Water/Ethanol Pervaporation Performance of Asymmetric Polyelectrolyte Complex Membrane Constructed by the Diffusion of Poly(acrylic acid) in Chitosan Membrane

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ABSTRACT: Asymmetric polyelectrolyte complex (PEC) membranes composed of chitosan membrane and absorbed poly(acrylic acid) (PAA) were constructed. Absorption and therefore PEC formation were performed by bringing a chitosan membrane into contact with a PAA aqueous solution. The mean molecular weight (MW) of PAA employed was 5,000, 25,000 or 250,000. Absorption of PAA and asymmetry of PEC membranes were confirmed and evaluated by Fourier transform infrared (FTIR) spectra and electron spectroscopy for chemical analysis (ESCA). The absorption quantity of PAA decreased while the water selectivity of the PEC membrane increased with an increase in the MW of constituent PAA. In a pervaporation experiment, the water selectivity of the membrane was so high that no ethanol was detected by gas chromatography (GC). Such selectivity was attained by just a small quantity of PEC formation at the surface of the chitosan membrane. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 265–271, 2002

Key words: FT-IR; membranes; polyelectrolytes; selectivity; swelling

INTRODUCTION

Pervaporation (PV) is a separation process for liquid mixtures and is effective especially for azeotropic mixtures. But PV has not been widely used on an industrial scale because of the high energy cost arising from the latent heat of vaporization and the cost for coolant necessary for condensation. If a high performance membrane that has both large permeability and high selectivity can be developed, PV will become a practical liquid separation process. Among PV processes for liquid mixtures, water/ethanol separation has attracted a huge interest because this process is necessary for the utilization of biomass energy. So far, many highly water-selective membranes have been invented. Mochizuki et al. found that the selectivity of chitosan membrane was improved by introducing multivalent anionic molecules in the membrane.[1,2] They found a similar effect for cationic molecules on alginate membrane.[3] On the basis of their findings, the authors developed highly selective chitosan membranes whose surface is converted to the polyelectrolyte complex (PEC) by incorporating poly(acrylic acid) (PAA) into the membrane.[4] Ethanol could not be detected in the liquid permeated through that membrane

by a gas chromatography method. Karakane et al. also directed their attention to PEC membrane. They reported that PAA-based membranes treated with several kinds of cationic polymers have high water selectivity.[5] Nowadays, PEC formation has been recognized as a very useful method to make highly water-selective membranes.

Membranes neutralized by small molecular counterions usually turn out to be mechanically weak in water-rich solutions owing to a high swelling degree that is brought about by the dissociation of counterion. On the other hand, PEC membranes can maintain their mechanical strength because electrostatic interactions between polyelectrolytes is so strong that the PEC cannot be dissolved even in water. Nam et al. intensively investigated the PV performance and the structure of chitosan–PAA PEC membranes prepared by mixing chitosan and PAA aqueous solutions.[6] PEC is usually a compact precipitate that is insoluble in water even at high salt concentrations; therefore, a few solvent/PEC system are known.[7] Even if PEC membrane can be formed from the solution, the counterions yielded from additive salts cannot be removed easily from the membrane that is a kind of biionic membrane.

We report on the high performance of the chitosan–PAA membrane constructed by the diffusion of PAA in chitosan. Here, the relationship between membrane performance and membrane construction conditions such as temperature, diffusion time, and MW of PAA

is clarified by examining the structure of constructed membranes. Then, the most preferable condition that yields a high performance membrane is discussed.

EXPERIMENTAL

Sample preparation

Chitosan, with a deacetylation degree more than 99%, was purchased from Katayama Chemical. PAA (MW = 5,000 and 25,000) and PAA (MW = 250,000) were purchased from Wako Pure Chemical Industries, Ltd., and Aldrich Chemical Company, Inc., respectively, and they are abbreviated as PAA5000, PAA25000, and PAA250000, respectively.

