EFFECT OF INTRAMEMBRANE STRUCTURE ON TRANSPORT PROPERTIES OF CATION EXCHANGE MEMBRANE PREPARED BY PASTE METHOD

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Cation exchange membranes were prepared using styrene and divinylbenzene as respective components and polyvinyl chloride cloth and microporous polyethylene film as respective backing materials. The intramembrane structures of synthetic and commercial membranes were analyzed using Tye's treatment by considering the non-homogeneous charge distribution within the membrane. Volume fractions of the pore, polyelectrolyte and inert polymer phases within the membrane were determined by using the water content of the membrane and the Donnan sorption concentration. The diffusion coefficients of the cupric ion within the pore and resin (*i.e.*, polyelectrolyte and inert polymer) phases were correlated with the respective volume fractions of the membrane. A simplified model of the intramembrane structure was found to be useful for evaluating the sorbed concentration and the membrane conductivity.

Introduction

Ion exchange membranes are generally produced by a chemical modification of the selected copolymer. The physical and transport properties of the ion exchange membrane are mainly affected by the intramembrane structure. The relationship between the membrane conductivity and the external concentration has been examined by using several models of intramembrane structure. Spiegler et al.[9] assumed the membrane to be composed of two components: the crosslinked insoluble polyelectrolyte and the electrolyte filling in the macropores. Arnold et al.[1] proposed a different equivalent circuit containing the resin and void phases. Narebska et al.[7,13] evaluated the difference among the models proposed so far and considered a multilayer model having a two-dimensional profile.

To identify the effective factor governing the ionic transport through the membrane, it is necessary to test membranes prepared by the same method and having different structures. Therefore, cation exchange membranes were prepared according to the paste method,[5] using different components and different backing materials. A simple model of the intramembrane structure based on Tye's treatment[12] was proposed. The Donnan sorption equilibrium

within the membrane and the membrane conductivity were measured. Using the equivalent circuit of the charge transport through the membrane, the diffusion coefficient within the membrane was correlated with the volume fraction related to its transport.

1. Theory

1.1 Intramembrane structure model

Figure 1 shows a conceptual schema of the inner part of a cation exchange membrane. The inner part of the membrane is divided into pore, polyelectrolyte and inert polymer phases. The inert polymer phase consists of the polymer and the backing material. The pore and polyelectrolyte phases are filled by the electrolyte, and correspond to zones where electric fields are ineffective and effective, respectively. Electrolyte components in the pore are the same and
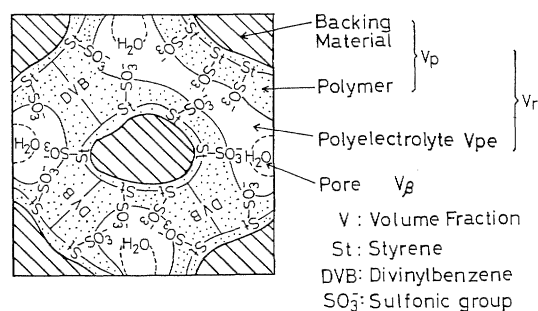
Fig. 1. Conceptual schema of inner part of cation ecchange membrane

those in the external solution. **Figure 2** shows schematically a simplified structure of the membrane. When the volume fraction of the inert polymer phase is designated by V_p, and the volume ratio of the pore phase to the total volume filled by the electrolyte is designated by β, volume fractions V_β and V_{pe}, of the pore and polyelectrolyte phases are expressed as follows.

$$V_\beta = \beta(1 - V_p) \qquad (1)$$

$$V_{pe} = (1 - \beta)(1 - V_p) \qquad (2)$$

The combination of the polyelectrolyte, the polymer and the backing material is called the resin phase. The volume fraction of the resin phase is

$$V_r = V_p + V_{pe} = 1 - V_\beta \qquad (3)$$

Figure 3 shows a parallel circuit of ionic transports through the pore and resin phases within the membrane. The electrical conductivity $\bar{\kappa}$ of the membrane is expressed by the summation of respective products of volume fractions V_β and V_r and conductivities κ_β and κ_r of the pore and resin phases, if the charge transport is assumed to obey the parallel circuit shown in Fig. 3.

