Mechanochemistry and Permeability of Polyelectrolyte Complex Membranes Composed of Poly(vinyl Alcohol) Derivatives

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Synopsis

Two polyanions and two polycations were prepared by the esterification of poly(vinyl alcohol). Properties of their neutral polyelectrolyte complex membranes were compared with those of polyelectrolyte membranes. The charged state on the membranes was related closely to the mechanochemical reaction, the salt rejection, and the solution permeability. Both the salt rejection and the water flux of neutral polyelectrolyte complex membranes were lower than those of the corresponding acidic or basic complex membranes.

INTRODUCTION

With regard to the practical and industrial applications of reverse osmosis, a large number of papers have been published recently on the permeability of ionic and nonionic membranes of various structures and functional properties. However, there are not so many papers on membranes that contain both positive and negative charges, for example, polyelectrolyte complex membranes[1-3] and charge mosaic membranes as used for piezodialysis.[4-6] The former membranes are of interest mainly in ultrafiltration and biomedical materials, while the latter membranes are of interest in negative reverse osmosis and biology.

As reported in our preceding paper,[3] the polyelectrolyte complex membrane composed of a weakly or strongly acidic polysaccharide and a weakly basic polysaccharide had a similar permeability dependence on pH to that of the charge mosaic membranes, like polyampholytes, despite their different distribution of charged groups. It is well known not only that the presence of ionized and ionizable groups on membranes has an influence on the permeability, but also that ionized groups play an important role in the mechanochemical reaction of polyelectrolyte membranes.[7,8] Therefore, it is interesting to investigate the effect of ionized and ionizable groups on neutral polyelectrolyte complex membranes in which ionizable basic groups are contained in equivalence to ionizable acidic groups. For this purpose, four kinds of partially esterized poly(vinyl alcohol) (PVA) derivatives were prepared: sulfated PVA (PVAS) as a strongly acidic polyelectrolyte, carboxymethylated PVA (PVAC) as a weakly acidic polyelectrolyte, PVA reacted with diethoxy ethyltrimethylammonium iodide (PVAT) as a strongly basic polyelectrolyte, and aminoacetalyzed PVA (PVAA) as a weakly basic polyelectrolyte. The properties of the neutral polyelectrolyte complex membranes were compared with an individual ionic PVAC and PVAA membrane.

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EXPERIMENTAL

Materials. A part of smaller molecular weight in a PVA sample was removed by the addition of acetone, and the degree of polymerization of PVA used was estimated as 2010 from viscometric measurement.[9] PVAA and PVAS were prepared in a similar method to one of our previous papers except for a reaction time of 1.5 hr and catalysis of hydrochloric acid. PVAT and PVAC were prepared according to the method proposed by Hosono et al.[11,12] The reaction reagents of PVA derivatives and the number of ionic groups of the obtained PVA derivatives per 100 PVA repeating unit are listed in Table I, where the numerals indicate half the degree of esterification. PVA derivatives were purified by a mixed-bed column filled with ion exchange resins after dialysis for several days. The degree of esterification of the samples was estimated conductometrically and potentiometrically.

Preparation of Membranes. For the preparation of an equimolar complex membrane, it was necessary to avoid the precipitation of polyelectrolyte complexes, in other words, to weaken the electrolyte interaction between positive and negative charges. Therefore, 12.8% HCl, 8.3% NH_3, and 3.1% HCl were added to the PVAS–PVAT, PVAS–PVAA, and PVAA–PVAC systems, respectively, and the polymer solution concentration was in a range from 0.9% to 1.4%. After casting the mixtures and drying, the membranes were washed in an equivolume mixture of ethyl alcohol and water so as to remove ammonia and hydrochloric acid.

The complex membranes were immersed and crosslinked in 0.06% aqueous glutaraldehyde aqueous solution at 30°C for 3 min. In the case of PVAA and PVAC ionic membranes, each polyelectrolyte solution was cast with 0.025% glutaraldehyde. The excess glutaraldehyde was removed by washing in water.