One weight percent of chitosan aqueous solution containing acetic acid whose molar quantity was equivalent to that of the chitosan monomer unit was filtered to get rid of insoluble materials. Then the filtered solution was poured onto a flat glass laboratory dish. After being dried at room temperature, the membrane was immersed twice in about 30 mL of 1MNaOH/ethanol = 50/50 (v/v) solution to remove acetic acid and then rinsed with water. The thickness of a dry chitosan membrane was about 15 μm.

PAA was dissolved in water so that the concentration of PAA monomer unit was 0.03M. The solution was filtered if necessary. A 25 mL PAA solution was transferred into a membrane holder to which the chitosan membrane was attached, and therefore the chitosan membrane was in contact with PAA solution at the top surface only. The effective membrane surface was a circle with a diameter of 80 mm for a wet chitosan membrane. Absorption of PAA was conducted at room temperature for 5 min, at 60°C for 1 and 4 h, and at 80°C for 1 and 4 h. Then the membrane was washed using water to remove residual PAA uncombined with chitosan polymer. We here denote the surface contacted with PAA solution as *upside* surface and the opposite side that was not contacted with the solution as *downside* surface.

Measurements

Membranes were dried in vacuum overnight prior to the weight measurement. The weight increase of the whole membrane before and after PEC formation gives the PAA absorption quantity, w. From w and the weight of dry chitosan membrane before PEC formation, W, an approximate neutralization degree of the membrane as a whole, ND, was estimated by the following equation:

$$\text{N.D.} = 100(w/72)/(W/161) \qquad (1)$$

where 72 and 161 are the molecular weights of PAA and chitosan monomer unit, respectively.

Verification of PAA absorption and PEC formation was carried out by Fourier transform infrared (FTIR) (BIO RAD FTS-60A/896) measurement of both the spectra through the membrane and the attenuated total reflectance (ATR) spectra from the upside and downside membrane surfaces. All the spectra were represented in absorbance, and the ATR absorbance directly obtained was multiplied by the wave number for convenience in comparing with the total absorbance. When the intensity of the ATR signal was too weak to obtain significant spectra, the surface structure of the polymer membrane was determined by X-ray photoelectron spectroscopy using a Shimadzu ESCA 750 (ESCA: electron spectroscopy for chemical analysis).

The PV experiment was conducted in the usual way.[5,6] The membrane cell was dipped in a water bath kept at 30°C. The upstream pressure was atmospheric and vacuum was applied to the downstream. The permeation quantity Q (kg) was determined from the weight of the liquid condensed in dual glass tubes that were cooled by liquid nitrogen and used alternately. The permeated liquid was returned to the feed to maintain its composition at a constant level. The composition of permeated liquid at a steady permeation state was analyzed by gas chromatography with Thermal Conductivity Detector (TCD) kept at 150°C. The temperatures of the column and the injection were 105°C and 150°C, respectively. The column packing material was Porapak-Q and the carrier gas was He of which flow rate was 50 mL/min. The permeation flux J (kg/mh) was calculated by normalizing with the membrane thickness d (m) from the following equation:

$$J = (Qd)/(At) \qquad (2)$$

where A (m^2) and t (h) are the effective membrane area and the permeation time, respectively.

RESULTS AND DISCUSSION

Weight increase

The effects of absorption time and temperature have been examined for three kinds of PAA. The results are depicted in Table I, which shows the weight increase and ND of membranes. The chitosan membrane partially dissolved and turned porous at 60°C for 4 h or at 80°C for 1 h in PAA5000 solution, and at 80°C for 4 h in PAA25000 solution. Therefore weight increases under these conditions are not listed in the table. No significant weight increase was obtained for membranes treated at room temperature (rt) for 5 min with any MW of PAA.