$$\bar{\kappa} = V_\beta \kappa_\beta + V_r \kappa_r \qquad (4)$$

In general, the conductivity κ of the electrolyte is expressed as follows according to the Nernst-Planck equation.[8]

$$\kappa = \frac{F^2}{RT} \sum_i z_i^2 D_i C_i \qquad (5)$$

For a binary electrolyte of cation A and anion B, ν_A moles of cation A and ν_B moles of anion B are dissociated per mole of the salt. The conductivity κ_β of the pore phase is described as

$$\kappa_\beta = \frac{F^2}{RT}(z_A^2 D_{\beta A}\nu_A C_0 + z_B^2 D_{\beta B}\nu_B C_0) \qquad (6)$$

The conductivity κ_r of the resin phase is expressed by use of diffusion coefficients and concentrations of concerned ions in the resin phase:

$$\kappa_r = \frac{F^2}{RT}(z_A^2 D_{rA} C_{rA} + z_B^2 D_{rB} C_{rB}) \qquad (7)$$

Since the electrolyte is filled in the polyelectrolyte within the resin phase, the concentration C_r in the resin volume is calculated using the concentration C_{pe} in the polyelectrolyte volume.

$$C_{ri} = \frac{V_{pe}}{V_r}C_{pei} \qquad (i = A \text{ and } B) \qquad (8)$$

The concentration $\bar{C}$ within the membrane is given by the summation of the concentration in the pore and polyelectrolyte phases.
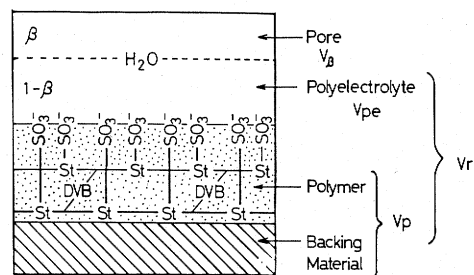
Fig. 2. Simplified model of intramembrane structure
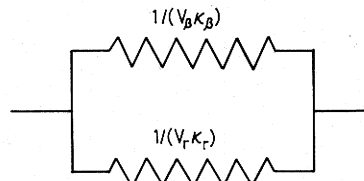
Fig. 3. Equivalent circuit of membrane conductivity

$$\bar{C}_i = V_\beta \nu_i C_0 + V_{pe} C_{pei} \qquad (i = A \text{ and } B) \qquad (9)$$

From the electroneutrality within the membrane,

$$\sum_i z_i \bar{C}_i + z_m Q = 0 \qquad (10)$$

Using Eqs. (8) to (10),

$$C_{rA} = \frac{1}{V_r}\left(\frac{-z_m Q - z_B \bar{C}_B}{z_A} - V_\beta \nu_A C_0\right) \qquad (11)$$

$$C_{rB} = \frac{\bar{C}_B - V_\beta \nu_B C_0}{V_r} \qquad (12)$$

By substituting Eqs. (11) and (12) into Eq. (7), we have

$$\kappa_r = \frac{F^2}{RT}\frac{1}{V_r}\{-z_A z_m D_{rA}Q - z_A D_{rA}(z_B \bar{C}_B + z_A V_\beta \nu_A C_0)$$
$$+ z_B^2 D_{rB}(\bar{C}_B - V_\beta \nu_B C_0)\} \qquad (13)$$

By substituting Eqs. (6) and (13) into Eq. (4), the membrane conductivity $\bar{\kappa}$ is described as follows.

$$\bar{\kappa} = \frac{F^2}{RT}\{V_\beta(z_A^2 D_{\beta A}\nu_A C_0 + z_B^2 D_{\beta B}\nu_B C_0) - z_A z_m D_{rA}Q$$
$$- z_A D_{rA}(z_B \bar{C}_B + z_A V_\beta \nu_A C_0)$$
$$+ z_A^2 D_{rB}(\bar{C}_B - V_\beta \nu_B C_0)\} \qquad (14)$$

