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Correlation between structure and properties of cation-exchange membranes prepared by the paste method

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By using cation-exchange membranes prepared by the paste method, a study was made of the influence of the distribution of polyvinyl chloride (PVC) on the electrical conductivity of the membranes and on the structure of the cation-exchange resin component (R-resin). Four kinds of cation-exchange membranes with different PVC contents and degrees of cross-linking were used. The experimental method involved treatment with hydrogen peroxide for selective decomposition of the R-resin. The estimated ratio of the specific electrical conductivity of the R-resin to that of the membrane varied from 2.2 to 4.4, depending upon the volume ratio of PVC in the membrane (0.33–0.45). Each of the membranes had a very high concentration of ion-exchange groups for cross-linking. This could be explained in terms of the mechanical and chemical restraint imposed by the PVC against the swelling of the R-resin. The structure of the R-resin, however, was almost independent of the PVC volume ratio over the range investigated.

1. Introduction

In previous papers [1, 2] concerned with our continuing efforts to improve cation-exchange membranes prepared by the paste method, it was shown that they have a microheterogeneity: the cation-exchange resin component (R-resin, sulfonated styrene (St)-divinylbenzene (DVB) copolymer) is finely distributed in polyvinyl chloride (PVC). This is verified by the fact that the cation-exchange membranes in the Fe^{3+} form are converted to PVC microporous membranes by treatment with hydrogen peroxide.

The inert polymer of PVC usually occupies a considerable proportion of the total membrane volume, and gives sufficient mechanical strength, excellent flexibility and dimensional stability, etc. to the membrane. On the other hand, it inevitably shields some considerable cross-sectional area of the membrane, causing a decrease in the electrical conductivity of the membrane. In addition, it may exert a significant influence on the structure of the R-resin which influences the electrochemical properties of the membrane.

In the present investigation, four kinds of cation-exchange membranes with different PVC contents and degrees of cross-linking have been used to elucidate the influence of the microheterogeneity on the ion-transfer and the structure of the R-resin. The experimental method involved an interpretation of the structure and the electrical resistance of the PVC porous membranes obtained by treatment with hydrogen peroxide.

2. Experimental

2.1. *Cation-exchange membranes*

The cation-exchange membranes (CEM-1–4) were prepared by the paste method [3–5]. Table 1 shows the compositions of the base membranes before sulfonation. Table 2 lists their characteristics measured by the usual methods [6, 7].

2.2. *Determination of specific conductivity and equivalent conductivity*

The electrical resistance of the cation-exchange

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Table 1. Compositions of the base membranes for the cation-exchange membranes (CEM-1–4)

	CEM-1	*CEM-2*	*CEM-3*	*CEM-4*
DVB content* (wt%)	1	5	15	5
PVC content† (wt%)	56	55	55	71

* Calculated from the amount of DVB used to prepare the membrane, based on the total monomer weight.
† Calculated from mean chlorine content of the membrane.

membranes was measured in 0.5, 0.25 and 0.1 N NaCl solutions at 25° C with an alternating current of 1 kHz. The cell used was similar to that described in an earlier paper [8]. It was made of methyl methacrylate. The effective membrane area was 1.0 cm^2. The platinized platinum electrodes were fixed close to the membrane (about 0.075 cm away), which enabled accurate readings of membrane resistance, even in dilute solutions.

The electrical resistance obtained was plotted against the square root of the external NaCl solution concentration. The electrical resistance of the membrane equilibrated with water, R_0(Ω cm^2), was estimated by extrapolation. The equivalent conductivity, Λ(Ω^{-1} cm^2 eq^{-1}), of Na$^+$ ions in the membrane can be calculated by the formulae

$$\Lambda = 1000\kappa/C \quad (1)$$

$$\kappa = L_m/R_0 \quad (2)$$

where κ is the specific electrical conductivity of the membrane (Ω^{-1} cm^{-1}), C is the capacity of the swollen membrane (meq cm^{-3}) and L_m is the membrane thickness (cm).

2.3. *Hydrogen peroxide treatment and characterization of porous membranes*

The cation-exchange membrane of the Fe^{3+} form was clamped between two half-cells to prevent any contraction in membrane area and then treated with 5% hydrogen peroxide solution for 100 min. The porosity ϵ of the resultant PVC porous membrane is calculated from the relation

$$\epsilon = \frac{W_e - W_d}{SLd_w} \quad (3)$$

where W_e is the wet weight of the membrane (g), W_d is the dry weight of the membrane (g), S is the area of the membrane (cm^2), L is the thickness of the membrane (cm) and d_w is the density of water (0.997 g cm^{-3} at 25° C).