Smaller PAA can be absorbed more easily. This can be understood quantitatively by the comparison of

TABLE I
Neutralization Degree Estimated from PAA Weight Absorbed in Chitosan

Membrane no.	Mean MW of PAA	Condition	Weight increase (mg)	Neutralization degree (%)
1	5,000	rt, 5 min	1.2	3.4
2	5,000	60°C, 1 h	32.6	83.5
3	25,000	rt, 5 min	0.2	0.5
4	25,000	60°C, 1 h	26.4	75.6
5	25,000	60°C, 4 h	47.3	123.4
6	25,000	80°C, 1 h	28.7	74.7
7	250,000	rt, 5 min	−1.0	−2.6
8	250,000	60°C, 1 h	0.1	0.3
9	250,000	60°C, 4 h	0.4	1.1
10	250,000	80°C, 1 h	0.2	0.5
11	250,000	80°C, 4 h	0.8	2.2

membranes 2, 4, and 8. This tendency can be qualitatively applicable to membranes treated at higher temperature or for a longer time: the absorption quantity of PAA25000 at 80°C for 1 h was not very different from that at 60°C, but in the case of PAA5000, this temperature difference had a great effect and at 80°C partial dissolution of membrane took place. Interestingly, membranes treated with PAA250000 exhibited no significant weight increase under any absorption conditions. This strongly implies that between 25,000 and 250,000 there is a cutoff MW that determines whether the diffusion of PAA into chitosan can occur.

Notably, the ND of membrane 5 exceeds 100%. The absorption of one polymer into the membrane composed of another polymer is not a common phenomenon. Obviously this should be ascribed to the specific interaction between the chitosan and PAA. Chitosan has a high affinity to PAA because it is soluble in an aqueous solution of acrylic acid monomer. The glass transition temperature T_g of chitosan that contains 8–30% of water was estimated as $T_g = 303$ K.[8] Hence the chitosan membrane is in a rubbery state and PAA is able to diffuse into it at temperatures higher than 30°C. But at the same time the dissolution of chitosan polymer is brought about under such conditions. If the MW is lower or the temperature becomes higher, the dissolution proceeds and eventually the membrane turns porous. Therefore, optimum absorption conditions should be adopted depending on the MW of PAA to obtain an objective ND.

IR spectra

Figures 1 and 2 represent FTIR absorbance spectra of chitosan membranes treated with PAA5000 and PAA25000 respectively. Figure 1 contains the spectra of native chitosan and PAA for the sake of comparison. As ND increases from membrane 1 to 2, the characteristic peak of —OH at 3454 cm^{-1} in chitosan loses sharpness, while the peak at 2910 cm^{-1} becomes greater than the peak at 2868 cm^{-1}. The existence of

PAA was confirmed most distinctly by the characteristic peak around 1716 cm^{-1} that is assigned to the stretching mode of C=O in PAA.[6] These results are in good agreement with those in Table I. The membranes having large ND show large absorbance at the characteristic wave number and vice versa. The membranes treated with PAA250000 showed no sign of absorbed PAA (data not shown) due to negligibly small weight increases. The group —NH^{3+} (3B, +P) has an N—H asymmetric deformation peak at 1650–1550 cm^{-1} and symmetric deformation peak at 1550–1504 cm^{-1}, while —COO^{-} has an asymmetric stretching peak at 1650–1550 cm^{-1}. The prominent 1555 cm^{-1} peak that is not found in chitosan or PAA spectrum can be assigned to these groups. These results indicate that PAA was certainly absorbed and formed polyelectrolyte complex with chitosan.

It is plausible to think that the diffusion of PAA is slow owing to its large molecular weight and the resulting membrane is asymmetric in the direction perpendicular to the membrane. This can be evaluated by ATR whose sampling depth is about 0.3–3 μm and
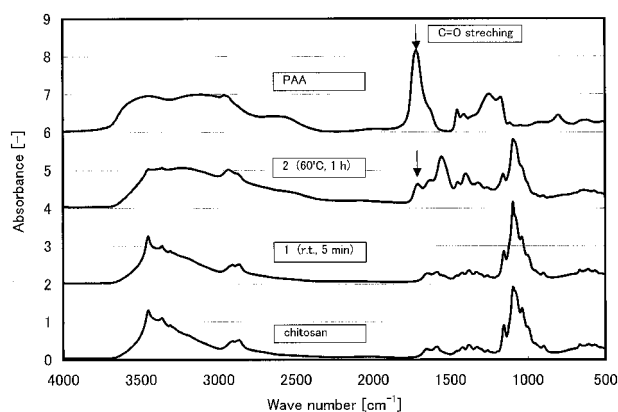

