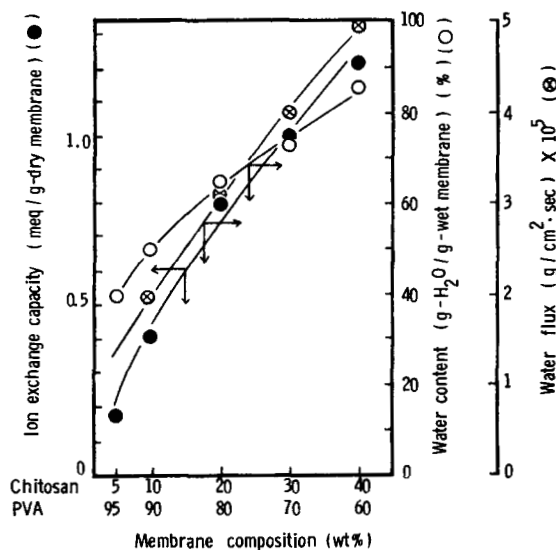$$\text{ion exchange capacity (meq/g)} = 0.2 V_s (V_b - V_m)/1000 W_d \qquad (1)$$

Fig. 1. Effect of chitosan/PVA ratio on the ion exchange capacity and water content, and water flux under pressure of the chitosan–PVA membrane.

where V_b (mL) and V_m (mL) are the titration value of $0.2N$ HCl for $0.2N$ NaOH in the blank test and in the solution with the membrane, respectively. V_s (mL) is the volume of $0.2N$ HCl aqueous solution with the membrane and W_d (g) is the weight of dry membrane.

The water content of the membrane was measured by the usual method shown as follows:

$$\text{water content } (\%) = (W_w - W_d) \times 100/W_w \qquad (2)$$

where W_w (g) and W_d (g) are the weight of wet membrane and dry membrane, respectively.

The degree of swelling of the membrane was determined by the following equation.

$$\text{swelling degree} = S_m/S_0 \qquad (3)$$

where S_0 (cm³) is the volume of the membrane swollen with the mixed aqueous solution of $0.1M$ NaCl and $0.1M$ NaOH and S_m (cm³) is the volume of the membrane swollen with a desired pH solution adjusted by adding $0.1M$ HCl to the above-mixed aqueous solution.

RESULTS AND DISCUSSION

Membrane Character

The membrane prepared by only chitosan dissolved easily in an acidic solution. The membrane which is suitable for the transport experiments must be insoluble in both acidic and alkaline solutions. Thus, chitosan was crosslinked with poly(vinyl alcohol) and glutaraldehyde. The relation between the ion exchange capacity and water content of the membrane and membrane composition is shown in Figure 1. Both the ion exchange capacity and the water content in-
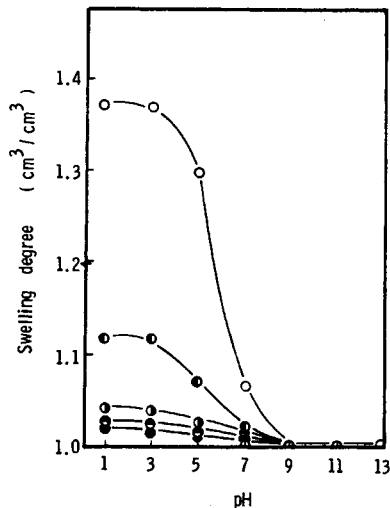
Fig. 2. Effect of H$^+$ ion concentration in the solution immersed the membrane on the swelling degree of the chitosan–PVA membrane. Chitosan/PVA; (O) 40/60; (◑) 30/70; (◐) 20/80; (◕) 10/90; (◒) 5/95.