Measurement of the Degree of Ionization of the Membranes. The titration curve of membranes was obtained with a Hitachi-Horiba F-7ss pH meter at 25°C. The degree of ionization of the membranes was calculated on the assumption that the activities of hydrogen and hydroxide ions in aqueous solution were the same as those in the presence of the membrane.

Measurement of Mechanochemical Reactions. The extension of a membrane sample 5–6 mm wide and 10–20 mm long under a given weight was measured with a cathetometer and the apparatus as shown in Figure 1. The pH value of the surrounding medium was adjusted by the addition of NaOH or HCl. The medium was stirred by bubbling nitrogen gas. The membranes were contracted or extended with reproducibility of a few percentages.

TABLE I
PVA Derivatives

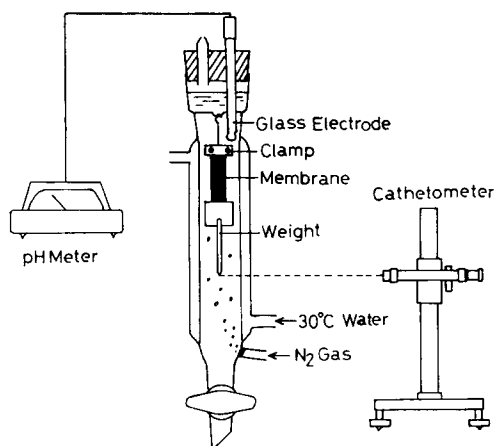| Derivative	Reaction reagents	Number of ionic groups per 100 PVA repeating unit
PVAS	80% sulfonic acid	21.0
PVAC	sodium hydroxide, sodium monochloroacetate	3.92
PVAT	hydrochloric acid, diethoxyethyl trimethylammonium iodide	13.8
PVAA	hydrochloric acid, aminoacetal	16.7

Fig. 1. Apparatus for measurement of mechanochemical reaction.

Measurement of Permeability. The reverse osmosis measurements were made by using a RO test loop for membranes equipped with three cells made by Tama Seiki Ind. Co. Ltd., as reported previously.[3] The feed solution, the applied pressure, and the membrane area were 0.2% NaCl aqueous solution, 83 kg/cm^2, and 11.9 or 19.6 cm^2, respectively.

RESULTS AND DISCUSSION

The state of ionized and ionizable groups on a polyelectrolyte or complex membrane immersed in an aqueous solution is presumably different from that of a homogeneous solution of the corresponding polyelectrolyte. Therefore, potentiometric titration was tried with small strips of membranes placed in aqueous solution. In Figure 2 the degree of ionization of PVAS–PVAT, PVAS–PVAA, and PVAC–PVAA complex membranes is plotted against pH, in comparison with PVAC and PVAA ionic membranes having weakly ionizable groups. In this figure Z_0 designates the total number of both ionized and ionizable groups and is calculated from the weight of the dry membrane, and Z is the number of ionized groups at a given pH value.

The Z/Z_0 values of the PVAS–PVAT complex membrane are almost constant and indicate that the positive and negative charges are almost neutralized in the overall pH region, as shown in curve 1. Some scatter of the data may have been caused not only by experimental error because of the slow diffusion of ions into the membrane, but by the heterogeneous distribution of positive and negative charges depending on the preparation conditions (relatively high concentration of HCl).