The tortuosity factor σ is defined as follows

$$\sigma = R/R_i \quad (4)$$

$$R_i = \rho_s L/\epsilon \quad (5)$$

where R(Ω cm^2) is the electrical resistance of the porous membrane in 0.5 N NaCl solution at 25° C,

Table 2. Characteristics of the cation-exchange membrane

	CEM-1	*CEM-2*	*CEM-3*	*CEM-4*
Thickness* L_m(10^{-2} cm)	1.60	1.50	1.28	1.45
Capacity* C (meq cm^{-3} wet membrane)	1.17	1.82	1.50	1.50
Water content* Q (cm^3 cm^{-3} wet membrane)	0.44	0.31	0.18	0.25
Transport number†	0.91	> 0.98	> 0.98	> 0.98

* All quantities refer to the membrane in the Na$^+$ form equilibrated with water.
† Measured by electrodialysis in 0.5 N NaCl at 25° C, at a current density of 2.0 A dm^{-2}.

measured by using the above-mentioned cell, and ρ_s is the specific electrical resistance of the same solution (about 21.5 Ω cm). It was first ascertained that the electrical resistance of each of the porous membranes was proportional to the specific electrical resistance of the external NaCl solution in the concentration range 0.25–3 N. This indicates that the contribution of the surface conductivity is negligible in the concentration range, which justifies the experimental method used for determining the tortuosity factor. If the pores in the membrane were in the form of straight tubes perpendicular to the membrane surface, the σ value would be equal to unity.

The conversion of any of the cation-exchange membranes of the Na^+ form into the Fe^{3+} form caused no significant changes in the dimensions of the membrane. The hydrogen peroxide treatment, however, results in an appreciable decrease in the membrane thickness. Then, the thickness ratio δ is defined as follows

$$\delta = L/L_m \tag{6}$$

where L_m is the thickness of the original cation-exchange membrane (cm).

3. Results and discussion

3.1. *Microheterogeneity*

The hydrogen peroxide treatment converted the cation-exchange membranes into porous membranes with no ion-exchange ability and with a chlorine content (55.1–55.7%) almost the same as that of PVC (56.8%). The residues after evaporation of the hydrogen peroxide solutions were found to be linear polystyrene sulfonates and were free from chlorine. These findings indicate that some active intermediates, formed by the iron-catalysed decomposition of hydrogen peroxide, brought about the breaking of the cross-linked polymer chains of the R-resin without substantial degradation of the PVC.

Table 3 shows the characteristics of the porous membranes. The change in the membrane thickness by the hydrogen peroxide treatment (shown by the δ value) must be due to the loss of swelling pressure of the R-resin. According to the increasing order of pore size (r) of the porous membranes, the cation-exchange membranes can be arranged in the following series: CEM-3 < CEM-2 < CEM-1, which is the same as the decreasing order of the degree of cross-linking, and CEM-4 < CEM-2, which is the same as the decreasing order of the PVC content. The pore radii of the four porous membranes are of comparable order. So, the CEM-1–4 cation-exchange membranes have heterogeneities of about the same dimensions (< 0.1 μm). This is due to the microphase separation during copolymerization of St and DVB in the PVC gel phase of both the cloth part and the other part [2]; a PVC cloth and a PVC powder were used to prepare the CEM membranes.

3.2. *Influence of PVC on ion-transfer*

The resistance factor of PVC (f_r) is defined as

Table 3. Characteristics of the porous membranes obtained from the cation-exchange membranes (CEM-1–4)

	CEM-1	*CEM-2*	*CEM-3*	*CEM-4*
Thickness L (10^{-2} cm)	1.44	1.31	1.13	1.30
Thickness ratio δ	0.900	0.873	0.883	0.897
Porosity ϵ	0.635	0.605	0.527	0.500
Apparent pore radius* r (μm)	0.031	0.028	0.020	0.013
Electrical resistance R (Ω cm²) (0.5 N NaCl, 25° C)	0.90	0.90	1.05	1.65
Tortuosity factor σ	1.8	1.9	2.3	3.0

* Determined from the water permeability by applying Hagen-Poiseuille's law [2].

