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Tadashi Uragami[a]; Fumihiko Yoshida[a]; Mizuho Sugihara[a]
[a] DEPARTMENT OF CHEMISTRY FACULTY OF ENGINEERING, KANSAI UNIVERSITY, SUITA, OSAKA, JAPAN

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Studies on Syntheses and Permeabilities of Special Polymer Membranes. 59. Active Transport of Organic Ions through Crosslinked Chitosan Membrane

TADASHI URAGAMI, FUMIHIKO YOSHIDA, and
MIZUHO SUGIHARA

DEPARTMENT OF CHEMISTRY
FACULTY OF ENGINEERING
KANSAI UNIVERSITY
SUITA, OSAKA 564, JAPAN

Abstract

Active transport of organic ions such as benzenesulfonate and benzoate ions and amino acids was studied through a chitosan-PVA membrane under various conditions. The organic anions of benzenesulfonate and benzoate ions were actively transported through the chitosan-PVA membrane from the acidic side to the alkaline side, but the active transport of amino acid occurred from the alkaline side to the acidic side. These active transports were significantly dependent on a pH difference and electric potential difference between the two sides of the membrane.

INTRODUCTION

Separation and transport of materials through polymer membranes are achieved by various driving forces. Reverse osmosis and ultrafiltration are due to a pressure difference, diffusive dialysis and electrodialysis depend on concentration and voltage differences, and gas permeation is due to a pressure difference. In the active and selective transport of materials with polymeric membranes having a functional fixed carrier, pH and electric potential differences are applied to the source of the driving force.

The authors have been studying the active and selective transport of metal ions (*1*, *2*), halogen ions (*3*), and organic ions (*4*, *5*) through ion-exchange membranes which have the simplest fixed carrier that can be reversed and changed rapidly through pH changes. Many studies on the active and selective transport of metal and halogen ions with polymer membranes having functional fixed carriers have been presented (*1–3*, *6–13*), but studies of organic ions (*4*, *5*, *16*) through such functional membranes are few. In earlier papers we reported on the active transport and mechanism of amino acids such as glycine (*4*) and L-phenylalanine (*4*, *5*), ammonium ion (*4*), and aniline (*4*) through cation-exchange membranes. For the purpose of learning more about the mechanism of active transport of organic ions through ion-exchange membranes, the present paper is concerned with the active transport of organic anions such as benzenesulfonate, acetate, and benzoate ions and amino acids such as L-phenylalanine through a chitosan–PVA membrane (an anion-exchange membrane).

EXPERIMENTAL

Materials

Chitosan with 92% free amino groups was prepared from chitin powder (Sigma Chemical Co.) by the method reported in an earlier paper (*3*). Poly(vinyl alcohol) (PVA) (identified as PVA 217) from Kurarey Co. was used. All the reagents used in this work were supplied by commercial sources.

Preparation of Membranes

The casting solution was prepared by combining a solution of chitosan (2.5 wt%) in 2.0 vol% acetic acid, an aqueous PVA solution (5.0 wt%), and an aqueous glutaraldehyde solution (5.0 wt%). Membranes were made by pouring the casting solutions onto a rimmed glass plate, evaporating the water at 40°C for 5 h in an oven, and immersing the membranes in 1 *N* NaOH for 3 d. They were then washed repeatedly with water and stored in pure water at 25°C. The chitosan–PVA membrane used in this work had an anion-exchange capacity of 1.23 meq/g and 85% water content.

Apparatus and Measurements

The transport apparatus (*1*) used, the experimental procedure (*1–3*), the determination of the concentrations of metal and halogen ions (*1–3*), and the measurement of the electric potential difference between the left and the right part of the membrane in a diaphragm cell (*1–3*) were described in earlier papers.

The concentrations of benzenesulfonate ion, benzoate ion, and L-phenylalanine, in both the left and right parts of the cell, were determined by ultraviolet absorption photometry; 262 nm in 0.2 *M* HCl for benzenesulfonate ion, 227 nm in 0.2 *M* HCl for benzoate ion, and 258 nm in 0.2 *M* HCl for L-phenylalanine.