In the case of the PVAA ionic membrane, the titration curve of the membrane is almost the same as that of PVAA in aqueous solution,[13] while the ionization of all carboxylic groups on a PVAC membrane shifts to higher pH value (curve 4 in Fig. 2) compared with that of PVAC in aqueous solution.[13] If the ionization of the amino groups on a PVAS–PVAA complex membrane is independent of the presence of PVAS, the titration curve of the equimolar mixture should be given by curve 5′, where values of Z/Z_0 of a PVAA ionic membrane subtracted from Z/Z_0 of a PVAS membrane are plotted against the pH. As shown in curve
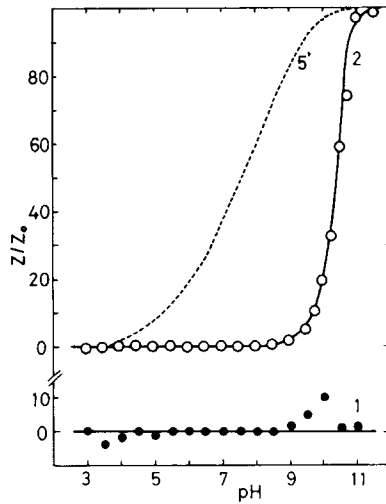
(a)
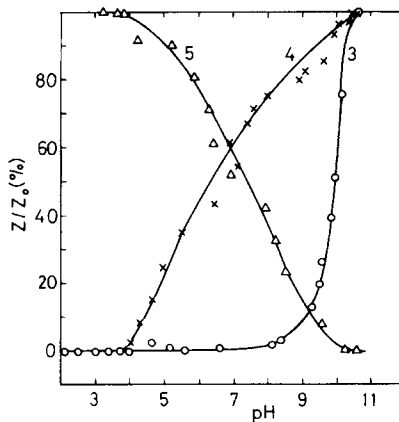
(b)

Fig. 2. Titration curves of PVAS–PVAT (1), PVAS–PVAA (2), and PVAC–PVAA (3) complex membranes and PVAC (4) and PVAA (5) ionic membranes. Curve 5′ is obtained by subtracting Z/Z_0 value of PVAA from unity.

2, however, Z/Z_0 of the PVAS–PVAA membrane increases steeply in the pH region from 8.5 to 11.5, particularly in comparison with curve 5′. Though the amino groups in the PVAA membrane are deionized gradually in the pH region from 3.6 to 11, they are disturbed by the presence of sulfuric groups in the PVAS–PVAA complex membrane. In other words, the ionization of amino groups is induced strongly by ionized sulfuric groups, as is also observed in a system of carboxymethyl cellulose and polyethyleneimine.[14]

Considering the charge state, the PVAS–PVAA membrane changes to an acidic ionic membrane above pH 11.5, to an acidic complex membrane at pH 8.5 to 11.5, and to a neutral complex membrane below pH 8.5 (curve 2). In the case of

PVAC–PVAA, an acidic membrane, an acidic complex membrane, and a neutral complex membrane are formed above pH 10.5, in the pH region from 7 to 10.5, and below pH 7, respectively.

The pH dependence of the membrane extension, $\Delta L/L_0$, is shown in Figure 3, where L_0 indicates the length of a membrane strip on which negative and positive charges are neutralized and ΔL is the extension of the membrane strip at a given pH value. All membranes except that of curve 2′, which is crosslinked in 0.09% glutaraldehyde for 5 min, have the same crosslinking condition. The membrane of curve 2′, crosslinked more densely, extends less than the membrane of curve 2.

The change of $\Delta L/L_0$ in Figure 3 is obviously in accord with the change of the titration curves for the charged state on membranes shown in Figure 2. For example, $\Delta L/L_0$ of a PVAT–PVAS membrane, swollen naturally by itself in
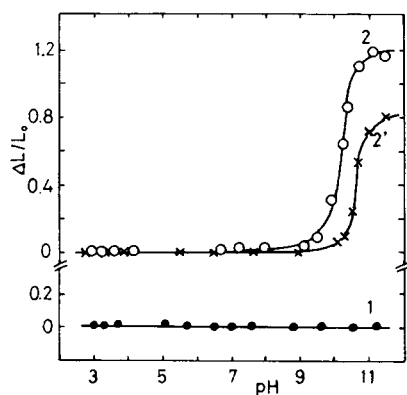
(a)
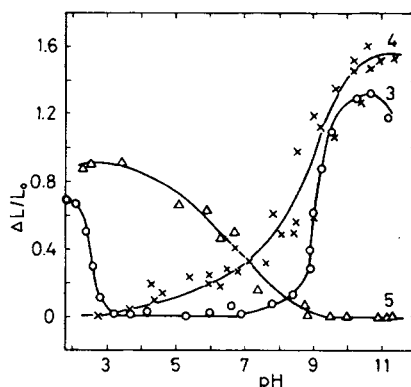
(b)