Figure 1 FTIR spectra of chitosan–PAA5000 membranes. Chitosan and PAA spectra are drawn for the sake of comparison. Aside from the PAA spectrum that was obtained using a KBr method, all spectra were taken on film samples.
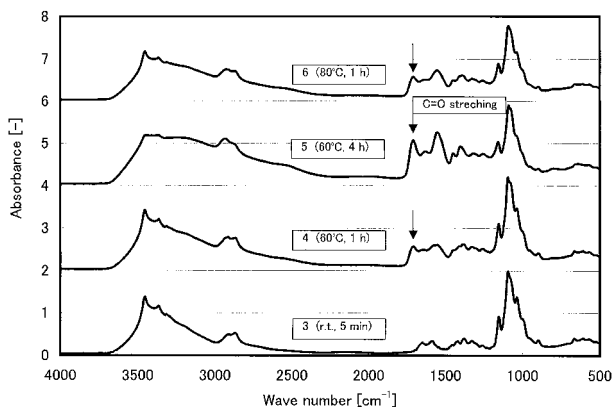
Figure 2 FTIR spectra of chitosan–PAA25000 membranes.

Figure 4 ATR spectra of chitosan–PAA25000 membranes.

is proportionally dependent on wavelength.[9] The results are shown in Figures 3–5, where (u) means upside surface that was in contact with PAA solution while (d) means downside surface. As shown in Figure 3, membrane 2 has a characteristic absorbance peak around 1716 cm^{-1} at (u) whereas it does not have this peak at (d). Accordingly, absorbed PAA5000 does not reach the downside surface, and hence the local ND at (u) of this asymmetric membrane can be estimated to be larger than 83.5%; i.e., the mean ND of this membrane.

Similarly in Figure 4, all the membranes except membrane 3 have characteristic peaks at (u). It should be noted that membrane 6 has a shoulder at the characteristic wave number even at (d). This means that PAA migrated to the downside of the membrane and the whole membrane changed into a PEC. Since the weight increase of this membrane is smaller than that of membrane 5, the migration of PAA25000 is mainly dependent on temperature. In Figure 5, membranes 8–10 about which transmission type FTIR gave no information on the absorbed PAA showed shoulder peaks around the characteristic wave number 1716 cm^{-1} at (u). This result indicates that a very small quantity of PAA250000 has been absorbed at the up-
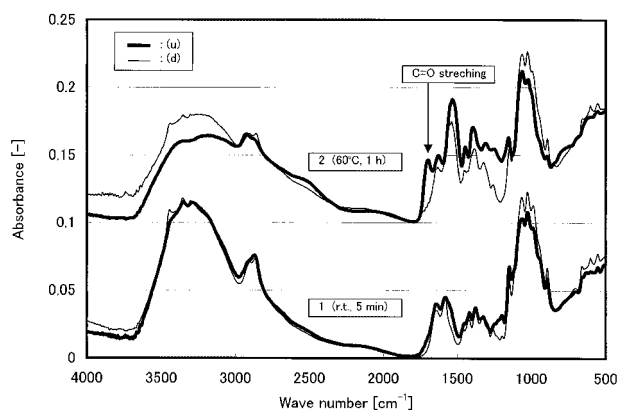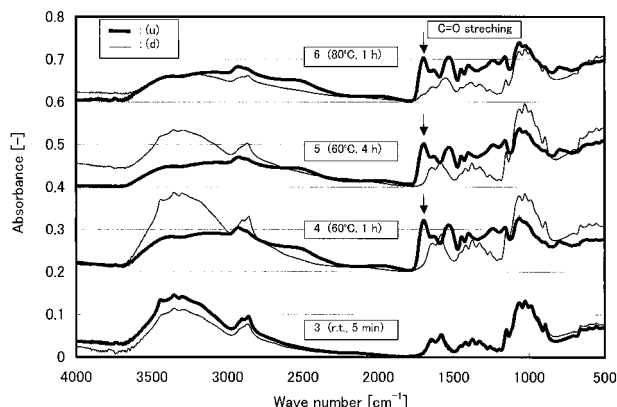
side of these membranes. Since PAA250000 cannot diffuse deeply into chitosan owing to its high MW, the PEC will be formed only near the upside surface. The existence of PAA was confirmed more directly by ESCA observation. Figure 6(a) and Figure 6(b) depict ESCA results for chitosan and membrane 11 (u), respectively. In each figure, the measured ratios of elements O, N, and C are given in the first row and the ratios calculated from the structural equation are given in the second row. In Figure 6(b), the nitrogen peak that arises from chitosan is very weak compared with that in Figure 6(a). Furthermore, from the chemical shift calculation of carbon in PAA, the peak of C should split into two peaks as depicted in Figure 6(b). The distance of each peak should be 4.48 eV while the relative strength should be 2:1, which is in accordance with Figure 6(a). Therefore PAA is certainly absorbed at membrane 11 (u). Since the ESCA signal arises from a depth on the order of a nanometer,[9] the surface is almost certainly occupied by PAA.