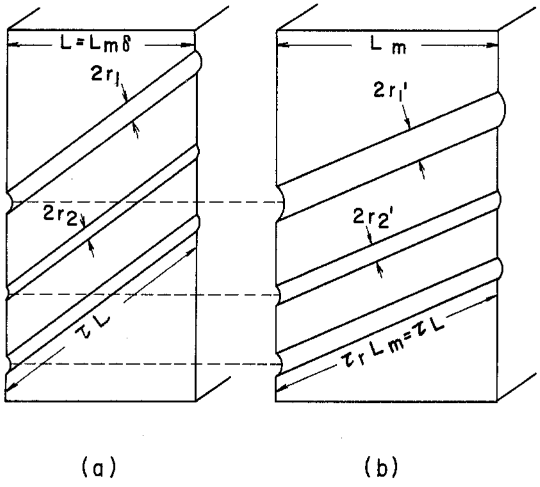

Fig. 1. 'Spaghetti model' of the porous membrane: (a) porous membrane obtained by hydrogen peroxide treatment of the cation-exchange membrane; (b) hypothetical porous membrane which might be obtained by the selective removal of the R-resin from the cation-exchange membrane without any deformation of the PVC part.

$$f_r = \frac{\kappa_r}{\kappa} \tag{7}$$

where κ is the specific electrical conductivity of the cation-exchange membrane ($\Omega^{-1}\,\mathrm{cm}^{-1}$) and κ_r is the true electrical conductivity of the R-resin ($\Omega^{-1}\,\mathrm{cm}^{-1}$). If the whole R-resin in the membrane were in the form of straight cylinders perpendicular to the membrane surface, f_r would be equal to $1/\epsilon_r$, where ϵ_r is the volume fraction of the R-resin. At this point, it is reasonable to define a tortuosity factor of the R-resin (σ_r) by the following equation

$$f_r = \frac{\sigma_r}{\epsilon_r}. \tag{8}$$

For elucidating the obstructive effect of PVC in the membrane, it seems convenient to imagine a porous membrane which might be obtained by the selective removal of the R-resin from the cation-exchange membrane without any deformation of the PVC part. The R-resin in the cation-exchange membrane should certainly function as a polyelectrolyte gel where water-filled pores are open in all directions. Therefore, it may be assumed that the σ_r value is equal to the σ value of the hypothetical porous membrane. On the basis of this assumption, the ϵ_r and σ_r values for the CEM membranes were estimated from the porosity (ϵ) and the tortuosity factor (σ) of the porous membranes obtained by hydrogen peroxide treatment, as will be shown below.

Table 4. The ϵ_r, σ_r, and f_r values of the cation-exchange membranes

	CEM-1	*CEM-2*	*CEM-3*	*CEM-4*
ϵ_r	0.67	0.65	0.58	0.55
σ_r	1.5	1.5	1.8	2.4
f_r	2.2	2.3	3.1	4.4

The tortuosity factor (σ) and porosity (ϵ) of the porous membrane were interpreted in terms of the spaghetti model (Fig. 1a). This model describes the porous medium as bundles of tubes all of length τL [9]. The radii are not necessarily equal. Correspondingly, the model shown in Fig. 1b, which has the following relations, was chosen to describe the above hypothetical porous membrane (thickness L_m, porosity ϵ_r, tortuosity factor σ_r, tube length $\tau_r L_m$):

$$\epsilon_r = (1-\delta) + \epsilon\delta \tag{9}$$

$$\tau_r L_m = \tau L. \tag{10}$$

There are also the following relationships [9]†:

$$\tau^2 = \sigma \tag{11}$$

$$\tau_r^2 = \sigma_r. \tag{12}$$

Combination of Equations 6, 10, 11 and 12 leads to the following equation:

$$\sigma_r = \sigma\delta^2. \tag{13}$$

Table 4 shows the ϵ_r, σ_r, and f_r values calculated from the δ, ϵ and σ values shown in Table 3 by using Equations 9, 13 and 8, respectively. As the degree of cross-linking is increased (CEM-1 < CEM-2 < CEM-3), the ϵ_r value decreases; cross-linking influences the extent of sulfonation of the St-DVB copolymer and the swelling behaviour of the R-resin. Concomitantly, the f_r value increases from 2.2 to 3.1. Increasing the PVC content of the base membrane

