

Studies on Ion-Exchange Membranes. XXXII. Heterogeneity in Ion-Exchange Membranes*

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Synopsis

Twelve kinds of cation-exchange membranes were treated with hydrogen peroxide. Some of them (Selemion CMV, Nepton CR-61, Sciron C-100, SAM-1) were completely destroyed. Heterogeneity is believed to be present in that part of their chemical structures that is decomposable by the treatment. The other membranes were converted into porous membranes by the decomposition of the resinous part. Water permeabilities and electric resistances of the porous membranes were examined to evaluate the pore radius. It was concluded that the "paste method" membranes have a heterogeneity or localized distribution of the resinous part under 50 μ . The "paste method" membranes seemed to resemble the "graft method" membranes in chemical structure and to be much different from the mosaic-type membranes such as Permaplex and MC-3142. These results were also supported by extraction of the membranes with appropriate solvents and observation by electron microscopy.

INTRODUCTION

Although ion-exchange membranes are generally classified into homogeneous and heterogeneous types, interpretations of membrane phenomena have frequently been based upon the assumption that they are homogeneous. On the other hand, Reichenberg and McCauley,¹ Glueckauf and Watts,² and Koschell and Schlögl³ have shown an unavoidable heterogeneity or localized distributions of the ion-exchange group density and of cross-linking degree.

The ion-exchange membranes, prepared by the "paste method"⁴⁻⁸ or the "graft method,"⁹ show excellent flexibility. This feature cannot be well explained by a simple model of tightly crosslinked gel structure. In the present study, the heterogeneity of ion-exchange membranes was studied by making use of treatment with hydrogen peroxide and extraction with an appropriate solvent.

EXPERIMENTAL

Ion-Exchange Membranes

Table I lists the characteristics of ion-exchange membranes measured by the ordinary methods.¹⁰⁻¹⁴

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TABLE I
Observed Characteristics of Sample Membranes

Trade name	Manu- facturer	Matrix ^a	Reinforcing material ^a	Ion-exchange			Remarks
				capacity, meq/g dry membrane	Electric resistance, ohm cm ² (0.5N NaCl)	Thickness mm	
Selemon CMV	Asahi Glass Co.	styrene-butadiene copolymer	poly(vinyl chloride)	1.5	5.2	0.25	31 ^b
Nepton CR-61	Ionics Inc.	polystyrene	acrylic synthetic fiber	1.9	6.2	0.60	54 ^b
Serion C-100	Organo Co.	polystyrene	polyethylene	0.6	2.7	0.21	62 ^b
SAM-1	Tokuyama Soda Co.	phenolic resin	glass fiber	0.5	—	0.15	— experimental membrane
Neosepta CL-25T	Tokuyama Soda Co.	poly(vinyl chloride) -styrene	poly(vinyl chloride)	1.75	3.0	0.19	31 "paste method"
Neosepta CH-2T	Tokuyama Soda Co.	poly(vinyl chloride) -styrene	poly(vinyl chloride)	2.05	1.8	0.16	35 "paste method"
SAM-2	Tokuyama Soda Co.	poly(vinyl chloride) -styrene	poly(vinyl chloride)	1.45	4.0	0.18	28 experimental membrane "paste method"
Neosepta, CLE-E	Tokuyama Soda Co.	polyethylene-styrene	polyethylene	1.3	25.0	0.81	18 "paste method"
MC-3142	Ionac Co.	vinyl chloride-vinyl acetate copolymer, polystyrene	poly(ethylene terephthalate)	0.9	7.7	0.18	21 heterogeneous membrane
Permaplex	Permutit Co.	polyethylene, polystyrene	nylon 6,6	2.3	20.0	0.80	35 heterogeneous membrane
AMFion C-60	AMF Co.	polyethylene-styrene	none	1.55	4.5	0.30	31 "graft method"
AMFion C-310	AMF Co.	polyfluorocarbon- styrene	none	0.65	3.8	0.30	26 "graft method"

^a Some compositions were inferred from IR spectra.

^b These values are given in g H₂O per g dry membrane.

