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Properties of Hydrogel Membranes of Poly(vinyl alcohol) and Poly(acrylic acid) under a Pressure Gradient

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The dependence of the electric potential difference on time under a pressure gradient across hydrogel membranes, obtained by esterification of poly(vinyl alcohol) and poly(acrylic acid), was measured. At the moment when a pressure difference was applied, a sharp spike of the electric potential difference was observed. The overall variation of the electric potential difference on time consisted of two different processes. One of them, which gradually increased with time, and finally reached a steady-state value, reflects a relaxation of polymer chains dissolved in the liquid phase of the gel membrane under the pressure difference. The other, which showed a sharp inverse spike just after applying the pressure difference, and reached zero immediately, may have been caused by a transformation of the membrane matrix due to a sudden change in pressure before the migration of the water, that is, by compaction of the membrane matrix. When hydrogen molecules of the carboxyl groups in the gel membrane were exchanged with potassium ions, the gel membrane expanded. The relationship between the magnitude of the electric potential difference for each of the forms and the properties of the membranes is discussed.

When two solutions having the same composition and at the same temperature, but at different pressures, are separated by a membrane, an electric-potential difference appears across the membrane. This electric-potential difference is called the streaming potential,[1)] which is known to depend on time when a polymer membrane is used.[2—6)] We have studied the mechanism of the time dependence of the streaming potential.[4—6)] Suppose a porous membrane model comprising a solid polymer matrix (solid phase) and cylindrical micropores throughout the membrane-containing liquid (liquid phase). If a hydrostatic pressure difference is applied across the porous membrane, solution flow occurs through the micropores, causing a conformational change of the polymer chains dissolved in the liquid phase of the membrane. In this case, if the membrane has fixed charges, the counterions are forced to move toward the lower pressure side due to the solution flow, although the fixed charges cannot move. Therefore, the electric-potential difference appears in such a way that the sign of the electric-potential of the lower pressure side is the same as that of the counterions. Under a pressure gradient the conformation of polymer chains changes so that the friction between the polymer chains and the solution flow decreases. The force necessary to drag the counterions is proportional to the velocity of the solution flow. Thus, the force becomes large with time, and reaches a steady state. In previous papers[4—6)] we have shown that the dependence of the streaming potential on time can be assigned to the relaxation of polymer chains dissolved in the liquid phase of membranes under a pressure difference. If more flexible and longer polymer chains are dissolved in the liquid phase of the membrane, the relaxation time becomes longer.[4,5)] The relaxation time also became longer with an increase in the average molecular weight per cross-linked unit.[6)] Moreover, if the membrane is made of different kinds of polymer chains, the overall relaxation consists of the sum of the relaxation components of their polymer chains.[5)] A measurement of the electric-potential difference under a pressure difference on time permits us to obtain information concerning the properties of polymer chains in the membrane.

In this study, the time dependence of the electric-potential difference across hydrogel membranes, obtained by esterification of poly(vinyl alcohol) and poly(acrylic acid), was measured under a pressure gradient. When hydrogen molecules of carboxyl groups in the esterified gel membrane are changed to alkali metallic ions, the membrane expands, because of a conformation change of the polymer chains, due to an electric repulsion among the fixed charges. These gels have been used for various chemomechanical systems. Although the macroscopic behavior and thermodynamics of contraction have been investigated,[7,8)] there have been very few efforts to directly measure the conformation change of the polymer chains. Furthermore, a different kind of time dependence of the streaming potential is sometimes observed for esterified gel membranes. The purpose of this study was to elucidate the time-dependence mechanism of the electric-potential difference across these gel membranes under a pressure gradient and to understand the conformation change of the polymer chains in the membrane.

