

## Microheterogeneity of Anion Exchange Membranes

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### Synopsis

Anion exchange membranes (ferricyanide ion type) prepared by the "paste method" were treated with an aqueous solution of hydrogen peroxide, and the resultant microporous membranes had no ion exchange capacity but water permeability. By measuring the water permeability of the membranes and observing the electron microphotographs of the membrane surfaces, it was elucidated that the anion exchange membranes contained microheterogeneity of colloidal dimension.

### INTRODUCTION

So far, some studies have shown that ion exchangers have unavoidable microheterogeneity or localized distributions of ion exchange group density and of crosslinking degree.<sup>1-3</sup> Also, we have already elucidated that cation exchange membranes prepared by the "paste method"<sup>4-8</sup> and the "graft method"<sup>9</sup> contain microheterogeneity of colloidal dimension.<sup>10-12</sup> In the "paste method," the paste is first prepared by mixing a fine powder of poly(vinyl chloride) (PVC) and monomer mixture consisting mainly of styrene (St)-divinylbenzene (DVB)-benzoylperoxide (BPO, a polymerization initiator) or vinylpyridine (VP)-DVB-BPO. The paste is then coated onto Tevion cloth (PVC cloth from Teijin Co., Ltd., a reinforcing material), the resultant composite is heated to polymerize the monomers, and thus the base membrane is prepared. Ion exchange groups are introduced onto the base membranes by the ordinary method.<sup>4,5</sup> The ion exchange membranes are prepared by using DVB as a crosslinking agent, but the membranes obtained are not brittle but flexible. This fact has suggested that the chemical structure of the ion exchange membranes is different from that of the ion exchangers of gel type with three-dimensional matrix. So, in order to make the difference clearer, the ion exchange membranes were extracted with tetrahydrofuran (THF), and the following facts were elucidated: the cation exchange membranes, prepared by using a paste consisting of PVC powder-St-DVB, contained fine particles of the cation exchange resin component able to get through filter paper, but only a small amount of the anion exchange resin component got through the filter paper in the case of the anion exchange membranes prepared from a paste consisting of PVC powder-2-methyl-5-vinylpyridine-DVB.<sup>10</sup> Furthermore, owing to the facts that cation exchangers (gel type) of ferric styrene sulfonate type could be completely decomposed by hydrogen peroxide treatment and, on the other hand, PVC was substantially resistant

TABLE I  
Anion Exchange Membranes

|  | Neosepta AV-4T <sup>a</sup>  | Neosepta AF-4T <sup>a</sup>  | Neosepta ACH-45T <sup>a</sup>  |
|--|------------------------------|------------------------------|--------------------------------|
| Anion exchange group                                     | quarternary pyridinium group | quarternary pyridinium group | Trimethylbenzyl-ammonium group |
| Electric resistance, <sup>b</sup><br>ohm cm <sup>2</sup> | 3-4                          | 2-3                          | 2-3                            |
| Transport number <sup>c</sup>                            | >0.98                        | >0.98                        | >0.98                          |
| Ion exchange capacity,<br>meq/g dry membrane             | 1.5-2                        | 1.5-2                        | 1.5-2                          |
| Water content,<br>g H <sub>2</sub> O/g dry membrane      | 0.25-0.3                     | 0.25-0.3                     | 0.3-0.35                       |

<sup>a</sup> Commercial anion exchange membranes manufactured by Tokuyama Soda Co., Ltd.

<sup>b</sup> Measured in a 0.5*N* NaCl solution at 25°C.

