

Studies on Elastic Hydrogel Membrane. I. Effect of Preparation Conditions on the Membrane Performance

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Synopsis

The properties and the permeation characteristics of poly(vinyl alcohol) hydrogel membranes were investigated. The membranes have excellent elasticity and showed reversible compaction by operating pressure. The membrane performance was also changed reversibly by pressure, and was held stable at ambient temperature for more than 12 months. The hydrogel membrane was stable against temperature up to 40°C, and was melted down at 70°C. Rejection increased with operating pressure. In the case of 1% (w/w) aqueous solution of poly(ethylene glycol) whose degree of polymerization is 400, the rejection increased from 30 to 85% by changing operating pressure from 5 kg/cm² to 60 kg/cm². These results suggested the possibility for the pressure-controlled fractionation of molecular weight.

INTRODUCTION

In recent years, poly(vinyl alcohol) (PVA)-hydrogel having high elasticity and high water content has been found to be prepared from PVA aqueous solution by repetition of freezing and thawing.¹⁻⁴ It was also reported that the PVA-hydrogels that have various strengths can be prepared by thawing the frozen PVA aqueous solution at various rates.⁵ Despite the fact that this gel is not chemically crosslinked, the water content and elasticity of the gel change scarcely by soaking over a long period of time in water. Because of the interesting properties, the PVA-hydrogel has been investigated with regard to rheological properties⁶⁻⁸ and to the state of water in the gel.⁹⁻¹¹ This gel is also utilized in the medical field because of its good biosuitability.¹²

PVA has good film-forming, highly hydrophilic properties and as such has been studied as a membrane in various ways. The studies have mainly been carried out on dense membranes or porous membranes of low void volumes in aqueous system. The authors reported on the preparation of highly porous PVA membrane from poly(vinyl acetate) latex polymerized under the presence of PVA as a protective colloid.¹³ The grafted PVAc in the PVA membrane was found to behave like a valve in organic solution.¹⁴

PVA as a highly elastic hydrogel membrane has, however, not been investigated. The PVA-hydrogel has characteristics such as high water content, entropic elasticity, and high mechanical strength,⁶⁻⁸ it is very interesting as a

functional membrane material, and the unique behaviors can be expected as a membrane. In this article, we investigated the gel as a membrane material.

EXPERIMENTAL

Materials

The partially saponified poly(vinyl acetate) used (PVA-117) was obtained from Kuraray Co., Ltd. (degree of polymerization (DP) about 1700 and degree of saponification 98.5 mol %). Other reagents were extra-pure grade chemicals and used without further purification. Polyethylene glycols (PEG) (DP = 400) was purchased from Waco Chemicals.

Membrane Preparation

PVA aqueous solutions (7, 5, 10, 12, 20 wt%) were prepared. PVA-hydrogel membranes were prepared by casting the PVA aqueous solutions on the petri dishes and repeating freezing-thawing for 7 days. One freezing cycle was comprised of freezing at -20°C for 23 h and thawing at ambient temperature for 1 h.

Thermal Stability of the Membrane

Thermal stability of the membrane was investigated by measuring an elongation of a piece of a membrane. A strip of PVA-hydrogel membrane (1×3 cm) was suspended with a weight (6.1 g) in a thermostatted soaking solution. The length of membrane was measured with a cathetometer after 5 h incubation in the thermostatted solution. The gel size reached stable value in 3 h. The temperature of the solution was changed from 10 to 70°C . The elongation value was defined by the following equation:

$$\text{Elongation (\%)} = \left(\frac{\text{membrane length at } t^{\circ}\text{C}}{\text{membrane length at } 10^{\circ}\text{C}} - 1 \right) \times 100$$

Permeation Measurements

The permeability of a membrane was investigated at room temperature at various pressure using a diaphragm type permeation cell (Model RO-3 of Bio-engineering Co.; cell volume = ca. 200 mL; effective membrane area = 28.27 cm^2). The solution in the cell was vigorously stirred with a magnetic stirrer to dissipate the filter cake of retained solutes which can possibly be formed on the membrane surface. The concentrations of the solutions were determined by weight method or by means of high performance liquid chromatography. Employed chromatograph, column, and refractometer as a detector were Type 638-50 of the Hitachi Co., TSK-gel 3000SW of the Toyo-Soda Co., Ltd., and Shodex RI, Model SE-11, of the Showa Denko Co., respectively. The permeation rate was determined by measuring the permeate volume. The

rejection value (R_j) of a membrane was defined as follows¹⁵:

$$R_j(\%) = 100(1 - C_p/C_f)$$

where C_f is the solute concentration in the feed and C_p is that in the permeate. C_p was estimated from the solid content in the permeate.