The first term within large brackets of the right side of the above equation is the ionic transport in the pore, the second term is the transport of the charge balanced with the fixed ion, and the other terms are the transport of the ions sorbed by Donnan equilibrium. When cupric chloride is the concerned salt, $z_A = +2$, $z_B = -1$, $\nu_A = 1$ and $\nu_B = 2$. If the ratio r_D of the diffusion coefficient within the membrane is equal to the ratio for infinite dilution, Eq. (14) is transformed into Eq. (15).

$$\bar{\kappa} = \frac{2F^2}{RT}\left[(2+r_D)V_\beta C_0 D_{\beta A} + \left\{-z_m Q\right.\right.$$

$$\left.\left. + \left(1+\frac{r_D}{2}\right)(\bar{C}_B - 2V_b C_0)\right\}D_{rA}\right] \qquad (15)$$

1.2 Donan sorption

According to Tye's treatment,[12] the volume fraction β of the pore space within a membrane can be calculated from the concentration of the sorbed electrolyte. The internal part of the membrane filled with the electrolyte is divided into the polyelectolyte phase at an electrical potential $\bar{\phi}$ and the pore phase at zero electrical potential. The concentration of the ion within the membrane is assumed to be given by the Boltzmann distribution law. The concentrations of cation and anion in the pore phase are equal to those in external solution. Then the average concentrations of cation and anion in the sorbed electrolyte are

$$\bar{C}_i' = \beta v_i C_0 + (1-\beta)\{v_i C_0 \exp(-z_i e\bar{\phi}/kT)\} \qquad (16)$$

By eliminating $\bar{\phi}$ from Eq. (16) when $i = A$ and B,

$$\left[\frac{\bar{C}_A' - \beta v_A C_0}{(1-\beta)v_A C_0}\right]^{z_B} = \left[\frac{\bar{C}_B' - \beta v_B C_0}{(1-\beta)v_B C_0}\right]^{z_A} \qquad (17)$$

When β is equal to zero, Eq. (17) expresses the relationship of simple Donnan equilibrium[3] of homogeneous charge distribution. The concentration $\bar{C}_i'$ based on the internal electrolyte of the membrane is related to the concentration $\bar{C}_i$ based on the membrane volume.

$$\bar{C}_i' = \frac{\bar{C}_i}{1-V_p} \qquad (18)$$

Using the electroneutrality within the membrane,

$$\left[\frac{Q}{z_A v_A C_0} - \frac{z_B \bar{C}_B}{z_A v_A C_0} - \beta(1-V_p)\right]^{z_B}$$

$$[(1-V_p)(1-\beta)]^{z_A - z_B} = \left[\frac{\bar{C}_B}{v_B C_0} - \beta(1-V_p)\right]^{z_A} \qquad (19)$$

The relationship of Donnan sorption between $\bar{C}_B$ and C_0 is obtained experimentally and β is determined by fitting the data to the expression described by Eq. (19).

2. Experimental

Four commercial membranes, Neosepta C66-5T. CM-2 (Tokyyama Soda, Japan), Naflon N-117 (Du Pont, USA) and MC-3470 (Ionac, USA), were used in preliminary experiments. Synthetic membranes were prepared by the paste method[5,11]. The paste, which consisted of styrene (St), divinylbenzene (DVB), di-n-butyl phthalate (DBP), polyvinyl chloride (PVC) powder and benzoyl peroxide (BPO) as polymerization initiator, was coated on a backing material and
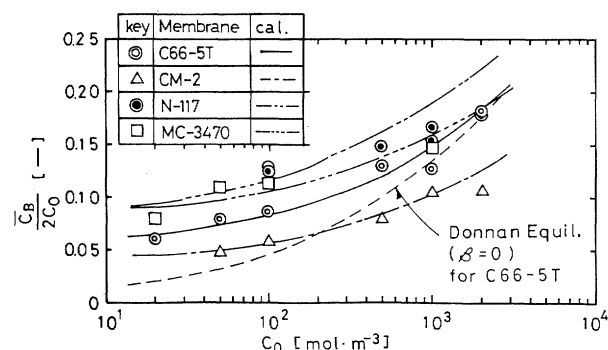

Fig. 4. Concentration change of chloride ion sorbed in commerical membrane with external concentration

the monomers were copolymerized by heating. Both the polyvinyl chloride cloth Teviron 7075 (Teijin), and the microporous poly(ethylene) film Hipore 1100A (Asahi Chem. Ind.) were used as backing materials. The degree of crosslinking (DOC) was changed in the range of 0 to 0.20. The contents of DBP, PVC and BPO added in the resin mixture were, respectively, 0.1—0.7, 0.152 and 0.015.