creased with an increase in the content of chitosan in the membrane. These increases are dependent on the increase of the content of amino group. Figure 1 also includes the water flux under pressure of the membranes from chitosan and poly(vinyl alcohol), where the water flux was determined at 40°C and 10 kg/cm^2 after the membranes were pressure treated in the normal manner[11] at 40°C and 50 kg/cm^2 for 3 h. The water flux increased with an increase in the water content of the membrane. This result can be understood by the following equation reported by Yasuda et al.[12]

$$P_w = H D_w \qquad (4)$$

where P_w is the membrane permeability constant, H is the water content of the membrane, and D_w is the diffusion coefficient for water. Since glutaraldehyde could react with the amino group and hydroxyl group in chitosan molecule, and with the hydroxyl group in PVA molecule, the crosslinks between chitosan and PVA molecules, chitosan molecules, and PVA molecules might be formed. Therefore, it was very difficult to determine chemical structure of the resulting membrane.

The effect of pH of the solution on the swelling degree of various membranes is shown in Figure 2. The membrane swelled in the acidic solution but not in the alkaline solution. The increase of swelling degree with the increase of the chitosan content in the membrane is due to the increase of the content of amino group.

Active Transport of Halogen Ions

An example of the concentration changes of Br$^-$ ion and Na$^+$ ion and the pH changes in both L side (alkaline side) and R side (acidic side) with time due to the transport through the membrane is shown in Figure 3, where the membrane was prepared from chitosan/PVA ratio of 40/60 (wt %), the L side was 0.1M NaBr
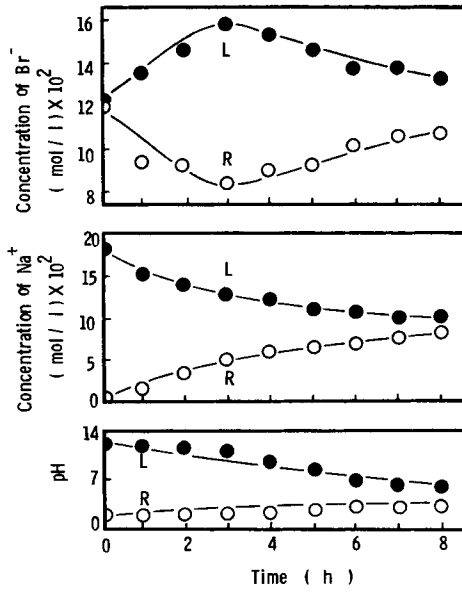
Fig. 3. Changes of the Br^- and Na^+ ion concentrations and pH with time in both sides through the membrane from the chitosan/PVA ratio of 40/60. L side: $0.1M$ NaBr and $0.1M$ NaOH; R side: $0.1M$ HBr.

in $0.1M$ NaOH and the R side $0.1M$ HBr. The concentration of Br^- ion in the L side increased up to a maximum and then decreased with time, the concentration changes of Br^- ion in both sides were in the opposite direction. The increase of the Br^- ion concentration in the L side suggests that Br^- ions were
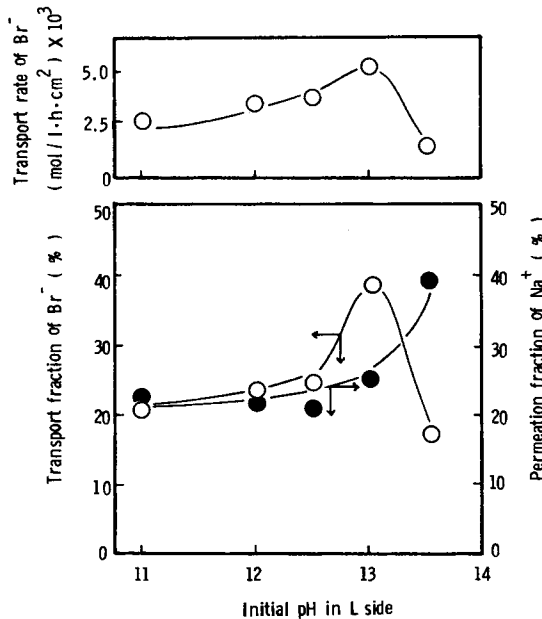