RESULTS AND DISCUSSION

Transport of Strong Organic Acid Anion

Benzenesulfonate ion was selected as a strong organic ion species. Figure 1 shows changes in the concentration of benzenesulfonate ion and pH with time on the left side (L side) and the right side (R side) of the chitosan–PVA membrane in the diaphragm cell. The L side was 0.1 *M* sodium benzenesulfonate and 0.1 *M* NaOH and the R side was 0.1 *M* sodium benzenesulfonate and 0.1 *M* HCl initially. The concentration of benzenesulfonate ion on the L side, which was alkaline, increased up to a maximum and then decreased. In contrast, that on the R side decreased and then increased with time. This result suggests an active transport of benzenesulfonate ion from the alkaline side to the acidic side through the chitosan–PVA membrane. Such a transport phenomenon is similar to that of halogen ions through the chitosan–PVA membranes (*3*), membranes with *N*-hydroxyethyl amide groups (*10*), and copoly(vinylpyridine–styrene) membranes (*11*).

In order to estimate the extent and rate of active transport of benzenesulfonate ion, the transport fraction and transport rate were defined as:

$$\text{Transport fraction of organic anion species (\%)}$$

$$= \{([\mathrm{OAS}]_{\max} - [\mathrm{OAS}]_0)/[\mathrm{OAS}]_0\} \times 100 \qquad (1)$$

$$\text{Transport rate of organic anion species (mol/L}\cdot\text{h}\cdot\text{cm}^2\text{)}$$

$$= ([\mathrm{OAS}]_{\max} - [\mathrm{OAS}]_0)/At_{\max} \qquad (2)$$

where $[\mathrm{OAS}]_0$ (mol/L) and $[\mathrm{OAS}]_{\max}$(mol/L) are the initial and maximum concentrations of organic anion species on the L side, respectively, A

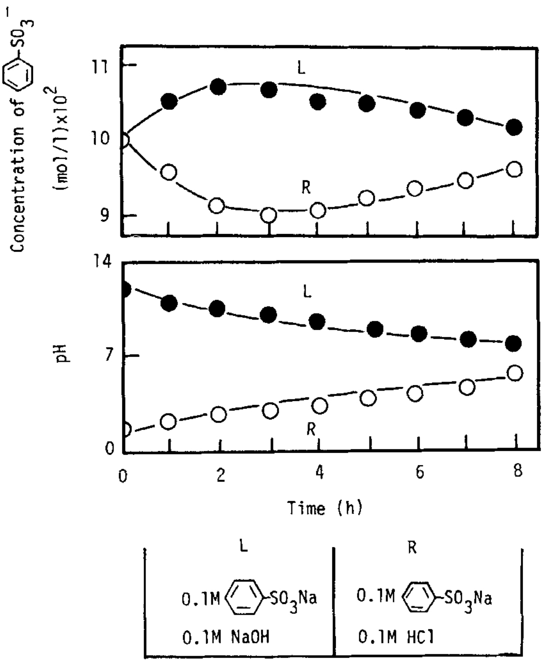


FIG. 1. Changes of the benzenesulfonate ion concentration and pH with time on both sides through the chitosan-PVA membrane. L side: 0.1 *M* sodium benzenesulfonate and 0.1 *M* NaOH; R side: 0.1 *M* sodium benzenesulfonate and 0.1 *M* HCl.

(cm^2) is the effective membrane area, and t_{max}(h) is the transport time for $[OAS]_{max}$.

The permeation fraction of Na^+ ion from the L side to the R side due to diffusive transport based on the concentration gradient of Na^+ ion across the chitosan-PVA membrane was also defined as

$$\text{Permeation fraction of } Na^+ \text{ ion } (\%) = ([Na^+]_{R,t}/[Na^+]_{L,0}) \times 100 \qquad (3)$$

where $[Na^+]_{L,0}$ (mol/L) is the initial concentration of Na^+ ion on the L side and $[Na^+]_{R,t}$ (mol/L) is the Na^+ ion concentration on the R side after *t* hours when the concentration of organic anion on the L side is maximum.

The permeation fraction of Cl^- ion from the R side to the L side through the chitosan-PVA membrane was defined as

$$\text{Permeation fraction of } Cl^- \text{ ion } (\%) = ([Cl^-]_{L,t}/[Cl^-]_{R,0}) \times 100 \qquad (4)$$

where $[Cl^-]_{R,0}$ and $[Cl^-]_{L,t}$ (mol/L) are the initial concentrations of Cl^- ion on the R side and on the L side after t hours when the concentration of organic anion on the L side is maximum.

In Fig. 2 the transport fraction and the transport rate of benzene sulfonate ion, calculated from Eqs. (1) and (2), respectively, and the permeation fraction of Na^+ and Cl^- ions, determined from Eqs. (3) and (4), are plotted against the initial pH on the L side.

