Ionic Salt Permeability Through Phase-Separated Membranes Composed of Amphoteric Polymers

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ABSTRACT: Amphoteric copolymers composed of hydrophilic poly(dimethyl acrylamide) and hydrophobic poly(dimethyl siloxane) formed phase-separated membranes. The hydrophilic and hydrophobic components formed continuous phase-separated domains in the membranes. The hydrated poly(dimethyl acrylamide) domains formed membrane-spanning pathways, which permitted an ionic salt to permeate the membranes. The permeability of the ionic salt through the amphoteric copolymer membranes was studied. On the basis of the results, the mechanism of salt transport could be explained by the free-volume theory, which was used for the analysis of diffusive transport in the hydrated, homogeneous membranes. The diffusion coefficient of the ionic salt increased exponentially as the volume ratio of the hydrophilic polymer to water [$(1 - H)/H$, where H is the degree of hydration] decreased in the membrane. It was possible to postulate that the diffusion of the ionic salt through the membranes was dependent on the free-volume fractions of water and hydrophilic poly(dimethyl acrylamide) domains in the membranes. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 79–85, 2011

Key words: diffusion; membranes; phase separation

INTRODUCTION

Membranes have gained importance in chemical engineering and are used in a wide range of applications, such as water purification and the recovery of valuable components from various industrial effluents used in the food and pharmaceutical industries.[1–3] Copolymers composed of hydrophilic and hydrophobic components are used to form microphase-separated membranes.[4] Recently, phase-separated membranes with specific permeability for target molecules have been attracting interest for medical materials.[5,6] In particular, phase-separated hydrogel membranes composed of hydrophilic and hydrophobic domains are promising materials for contact lenses.[7] The continuous phase in the membranes acts as an independent permeable pathway for individual permeants. That is, the hydrophilic continuous phase in the membranes provides an efficient permeable pathway for aqueous solutes such as ionic salts. In this study, we prepared microphase-separated membranes composed of amphoteric polymers with independent permeable pathways. The membranes were designed so that the hydrophilic domains, consisting of poly(dimethyl acrylamide), acted as permeation pathways for aqueous solutes, and the hydrophobic domains, consisting of poly(dimethyl siloxane) (DMS), formed effective oxygen-permeable pathways.[8] It has been reported[9–12] that the permeability of aqueous solutes through hydrogel membranes is strongly dependent on the water content of the membranes. The transport phenomena of aqueous solutes through hydrogels can be explained by free-volume theory.[13] The mechanism of salt transport through microphase-separated membranes composed of amphoteric polymers is discussed in connection with the membrane structures.

EXPERIMENTAL

Materials

Amphoteric copolymer membranes composed of hydrophobic bi-functional acrylated poly(dimethylsiloxane) (DMS), methacrylate having a bulky siloxanylalkyl pendant group (Tris), and hydrophilic dimethylacrylamide (DMAA)[14] (Figure 1) were kindly provided from Menicon Co., Ltd., Nagoya, Japan. The average molecular weight of DMS was 5400 (the average degree of polymerization, n = 40, determined by gel permeation chromatography). The

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Hydrophobic Components

bi-functional acrylated poly(dimethylsiloxane) (DMS)

methacrylate having a bulky siloxanylalkyl pendant group (Tris)