Fig. 4. Effect of the initial pH in the L side on the transport fraction and transport rate of Br^- ion, and the permeation fraction of Na^+ ion through the membrane from the chitosan/PVA ratio of 40/60. L side: $0.1M$ NaBr, NaOH aq. soln; R side: $0.1M$ HBr.

actively transported across the membrane from the R side to the L side against its concentration gradient between both sides of the membrane because the initial concentration of Br$^-$ ion was originally identical in both sides. The pH in the R side and the L side kept acidic and alkaline, respectively, for a long time. This result is attributed to the fact that the initial concentration of OH$^-$ ion in the L side is equal to that of H$^+$ ion in the R side. The Na$^+$ ion concentration in the L side decreased with time caused by the diffusion through the membrane on the basis of its concentration gradient between both sides of the membrane. Since the membrane used in this work is an anion exchange membrane, it should be difficult to transport Na$^+$ ions across the membrane. However, Na$^+$ ions were transported from the L side to the R side across the membrane. This is due to the fact that the membrane is relatively open. In other words, this result also contains a possible mechanism which would counter diffuse Br$^-$ ions in the L side transported actively across the membrane. Also in the system of Cl$^-$ ion and I$^-$ ion, similar results were obtained. It is expected that the transport of halogen ions in such system, where one side was acidic and the other alkaline, is significantly influenced by a pH difference between both sides and the diffusion of counter cation, such as Na$^+$ ion in Figure 3, for halogen ion.

In Figure 4, the transport fraction and transport rate of Br$^-$ ion, calculated from eqs. (5) and (6), respectively, and the permeation fraction of Na$^+$ ion are plotted against the initial pH in the L side.

$$\text{transport fraction (\%)} = ([\text{X}^-]_{\max} - [\text{X}^-]_0) \times 100/[\text{X}^-]_0 \qquad (5)$$

$$\text{transport rate (mol/L·h·cm}^2) = ([\text{X}^-]_{\max} - [\text{X}^-]_0)/At_{\max} \qquad (6)$$

where $[\text{X}^-]_0$ and $[\text{X}^-]_{\max}$ are the initial and maximum concentrations of halogen ion in the L side, respectively, and A is the membrane area and $t_{\max}$ is the transport time for $[\text{X}^-]_{\max}$.

$$\text{permeation fraction (\%)} = ([\text{Na}^+]_{\text{R},t}/[\text{Na}^+]_{\text{L},0}) \times 100 \qquad (7)$$

where $[\text{Na}^+]_{\text{L},0}$ is the initial concentration of Na$^+$ ion in the L side and $[\text{Na}^+]_{\text{R},t}$ is the Na$^+$ ion concentration in the R side after t hours when the Br$^-$ ion concentration in the L side is maximum.

The transport fraction and transport rate of Br$^-$ ion had maximum values at the initial pH 13.0 in the L side. These results under such conditions are caused by the fact that the pH in the L side and the R side kept alkaline and acidic, respectively, for a long time. When the initial pH in the L side was lower or higher than 13.0, the pH in both sides became rapidly acidic or alkaline with time. These pH changes are attributed to a transport of H$^+$, OH$^-$, and Na$^+$ ions, caused by a proton-jump mechanism,[13] specific diffusion mechanism,[13] and diffusive transport, respectively, as well as the transport of Br$^-$ ion caused by the active transport, in both sides. Consequently, both the transport fraction and transport rate of Br$^-$ ion were smaller than those at pH 13.0. The permeation fraction of Na$^+$ ion from the L side to the R side through the membrane increased as the Na$^+$ ion concentration in the L side increased.

The transport amount of each ion through the membrane against the initial pH in the L side is summarized in Table I. When the initial pH was 13.0, the rate of transported amount of H$^+$ ion and OH$^-$ ion was unity. This result is caused by the neutralization between H$^+$ ion and OH$^-$ ion in the membrane.