The transport fraction and the transport rate of benzenesulfonate ion were optimum with an initial pH of 13.0 on the L side. Figure 1 also

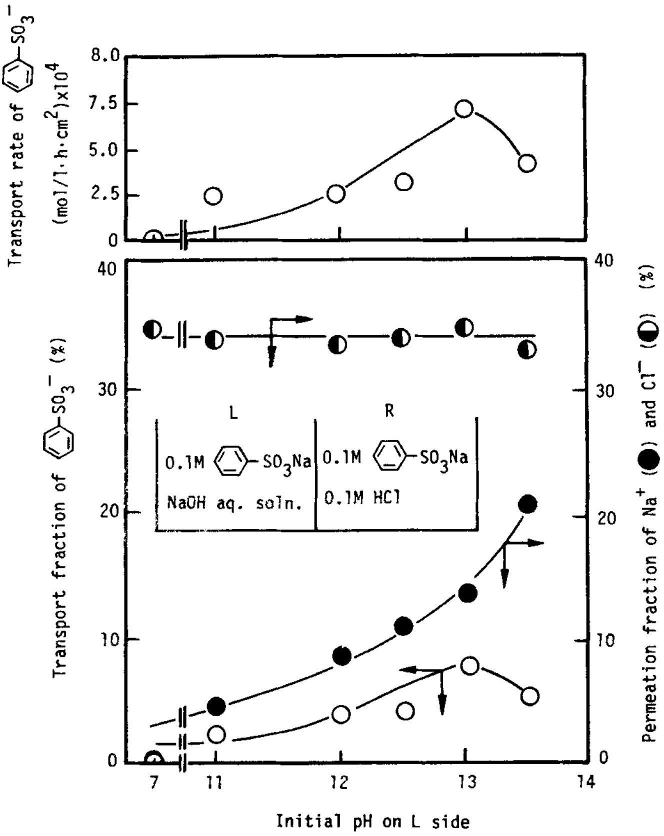


FIG. 2. Effect of the initial pH on the L side on the transport fraction and transport rate of benzenesulfonate ion, and the permeation fractions of Na^+ and Cl^- ions through the chitosan-PVA membrane. L side: 0.1 *M* sodium benzenesulfonate and NaOH aqueous solution; R side: 0.1 *M* sodium benzenesulfonate and 0.1 *M* HCl.

includes the pH changes on both sides with time when the initial pH on the L and R sides were 13.0 and 1.0, respectively. As can be seen from the pH changes in Fig. 1, the pH on the L and R sides remained alkaline and acidic, respectively, for a long time. The appearance of the optimum in Fig. 2 is dependent on keeping a large pH difference between the two sides for a long time, but when the initial pH on the L side was lower or higher than pH 13.0, both the L and R sides rapidly became alkaline or acidic. As will be shown in Fig. 9, the active transport of benzenesulfonate ion is due to interactions with a fixed carrier, the amino group, in the chitosan–PVA membrane. Incorporation into the membrane and release from the membrane of benzenesulfonate ion are significantly influenced by the pH's on both sides. The large pH difference between sides across the membrane is favorable for the incorporation and release of benzenesulfonate ion. The optimum phenomenon appearing at pH 13.0 in the active transport of benzenesulfonate ion may be attributed to the above factors. The permeation fractions of Cl^- ion in Fig. 2 were approximately constant regardless of the initial pH on the L side. This is due to a constant initial concentration of Cl^- ion on the R side and supports a diffusive transport of Cl^- ion from the R side to the L side based on the concentration difference between the sides.

The permeation fraction of Na^+ ion increased as the initial pH on the L side became higher. This depends on an increase of the concentration difference of Na^+ ion between the sides, because sodium hydroxide was used as the control reagent of pH on the L side.

When benzenesulfonic acid was used instead of a mixture of sodium benzenesulfonate and hydrochloric acid on the R side in Fig. 2, benzenesulfonate ion was actively transported from the R side to the L side (Fig. 1). Figure 3 shows the transport fraction, the transport rate of benzenesulfonate ion, and the permeation fraction of Na^+ ion through the chitosan–PVA membrane when benzenesulfonic acid was used on the R side. The transport fraction and transport rate of benzenesulfonate ion and the permeation fraction of Na^+ ion in Fig. 3 were greater than those appearing in Fig. 2. The improvement of the transport fraction and transport rate of benzenesulfonate ion appearing in Fig. 3 is mainly caused by the fact that an electric potential difference across the chitosan–PVA membrane is maintained for a long time, as shown in Fig. 4 which compares both systems. The transport of benzenesulfonate ions shown in Figs. 2 and 3 involves H^+ ions. The primary chemical species which induces the active transport of benzenesulfonate ions are OH^- ions on the L side. Therefore, OH^- ions play important roles as the driving force in the active transport of benzenesulfonate ions and as the controlling reagent for chemical and physical structures of the chitosan–