PV performance

As shown in Figures 7(a) and (b), even a small absorption of PAA5000 slightly decreases the permeation
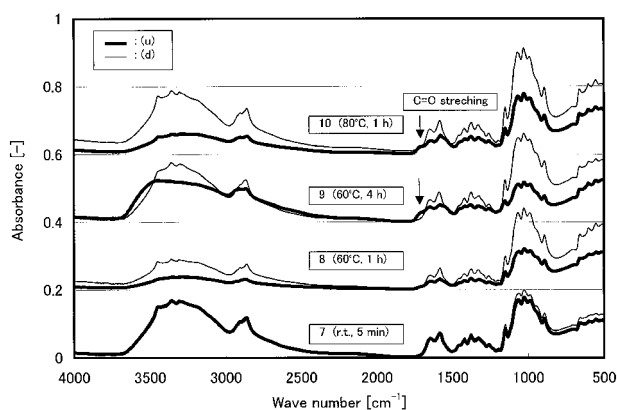

Figure 3 ATR spectra of chitosan–PAA5000 membranes.

Figure 5 ATR spectra of chitosan–PAA250000 membranes.

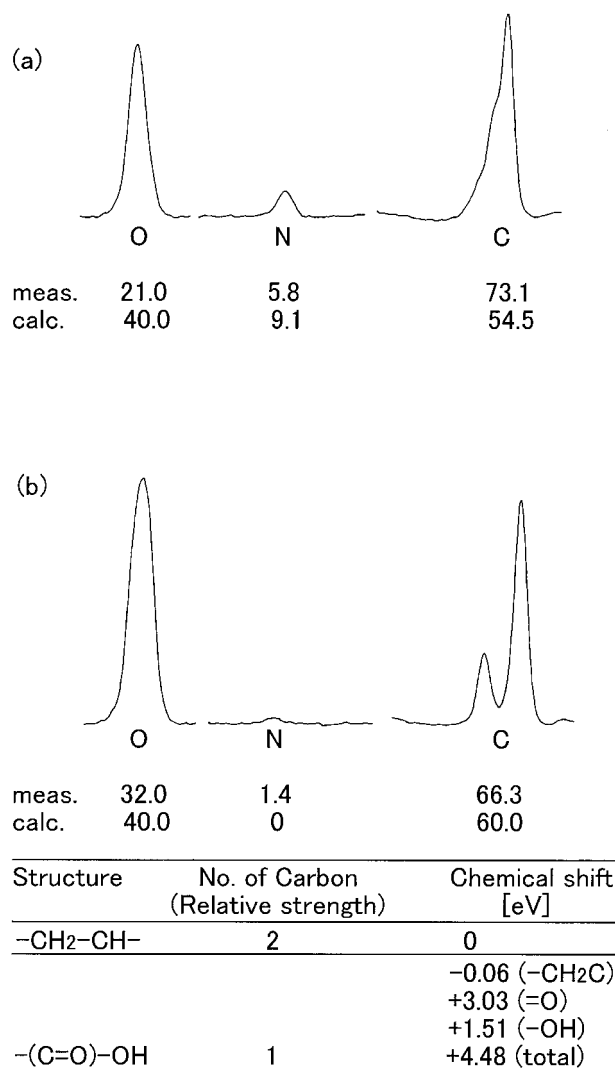| Structure	No. of Carbon (Relative strength)	Chemical shift [eV]
$-CH_2-CH-$	2	0
		$-0.06\ (-CH_2C)$
		$+3.03\ (=O)$
		$+1.51\ (-OH)$
$-(C=O)-OH$	1	$+4.48\ (total)$