TABLE I
Transported Amount of Each Ion through the Membrane

Initial pH[a]	13.5	13.0	11.0
$\overleftarrow{Br^-}$[b] [(mol/L) × 10⁴]	3.5	7.6	3.9
$\overrightarrow{Na^+}$[b] [(mol/L) × 10⁴]	16.6	10.0	4.5
$\overleftarrow{H^+}$[b] [(mol/L) × 10⁴]	—	14.3	9.8
$\overrightarrow{OH^-}$[b] [(mol/L) × 10⁴]	23.3	14.3	—

[a] in the L side.
[b] ← = transport from the R side to the L side; → = transport from the L side to the R side.

Under this condition, the amount of OH⁻ ion transferred from the L side to the R side was greater than that of Na⁺ ion, because OH⁻ ion was easily diffused by a specific diffusion mechanism,[13] but Na⁺ ion was repelled by the charge fixed to the membrane. On the other hand, the amount of H⁺ ion transported from the R side to the L side was significantly greater than that of Br⁻ ion. This result is attributed to H⁺ ions being easily transferred by a proton-jump mechanism.[13] At the initial pH 13.5, OH⁻ ion was transported the greatest of all ions, and H⁺ ion the greatest at pH 11.0. Since there is a difference between the transported amounts of each ion and Donnan equilibrium is set up between the solution and the membrane, which has a fixed charge, it is expected that an electric potential difference between both sides occurs, and, consequently, its potential difference may be related to the transport of halogen ions. The change of the electric potential difference between both sides with time is shown in Figure 5. In all conditions an electric potential difference occurred between both sides. The extent of transport fraction of Br⁻ ion was dependent on that of its potential
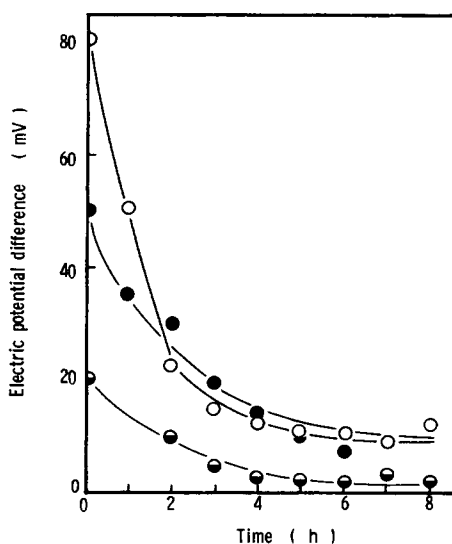

Fig. 5. Changes of the electric potential difference between both sides with time across the membrane from the chitosan/PVA ratio of 40/60. Initial pH in L side: (O) 13.5; (◓) 13.0; (●) 11.0. L side: 0.1M NaBr, NaOH aq. soln; R side: 0.1M HBr.
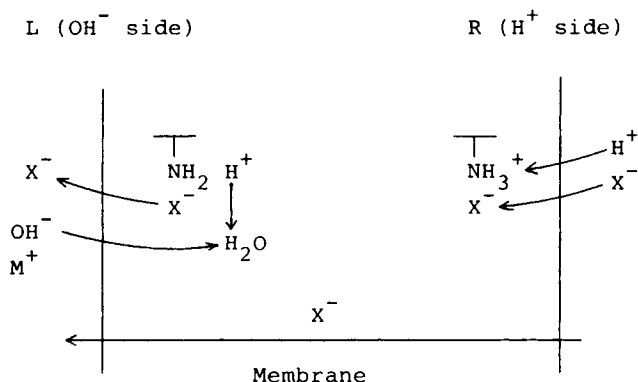
Fig. 6. Tentative mechanism of the transport of halogen ions through the chitosan–PVA membrane. (X^-) halogen ion; (M^+) metal ion.

difference. The decrease of electric potential difference with time was due to the diffusive transport of Na^+ ion from the L side to the R side.