Experimental

Membranes. Gel membranes were obtained by the esterification of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA). A 25 wt% aqueous solution of PVA (degree of saponification: 99.9 mol%, Kuraray Co., Ltd) and a 25 wt% aqueous solution of PAA (molecular weight: 8000—12000, Wako Pure Chemical Industries, Ltd) were mixed, and cast onto a glass plate. The cast membrane was dried at 25 °C for about one day. The esterification between PVA and PAA was catalyzed by the addition of small amounts of hydrochloric acid in an inert oven at 120 °C for several hours in order to obtain a gel membrane, GVA, with the H^+ form. The K^+-form membrane was prepared by immersing the H^+-form membrane in a 0.01 $\mathrm{mol\,kg^{-1}}$ aqueous KOH solution for one day. By varying the weight fraction of PAA and the conditions for esterification, various gel membranes GVA (20-80) were prepared. The number in the parentheses indicates the weight fraction of PAA. The properties of the membranes are summarized in Table 1.

An oxidized collodion membrane (Ox-C) was also used as a reference. It was obtained by immersing a collodion membrane in a 0.01 $\mathrm{mol\,kg^{-1}}$ KOH solution, which was prepared by casting a collodion (Wako Pure Chemical Industries, Ltd) on a glass plate, and subsequently air-dried for about ten minutes at room temperature.

Measurements of the Electric-Potential Difference under a Pressure Difference. A membrane was mounted between two 50 $\mathrm{cm^3}$ compartments of a cell made of poly(vinyl chloride), and equipped with silver-silver chloride electrodes, a thermometer and joints to a pressurizing unit employing a hydrostatic pressure difference, as described in previous papers.[4—6] The membrane area was 3.1 $\mathrm{cm^2}$. The electric-potential difference across the membrane was measured using a vibrating-reed electrometer (Takeda Riken TR-8411). The output signal from the electrometer was digitized through a digital multimeter (Takeda Riken TR-6841) and fed into a personal computer at intervals of 1 or 2 s. The measurements were carried out at 25 °C in an air-conditioned thermostat. The bathing solution was a 0.001 $\mathrm{mol\,kg^{-1}}$ KCl solution.

Electron Micrograph. Cross sections of the membranes were observed using a Nippon Denshi Scanning Electron Microscope (JSM 890).

Results and Discussion

The time dependences of the electric-potential difference across a PAA-PVA membrane (GVA(30)B) and an oxidized collodion membrane (Ox-C) in the K^+ form under a pressure gradient are shown in Figs. 1 and 2, respectively. For the Ox-C membrane, the absolute value of the electric-potential difference increased rapidly after switching the pressure difference from 0 to 5.89 kPa, and then gradually increased up to a steady-state value. The electric-potential of the low-pressure side was always higher than that of the high-pressure side, because the Ox-C membrane has negative fixed charges. This time dependence of the electric-potential difference could be analyzed as the relaxation of polymer chains dissolved in the liquid phase of the membrane due to the pressure difference described in previous papers.[5)]

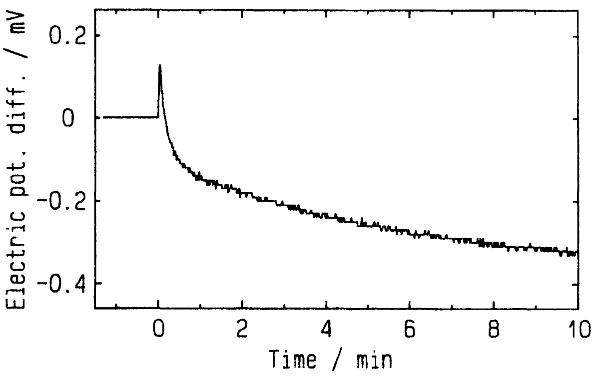

Fig. 1. The dependence of the electric-potential difference on time across GVA(30)B membrane in the K^+ form.

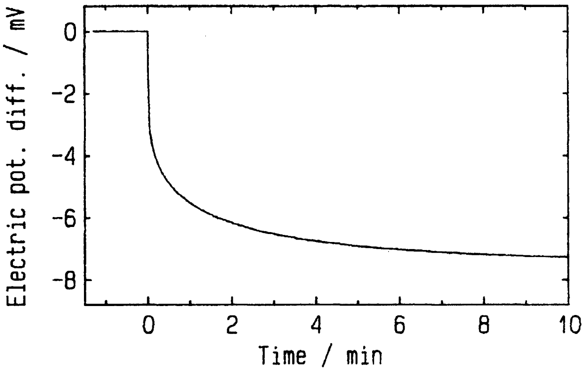

Fig. 2. The dependence of the electric-potential difference on time across Ox-C membrane in the K^+ form.