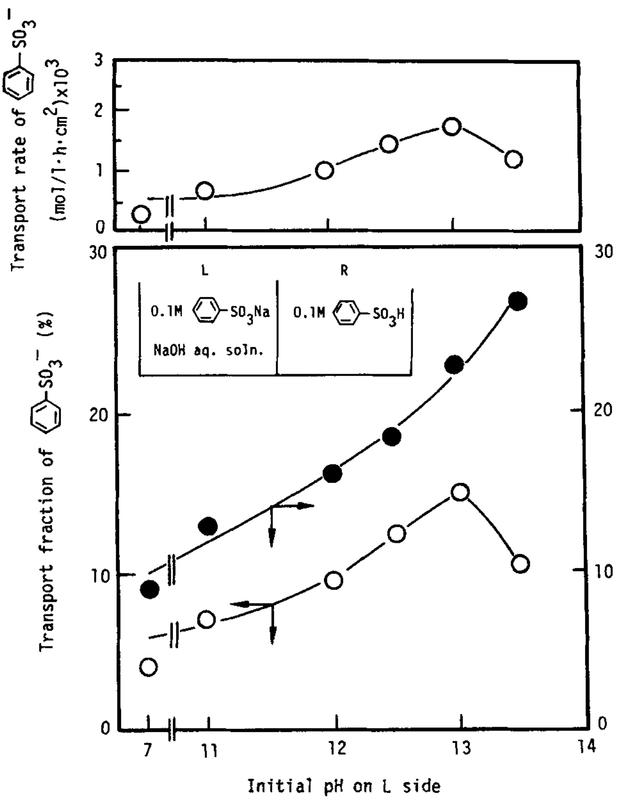


FIG. 3. Effect of the initial pH on the L side on the transport fraction and transport rate of benzenesulfonate ion, and the permeation fraction of Na^+ ion. L side: 0.1 *M* sodium benzenesulfonate and NaOH aqueous solution; R side: 0.1 *M* benzenesulfonic acid.

PVA membrane. The electric potential difference between the two sides is significantly governed by the transport of OH^- ions through the chitosan–PVA membrane.

Transport of Weak Organic Acid Anion

Figure 5 shows an example for time changes of concentration of acetate ion, pH, and K^+ ion through the chitosan–PVA membrane, where the L side was 5.0×10^{-2} *M* CH_3COOK and 0.1 *M* KOH, and the R side was 5.0×10^{-2} *M* CH_3COOH. From Fig. 5 it can be seen that the pH on both sides changed and K^+ and OH^- ions were transported diffusively

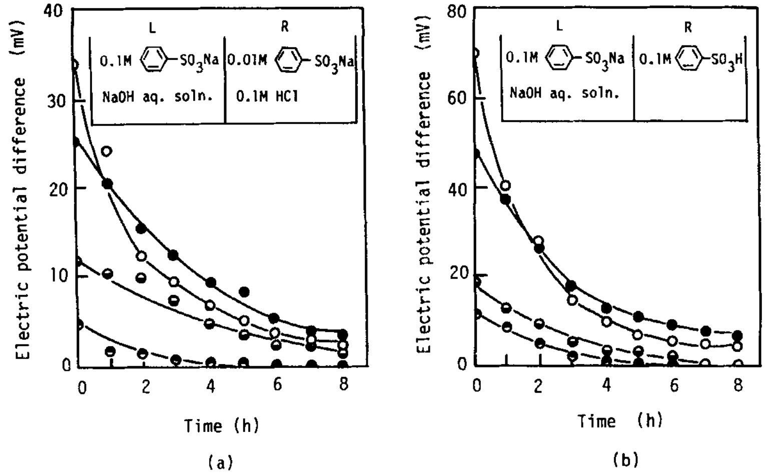


FIG. 4. Changes of the electric potential difference between both sides with time across the chitosan-PVA membrane. Initial pH: (○) 13.5; (●) 13.0; (⊖) 11.0; (◒) 7.0. L side in (a) and (b): 0.1 *M* sodium benzenesulfonate and NaOH aqueous solution; R side in (a) and (b): 0.1 *M* sodium benzenesulfonate and 0.1 *M* HCl, and 0.1 benzenesulfonic acid, respectively.

from the L side to the R side, but the acetate ion could not be entirely transported. Even if the initial pH on the L side was changed, similar results were obtained. When the acetic acid on the R side in the system of Fig. 5 was changed to a mixture of potassium acetate and hydrochloric acid, transport of the acetate ion was not observed. The electric potential differences across the membrane rapidly decreased with time in these systems.