The membranes were immersed into 1 kmol·m^{-3} CuCl$_2$ solution and allowed to equilibrate for half a day before measurements. The thickness, density, water content and ion exchange capacity of the wet membrane and the fixed ion concentration based on dry membrane weight were measured as described in the previous work[10].

2.1 Measurement of sorbed electrolyte

Two membrane sheets (2 cm × 2 cm) were immersed into a CuCl$_2$ solution and allowed to equilibrate at 298 K for a day. After measurement of physical properties, the surfaces of the membrane were wiped with filter papers and immersed into deionized water of 10 cm^3 in volume at 298 K for a day. The concentration of the cupric ion desorbed from the membrane was determined by a chelate titration. The concentration of the CuCl$_2$ solution was varied in the range of 0.02 to 2 kmol·m^{-3}.

2.2 Measurement of membrane conductivity[2]

The cell consisted of two platinum electrodes of 1 cm diameter and a detachable cartridge as membrane holder. The electrodes could be moved forward and backward in the cell by means of a screw-driven mechanism and the distance between the two electrodes could be changed from 3 cm to 0.2 cm. The resistance of the cell at 1 kHz A.C. was measured as a function of the distance of the electrodes, with and without the membrane.

3. Results and Discussion

3.1 Intramembrane structure

Figure 4 shows the sorbed concentration of chloride ion within the membrane as a function of the external concentration of CuCl$_2$ for commercial membranes.

The chloride ion is a co-ion of a cation exchange membrane and is excluded from the membrane. When the external concentration was increased, the sorbed concentration increased according to the Donnan equilibrium. Experimental results for sorption equilibrium showed that the sorbed concentration was higher than that calculated from the simple Donnan equilibrium where a homogeneous charge distribution was assumed, i.e., $\beta = 0$. The curves described in Fig. 4 are the calculated results from Eq. (19) according to the non-homogeneous model described in Section 1.2. For comparison, the broken line was calculated according to the simple Donnan equilibrium for the C66-5T membrane.

Table 1 shows the parameters of intramembrane structure of commercial membranes. The V_p value was calculated by the following equation.

$$V_p = 1 - \frac{W \rho_{wm}}{(W+1)\rho_w} \tag{20}$$

where W was water content, ρ_{wm} the density of wet membrane and ρ_w the density of water. V_{pe}, V_β and V_r were given by Eqs. (1) to (3). The volume fraction V_β of the pore phase was found to be less than 0.1 for every membrane. Since MC-3470 is a heterogeneous membrane made by compressing a powdered mixture of inert polymer and polystyrensulfonic acid resin, V_β of the MC-3470 was the largest.

Figures 5 and **6** show the sorption equilibrium for synthetic membrane using Teviron cloth or Hipore film, respectively, as a backing material. The sorbed concentration decreased with increasing DOC. The term DVB/Re in figures refers to the DOC. The relationship between $\bar{C}_B/2C_0$ and C_0 indicated a similar tendency for the two reinforcing materials, but the sorbed concentration in the membrane with Hipore film was higher than in that with Teviron cloth.

Figure 7 shows the relationship of β and V_p to the DOC. V_p increased gradually with the DOC. When Hipore film was used as a backing material, V_p of the synthetic membrane was relatively low because of the high water content. The relationship between β and the DOC is shown as a curve which passed through a minimum. Its tendency to have a minimum with respect to the DOC was in accordance with Tye's result,[12] and might be due to the result that V_{pe} had a maximum relative to the DOC. Details of V_{pe} are shown later.