Hydrogen Peroxide Treatment

The ion-exchange membranes of the H^+ form were converted into the Fe^{3+} form by dipping them in an aqueous solution of ferric chloride (0.15 mole/l.) and then in an aqueous solution of hydrogen peroxide (5%–10%); thus the porous membranes resulted, having no ion-exchange capacity but having water permeability.

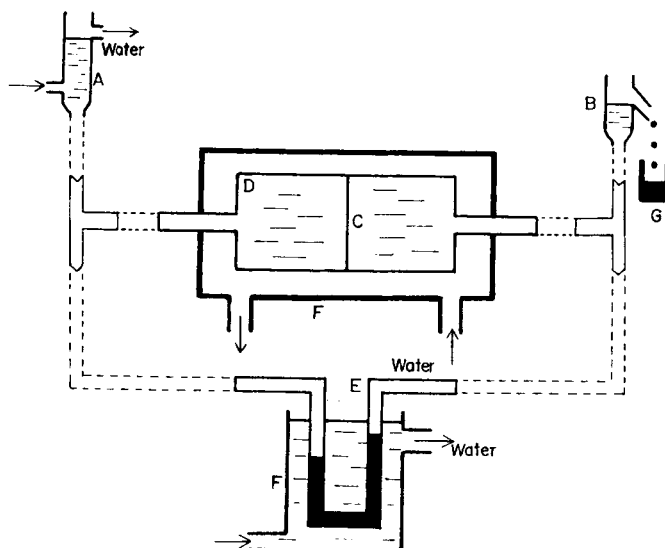


Fig. 1. Apparatus for measuring water permeabilities: (A,B) leveling bulbs; (C) sample membrane; (D) cell; (E) Hg differential manometer; (F) thermostat; (G) weighing bottle.

Measurements of Water Permeability and Electric Resistance

Figure 1 shows the apparatus for measuring the water permeability of the porous membranes. The effective area of the membrane was 20 cm^2 and the measurement was carried out at 25°C .

Electric resistance of the porous membrane in a $0.5N$ aqueous solution of sodium chloride was measured at 25°C with alternating current of 1000 C/S .

Determination of Apparent Pore Size and Tortuosity Factor of Pore

Concerning water permeation through a porous membrane, D'Arcy's law is well known:

$$K_p = \frac{Q\eta L}{A\Delta p} \quad (1)$$

where K_p is the specific permeation rate (cm^2), Δp is the pressure difference (dyne/cm^2), Q is the permeation rate (cm^3/sec), η is the viscosity of water (poise), and L is the thickness of the membrane (cm).

Porosity of the membrane is given as follows:

$$\epsilon = \frac{W_e - W_d}{AL\rho_w} \quad (2)$$

where ϵ is the porosity of the membrane, W_e is the wet weight of the membrane (g), W_d is the dry weight of the membrane (g), A is the effective area of the membrane (cm^2), and ρ_w is the density of water (g/cm^3).

By assuming that the pores in the membranes are circular tubes with the equal radius perpendicular to the membrane surface, Hagen-Poiseuille's law can be applied to one tube:

$$V = \frac{\pi\gamma^4\Delta p}{8\eta L} \quad (3)$$

where V is the permeation rate through a pore (cm^3/sec) and γ is the pore radius (cm).

Clearly, the following relation can be applied to the membrane:

$$Q = \frac{nA\pi\gamma^4\Delta p}{8\eta L} \quad (4)$$

where n is the number of the pores per unit surface area.

The porosity ϵ is expressed as follows:

$$\epsilon = \pi\gamma^2n. \quad (5)$$

From eqs. (1), (4), and (5) we obtain

$$\gamma = \left(\frac{8\eta LQ}{\epsilon A \Delta p}\right)^{0.5} = \left(\frac{8}{\epsilon} K_p\right)^{0.5} \quad (6)$$

On the other hand, the tortuosity factor is defined as follows:

$$\sigma = \frac{R_m}{R_I} \quad (7)$$

$$R_I = \frac{R_n L}{\epsilon} \quad (8)$$

where R_m is the electric resistance of the porous membrane in a 0.5*N* aqueous solution of sodium chloride (ohm cm^2) and R_n is the specific electric resistance of a 0.5*N* aqueous solution of sodium chloride (ohm cm).