Figure 6 (a) ESCA peaks of chitosan membrane. (b) ESCA peaks of the membrane 11 at (u). The peaks correspond to the photo electron energy of O1s, N1s, and C1s orbitals of the respective atoms. The energy (eV) increases toward the left-hand side. The total width of carbon signal ranges to 15eV.

flux while increasing the selectivity (membrane 1). However, the large absorption of PAA5000 leads to a decrease in selectivity at high ethanol concentrations in spite of the decrease of permeation flux. The selectivity increased only at 56% ethanol in the feed. Though this reason is not obvious, it is a peculiar phenomenon for a small MW of PAA because the decrease of selectivity is not observed for larger MW of PAA as mentioned in the following. The effect of PEC formation with PAA25000 was more outstanding, as shown in Figures 8(a) and (b). The permeation fluxes of membranes 5 and 6 have been reduced to less than half that of native chitosan, while the selectivity increased so drastically that no ethanol was detected by GC analysis. The results of PAA250000 treated membranes [membranes 9–11 in Figures 9(a) and (b)]

are most noteworthy. In spite of the small PAA quantity near the surface as clarified in Table I and Figures 5 and 6, the selectivity was so high that no ethanol was detected by GC analysis at all feed compositions examined in this experiment. The permeation fluxes of these membranes are reduced to less than half of that of chitosan membrane in spite of the very thin PEC layer. Probably this PEC is more rigid compared with another PEC prepared from PAA5000 or PAA25000, so the uptake of water/ethanol at the feed interface will be most reduced.

Consideration

Needless to say, the results shown above indicate that selectivity stems from PEC formation because native chitosan has a low selectivity and PAA is soluble in water/ethanol. The PEC membranes will be homogeneous when made by a solution mixing method, whereas PEC membranes made by this diffusion method are asymmetric. The extent of asymmetry will be regulated by varying the MW, temperature, and absorption time. Owing to electrostatic interaction be-
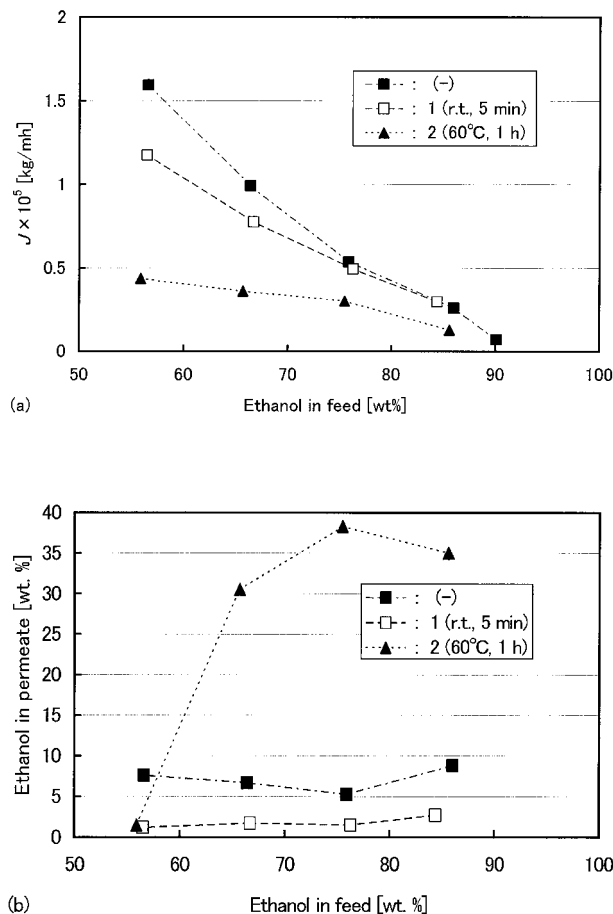