Fig. 3. pH Dependence of membrane extension for PVAS–PVAT (1), PVAS–PVAA (2), PVAS–PVAA (2′), PVAC–PVAA (3), PVAC (4), and PVAA (5) membranes. Complexes 1, 2, and 3 were crosslinked in 0.06% glutaraldehyde for 3 min; complex 2′ was crosslinked in 0.09% glutaraldehyde for 5 min; 4 and 5 were cast with 0.025% glutaraldehyde.

aqueous solution, is not dependent on pH. In the case of individual PVAC or PVAA ionic membranes, $\Delta L/L_0$ increases with increasing degree of ionization of the membranes. This relationship in the mechanochemical reaction was previously regarded as a result of the extension of polyelectrolyte chains due to the repulsion among ionized groups[15] and of the membrane swelling by the increasing osmotic pressure caused by counter ions.[16] Taking the membrane swelling into consideration from both this standpoint and our data on mechanochemical reaction, the swelling of ionic membranes is supposed to be larger than in the complex membranes for the PVAS–PVAA and PVAC–PVAA systems.

With respect to ionic linkages, the extension of the neutral complex membranes is suppressed more than that of the ionic membranes, as observed in curves 2, 2′, and 3 in Figure 3. Hence, ionic linkages seem to behave like crosslinkages, as presumed in complex coacervation.[10] The result that the $\Delta L/L_0$ of the PVAC–PVAA membrane increases in the pH region below 3.2 seems to be contradictory to the constant Z/Z_0 in curve 3 of Figure 2. This, however, suggests that ionic linkages are loosened because of the deionization of carboxylic groups.

The change in the degree of swelling of membranes has a large influence on the permeability of the membranes.[2,4,17] Figures 4 and 5 show respectively the salt rejection R_s and the flux as functions of pH. Generally speaking, with respect to the PVA derivative membranes, the salt rejection decreases slightly with increasing pH for neutral complex membranes, and the ionic membranes show better salt rejection than the neutral complex membranes and the nonionic membranes. In comparison with membranes composed of oppositely charged polysaccharides,[3] and membranes composed of block copolymers containing 2-vinylpyridine and trimethylsilyl methacrylate,[5] the neutral pH region in the membranes is broader in our PVA derivative membranes. This is attributed to the more effective ionization induced by ionized groups. In other words, ionic linkages may exist in a more optimum distance because of the flexible backbone chains of PVA and the absence of microphase separation.

Curiously enough, the flux also increases with increasing R_s, as is obvious from curves 2, 3, 4, and 5 in both Figures 4 and 5. The same behavior was also observed for polyelectrolyte complex membranes[3] composed of oppositely charged polysaccharides. The relationship between the R_s and the permeability coefficient K_1 is denoted by the following equation[17]:

$$K_1 = A \exp(-BR_s) \tag{1}$$

where A and B are the constants. Although attempts were made to obtain the permeability coefficient K_1, it was very difficult with our apparatus to measure the thickness under pressure and, in addition, to prepare membranes having the same charge density in the same condition of the preparation. Therefore, the absolute values of the R_s and the flux cannot be compared in Figures 4 and 5. However, the cause of the phenomenon that the R_s increases with the increase in flux, in contrast to eq. (1), may not be attributed only to the change in the membrane thickness but more likely to the change in pH. That is, for PVAC and PVAA membranes, the feature of the membranes changes from a nonionic character to an ionic one with change in pH. Similarly, in the case of PVAS–PVAA and PVAC–PVAA complex membranes, the neutral complex membranes change to ionic membranes with change in pH.
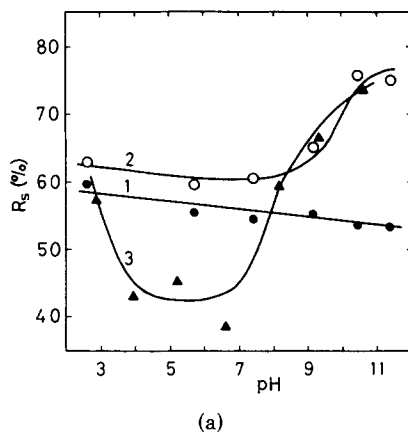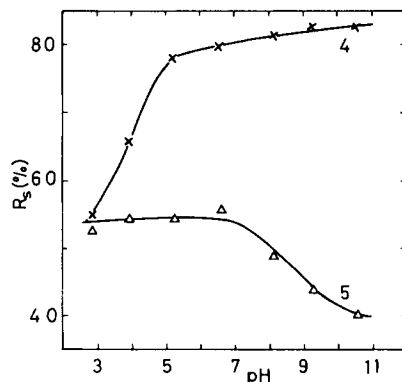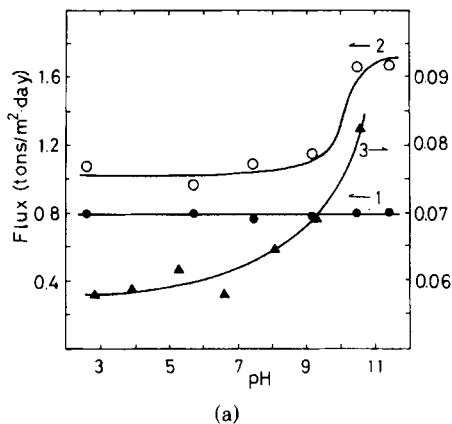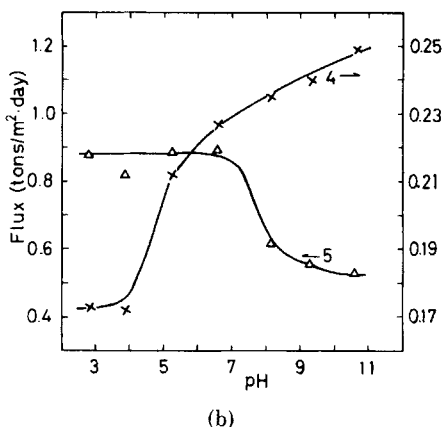
Fig. 4. Effect of pH on salt rejection for PVAS–PVAA (1), PVAS–PVAA (2), and PVAC–PVAA (3) complex membranes and PVAC (4) and PVAA (5) ionic membranes.

With respect to the ionic membrane, coions are less permeable, and moreover the free volume for the transport of salt is smaller than that of nonionic membrane.[17] In the case of the neutral complex membrane, no repulsive force exists between microions and charges on the membranes; rather, attractive force may act between them. Thus, microions are more permeable in a complex membrane than in an ionic membrane. Although we could not prepare nonionic and complex membranes in comparable condition, a complex membrane is presumably more permeable to microions than is a nonionic membrane. Namely, the salt rejection of PVA derivative membranes is in the following order: ionic membrane > nonionic membrane > neutral complex membrane.

On the other hand, as observed in curves 4 and 5 in Figure 5, the flux of an ionic membrane is larger due to its higher degree of swelling than that of a nonionic membrane. With respect to neutral complex membranes, ionic linkages in a polyelectrolyte complex behave not only like crosslinks, as mentioned above, but also reduce the extension of polyelectrolyte chains.[18] Therefore, the degree

(a)

(b)

Fig. 5. pH Dependence of flux for PVAS–PVAT (1), PVAS–PVAA (2), and PVAC–PVAA (3) complex membranes and PVAC (4) and PVAA (5) ionic membranes.

of swelling of neutral complex membrane seems smaller than that of nonionic membrane in aqueous solution. Thus, the order of the solution permeability of PVA derivative membranes is as follows: ionic membrane > nonionic membrane > neutral complex membrane.

In conclusion, the ionic membrane is much better for reverse osmosis than the neutral complex membrane; the permeability of microsalts is very high in the neutral complex membrane.

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