Solvent Extraction

After preliminary extraction with methanol, SAM-2 and Permaplex were extracted respectively with tetrahydrofuran and benzene for 30 hr by the use of a Soxhlet extractor. The cylindrical filter paper used was Toyo Filter Paper No. 84, which retains particles larger than 8 μ .

RESULTS AND DISCUSSION

Previously, the following facts were experimentally ascertained: (1) Amberlite IR-120 (Fe^{3+} form), which is regarded as an ion-exchange resin having crosslinked gel structure, is easily decomposed by hydrogen peroxide treatment. (2) Polymer (P-polymer) other than the ion-exchange resin component (R-resin) in an ion-exchange membrane, for example poly(vinyl chloride) (PVC) or polyethylene (PE), is not substantially decomposed by the same treatment.

Table II shows the results of the hydrogen peroxide treatment of the various ion-exchange membranes. The membranes were divided into two groups. The membranes in group I were completely decomposed within several hours, leaving only reinforcing materials. The chemical structures of these membranes may be considered to be rather homogeneous. However, the ion-exchange capacities of these membranes are smaller than those of the corresponding ion-exchange resins based upon the styrene (St)-divinylbenzene (DVB) copolymer or the phenol-formaldehyde copolymer. This fact suggests that some kind of heterogeneity is present in these membranes. With respect to this problem, Koschell and Schlögl³ have already pointed out heterogeneity of colloidal dimensions in ion-exchange membranes of the phenol sulfonate type. Even in ion-exchange resins based on the St-DVB copolymer such heterogeneity has been reported.^{1,2} From the above facts it is concluded that in group I heterogeneity is present in the chemical structures decomposable by the hydrogen peroxide treatment in spite of their apparent homogeneous nature.

TABLE II
Result of Hydrogen Peroxide Treatment

Group	Membrane
Group I: membranes destroyed, leaving only reinforcing materials	Selecion CMV Nepton CR-61 Sciron C-100 SAM-1
Group II: membranes converted into porous membranes with decomposition of resinous part	Neosepta CL-25T Neosepta CH-2T Neosepta CLE-E MC-3142 Permaplex AMFion C-60 AMFion C-310

On the other hand, the ion-exchange membranes in group II were converted by the hydrogen peroxide treatment into porous membranes that have no ion-exchange capacity but have water permeability. This shows the existence of some heterogeneity in the membranes. Because the pore size of the porous membranes were reasonably considered to show the de-

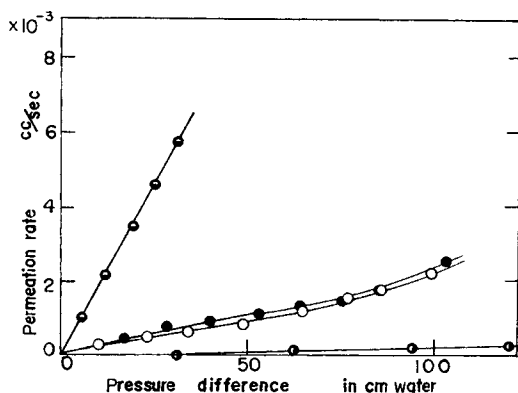


Fig. 2. Permeation rate of water vs. pressure difference between both sides of membrane: (●) Neosepta CH-2T; (●) Neosepta CLE-E; (○) Neosepta CL-2→5T; (○) AMFion C-310.

gree of the heterogeneity, the apparent pore size of the porous membranes were determined.

To begin with, the water permeability of the ion-exchange membranes themselves was verified to be negligibly small in comparison with that of the corresponding porous membranes. Figures 2 and 3 show the relations between the Q values of the porous membrane and Δp . From the slopes of the linear parts of these curves, the K_p values were calculated. Table III shows the experimental results. The Q value of the porous membrane from AMFion C-310 was very small, so its apparent pore radius could not be evaluated. AMFion C-60 shrank more than 15% in length by the hydrogen peroxide treatment and, what is worse, it became so brittle that its water permeability could not be measured. Table IV shows the tortuosity factor σ , which shows the complexity of the heterogeneity of the membrane.