Figure 7 PV performance of chitosan-PAA5000 membrane: (a) permeation flux J; (b) ethanol in permeate. The (–) denotes chitosan as a reference.
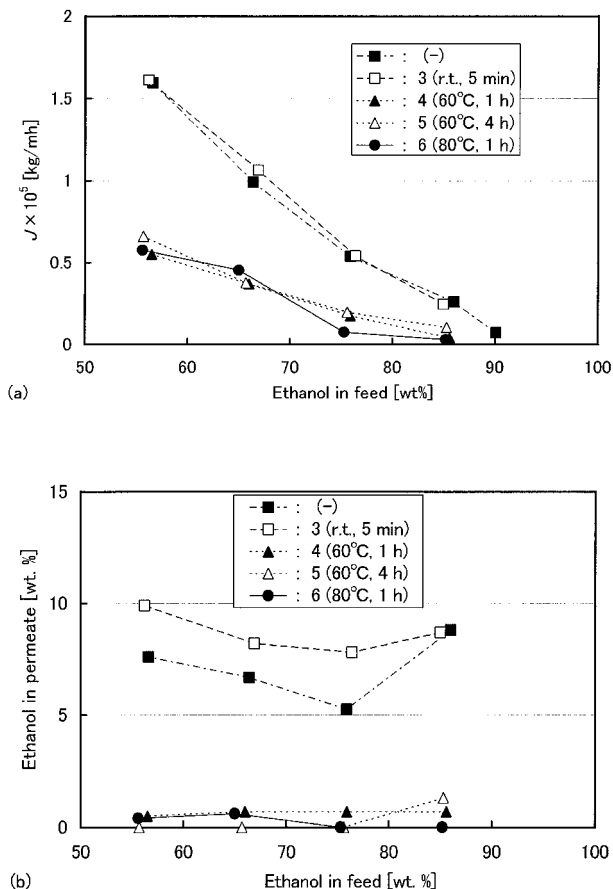
Figure 8 PV performance of chitosan–PAA25000 membrane: (a) permeation flux *J*; (b) ethanol in permeate. The (–) denotes chitosan as a reference.

tween oppositely charged polymer species, a very small quantity of PAA is adsorbed only on the chitosan surface at room temperature. Not all the PAA forms PEC because the salt bonds exist only at the interface between the chitosan and the adsorbed PAA without the entanglement between the constituting polymer chains. Hence, those membranes have low selectivity. At temperatures higher than T_g, the PAA diffuses into chitosan and forms a PEC whose selectivity increases with an increase in PAA absorption. The highest selectivity of homogeneous PEC will be attained at a stoichiometric composition.

$$(\text{chitosan unit}):(\text{PAA unit}) = 1:1 \ (\text{mol:mol})$$

If the polymer composition deviates from this ratio, residual polymers whose ionic groups do not have a salt bond will spoil selectivity. Membranes constructed here are asymmetric and therefore the local composition of the PEC inside the membrane could not be estimated. Even though the upside becomes PAA rich, there will be a certain depth at which the PEC composition is 1:1 because the downside is chitosan rich. The PEC at this depth is most relevant to

high selectivity. For this reason, membranes 5 and 6 had high selectivity in spite of their different absorption conditions and ND.