Figure 8 shows volume fractions within the membrane as a function of the DOC. V_β decreased with increase in the DOC. V_r, however, increased with increasing DOC and approached a maximum value. V_{pe} had a maximum with repect to the DOC. To improve the selective transport and ionic transport flux through the membrane, an increment of V_{pe}

Table 1. Volume fractions within commercial membranes

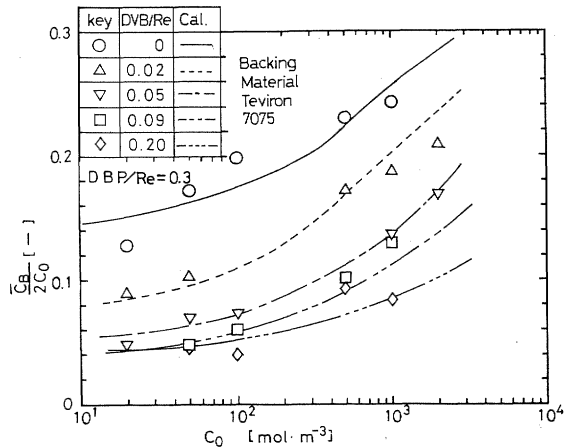| Membrane	C66-5T	CM-2	N-117	MC-3470
β	0.18	0.18	0.26	0.33
V_p	0.73	0.80	0.71	0.76
V_{pe}	0.22	0.16	0.21	0.16
V_r	0.95	0.96	0.92	0.92
V_β	0.049	0.036	0.075	0.079

Fig. 5. Concentration change of chloride ion sorbed in synthetic membrane reinforced by Teviron cloth with external concentration
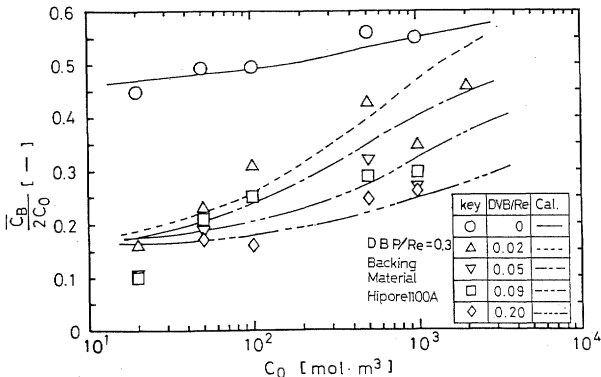

Fig. 6. Concentration change of chloride ion sorbed in synthetic membrane reinforced by Hipore film with external concentration
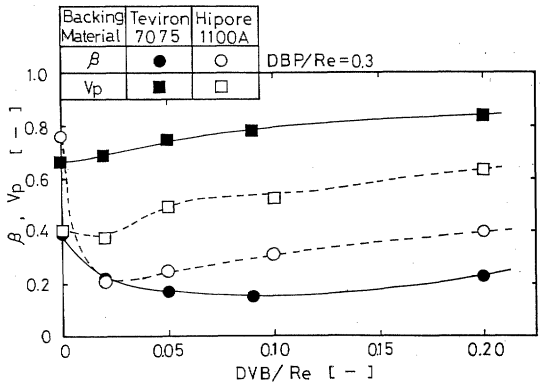

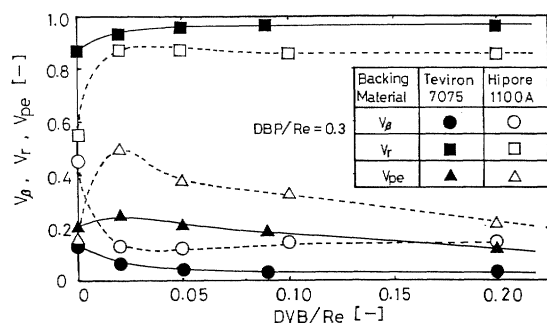**Fig. 7.** Relationship of β and V_p to degree of cross-linking

Fig. 8. Relationship between volume fractions and degree of cross-linking

Fig. 9. Membrane conductivity of synthetic membrane reinforced by Teviron cloth as a function of conductivity of external solution

Fig. 10. Membrane conductivity of synthetic membrane reinforced by Hipore film as a function of conductivity of external solution

effective for ion exchange, and the decrease in V_β and V_p ineffective for ion exchange are required. Since V_{pe} maximized and V_β showed a lower value at a DOC of 0.02, the membrane with a DOC of 0.02 was considered to have superior properties.

