

# Preparation of Microporous Membrane-Containing Sulfonic Acid Group

## INTRODUCTION

As has been shown in previous papers,<sup>1-5</sup> poly(vinyl chloride) (PVC) microporous membranes were obtained from cation-exchange membranes prepared by the paste method<sup>6,7</sup> or the soaking method.<sup>8</sup> The method was based on the findings that (1) polymerization of styrene (St) and divinylbenzene (DVB) in a PVC gel phase brought about microphase separation of the copolymer from PVC; (2) the cation-exchange resin component (R-resin) resulting from the sulfonation of the copolymer was selectively decomposed by treatment with hydrogen peroxide.

We have recently developed a modification of this method to control the degree of decomposition of the R-resin. In this connection, the present paper deals with the preparation and some properties as filter of PVC microporous membranes with different quantities of sulfonic acid groups.

## EXPERIMENTAL

### Cation-Exchange Membrane

The membrane used was Neosepta CH-45T (Tokuyama Soda Co.) prepared by the paste method. Its characteristics are as follows: cation-exchange capacity (Na<sup>+</sup> form), 2.1 mEq/g dry membrane; water content (Na<sup>+</sup> form), 0.35 g H<sub>2</sub>O per gram dry membrane; transport number (measured by electrodialysis in 0.5 N NaCl at 25°C, at a current density of 2.0 A/dm<sup>2</sup>), >0.98; and thickness, 0.17 mm.

### Hydrogen Peroxide Treatment

Several pieces (7 × 7 cm) of Neosepta CH-45T were immersed in each of various mixed solutions of FeCl<sub>3</sub> + MCl<sub>n</sub> (MCl<sub>n</sub>: KCl, NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, BaCl<sub>2</sub>) at room temperature for a long time. They were then treated with 5% hydrogen peroxide solution at room temperature for different times (—1300 min).

### Water Permeability Measurement

For measurement of water permeability of porous membranes, a batch-type ultrafiltration cell, which was similar to that described in an earlier paper,<sup>9</sup> was used without stirring. The effective membrane area was 6.15 cm<sup>2</sup>, and the applied pressure was 3 kg/cm<sup>2</sup>.

## RESULTS AND DISCUSSION

Figure 1 shows the change in the residual cation-exchange capacity of Neosepta CH-45T with the time of the hydrogen peroxide treatment. It is noteworthy that the decreasing curves in case of Fe<sup>3+</sup>–Ca<sup>2+</sup> and Fe<sup>3+</sup>–Ba<sup>2+</sup> systems approach constant values after 400 min or so. It has already been shown that the hydrogen peroxide treatment effectively converted the Fe<sup>3+</sup> form of the Neosepta membrane into a PVC porous membrane owing to the rapid decomposition of the R-resin.<sup>2</sup> On the other hand, the membranes of the Na<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, and Mg<sup>2+</sup> forms were found almost unaffected by the treatment. This finding can be explained in terms of the cation-exchange equilibrium in the membrane. Generally, Ba<sup>2+</sup> and Ca<sup>2+</sup> ions are taken into cation exchangers with sulfonic acid group in preference to other cations. So, the Fe<sup>3+</sup> quantity in the Neosepta sample membrane should be less in case of the Fe<sup>3+</sup>–Ba<sup>2+</sup> and Fe<sup>3+</sup>–Ca<sup>2+</sup> systems.

Figure 2 shows the effect of the ratio of the ionic concentrations of Fe<sup>3+</sup> and Ca<sup>2+</sup> ions in

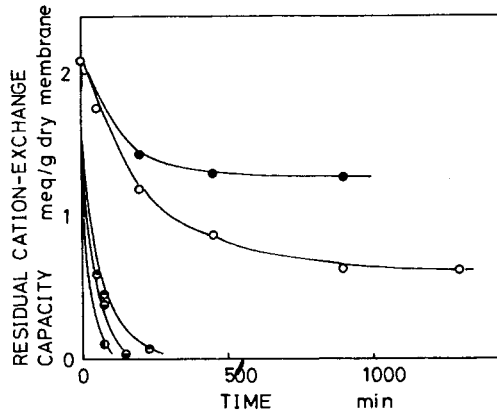


Fig. 1. Time-dependent curves of the residual cation-exchange capacity during  $\text{H}_2\text{O}_2$  treatment of Neosepta CH-45T previously immersed in the solutions containing  $0.075\text{ N Fe}^{3+}$  and  $0.925\text{ N M}^{n+}$  ( $\bullet$ ,  $\text{Ba}^{2+}$ ;  $\circ$ ,  $\text{Ca}^{2+}$ ;  $\bullet$ ,  $\text{Mg}^{2+}$ ;  $\circ$ ,  $\text{K}^+$ ;  $\circ$ ,  $\text{Na}^+$ ) ions.

the solution on the decreasing curve of the cation-exchange capacity. Evidently, the residual capacity after the hydrogen peroxide treatment longer than 600 min can be controlled by adjusting the ratio of the ionic concentrations ( $\text{Fe}^{3+}$ - $\text{Ca}^{2+}$ ).