For a membrane composed of one polymer species, the uptake of each liquid can be theoretically calculated and the reciprocity between swelling degree and selectivity is applicable.[10,11] In the present PEC membrane system such reciprocity seems to hold phenomenologically because the selectivity increased at the cost of permeation flux. The order of PAA that contributed to the selectivity as well as permeation flux *J* was PAA5000 < PAA25000 < PAA250000. Since chitosan is soluble in acrylic acid solution, low MW PAA can not improve selectivity. Besides, the thick PEC region suppresses the permeation flux. On the other hand, the improvement of selectivity with high MW PAA is brought about by the decrease of swelling of the PEC that has a strong electrostatic crosslinking. Owing to the large MW of PAA250000, it cannot diffuse into chitosan. Instead, segments of PAA diffuse to a shallow depth and a thin PEC layer can be generated near the surface. Hence the decrease in permeation flux is the smallest. From a practical point of view, a
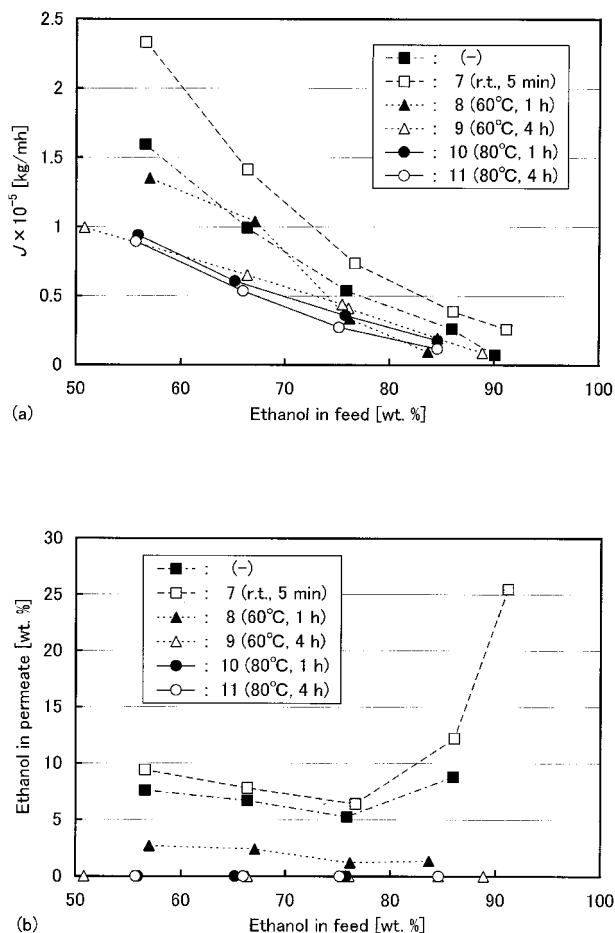

Figure 9 PV performance of chitosan–PAA250000 membrane: (a) permeation flux *J*; (b) ethanol in permeate. The (–) denotes chitosan as a reference.

large amount of PAA absorption will further reduce the permeation rate $Q/t = J/d$ through the increase of membrane thickness d. In this way, PAA250000 is most effective to improve both the selectivity and the permeation performance.

CONCLUSION

We investigated the PV performance of a chitosan–PAA membrane constructed by a simple interfacial formation of PEC by varying the temperature, diffusion time, and MW of PAA. The absorption of PAA was confirmed by FTIR and ESCA observations in addition to simple gravimetry. The asymmetry of the membrane was estimated by comparing the ATR spectra of both surfaces. Low MW PAA diffused into chitosan while high MW PAA remained only near the surface. As the MW of PAA increased, water selectivity was highly improved up to the extent that no ethanol was detected in the permeated liquid. Only a small quantity was enough to give high water selectivity if the MW of PAA was 250000. Owing to the thin PEC layer, the permeation flux of this membrane was highest. If the PEC of chitosan–PAA250000 is formed throughout the membrane by a solution mixing method, the resistance of the PEC will decrease the permeation flux. This interfacial PEC formation is a very simple and convenient method to construct a highly water-selective membrane without a considerable decrease of permeation flux.

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