<sup>c</sup> Measured by electro dialysis in a 0.5*N* NaCl solution at 25°C and current density of 2 A/dm<sup>2</sup>.

to the treatment, the cation exchange membranes of ferric ion type could be transformed by the hydrogen peroxide treatment into a microporous membrane with no ion exchange capacity but water permeability.<sup>11,12</sup>

These facts clearly showed that the cation exchange membranes contained microheterogeneity of colloidal dimensions. It is for this reason that cation exchange membranes prepared by the "graft method"<sup>9</sup> and the "paste method"<sup>4-8</sup> are not brittle. On the other hand, the microheterogeneity of the anion exchange membranes was suggested by the THF extraction but could not be clearly confirmed because the result of the THF extraction was pretty different from that of the cation exchange membranes and also the hydrogen peroxide treatment was not available for the anion exchange membranes. However, we have recently found a way to decompose only the anion exchange resin component of the anion exchange membranes and, for the first time, the presence of a microheterogeneity could be verified in this study.

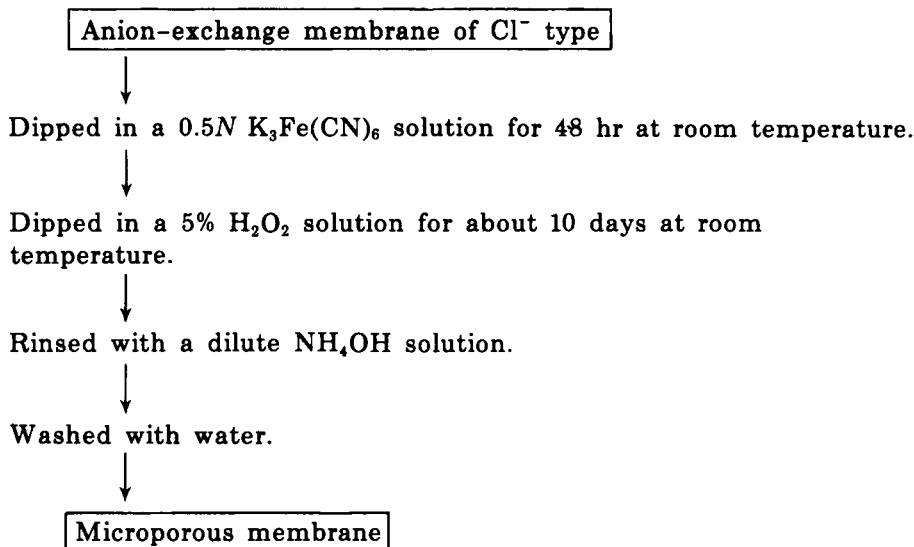
## EXPERIMENTAL

### Materials

The anion exchange membranes used are shown in Table I. All reagents used were of chemical grade.

### Hydrogen Peroxide Treatment

First, the anion exchange membranes were repeatedly washed alternately with 0.1*N* aqueous solutions of hydrochloric acid and ammonia and then water. The hydrogen peroxide treatment scheme is shown below:



### Measurement of Water Permeability

The apparatus used was the same as that shown in the previous papers.<sup>11,12</sup> The pressure difference was applied between both sides of the membrane, and the pressure difference was measured by means of a mercury differential manometer. The permeating rate of water through the membranes was measured at 25°C by applying a definite pressure difference.

### Calculation of Pore Size, Pore Number, and Tortuosity Factor of Pore

The size ( $\gamma$ , cm) and number ( $n$ , cm<sup>-2</sup>) of pores of the porous membrane were calculated by the aid of eqs. (1)–(3), as were used in the previous studies.<sup>11–13</sup> Equations (1) and (2) can be derived from D'Arcy's law and Poiseuille's law.

$$\gamma = \sqrt{\frac{8\eta LQ}{\epsilon A \Delta P}} = \sqrt{\frac{8}{\epsilon} K_p} \quad (1)$$

$$n = \frac{\epsilon^2}{8\pi K_p} \quad (2)$$

$$\epsilon = \frac{W_e - W_d}{AL\rho_w} = \pi\gamma^2 n \quad (3)$$

where  $L$  = thickness of the membrane (cm);  $Q$  = permeation rate of water through the membrane (cm<sup>3</sup>/sec);  $\epsilon$  = porosity of the membrane;  $A$  = effective area of the membrane (cm<sup>2</sup>);  $\Delta P$  = pressure difference between both sides of the membrane (dyne/cm<sup>2</sup>);  $K_p$  = specific permeability of the membrane (cm<sup>2</sup>);  $W_e$  = wet weight of the membrane (g);  $W_d$  = dry weight of the membrane (g);  $\rho_w$  = specific gravity of water ( $\approx 1$ ); and  $\eta$  = viscosity of water (poise, 0.00895 poise at 25°C).