RESULTS AND DISCUSSION

On Preparation Conditions of PVA-Hydrogel Membrane

Two methods have been reported by Nambu as the preparation method of the highly elastic hydrogel, which are the repetitive freezing-thawing method and the freezing partial dehydration method.¹² In this article, the method employed is made up of a combination of both; that is, the method should be called a partially dehydrating freezing-thawing method, and for convenience the method employed will be called freezing-thawing method in this article. The relationship between dehydration degree and holding time is shown in Figure 1. For the purpose of comparison, the membrane prepared by the continuous freezing method was also shown. The freezing-thawing cycle is made up by freezing at -20°C for 23 h and thawing at ambient temperature for 1 h, while the freezing partial dehydration method, which was carried out for comparison only, consists of successive freezing at -20°C . The results in

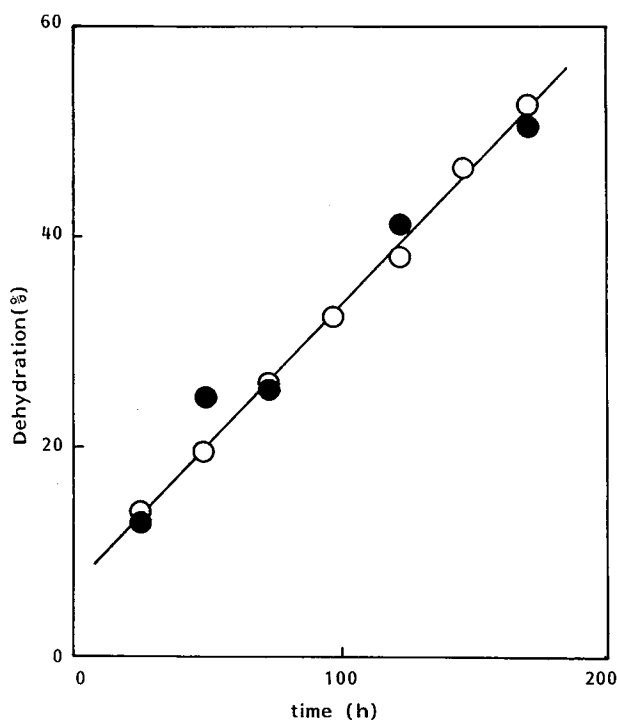


Fig. 1. Effect of freezing time on the dehydration rate: (○) repetitive freezing-thawing method; (●) continuous freezing method.

TABLE I
Characterization of PVA-Hydrogel Membranes

Membrane	PVA concentration (wt %) ^a	Water content (wt %)		Membrane thickness (mm)		Degree of deformation ^c	Lost PVA ^d (%)
		As cast	Compacted ^b	As cast	Compacted ^b		
1	7.5	91.4	82.8	0.93	0.14	0.85	69.3
2	10.0	87.8	80.5	1.21	0.50	0.59	32.7
3	12.0	87.8	81.0	0.89	0.55	0.38	12.8
4	20.0	76.1	68.1	0.91	0.68	0.09	0.0

^aIn casting solution.

^bAfter exposure at the pressure 60 kg/cm² for more than 50 h.

^cDegree of deformation = 1 - (thickness after compaction)/(thickness before compaction).

^dLost PVA (%) = [1 - (solid content after compaction)/(solid content estimated from degree of deformation)] × 100.

Figure 1 show that both methods resulted in the same dehydrating rate, although the gel membrane obtained by the freezing-thawing method is much tougher than that obtained by the other method, suggesting that the gel becomes tough by freezing-thawing in the preparation process.⁴ The membrane used in this article is therefore prepared by the former method.

The effect of the concentration of the casting solution of PVA and the effect of the compaction on the water content and the membrane thickness is tabulated in Table I. The compaction of the membrane was carried out at 60 kg/cm² in a reverse osmosis cell by permeating water for 50 h. The water content decreased with increasing the PVA concentration of the casting solution, and the compaction of PVA-hydrogel membrane caused a decrease of the membrane thickness, accompanying the decrease of the water content. The membrane thickness also decreased by compaction. The higher the water content of the gel, the higher the degree of deformation. In the case of membrane 1, the degree of deformation is much higher than the other membrane, although the decrease in the water content is comparable and does not differ so much from other membranes. This fact can be explained by the leakage of PVA from the gel membrane by compaction (Table I). Increase of water content in the gel membrane caused the increase of PVA leak by compaction, suggesting the decrease of PVA content increases the PVA portions that are not involved in the gel network formation. It will lead to the conclusion that the effective gel formation requires the higher PVA concentration of the casting aqueous solution. In this article, the investigations are carried out on the gel membrane prepared by the recipe of membrane 2, since the PVA leak was negligible after exposure at 60 kg/cm² for 50 h, and the pressure effect on the membrane compaction can be expected to be not too small.