Hydrophilic Component

dimethylacrylamide (DMAA)
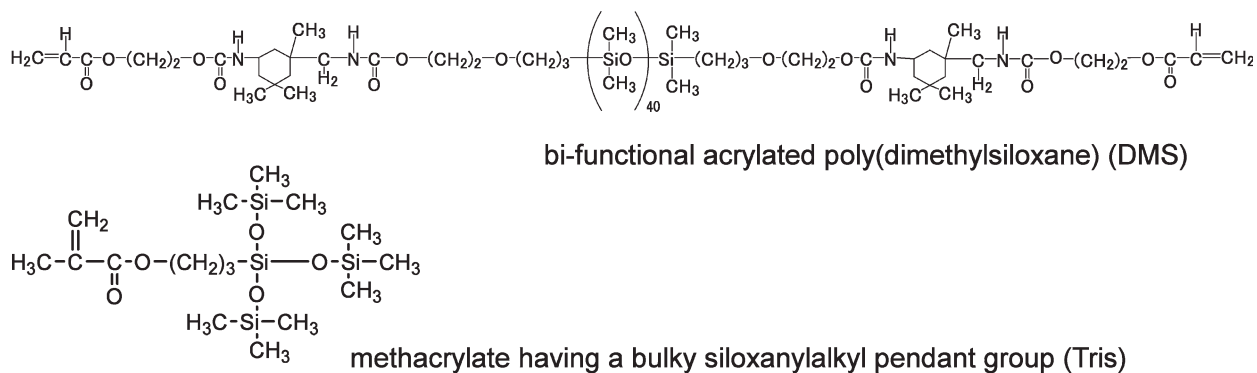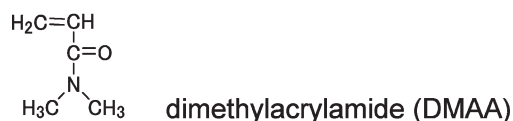
Figure 1 Chemical structures of hydrophobic, bifunctional, acrylated DMS, Tris, and hydrophilic DMAA, which composed the amphoteric copolymer membrane.

weight fraction of each component in the membranes is summarized in Table I.

Degree of hydration (H) of the membranes

The H values of the membranes used for the study of ionic salt permeability were calculated with the volume of the water-swollen domain ($[DMAA]_v$) and not with the volume of the whole membrane:

$$H = V_W/(V_{wm} + V_W) \qquad (1)$$

where V_{wm} is the volume of the hydrophilic domain in the dry membrane (calculated from the weight fraction and specific volume of the hydrophilic domain in the membrane) and V_W is the volume of water. The membrane was swollen in distilled water at $35 \pm 0.1°C$, blotted, and weighed repeatedly until a constant weight was obtained. V_W was calculated with the increased weight of the membrane after swelling and the specific volume of water.

### Partition coefficient with respect to salt for the membranes (K_S)

Approximately 0.02 g of an amphoteric copolymer membrane was immersed in a $0.1M$ NaCl solution. After sorption equilibrium was attained, the membrane was removed, rinsed, blotted, and immersed in distilled water. The desorption curve of NaCl from

the membrane with respect to water was obtained from the NaCl concentration changes in water, which were determined with an electroconductivity meter (MM-60R multifunction water quality meter, DKK TOA Co., Ltd., Tokyo, Japan) with a calibration curve for the NaCl concentration versus the conductance. The temperature was controlled at $35 \pm 0.1°C$ during the sorption and desorption measurements. From the concentration of NaCl in water at the desorption equilibrium, the amount of NaCl present in each water-swollen hydrophilic part of the membrane was calculated. K_S was defined as follows:

$$K_S = \frac{\overline{C} \text{ (mol/L)}}{C \text{ (mol/L)}} \qquad (2)$$

TABLE I
Weigh Fraction of Each Component in the Amphiphilic Block Copolymer Membranes

Sample	Weight fraction (%)		
	DMS	Tris	DMAA
p(DMS/DMAA)1	60	0	40
p(DMS/DMAA)2	50	0	50
p(DMS/DMAA)3	40	0	60
p(DMS/DMAA)4	20	0	80
p(DMS/Tris/DMAA)1	10	50	40
p(DMS/Tris/DMAA)2	10	47	43
p(DMS/Tris/DMAA)3	10	45	45
p(DMS/Tris/DMAA)4	20	40	40
p(DMS/Tris/DMAA)5	20	30	50
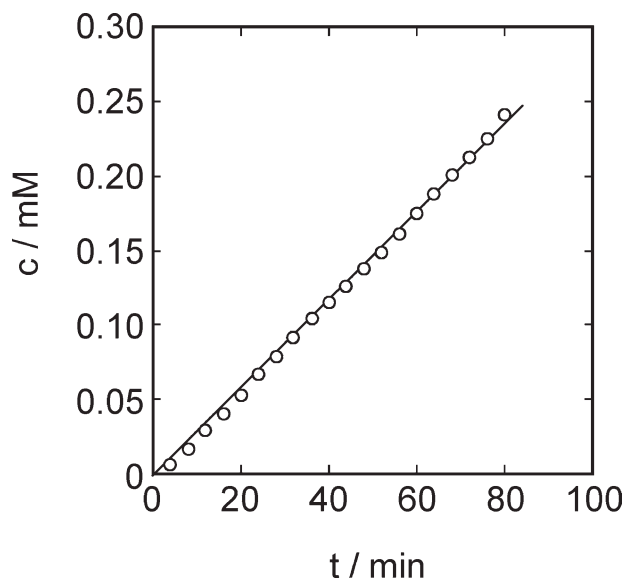
Figure 2 Permeation curve for NaCl through p(DMS/Tris/DMAA)3 at $35 \pm 0.1°C$ (c = concentration; t − time).