TABLE II  
Changes in Membrane Characteristics by Hydrogen Peroxide Treatment

|                       | Neosepta AV-4T |         | Neosepta AF-4T |         | Neosepta ACH-45T |         |
|-----------------------|----------------|---------|----------------|---------|------------------|---------|
|                       | Untreated      | Treated | Untreated      | Treated | Untreated        | Treated |
| Thickness, mm         | 0.16           | 0.15    | 0.16           | 0.15    | 0.17             | 0.16    |
| Area, cm × cm         | 7 × 7          | 6.8 × 7 | 7 × 7          | 6.8 × 7 | 7 × 7            | 6.9 × 7 |
| Elemental analysis, % |                |         |                |         |                  |         |
| N                     | 2.58           | 0.3     | 2.62           | 0.1     | 2.31             | 0.2     |
| Cl                    | —              | 54.36   | —              | 54.08   | —                | 54.12   |

Assuming the square array of the pores, the apparent pore distance ( $\delta$ , cm) can be given by eq. (4):

$$\delta = \frac{1}{\sqrt{n}} \quad (4)$$

Also, the tortuosity factor of pores ( $\sigma$ ) was defined as follows:

$$\sigma = \frac{R_m}{R_i} \quad (5)$$

$$R_i = \frac{RnL}{\epsilon} \quad (6)$$

where  $R_m$  = electric resistance of the microporous membrane in a 0.5*N* aqueous solution of sodium chloride at 25°C (ohm-cm<sup>2</sup>) and  $R_n$  = specific electric resistance of the 0.5*N* aqueous solution of sodium chloride at 25°C (ohm-cm).

## RESULTS AND DISCUSSION

The anion exchange membranes of chloride ion form were not easily decomposable by the hydrogen peroxide treatment, so the use of the promoters was considered to be advantageous. The method for cation exchange membranes in the previous papers<sup>11,12</sup> could not be applied to the anion exchange membranes. It was newly found that anions containing some heavy metals (for example, permanganate ion, ferricyanide ion, ferric chloride complex ion, and cupric chloride complex ion) were effective in promoting only the decomposition of the anion exchange resin component by the hydrogen peroxide treatment but not PVC. Accordingly, the experimental results by using ferricyanide ion as the promoter is shown in this paper. Regarding the hydrogen peroxide treatment, the decomposition rate of the anion exchange resin component was slower than that of the cation exchange resin component,<sup>11</sup> but the details of the decomposition reactions are still obscure.

Table II shows the changes in the membrane characteristics produced by the hydrogen peroxide treatment. The chlorine contents of the resultant membranes were a little less than that of PVC itself (56.4%) probably because of the partial degradation of PVC, as was similarly observed in the hydrogen

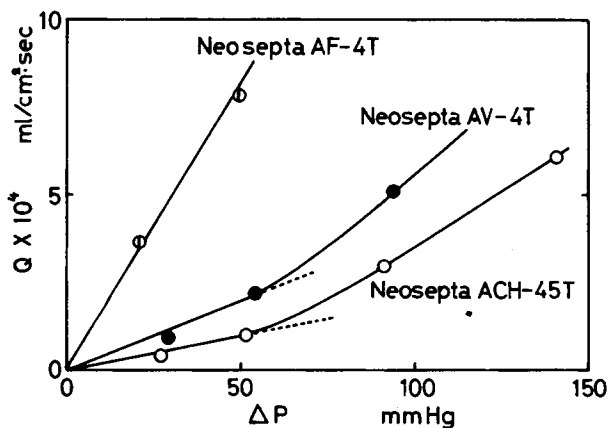


Fig. 1. Relation between permeation rates of water through the treated membranes and pressure differences.