However, for the GVA(30)B membrane in the K^+ form, a sharp inverse spike of the electric-potential difference was observed just after a pressure difference was applied, although the GVA membrane contains negative fixed charges, as does the Ox-C membrane. When an aqueous HCl solution was used as the external solution for the GVA membranes in the H^+ form, the electric-potential difference was not observed in the experimental error, because of the low degree of dissociation of the carboxyl groups. If the GVA membrane in the H^+ form is immersed in a KCl solution, protons in carboxyl groups are partially exchanged with K^+ ions. This membrane is denoted as a GVA membrane in the K^+/H^+ form. However, considering the facts that the water content and thickness of the GVA membrane in the K^+/H^+ form are equal to those of the GVA membrane in the H^+ form, we can suppose that the degree of dissociation of the carboxyl groups for the K^+/H^+-form membrane is the same as that for the H^+-form membrane. Measurements of the electric-potential dif-

Table 1. Properties of the Membranes

Membranes[a)]	Time of esterification/h	Water content[b)]		Thickness/mm	
		H^+ form	K^+ form	H^+ form	K^+ form
GVA(20)	6	1.53	2.80	0.16	0.18
(40)	6	0.86	1.78	0.11	0.13
(60)	6	0.96	1.13	0.16	0.16
(80)	6	1.38	1.55	0.13	0.14
(30)A	6	0.86	4.06	0.36	0.47
(50)A	6	0.63	2.47	0.27	0.37
(70)A	6	0.78	2.45	0.46	0.51
(30)B	4	1.13	2.89	0.33	0.35
(50)B	4	0.92	1.75	0.35	0.55
(70)B	4	1.18	2.51	0.32	0.37

a) The number in the parentheses indicates the weight fraction of PAA. b) g/g-dry membrane.

ference across the GVA membrane in the K^+/H^+ form were carried out in a KCl solution. For the GVA membrane in the K^+/H^+ form, similar results concerning the time dependence of the electric-potential difference were obtained as those for the K^+-form membranes, although the magnitude of the sharp inverse spikes was small compared with that for the K^+ forms.

Figures 3a and 3b show scanning electron microphotographs of sections perpendicular to the surface of the GVA(30)B and Ox-C membranes, respectively. Although a large number of micropores were observed for the Ox-C membrane, they were not observed for the GVA(30)B membrane.

For a porous membrane, when a hydrostatic pressure difference is applied, water flow through the pores occurs immediately. On the other hand, if the membrane is not porous, a membrane matrix is directly forced due to the initial pressure difference. The GVA membrane is made of such flexible polymers as PVA and PAA, although the Ox-C membrane consists of relatively stiff polymers of cellulose. Therefore, for the GVA membrane at the moment when a pressure difference is applied, a transformation of the membrane matrix containing fixed charges is faster than water flow in the liquid phase of the gel membrane; in other words, a rapid compaction of the membrane matrix occurs. This compaction causes the appearance of an inverse electric-potential difference across the GVA membranes. However, the electric-potential difference due to compaction rapidly approaches zero after that because the movement of counterions for maintaining electroneutrality is fast, and the thickness of the membrane is finite. Thus, the electric-potential difference due to compaction does not affect the observed electric-potential difference over the full range of time. Although the GVA membrane is not microscopically porous, a volume flow due to the pressure difference occurs. Thus, the electric-potential differences due to both compaction of the membrane matrix and relaxation of polymer chains is observed. Consequently, the electric-potential difference due to relaxation of the polymer chains is predominant after about 30 s.