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† Equation 11, for example, can be derived from Equations 4 and 5 and the following equation:

$$R = \rho_s \frac{\text{tube length}}{\text{area ratio of pores in a cross-section vertical to tubes}} = \rho_s \frac{\tau L}{(\epsilon/\tau)}.$$

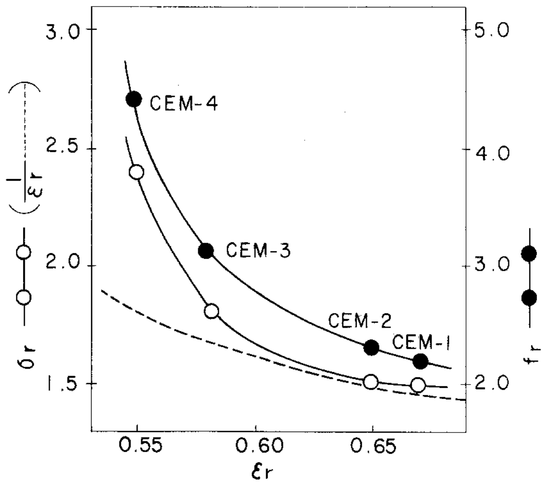

Fig. 2. Dependence of σ_r and f_r values on the ϵ_r values of the cation-exchange membranes.

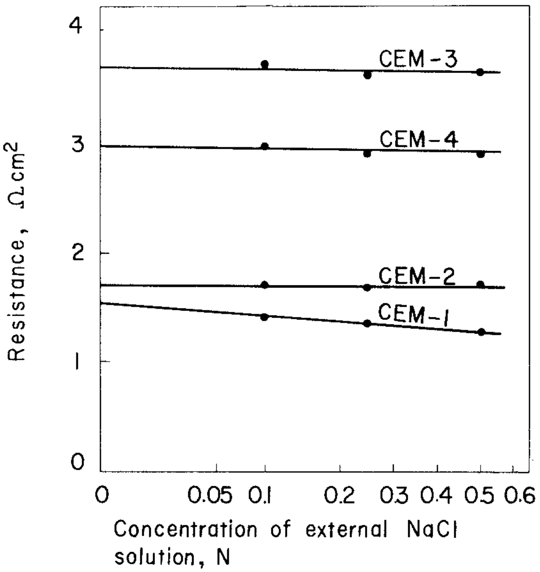

Fig. 3. Cation-exchange membrane resistance at 25° C as a function of external concentration of NaCl.

(CEM-2 < CEM-4) brings about a pronounced increase of the f_r value (from 2.3 to 4.4) attended by a large increase in the σ_r value. The σ_r and f_r values of the CEM membranes are plotted against their respective ϵ_r value (Fig. 2). It seems that, in general, the σ_r value has an interrelationship to the ϵ_r value, as is also the case with the f_r value. When the ϵ_r value is less than about 0.6, the f_r value becomes very large.

3.3. *Conductivity of the R-resin*

The dependence of the electrical resistance of the CEM membranes on the concentration of the external NaCl solution is shown in Fig. 3. The decrease in resistance with increasing concentration is most marked in the case of the CEM-1 membrane; this membrane is thought to contain regions of very low ionic group concentration, i.e. voids. Table 5 lists the values of κ and Λ of the CEM membranes calculated by using their respective R_0 values.

Table 5 also shows the κ_r value calculated by using Equation 7 and the corrected equivalent conductivity for the obstructive effect of PVC, $\Lambda_r(\Omega^{-1}\text{cm}^2\ \text{eq}^{-1})$; the latter was estimated as follows: Equation 14 holds for the R-resin:

$$\Lambda_r = \frac{1000\kappa_r}{C_r} \qquad (14)$$

where C_r is the volume capacity of the swollen R-resin (meq cm^{-3}). This is given by

$$C_r = C/\epsilon_r. \qquad (15)$$

Combining Equations 1, 8, 14 and 15 yields

$$\Lambda_r = \sigma_r\Lambda. \qquad (16)$$

As is to be expected, both the σ_r and Λ_r values decrease greatly with the increase in the degree of cross-linking. It is noteworthy that the σ_r and Λ_r values of the CEM-4 membrane are comparable to those of the CEM-2 membrane. Thus the differences in the apparent conductivity properties of the two membranes are mainly due to the different obstructive effect of PVC. In view of this, it is understandable that they have almost the same ratios of electrical resistance for different kinds of ions, as exemplified in Table 6.