where $\overline{C}$ and C are the NaCl concentrations in the water-swollen, hydrophilic part of the membrane and in the solution, respectively.

Ion-permeability measurements

The measurements of the permeation of NaCl through the amphoteric copolymer membranes were carried out with a Pyrex glass permeation cell at $35 \pm 0.1°C$. Each membrane was interposed between the two parts of the cell. A $0.1M$ aqueous solution of NaCl was introduced into one side of the cell, and salt-free water was introduced into the other side (the permeated side) of the cell. The change in the NaCl concentration with time on the permeated side was measured with an electroconductivity meter to determine the NaCl permeability coefficient (P_S) through the membrane. Figure 2 shows a typical example of the time-dependent changes of the NaCl concentration on the permeated side; these were obtained from the calibration curve for the NaCl concentration versus the conductance. From the slope of the straight line of Figure 2, the flux of NaCl [J_S (mol cm^{-2} s^{-1})] through the membrane was calculated. In this study, the membrane area was the area of the swollen hydrophilic domain for an effective permeation area. We postulated that the effective permeation area was proportional to the volume of a swollen hydrophilic domain in the membrane. P_S of NaCl (cm^2/s) was obtained as follows:

$$P_S = J_S \Delta x / \Delta c \qquad (3)$$

where Δx is the membrane thickness and Δc is the external concentration difference of NaCl across the membrane.

Transmission electron microscopy (TEM) observation

For TEM experiments, the ultrathin sections were cut off from amphoteric copolymer membrane specimens with an ultramicrotome and a diamond knife. The ultrathin sections were cut perpendicularly to the surface of the amphoteric copolymer membranes. To enhance the contrast, the ultrathin sections of the sample films were stained with ruthenium tetroxide (RuO$_4$). It is known that when ultrathin sections are stained with RuO$_4$, the DMAA domains produce dark contrast in TEM micrographs. For electron microscopy, a JEOL JEM-2000FX electron microscope (Tokyo, Japan) operating at 200 kV was used. The initial magnification was $100,000\times$. Furthermore, three-dimensional (3D) TEM observations were performed with a JEOL JEM-1400 electron microscope operating at 200 kV. Projection images with sample rotation from -60 to $+60°$ (with 1°increments) were automatically acquired with Inspect3D on a slow-scan charged coupling device camera (Gatan Orius). The initial magnification was $100,000\times$. In this experiment, ultrathin sections of sample films were stained with osmium tetroxide (OsO$_4$).