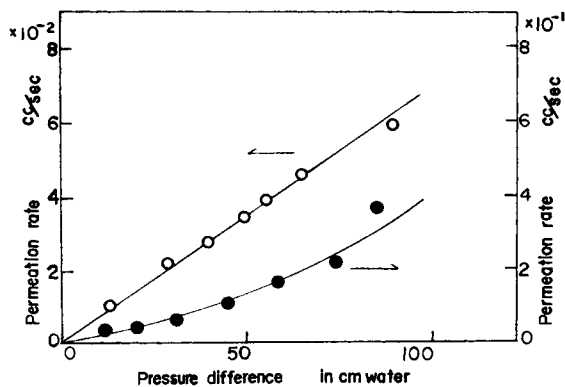


Fig. 3. Permeation rate of water vs. pressure difference between both sides of the membrane: (●) Permaplex; (○) MC-3142.

TABLE III
Apparent Pore Size of Porous Membranes, Calculated from Hydrodynamic Permeability

	Neosepta CL-25T	Neosepta CH-2T	Neosepta CLE-E	MC-3142	Permaplex	AMFion C-310
$Q/\Delta P, \frac{\text{cm}^3 \text{ sec}^2}{\text{g}}$	1.72×10^{-8}	1.84×10^{-7}	1.92×10^{-8}	6.04×10^{-7}	3.07×10^{-6}	very small
A, cm^2	2×10	2×10	2×10	2×10	2×10	2×10
L, cm	1.55×10^{-2}	1.4×10^{-2}	7.7×10^{-2}	1.7×10^{-2}	7.5×10^{-2}	2.9×10^{-2}
K_p, cm^2	1.19×10^{-13}	1.15×10^{-12}	6.18×10^{-13}	4.59×10^{-12}	1.03×10^{-10}	—
$\epsilon, \text{vol.-%}$	5.05×10^{-1}	5.96×10^{-1}	2.32×10^{-1}	3.42×10^{-1}	5.36×10^{-1}	3.20×10^{-1}
γ, cm	1.37×10^{-6}	3.95×10^{-6}	4.61×10^{-6}	1.09×10^{-5}	3.95×10^{-5}	very small

^a $\eta = 0.00895$ poise, $\rho_w = 0.997 \text{ g/cm}^3$ (at 23°C).

TABLE IV
 Tortuosity Factor of Porous Membranes

	R_m , ohm cm ²	σ^a
Neosepta CL-25T	1.6	2.4
Neosepta CH-2T	0.8	1.6
Neosepta CLE-E	17.1	2.5
MC-3142	4.1	3.8
Permaplex	20.7	6.9
AMFion C-310	4.0	2.1

^a $R_m \doteq 21.5$ ohm cm at 25°C (0.5N NaCl solution).

As is shown in Table III, the apparent pore radius becomes larger in the following order: Neosepta CL-25T < Neosepta CH-2T < Neosepta CLE-E < MC-3142 < Permaplex. The order of the σ -values is also consistent with the above order on the whole. The larger σ -values of the porous membranes derived from MC-3142 and Permaplex should suggest the presence of blocked and/or dead-ended pores, and this should be expected in view of their preparative process of milling and calendering with an inert binder.¹⁵

Both the γ - and σ -values of the Neosepta membranes, prepared by the "paste method," were considerably smaller. This shows the difference of microstructure or the degree of the heterogeneity of these membranes from those of the mosaic-type membranes such as MC-3142 and Permaplex. In the "paste method,"⁴⁻⁸ the fine powder of PVC or PE (P-polymer) is mixed