peroxide treatment of the cation exchange membrane.<sup>11</sup> Also, a small amount of nitrogen could be detected in the resultant membranes, though the membranes showed no capacity for ion exchange with neutral salts, and the chemical structure relating to the nitrogen is still obscure. This is surely one of the reasons for the lower chlorine content described above. Because of the hydrogen peroxide treatment, the thickness and the size of the membranes decreased somewhat owing to the loss of swelling pressure of the anion exchange resin component. Thus, it could be considered that the anion exchange resin component was almost decomposed. The resultant membranes showed water permeability, as shown in Figure 1. In advance, it was confirmed that the anion exchange membranes before the hydrogen peroxide treatment had no water permeability. From the slope of the linear part, the specific permeability ( $K_p$ ) could be determined and then the pore size, the pore number, the pore distance, and the tortuosity factor of the pore could be calculated with the aid of eqs. (1), (2), (4), and (5), respectively, as shown in Table III. The apparent order of the pore size was as follows: Neosepta AF-4T > Neosepta AV-4T > Neosepta ACH-45T. However, the pore sizes were determined by assuming that the pores were cylindrical and vertical to

TABLE III  
Characteristics of Resultant Porous Membranes

|   | Neosepta AV-4T <sup>a</sup> | Neosepta AF-4T <sup>a</sup> | Neosepta ACH-45T <sup>a</sup> |
|---|-----------------------------|-----------------------------|-------------------------------|
| Thickness, mm                                   | 0.15                        | 0.14                        | 0.16                          |
| Porosity  | 0.513                       | 0.497                       | 0.563                         |
| Specific permeability, cm <sup>2</sup>          | $4.2 \times 10^{-13}$       | $1.5 \times 10^{-12}$       | $2.2 \times 10^{-13}$         |
| Pore radius, cm                                 | $2.6 \times 10^{-6}$        | $4.9 \times 10^{-6}$        | $1.8 \times 10^{-6}$          |
| Pore number, cm <sup>-2</sup>                   | $2.5 \times 10^{10}$        | $6.6 \times 10^9$           | $5.7 \times 10^{10}$          |
| Pore distance, cm                               | $6.3 \times 10^{-6}$        | $1.2 \times 10^{-5}$        | $4.2 \times 10^{-6}$          |
| Electric resistance, $\Omega \cdot \text{cm}^2$ | 0.9                         | 0.7                         | 1.3                           |
| Tortuosity factor                               | 1.5                         | 1.2                         | 2.0                           |

<sup>a</sup> Treated membrane.

TABLE IV  
Results of Treating AMFion A-100 with Hydrogen Peroxide

|                    | Thickness,<br>mm | Ion exchange<br>capacity, meq/<br>g dry membrane | Specific<br>permeability,<br>cm <sup>2</sup> |
|--------------------|------------------|--|--|
| Untreated membrane | 0.15             | 1.5  | 0  |
| Treated membrane   | 0.14             | 0  | $1.68 \times 10^{-14}$                       |

the membrane surface, so a reasonable conclusion here should be that the pore sizes of these anion exchange membranes are of comparable order.

The base membrane for Neosepta ACH-45T was prepared by using the paste consisting of PVC-St-DVB, and a similar paste was used to prepare the base membrane for the cation exchange membrane, Neosepta CL-25T, which had a microheterogeneity of colloidal order.<sup>11</sup> Accordingly, the chemical structure of Neosepta ACH-45T could be expected to be similar to that of Neosepta CL-25T. On the other hand, the microheterogeneity of Neosepta AV-4T and Neosepta AF-4T was confirmed for the first time. This result means that, although PVC is more swellable and more compatible with the VP-DVB mixture than with the St-DVB mixture, the polymerization of VP-DVB resulted in phase separation, and DVB should play an important role in promoting the phase separation. Furthermore, Table III shows that the tortuosity factors obtained in this study were similar to the values (1.6–2.5) for the cation exchange membranes prepared by the “paste method” in the previous study.<sup>12</sup> The tortuosity factors of Neosepta AV-4T and Neosepta AF-4T were about same and smaller than that of Neosepta ACH-45T. It is likely that this difference could be ascribed to the better compatibility of the VP-DVB mixture with PVC than that of the St-DVB mixture.