A tentative mechanism of the active transport of halogen ions is shown in Figure 6. In order to simplify the explanation, we instance the transport of Br^- ion. When the Br^- ion is incorporated into the membrane on the R side (H^+ side), the hydrobromide is formed in the presence of hydrobromic acid and transferred through the membrane. As this hydrobromide reaches the L side (OH^- side), the hydrobromide changes to the amino group by neutralization and the Br^- ion is released. The released Br^- ion is transferred to the L side by the electric potential gradient between both sides. Consequently, it suggested that the Br^- ion is actively transported through the membrane from the acidic side to the alkaline side.

If a greater pH difference and electric potential difference between both sides could be kept for a longer time, that is, the diffusive transport of metal ion from the L side to the R side should be prevented, the active transport of Br^- ion might be promoted. This expection has revealed by Ogata et al.[14] They reported that the active transport of Cl^- ion through polymeric membranes having N-hydroxyethyl amide groups was promoted by trapping with crown ether metal ion in the alkaline side in order to prevent the diffusion of metal ion from the alkaline side to the acidic side.

Figure 7 shows the effect of the chitosan/PVA ratio on the transport fraction and transport rate of halogen ions, which increased with the increase in the content of chitosan in the membrane. These increase corresponded to the ion exchange capacity of the membrane shown in Figure 1. It is concluded that the extent of transport of halogen ions depends on the content of amino group in the membrane.

In the membranes with the lower ratio of chitosan and PVA, both the transport fraction and the transport rate of Cl^- ion were considerably smaller than those of Br^- and I^- ions. The difference between those of Cl^- ion and of Br^- and I^- ions decreased as the content of chitosan in the membrane increased. These phenomena are attributed to the difference of the hydrated size of each halogen ion. That is, in the membrane having lower ion exchange capacity the halogen ions (Br^- and I^-), which had smaller hydrated ionic radius might be preferen-
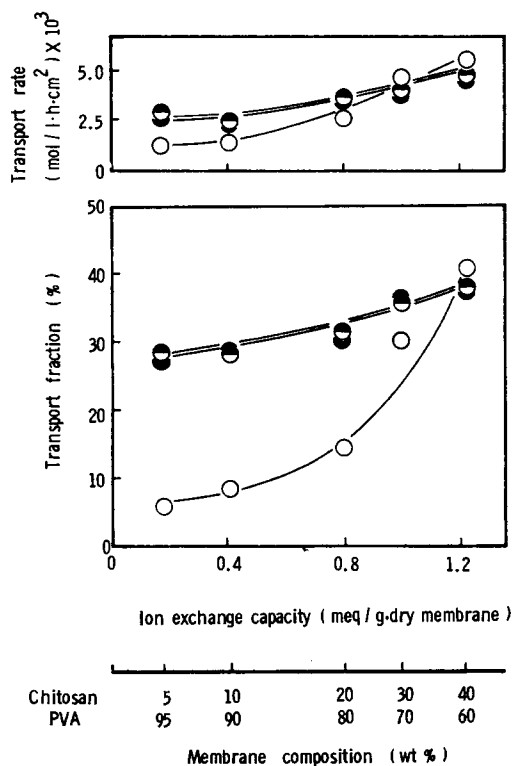
Fig. 7. Effect of the chitosan/PVA ratio on the transport fraction and transport rate of halogen ions: (O) Cl^-; (◉) Br^-; (●) I^-. L side: $0.1M$ NaX, $0.1M$ NaOH; R side: $0.1M$ HX.

tially transported because its halogen ion interacted more strongly with the amino group compared with the halogen ions (Cl^-) having larger hydrated size. On the other hand, in the membrane having higher ion exchange capacity, the effect of the hydrated ionic radius in the transport of halogen ion through the swollen membrane was diminished, and, consequently, the transport fraction and the transport rate for Cl^-, Br^-, and I^- ions became equal between one another.

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