3.2 Membrane conductivity

The membrane conductivity was calculated using the difference between the resistivities with and without the membrane, and the change in resistivity with distance between measuring electrodes.[2]

Figures 9 and **10** show the electrical conductivities of membranes as a function of electrolyte conductivity for synthetic membranes with Teviron cloth and Hipore film, respectively. The lines depicted in Figs. 9 and 10 represent the calculated results of Eq. (15) using V_β and the $\bar{C}_B$, which were determined experimentally, and a γ_D of 2.82. The membrane conductivity increased with electrolyte conductivity because the sorbed concentration increased with increasing external concentration. Using the nonlinear least squares method, $D_{\beta A}$ and D_{rA} values were calculated from the relationship between $\bar{\kappa}$ and κ_0, which was a function of C_0. As shown in Fig. 9, the $\bar{\kappa}$ value of the membrane with Teviron cloth decreased with increasing the DOC. The $\bar{\kappa}$ of non-crosslinked membrane was lower than that of the membrane having a DOC of 0.02. As depicted in Fig. 10, the $\bar{\kappa}$ value of the membrane with Hipore film was larger than that of the membrane with Teviron cloth, because V_p of the former was smaller than that of the latter. The noncrosslinked membrane indicated the remarkable dependency of $\bar{\kappa}$ and κ_0. The relationships between $\bar{\kappa}$ and κ_0 for commercial membranes were also obtained. N-117 was found to have the highest conductivity because of the large values of V_β and V_{pe}, and the highest concentration of Donnan sorption.

The effective diffusivity D_e in porous medium is expressed by using the tortuosity factor τ when the concentration of the diffusive species is based on the membrane volume.
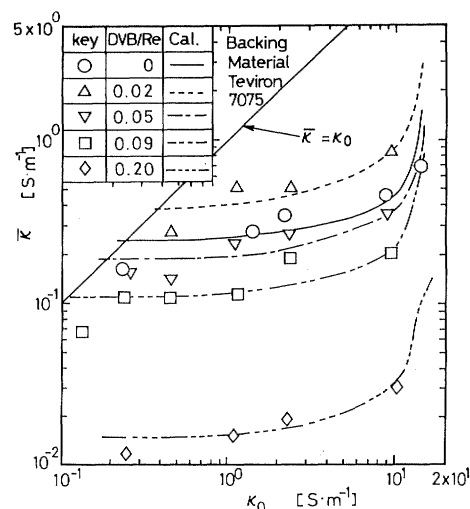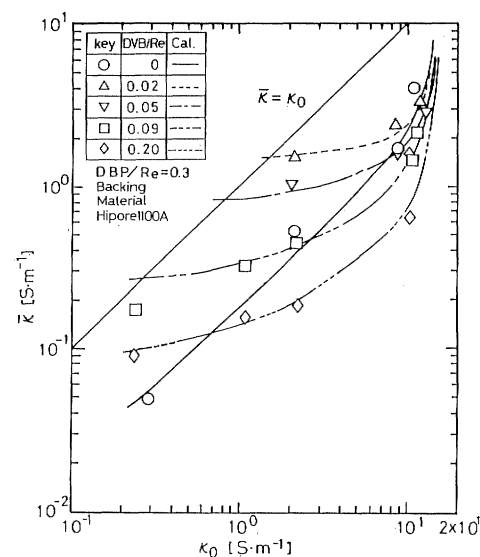
$$D_e = D/\tau \tag{21}$$

where D is the diffusivity in the bulk solution. Mackie and Meares[4] derived the following expression for τ in terms of the volume fraction V_{ip} inaccessible for charge transport.

$$\tau = \left(\frac{1 + V_{ip}}{1 - V_{ip}}\right)^2 \tag{22}$$

Generally τ is expressed by a function of the volume fraction of the phase effective to diffusion.[6]

Figure 11 shows the relationship between the diffusion coefficient in the resin phase and the volume fraction of polyelectrolyte phase within the membrane. The diffusion coefficient of the cupric ion was normalized through division by the diffusion coefficient D_{LA}° for infinite dilution of $7.2 \times 10^{-10}\,\mathrm{m^2 \cdot s^{-1}}$.