Table 5. Conductivity characteristics of the cation-exchange membranes (Na⁺ form, 25° C)

	CEM-1	*CEM-2*	*CEM-3*	*CEM-4*
R_0 (Ω cm^2)	1.55	1.70	3.65	3.00
κ ($10^{-3}\ \Omega^{-1}$ cm^{-1})	10.3	8.83	3.51	4.83
Λ (Ω^{-1} cm^2 eq^{-1})	8.80	4.85	2.34	3.22
κ_r($10^{-2}\ \Omega^{-1}$ cm^{-1})	2.3	2.0	1.1	2.1
Λ_r (Ω^{-1} cm^2 eq^{-1})	13.2	7.3	4.2	7.7
Λ_r/Λ_0^*	0.26	0.15	0.08	0.15

* Λ_0 is the limiting equivalent ionic conductivity of the Na⁺ ion in solution at 25° C (50.1 Ω^{-1} cm^2 eq^{-1}).

Table 6. Ratio of electrical resistances of the cation-exchange membranes for Ca^{2+} and Na^+ ions

	CEM-1	*CEM-2*	*CEM-3*	*CEM-4*
$R_{\mathrm{Ca}^{2+}}/R^{*}_{\mathrm{Na}^{+}}$	2.1	2.7	5.1	2.8

* $R_{\mathrm{Ca}^{2+}}$ and $R_{\mathrm{Na}^{+}}$ (Ω cm^2) are electrical resistances measured in 0.5 N $CaCl_2$ and NaCl (25° C), respectively.

3.4. *Structure of the R-resin*

Table 7 shows the volume fraction of polymer in the R-resin, V_p, the capacity of the swollen R-resin, C_r(meq cm^{-3}) and the concentration of ionic groups, $\bar{m}$ (meq g^{-1} H_2O); the V_p and $\bar{m}$ values were calculated according to the following equations:

$$V_p = 1 - \frac{Q}{\epsilon_r} \tag{17}$$

$$\bar{m} = \frac{C}{Qd_w} = \frac{C_r}{(1 - V_p)d_w} \tag{18}$$

where Q is the water content of the membrane (cm^3 cm^{-3} membrane, see Table 2).

The ionic group concentration of each of the membranes is higher than those of the usual cation-exchange resins with the same degree of cross-linking. This is most marked at lower degrees of cross-linking (1 and 5%), which is very favourable for preparing membranes with low electrical resistance and high ionic permselectivity. There are two possible explanations for this structural feature. One is the restraining force of the PVC opposing hydration and the consequent expansion of the R-resin. The other is that the chemical interaction between the R-resin and PVC, the presence of which has been proved by the solvent extraction method [2], brings the two components into tight contact; on the other hand, in the so-called heterogeneous membranes, interstices filled with water often develop between the R-resin and inert binder as a result of the difference in their volume swelling [10–12].

The data also indicate that the CEM-2 and CEM-4 membranes resemble each other in the structure of the R-resin. This is in accord with the above-mentioned relationship between their electrical conductivity, which suggests the validity of the present method. It can be said that PVC in the CEM-2 and CEM-4 membranes has almost the same effect on the structure of the R-resin. On the whole, the structure of the CEM-2 membrane seems very favourable; in fact, its electrical conductivity and ionic permselectivity are sufficient for its practical use in electrodialysis.

Table 5 also shows the ratios of the Λ_r values to the equivalent conductivity of Na^+ ion in dilute aqueous solution (Λ_0). It would be interesting to correlate these Λ_r/Λ_0 values with the structural characteristics of the R-resin, such as C_r, $\bar{m}$ and V_p values.

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Table 7. Some structural properties of the R-resin in the cation-exchange membranes

	CEM-1	*CEM-2*	*CEM-3*	*CEM-4*
Volume fraction of polymer* V_p	0.35	0.53	0.70	0.55
Volume capacity*† C_r (meq cm^{-3} swollen R-resin)	1.75	2.80	2.59	2.73
Concentration of ionic groups* $\bar{m}$ (meq g^{-1} H_2O)	2.67	5.89	8.36	6.00

* All quantities refer to membranes of the Na^+ form equilibrated with water.

† Calculated by using Equation 15.

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