In the mixture of potassium acetate and hydrochloric acid, the following reaction occurs:

$$CH_3COOK + HCl \rightarrow CH_3COOH + KCl$$

Therefore, the probable occurrence of acetate ion on the R side is low.

From these results it is presumed that the transport characteristic of weak acids through the chitosan-PVA membrane is due to the degree of dissociation of the acid, i.e., pK_a. Table 1 summarizes pK_a values (*17*) of some weak organic acids. It is expected that organic acids with low pK_a values will be actively transported through the chitosan-PVA membrane.

In this study, benzoic acid with a moderate pK_a value was used and its transport profile investigated. An example of the concentration changes of benzoate ion and the pH change on both the R and L sides with time

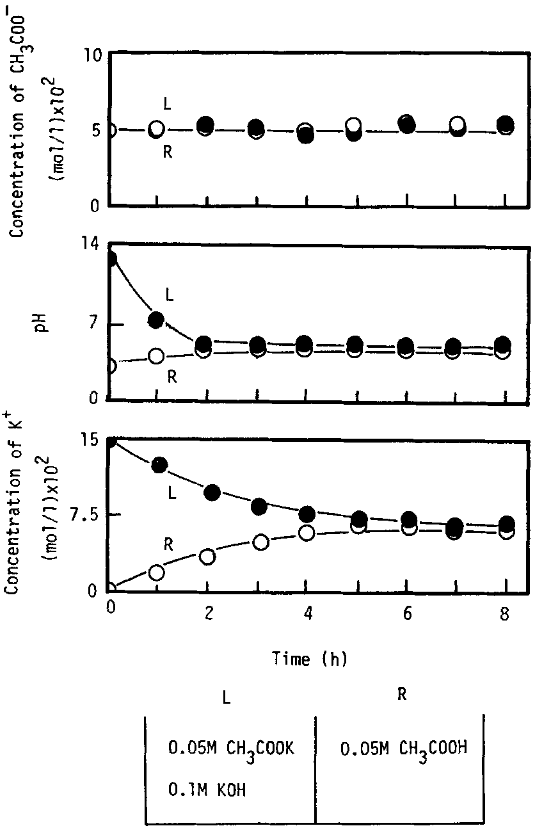


FIG. 5. Changes of the acetate ion concentrations, pH, and K^+ ion with time on both sides through the chitosan–PVA membrane. L side: 5.0×10^{-2} *M* CH_3COOK and 0.1 *M* KOH; R side: 5.0×10^{-2} *M* CH_3COOH.

due to the transport through the chitosan–PVA membrane is shown in Fig. 6, where the L side was sodium benzoate of 1.0×10^{-2} *M* and NaOH 1.0×10^{-3} *M*. As can be seen from Fig. 6, benzoate ion was actively transported from the R side to the L side against the concentration gradient across the membrane.

Figure 7 shows the effect of initial pH on the L side on the transport fraction, the transport rate of benzoate ion from the R side to the L side, and the permeation fraction of Na^+ ion from the L side to the R side. The transport fraction and the transport rate of benzoate ion were maxima at an initial pH of 11 on the L side. These results are mainly due to the pHs

TABLE 1
The pK_a Values of Some Weak Organic Acids

Organic acid		pK_a
Valeric acid	C_4H_9COOH	4.86
Propionic acid	C_2H_5COOH	4.87
Acetic acid	CH_3COOH	4.75
Benzoic acid	C_6H_5COOH	4.20
o-Chlorobenzoic acid	$C_6H_4(Cl)COOH$	2.94
o-Nitrobenzoic acid	$C_6H_4(NO_2)COOH$	2.17