For reference, AMFion A-100 (anion exchange membrane from American Machine and Foundry Co., probably prepared by the “graft method”<sup>9</sup>) was similarly treated with hydrogen peroxide. The treatment resulted in a microporous membrane which was brittle and water permeable, as shown in Table IV. This result clearly shows the microheterogeneity of AMFion A-100 and also means that the polymerization of St in filmy polyethylene to make its base membrane resulted in phase separation of colloidal order.

Figure 2 shows the electron microphotographs of the membrane surfaces after the hydrogen peroxide treatment, taken with the aid of a scanning electron microscope, JSM-50A from JEOL Ltd. The samples were freeze-dried in order to maintain the real state of the pores as long as possible. The membrane areas of Neosepta ACH-45T and Neosepta AV-4T did not change, but that of Neosepta AF-4T shrank a little by freeze-drying (5 cm × 5 cm → 4.65 cm × 4.75 cm). Clearly, the photographs show the presence of the micropores. There are some pores of relatively larger sizes than those calculated from the water permeability of the membranes, and a distribution of pore sizes can be observed. However, since the calculation of the pore size from the water permeability is based on the simple assumption described before and the water permeability is restricted by the pore size of the narrowest part along the water pathway, it might be considered that the calculated pore sizes were reasonable in comparison with the relatively smaller ones shown in the photographs. Also, the photographs show the respective patterns, which should be formed due to phase separation of the resulting polymer from the

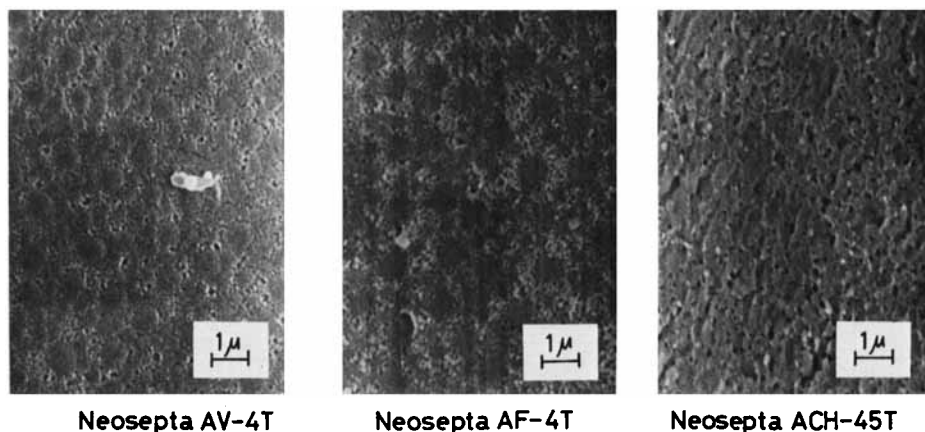


Fig. 2. Electron microphotographs of the microporous membrane surfaces.

monomers in the paste and the fusion of the PVC powder into continuous phase during the polymerization. The distribution of the pores and the pore sizes should be affected by various factors such as the PVC/monomer ratio, the DVB/monomer ratio, the polymerization temperature, etc. So, the details must be clarified in the future. In the polymerization of the monomers in the PVC paste, the graft polymer should be produced, as presumed by the fact that a graft polymer of St onto PVC was obtained in the polymerization of St in a PVC film.<sup>14</sup> However, it is obscure what kind of role the graft polymer plays in the phase separation during the polymerization or in the formation of the membrane microstructure. The results in this paper should be important not only in confirming the presence of microheterogeneity of the anion exchange membranes and in making it easier to consider the relation between the function and the chemical structure of the anion exchange membranes, but also to show an example of polymerization with phase separation.

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