The dependence of the electric-potential difference on time due to a relaxation of the polymer chains under a pressure gradient may be written as

$$\Delta\,\psi(t) - \Delta\,\psi(\infty) = k\,\exp\left(-t/\tau\right), \tag{1}$$

$$\ln\{\Delta\,\psi(t) - \Delta\,\psi(\infty)\} = -t/\tau + K, \tag{2}$$

where $\Delta\psi(t)$ and $\Delta\psi(\infty)$ are the electric-potential differences at time t and steady state, respectively, τ the relaxation time, and k and K are constants.[4)] If the overall relaxation comprises several relaxation components, Eq. 1 may be written as

$$\Delta\,\psi(t) - \Delta\,\psi(\infty) = \sum_i k_i\,\exp\left(-t/\tau_i\right). \tag{3}$$

In Fig. 4, the relationship between $\ln\{\Delta\psi(t) - \Delta\psi(\infty)\}$ and the time was shown for the GVA(30)B membrane in the K^+ form. The values of $\ln\{\Delta\psi(t) - \Delta\psi(\infty)\}$ could not be plotted before 10 s because of the negative values of $\{\Delta\psi(t) - \Delta\psi(\infty)\}$. A straight line was drawn by the least-squares method after about 1 min; values of 223 s for τ_1 and -1.51 for K_1 were obtained. Although the GVA membrane is made of two kinds of polymers, PVA and PAA, these polymer chains have nearly the same flexibility. Moreover, the gel GVA membranes seemed to be homogeneous based on an observation of electron microphotographs. Thus, the time dependence of the electric-potential difference due to a relaxation of the polymer chains may be expressed by a single component. However, during an early time period it could not be expressed by the single component, as shown in Fig. 4. In this time region, a relaxation of the compaction of the whole membrane matrix may be included. We introduced a second component with values of 10±5 s for τ_2 and -2.3 for K_2 to explain the time dependence. However, the values of τ_2 and K_2 may be arbitrary values.

In Fig. 5, the observed variation of the electric-potential difference across the GVA(30)B membrane in the K^+ form, indicated by line A, is divided into two lines

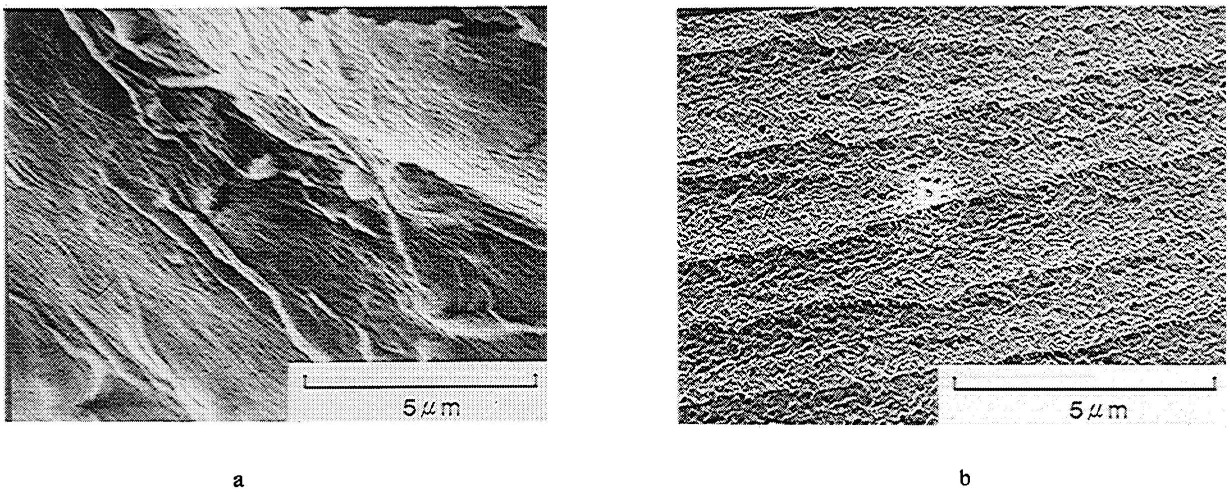

Fig. 3. Scanning electron microphotographs of the membranes (cut vertically to the surface). (a), GVA(30)B; (b), Ox-C.