Figure 3 shows the water permeability of the sample membranes with different residual cation-exchange capacity obtained by the above method. With decreasing the residual cation-exchange capacity, the water permeability expectedly enhances. When the residual cation-exchange capacity is more than 50% of the initial value, the water permeability is very small under the applied pressure of  $3\text{ kg/cm}^2$ . When the residual cation-exchange capacity is less than 20–30%, the water permeability becomes considerably large. It was also found that cane

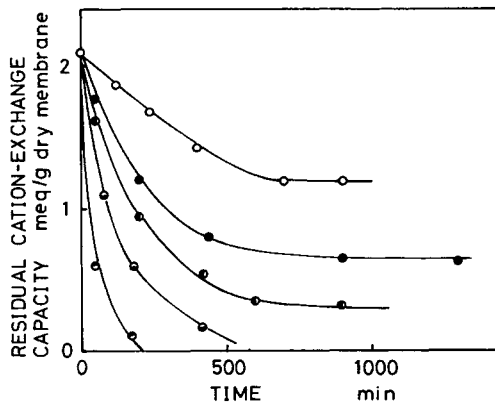


Fig. 2. Effect of the ratio of ionic concentrations ( $\text{Fe}^{3+}$ - $\text{Ca}^{2+}$ ) of the pretreating solution on the time-dependent curve of the residual cation-exchange capacity during  $\text{H}_2\text{O}_2$  treatment of Neosepta CH-45T.

$\text{Fe}^{3+}$ - $\text{Ca}^{2+}$ :

- |                            |                           |
|----------------------------|---------------------------|
| $\circ$ , 0.05 N-0.95 N;   | $\bullet$ , 0.75 N-0.925; |
| $\bullet$ , 0.10 N-0.90 N; | $\circ$ , 0.25 N-0.75;    |
| $\bullet$ , 0.50 N-0.50 N. |                           |

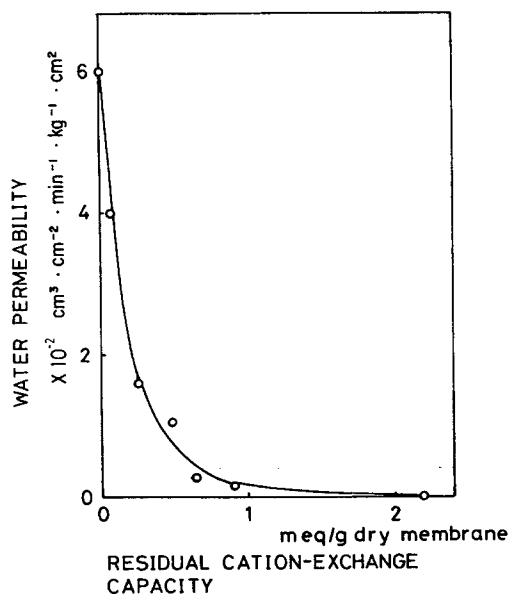


Fig. 3. Relation between water permeability and residual cation-exchange capacity of Neosepta CH-45T after different extents of  $H_2O_2$  treatment.

sugar could diffuse through such water-permeable membranes with the capacity less than 50% of the initial value. Though the flux is not so high, this means that the pore size is big enough as relatively high-molecular-weight neutral solutes like cane sugar can pass through.

Table I shows some properties of a microporous membrane with a sulfonic acid group. The cation-exchange capacity, more than half of the initial value, was lost. The apparent pore radius was calculated to be 25nm by using Hagen-Poiseuille's law, assuming that the pore was cylindrical and vertical to the membrane surface.<sup>2,3</sup> Here, it is very interesting that, although the membrane is porous and water-permeable, the membrane still has high cation permselectivity in a 0.5 *N* NaCl solution, suggesting the effect of the residual sulfonic acid group on the transfer of ionic species. This cation permselectivity should be dependent on the balance among the pore size, the residual cation-exchange capacity, and the ionic concentration of the external solution, among other factors. The practical applicability of the microporous

TABLE I  
Properties of a Microporous Membrane Containing Sulfonic Acid Group

Residual cation-exchange capacity <sup>a</sup> (mEq/g dry membrane)	Porosity	Transport number <sup>b</sup>	Apparent <sup>c</sup> pore radius (nm)
0.96	0.47	0.85	25

<sup>a</sup> Residual value/initial value = 0.46

<sup>b</sup> Determined by electro dialysis in a 0.5 *N* NaCl solution at 25°C.

<sup>c</sup> Determined from water permeability by using Hagen-Poiseuille's law.<sup>5,6</sup>

membrane with a sulfonic acid group must be investigated in detail, especially for the separation between ionic and neutral species.

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