RESULTS AND DISCUSSION

We investigated the morphology of the amphoteric copolymer membranes. Figure 3 shows typical electron micrographs of ultrathin sections cut perpendicularly to the surface of amphoteric copolymer membranes [p(DMS/DMAA)1 and p(DMS/DMAA)3]. The dark domains could be clearly observed in each membrane, which included a high-volume fraction of DMAA [p(DMS/DMAA)3; Fig. 3(a)] or a lower volume fraction [p(DMS/DMAA)1; Fig. 3(b)]. The size of the dark domain, which was composed of hydrophilic poly(dimethyl acrylamide), increased with increasing [DMAA]$_v$ in the membrane. We observed the 3D structure of the amphoteric phase-separated membrane by 3D TEM. Figure 3(c) shows a 3D TEM image of the p(DMS/DMAA)1 membrane. The continuous dark domains were poly(dimethyl acrylamide), which was embedded into the continuous hydrophobic DMS matrix. This result suggested that the amphoteric copolymer, composed of hydrophobic and hydrophilic components, formed phase-separated membranes. Moreover, the hydrophilic and hydrophobic components formed continuous phase-separated domains in the membrane. The DMS homopolymer membrane was not swollen in water. From these results, we think that the hydrophilic and continuous phase-separated domain composed of poly(dimethyl acrylamide) acted as a permeation pathway for the ionic salt in the membrane. In the following, we discuss the
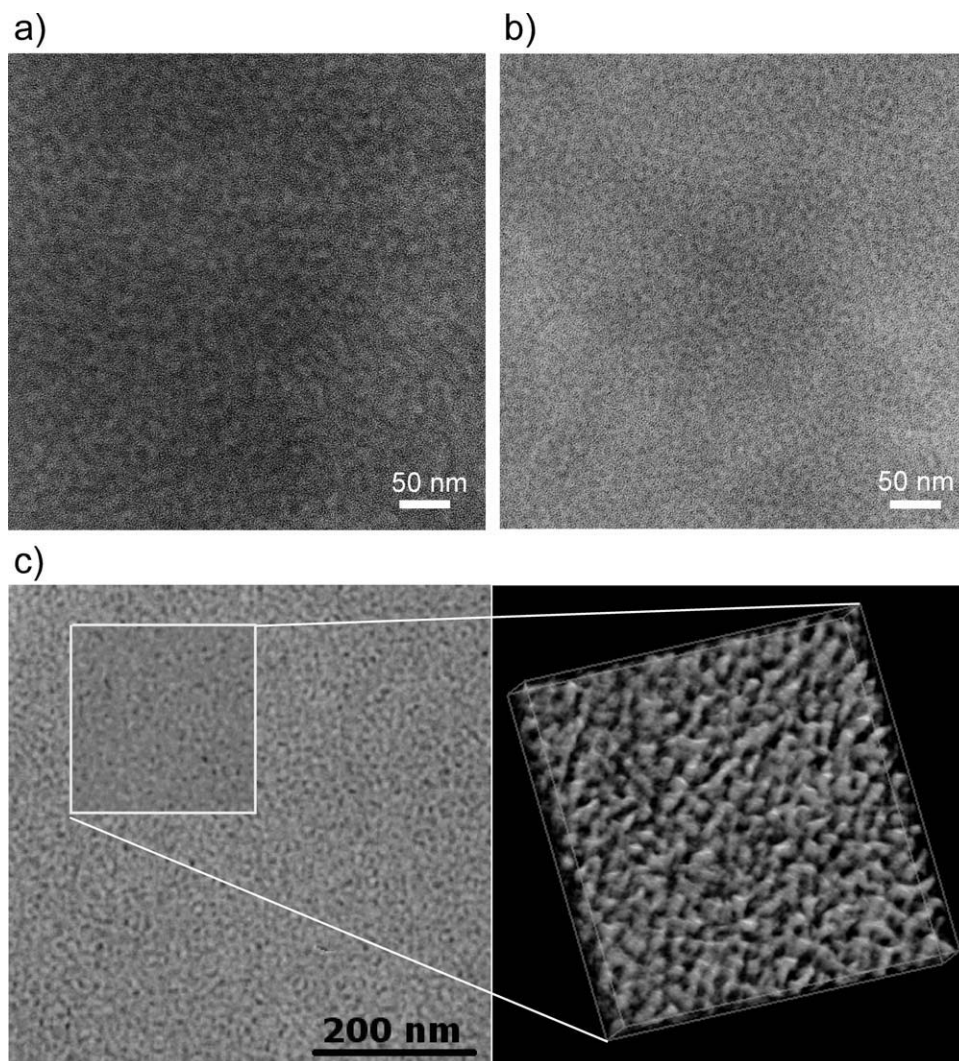
Figure 3 TEM images of ultrathin sections of (a) p(DMS/DMAA)3 and (b) p(DMS/DMAA)1 membranes. The samples were stained with RuO$_4$. The initial magnification was 100,000×. (c) 3D TEM image of the p(DMS/DMAA)1 membrane. The sample was stained with OsO$_4$. The initial magnification was 100,000×. The ultrathin sections were cut perpendicularly to the surface of the amphoteric copolymer membranes.

participation of the water-swollen hydrophilic poly (dimethyl acrylamide) domain in the permeability of the ionic salt.