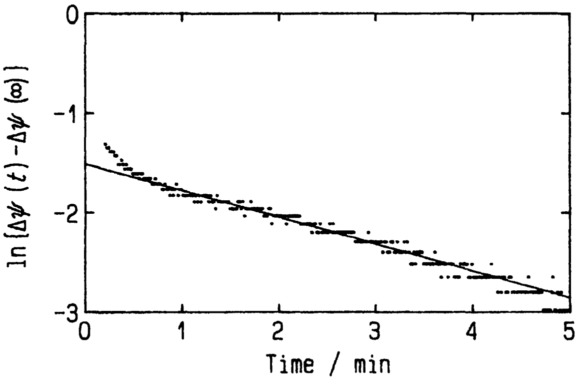

Fig. 4. The relationship between $\ln\{\Delta\psi(t)-\Delta\psi(\infty)\}$ and time for GVA(30)B membrane in the K^+ form.

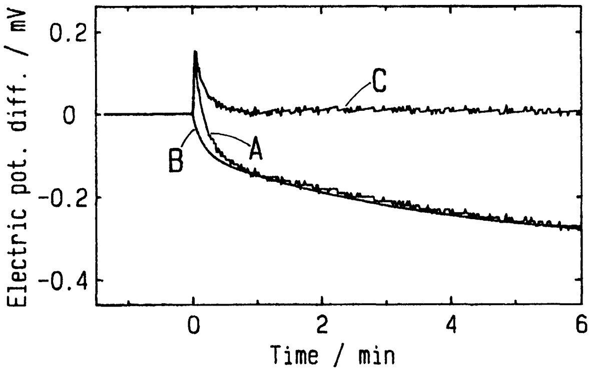

Fig. 5. The relationship between the electric-potential difference and time for GVA(30)B membrane in the K^+ form. A, observed; B, due to relaxation of polymer chains; C, due to compaction of membrane matrix.

due to a relaxation of the polymer chains, shown by line B, and due to compaction of the membrane matrix, shown by line C. Line B was calculated using Eq. 3 with $\tau_1=223$ s, $\tau_2=10$ s, $k_1=0.22$, and $k_2=0.1$, respectively. Line C was obtained by subtracting line B from the observed values. For the other membranes, the overall dependences of the electric-potential difference on time were also divided into two lines.

The value of τ_1 reflects the properties of the main polymer chains in the membrane. The values of τ_1, K_1, and $\Delta\psi(\infty)$ for the membranes in the K^+/H^+ and the K^+ forms were estimated, and are listed in Table 2. In general, the values of τ_1 for the membranes in the K^+/H^+ form were larger than those for the membrane in the K^+ form. Since the polymer chains in the K^+-form membrane are in the expanded state, because of an electric repulsion of the carboxyl groups, the degree of freedom of the polymer chains is lower than that in the K^+/H^+-form membrane. In Fig. 6, the relationship between $(\delta^K/\delta^{K/H})^3$and $\tau_1^K/\tau_1^{K/H}$ is shown, where δ^K and $\delta^{K/H}$ are the thicknesses, and τ_1^K and $\tau_1^{K/H}$ are the main relaxation times for the K^+- and the K^+/H^+-

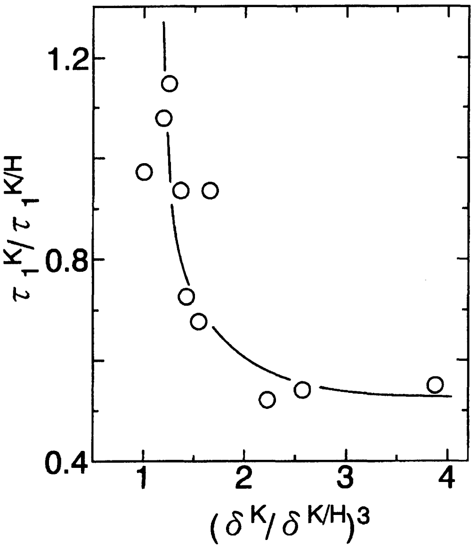

Fig. 6. The relationship between $(\delta^K/\delta^{K/H})^3$ and $\tau_1^K/\tau_1^{K/H}$.