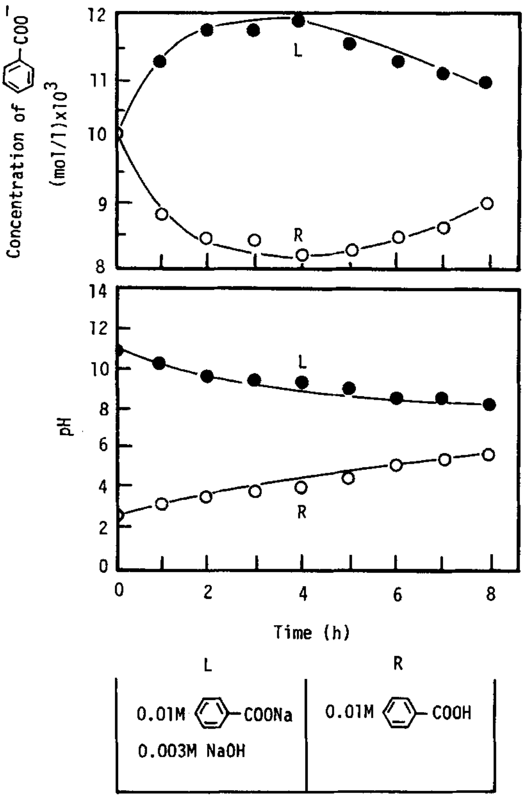


FIG. 6. Changes of the benzoate ion concentration and pH with time on both sides through the chitosan–PVA membrane. L side: 1.0 × 10^{-2} *M* sodium benzoate and 1.0 × 10^{-3} *M* NaOH; R side: 1.0 × 10^{-2} *M* benzoic acid.

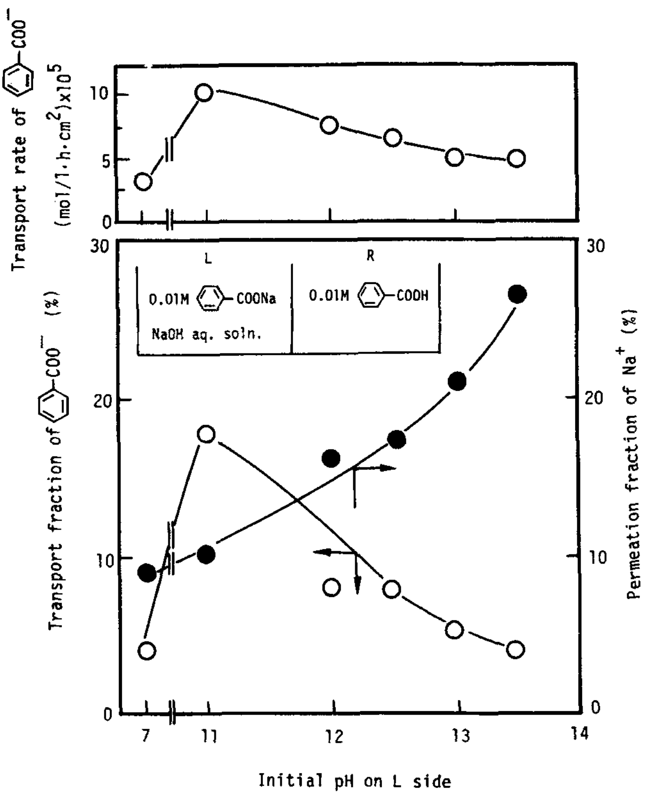


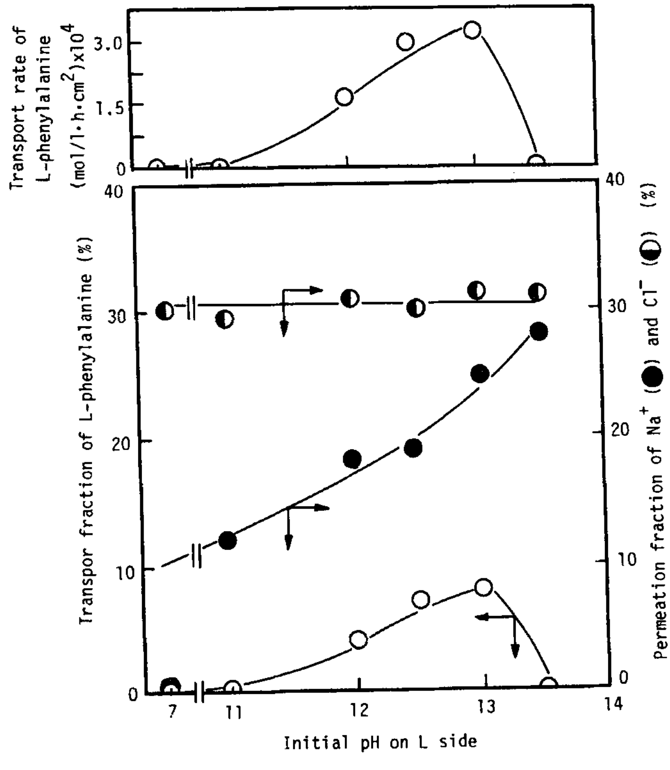
FIG. 7. Effect of the initial pH on the L side on the transport fraction and transport rate of benzoate ion, and the permeation fraction of Na^+ ion through the chitosan–PVA membrane. L side: 1.0×10^{-2} *M* sodium benzoate and NaOH aqueous solution; R side: 1.0×10^{-2} *M* benzoic acid.

on the L and R sides being alkaline and acidic for a long time, respectively. Also, the transport fraction of benzoate ion corresponded to the electric potential difference between the two sides, as well as those of halogenide (*3*) and benzenesulfonate ions.