Figure 4 shows the relationship between H of the amphoteric copolymer membranes and [DMAA]$_v$ of the hydrophilic poly(dimethyl acrylamide) component in the membranes. The H values of the membranes used for the study of ionic salt permeability were calculated with [DMAA]$_v$ and not with the volume of the whole membrane [defined by eq. (1)]. The [DMAA]$_v$ values were calculated with the weight fractions and specific volumes of each component in the membranes under the assumption of the additive property. H for the hydrophilic domain in the amphoteric copolymer membranes linearly increased with increasing [DMAA]$_v$.

The behavior of ionic salt permeation through the amphoteric copolymer membranes was investigated. Figure 5(a) shows the P_S values of NaCl through the amphoteric copolymer membranes, which had various [DMAA]$_v$ values. Figure 5(b) shows the relationship between K_S and [DMAA]$_v$. We obtained the diffusion coefficient (D_S) of NaCl in the membranes as follows (Fig. 6):

$$P_S = D_S K_S \qquad (4)$$

The values of P_S and D_S increased exponentially with [DMAA]$_v$ of the hydrophilic poly(dimethyl acrylamide) component increasing. Moreover, the value of K_S increased linearly with [DMAA]$_v$
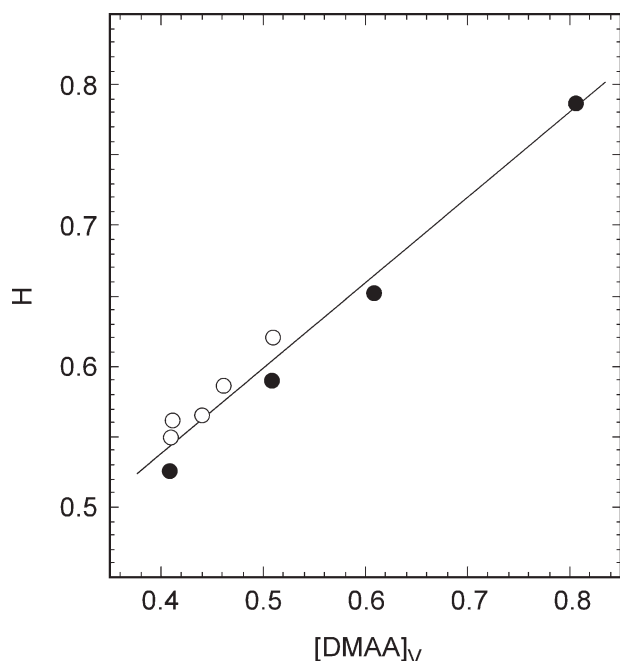
Figure 4 Relation between H of the amphoteric copolymer membranes and $[DMAA]_v$ of the hydrophilic poly (dimethyl acrylamide) component in the membranes. H was calculated with V_{wm} in the membrane by eq. (1): (○) p(DMS/Tris/DMAA) and (●) p(DMS/DMAA).

increasing. These results implied that the continuous and hydrated poly(dimethyl acrylamide) domain in the amphoteric membranes, which was formed by phase separation, acted as an effective permeable pathway through the membranes for the ionic salt.