Table 2. Values of τ_1, k_1, and $-\Delta\psi(\infty)$

Membranes	K^+/H^+ form			K^+ form		
	τ_1/s	k_1	$-\Delta\psi(\infty)$/mV	τ_1/s	k_1	$-\Delta\psi(\infty)$/mV
GVA(20)	406	0.31	0.72	295	0.32	0.45
(40)	542	0.15	0.34	337	0.15	0.19
(60)	185	0.09	0.27	180	0.05	0.16
(80)	242	0.31	0.48	278	0.09	0.14
(30)A	306	0.35	0.57	159	0.21	0.33
(50)A	198	0.17	0.49	107	0.23	0.23
(70)A	156	0.23	0.45	146	0.23	0.45
(30)B	204	0.37	0.66	223	0.22	0.28
(50)B	416	0.15	0.62	229	0.11	0.13
(70)B	195	0.26	0.62	132	0.13	0.21

form membranes, respectively. The value of $(\delta^K/\delta^{K/H})^3$ corresponds to the degree of expansion of the K^+-form membrane relative to the K^+/H^+-form one. When the degree of expansion increased, the ratio of the relaxation time became small.

Figure 7 shows the relationships between the electric-potential difference at a steady state ($\Delta\psi(\infty)$) and the water content for the K^+- and the K^+/H^+-form membranes. The volume of flow across a membrane increases with increasing the water content of the membrane. Therefore, the electric-potential difference which appears also increases along with an increase in the water content. The relationships between $\Delta\psi(\infty)$ and the water content were approximately linear for both form membranes. Straight lines were obtained by a least-squares method. However, the water contents obtained from the intercepts of the straight lines of the water-content axis were different from each other. For the K^+/H^+-form membranes there are a few counterions dissociated from the carboxyl groups. However, for the K^+-form membranes there are many K^+ ions in the membrane. The K^+ ions in charged membranes hinder the flow of water, because K^+ ions cannot move away far from the site of fixed charges if an electric current is not passed. Moreover, in the H^+-form membranes H^+ ions do not greatly hinder the flow of water, because they can exchange with the hydrogen of neighboring water, just as a proton jump in electric conductivity. A part of the water restricted around the K^+ ions and the fixed charges cannot contribute to the flow of water. The parts of water were estimated to be 0.22 and 0.91 g/g-dry membrane for the H^+/K^+-form and for the K^+-form membranes, respectively, from Fig. 7.

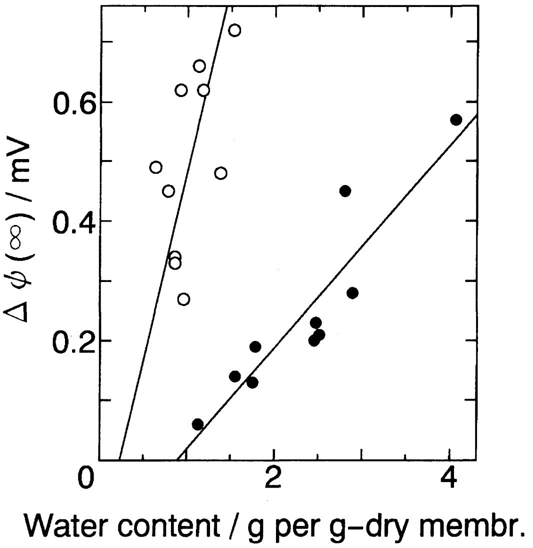

Fig. 7. The relationships between water content and the electric-potential difference at steady state, $\Delta\psi(\infty)$. ○, K^+/H^+-form membranes; ●, K^+-form membranes.

Conclusions

The time dependence of the electric-potential difference under a pressure gradient across hydrogel membranes obtained by esterification of poly(vinyl alcohol) and poly(acrylic acid) was measured. The time dependence consisted of two different processes due to compaction of the membrane matrix and relaxation of polymer chains dissolved in the liquid phase of the membrane. The main relaxation time of the polymer chains observed for the K^+/H^+-form membranes was larger than that for the K^+-form membranes.

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