From the above results it is suggested that the active transport of a weak organic acid ion is significantly related to its pK_a value, i.e., the degree of dissociation of an organic acid in an aqueous solution is a very important factor.

Transport of Amino Acid

The effect of the initial pH on the L side on the transport fraction and transport rate of L-phenylalanine, and the permeation fractions of Na^+ and Cl^- ions through the chitosan–PVA membrane are shown in Fig. 8, where the L side was L-phenylalanine of 5.0×10^{-2} *M* and aqueous solution of NaOH and the R side was L-phenylalanine of 5.0×10^{-2} *M* and 0.1 *M* HCl. The L-phenylalanine molecule was actively transported.



L	R
0.05M L-phenylalanine NaOH aq. soln.	0.05M L-phenylalanine 0.1M HCl

FIG. 8. Effect of the initial pH on the L side on the transport fraction and transport rate of L-phenylalanine, and the permeation fractions of Na^+ and Cl^- ions through the chitosan–PVA membrane. L side: 5.0×10^{-2} *M* L-phenylalanine and NaOH aqueous solution; R side: 5.0×10^{-2} *M* L-phenylalanine and 0.1 *M* HCl.

In this case, however, a direction of the active transport of L-phenylalanine across the chitosan-PVA membrane differed from those of halogen ions (*3*) and such organic anions as benzenesulfonate and benzoate ions, and was from the L side (alkaline side) to the R side (acidic side).

Tentative Mechanisms of Active Transport for Organic Anions and Amino Acids

A tentative mechanism of the active transport of organic anions such as benzenesulfonate and benzoate ions through the chitosan-PVA membrane is shown on Fig. 9. On the R side (H^+ side), the amino group in the chitosan-PVA membrane is positively charged. Benzenesulfonate

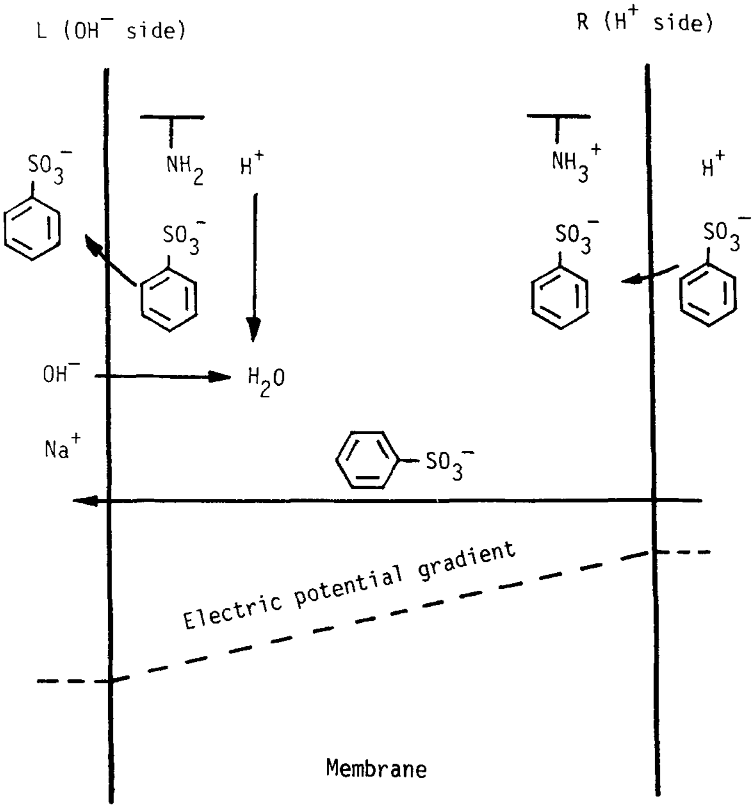


FIG. 9. Tentative mechanism of organic anions through the chitosan-PVA membrane.