We attempted to explain the ionic salt diffusion through the amphoteric phase-separated membrane

by the free-volume theory.[13] Generally, D_S is expressed by eq. (5) as a function of the free volume of the system (V_f) and the critical size of the diffusant ionic salt (V^*), which includes the overlapping factor of free volumes:

$$D_S = ART \exp(-V^*/V_f) \quad (5)$$

where A is a constant. The free volume fraction, V_f, is assumed to be the sum of the contribution of all components. R and T are gas constant and absolute temperature, respectively:

$$V_f = HV_{fw} + (1 - H)V_{fm} \quad (6)$$

where H is the volume fraction of water in the system and V_{fw} and V_{fm} are the free-volume fractions of pure water and the hydrophilic DMAA domain in the membrane, respectively.

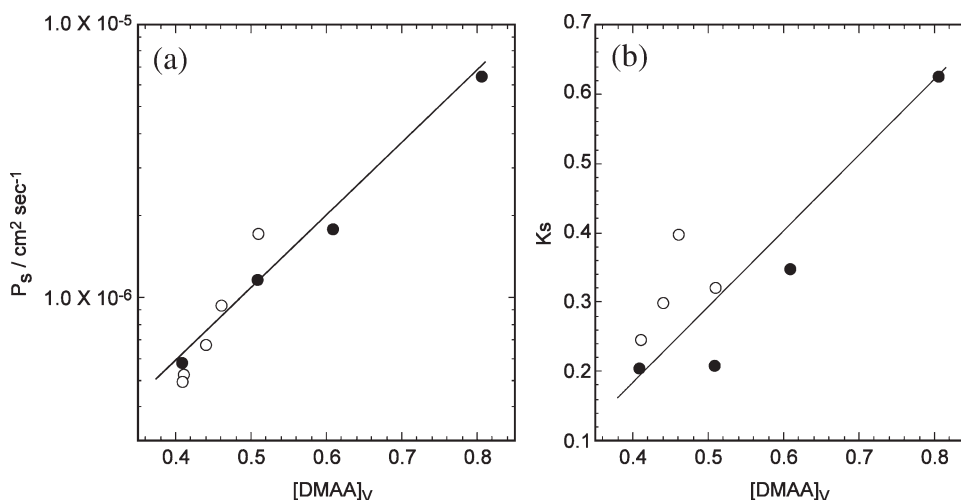On the other hand, the self-diffusion coefficient of the ionic salt (D_o) can be expressed as follows:

$$D_o = ART \exp(-V^*/V_{fw}) \quad (7)$$

On the basis of eqs. (5) and (7), D_S of the ionic salt through the membrane at a given temperature can be expressed as a function of D_o and the free volume:

$$D_s = D_o \exp\{-V^*(1/V_f - 1/V_{fw})\} \quad (8)$$

The combination of eqs. (5) and (8) leads to

$$\ln(D_s/D_o) = -\beta x(1 - \alpha)/(1 + x\alpha) \quad (9)$$

Figure 5 (a) Relation between P_S of NaCl through the amphoteric copolymer membranes and $[DMAA]_v$ of the hydrophilic poly(dimethyl acrylamide) component in the membranes. (b) Relation between K_S and $[DMAA]_v$ of the hydrophilic poly(dimethyl acrylamide) component: (○) p(DMS/Tris/DMAA) and (●) p(DMS/DMAA).
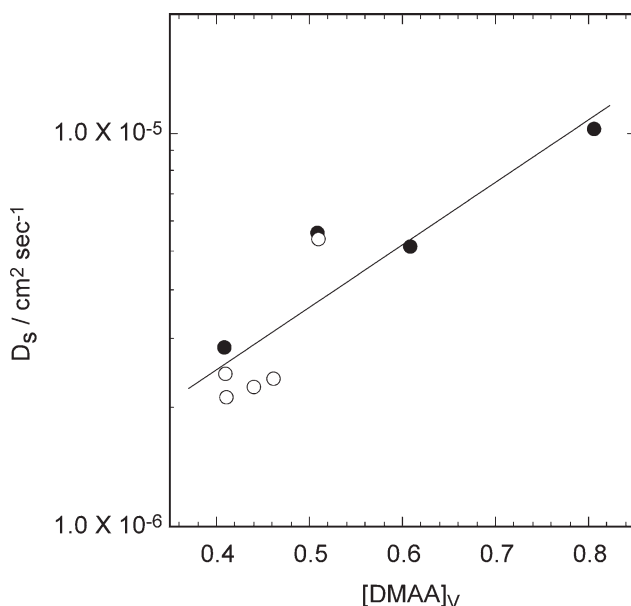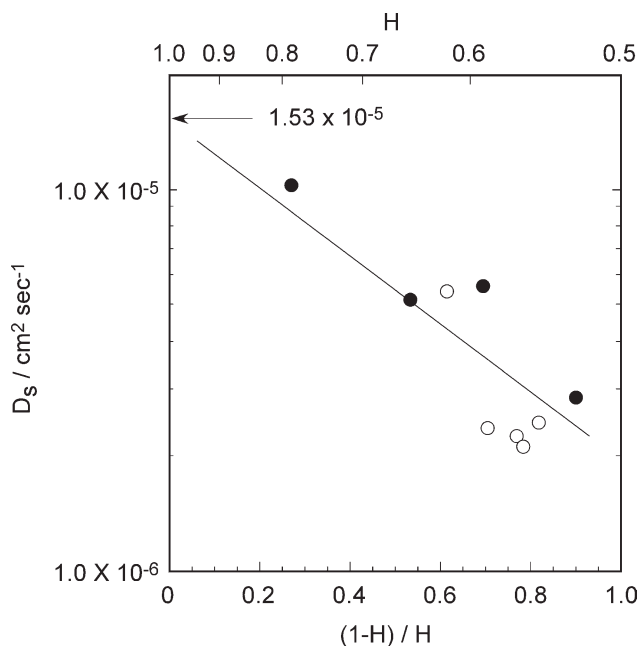
where

$$x = (1 - H)/H$$
$$\alpha = V_{fm}/V_{fw}$$
$$\beta = V^*/V_{fw}$$

Equation (9) indicates that ln D_S versus x, starting from D_o, approaches a straight line in the range of high H values ($x \rightarrow 0$) with a negative slope of $\beta(1 - \alpha)$. Figure 7 shows the relationship between the logarithm of D_S of NaCl through the membranes and the parameter $(1 - H)/H$ for the membranes. The arrow shows the self-diffusion coefficient of NaCl ($0.1M$) in an aqueous solution. The dependence of ln D_S on $(1 - H)/H$ for various membranes could be described by a single straight line without concern about the composition of the hydrophobic component in the membranes. The intercept of the straight line was 1.53×10^{-5} cm²/s, and this value was in fair agreement with the self-diffusion coefficient of NaCl in an aqueous solution. This result suggested that the diffusion of the ionic salt through the phase-separated amphoteric membrane could be explained by the free-volume theory, which was used for an analysis of diffusive transport through the homogeneous hydrogel membranes. That is, the continuous water-swollen hydrophilic domain, composed of poly(dimethyl acrylamide) in the amphoteric phase-separated membrane, acted as an effective permeation path for the ionic salt through the membrane. Furthermore, it was possible to postulate

Figure 7 Dependence of the D_S values of NaCl through the amphoteric copolymer membranes on the parameter $(1 - H)/H$, as approximated by eq. (9). The arrow shows the self-diffusion coefficient of NaCl ($0.1M$) in an aqueous solution.

that the diffusion of the ionic salt through the membrane was dependent on V_{fw} and on the free volume of the hydrophilic poly(dimethyl acrylamide) domain in the membrane.

CONCLUSIONS

An amphoteric copolymer can be used to form phase-separated membranes. The hydrophilic and hydrophobic components form continuous phase-separated domains across the membrane thickness. The water-swollen hydrophilic domain in the membranes acts as a continuous channel filled with water for the ionic salt. Phase-separated membranes, in which each continuous domain across the membrane thickness can act as an independent permeable pathway for individual permeants such as ionic salts or oxygen, are useful materials for contact lenses.

Figure 6 Relation between the D_S values of NaCl through the amphoteric copolymer membranes and $[DMAA]_v$ of the hydrophilic poly(dimethyl acrylamide) component in the membranes: (○) p(DMS/Tris/DMAA) and (●) p(DMS/DMAA).

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