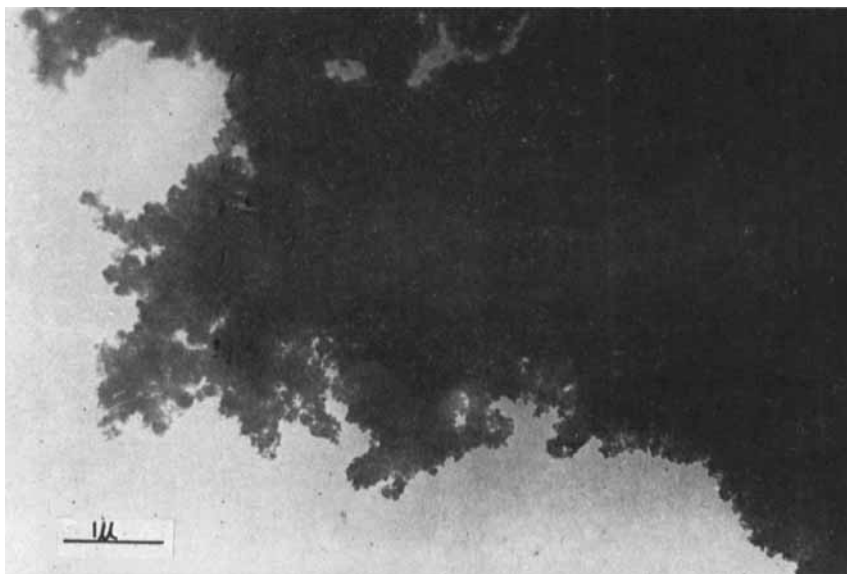


Fig. 4. Electron microphotograph of extraction residue of the "paste method" membrane.

with the monomer mixture, mainly consisting of St and DVB, to prepare a paste, and this is coated onto a reinforcing material. The thus obtained composite is heated to polymerize the monomers and to convert the powdery P-polymer into a filmy gel; then an ion-exchange group is introduced onto the St-DVB copolymer (M-resin). Inasmuch as the monomers are polymerized in the P-polymer gel phase, grafting of the monomers onto the P-polymer and entanglement of the M-resin with the P-polymer should occur. On the other hand, the gel of the P-polymer is comiscible with the monomers but not with polystyrene; so the M-resin should become a fine powder. This can be supported by the fact that when St and DVB are polymerized in kerosene, which is comiscible with the monomers but immiscible with polystyrene, a fine powdery polymer results.¹⁶ As is described above, it is clear that Neosepta membranes have a heterogeneity or a localized distribution of the R-resin under 50 μ .

In order to confirm the heterogeneity described above, SAM-2 and Permaplex were extracted respectively with tetrahydrofuran and benzene. The result is shown in Table V. The presence of PVC in the extraction residue means the presence of entanglement or grafting between the R-resin and the PVC chain. Furthermore, it is a very important fact that the R-resin was in the extracted portion. Since the R-resin is crosslinked, this fact shows that the R-resin is so powdery that some of the particles can pass through the filter paper. Figure 4 shows the existence of a fine, powdery R-resin smaller than 100 μ . These results show heterogeneity or localized distribution of R-resin in the Neosepta membranes, and agree with the results obtained by the hydrogen peroxide treatment. In the case of Permaplex, both the reinforcing material and the R-resin were separated as the extraction residue, and PE was completely extracted with benzene. This fact shows that Permaplex is only a mixture of PE and R-resin and that its chemical structure is clearly different from that of the Neosepta membranes and probably of the AMFion membranes also.

TABLE V
Result of THF Extraction of SAM-2 Membrane^a by the "Paste Method"

	Cl content, wt-%	Weight ratio, %	
		Theoretical ^b	Observed
Before extraction	29.93-30.35	—	—
After extraction			
residue	14.8	46.5-47.3	56.8
extracted portion	17.7	52.7-53.5	43.2

^a In Cu²⁺ form.

^b Calculated from chlorine content before extraction.

Goldring¹⁷ and Crabtree and Glueckauf¹⁸ have reported a heterogeneity or a localized distribution of R-resin in AMFion membranes. In view of their method of preparation, phenomena similar to those in the case of SAM-2 should occur in the polymerization of the M-resin in PE. So, both

the ion-exchange membranes prepared by the "paste method" and the "graft method" are considered to resemble each other in their chemical structures.

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