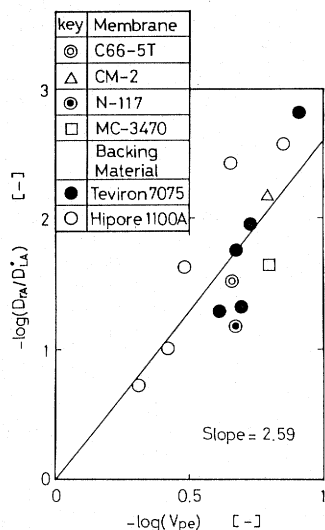| key	Membrane
◎	C66-5T
△	CM-2
◉	N-117
□	MC-3470
	Backing Material
●	Teviron7075
○	Hipore 1100A

Slope = 2.59

Fig. 11. Correlation of diffusion coefficient in resin phase

The correlation was given as follows within a deviation of $\pm 30\%$.

$$D_{rA} = D_{LA}^{\circ} V_{pe}^{2.59} \tag{23}$$

In spite of the fact that the correlation included commercial membranes prepared by different methods, the diffusion coefficient in the resin phase was well correlated with V_{pe}. Since $D_{\beta A}$ referred to the diffusivity in the open pore filled with electrolyte, the dependency of $D_{\beta A}$ or V_{β} was presumed to be small. The experimental relationship between $D_{\beta A}$ and V_{β} was expressed as follows within a deviation of $\pm 70\%$.

$$D_{\beta A} = D_{LA}^{0} V_{\beta}^{0.58} \tag{24}$$

Conclusion

A model of the intramembrane structure was proposed and each ·volume fraction within the membrane was determined from experiments in Donnan sorption equilibrium. When the external concentration was increased, the sorbed concentration within the membrane was larger than that estimated using the simple Donnan equilibrium of homogeneous charge distribution and was explained by the non-homogenous model of Tye. The intramembrane structure was afferent by the kind of the backing material and the degree of crosslinking. The membrane conductivity was analyzed by use of an equivalent circuit of the same model of intramembrane structure. The diffusion coefficients of the cupric ion through the pore and resin phases were correlated with the respective volume fractions. The simplified model of the intramembrane structure was found to be useful for evaluating the sorbed concentration and the membrane conductivity.

Nomenclature

C	= concentration	$[\text{mol}\cdot\text{m}^{-3}]$
D	= diffusion coefficient	$[\text{m}^2\cdot\text{s}^{-1}]$
D_e	= effective diffusion coefficient	$[\text{m}^2\cdot\text{s}^{-1}]$
D_L°	= diffusion coefficient for infinite dilution	$[\text{m}^2\cdot\text{s}^{-1}]$
e	= electron charge	$[\text{C}]$
F	= Faraday's constant	$[\text{C}\cdot\text{mol}^{-1}]$
k	= Boltzmann's constant	$[\text{J}\cdot\text{K}^{-1}]$
Q	= fixed ion concentration	$[\text{mol}\cdot\text{m}^{-3}]$
R	= gas constant	$[\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}]$
r_D	= ratio of diffusion coefficient of species B to species A	$[—]$
T	= temperature	$[\text{K}]$
V	= volume fraction	$[—]$
W	= water content	$[\text{kg-water}\cdot\text{kg}^{-1}\text{-dry mem.}]$
z	= number of charges	$[—]$
β	= ratio of pore volume to electrolyte volume within membrane	$[—]$
δ	= membrane thickness	$[\text{m}]$
$\bar{\phi}$	= electrical potential in membrane	$[\text{V}]$
κ	= electrical conductivity	$[\text{S}\cdot\text{m}^{-1}]$
v	= stoichiometric coefficient for dissociation of a binary electrolyte	$[—]$
ρ	= density	$[\text{kg}\cdot\text{m}^{-3}]$
τ	= tortuosity factor	$[—]$

⟨Subscripts⟩

A	= cation (Cu^{2+})
B	= anion (Cl^{-1})
ip	= ineffective part for charge transport
m	= fixed ion
p	= inert polymer phase
pe	= polyelectrolyte phase
r	= resin phase
w	= water
wm	= wet membrane
β	= pore phase
0	= value of external solution

⟨Superscripts⟩

$\bar{}$	= value within membrane
$\cdot$	= value based on internal electrolyte volume

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