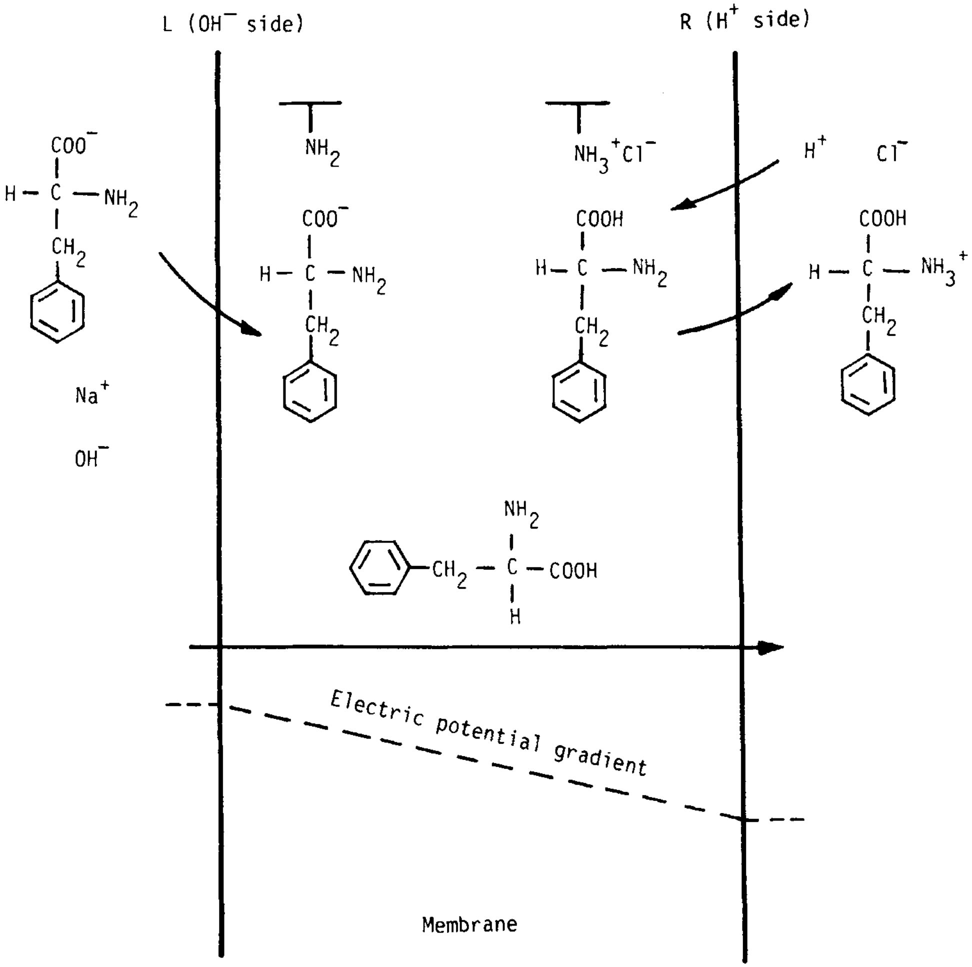


FIG. 10. Tentative mechanism of amino acids through the chitosan-PVA membrane.

ion on the R side is incorporated into the membrane by an electrostatic interaction with the positively charged amino group. The incorporated benzenesulfonate ion is transferred on the fixed carrier in the membrane according to the electric potential gradient between both sides of the membrane. When the benzenesulfonate ion that interacted electrostatically with the positively charged amino group reaches the interface of the membrane on the L side (OH^- side), neutralization between the proton and the hydroxide ion gives the amino group and the benzenesulfonate ion. This released benzenesulfonate ion is transferred to the L side by the electric potential gradient. The active transport of organic anions such as benzenesulfonate and benzoate ions from the acidic side to the alkaline side through the chitosan–PVA membrane is nicely explained by the above tentative mechanism.

Figure 10 shows the tentative mechanism of the active transport of amino acids such as L-phenylalanine and glycine through the chitosan–PVA membrane. The phenylalanine molecule is charged negatively on the L side and positively on the R side. On the other hand, the chitosan–PVA membrane is kept neutral on the L side and positive on the R side. Therefore, it is very difficult for the L-phenylalanine on the R side to enter the membrane on the R side because of electrostatic repulsion between the positively charged L-phenylalanine and the positively charged chitosan membrane. On the other hand, negatively charged L-phenylalanine and the amino group in the chitosan–PVA membrane transferred through the membrane. When the negatively charged L-phenylalanine reaches the R side (H^+ side), it is released by H^+ ion. Consequently, it is suggested that L-phenylalanine is actively transported through the chitosan–PVA membrane from the alkaline side to the acidic side.

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