Thermal Stability of PVA-Hydrogel Membrane

Thermal stability of the membrane was investigated through the elongation behavior under suspending the weight of 6.1 g in the thermostatted water-bath. In Figure 2, the effect of soaking temperature on the elongation of PVA-hydrogel membrane was shown, suggesting that the size of the gel

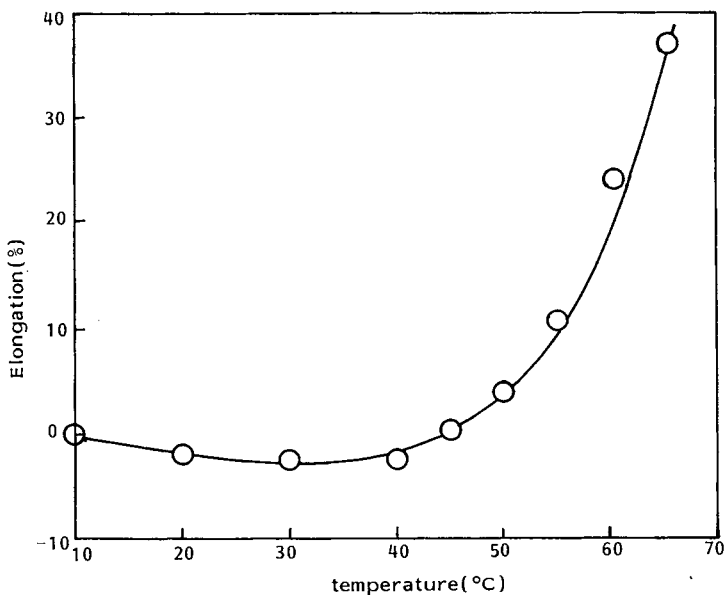


Fig. 2. Effect of temperature on the degree of elongation of PVA-hydrogel membrane. The degree of elongation was measured suspending a weight of 6.1 g, and the values were estimated as the relative size making that at 10°C as a control.

membrane is stable at ambient temperature, and it shrinks a little up to about 40°C, but becomes looser and melts down over 70°C. The curve in Figure 2 showed the similar inclination to that of the temperature dependence of the Young's modulus reported by Watase et al.² The contraction of the gel membrane up to ca. 40°C is attributable to the entropic nature of the gel, while the elongation of the gel membrane at high temperature is attributable to the decay of the gel network structure, since the swollen membrane at high temperature did not restore the original size when it cooled to ambient temperature. Further measurements were, therefore, carried out at ambient temperature in order to avoid the deterioration of the membrane.

Pressure Dependence of Water Flux

In order to attain the stable performance, the membrane was exposed under high pressure (60 kg/cm²) for 50 h prior to the further permeation experiments. In Figure 3, the time course of the water permeability of a membrane was shown [Fig. 3(a)] together with the Merten plots [Fig. 3(b)].¹⁶ The plots in Figure 3(a) are scattered. However, the flux decreased significantly, then increased slightly, and attained a constant value. This shows that the membrane is stabilized after compaction. The Merten plots in Figure 3(b) were plotted according to the following equation:¹⁶

$$J/J_0 = (t/t_0)^{-m} \quad (1)$$

where J , t , and m are the flux, the operation time, and the decreasing

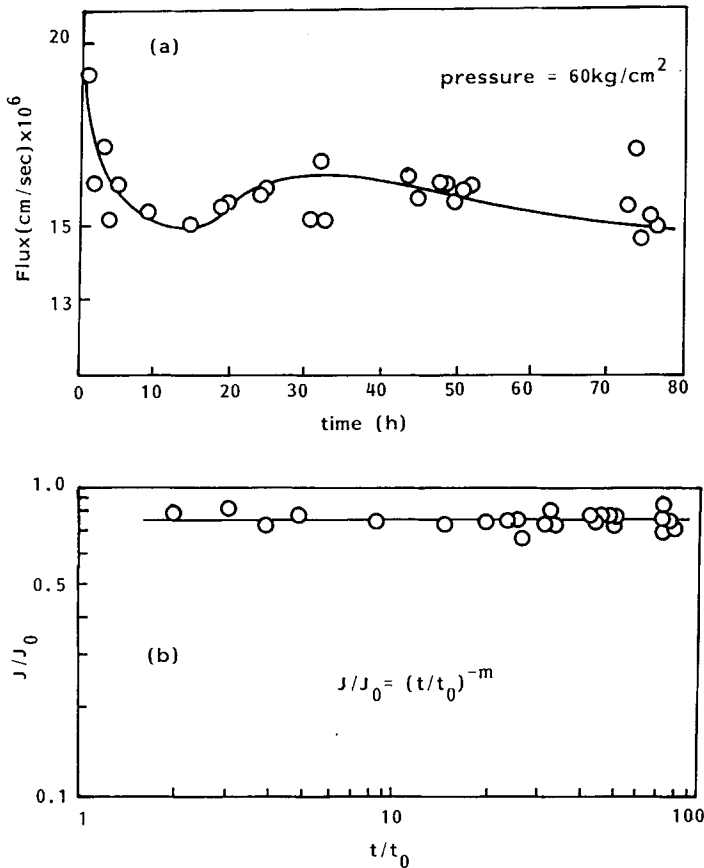


Fig. 3. Time dependence of flux (a) and the Merten plots (b). Permeant is water, and applied pressure is 60 kg/cm².

coefficient, respectively, and J and t with subscript zero means initial value. The J/J_0 value is constant irrespective of the permeation time. This result indicates that the flux reached steady value rather quickly, and the further compaction did not proceed any more. The Merten plots exhibits the stabilized stage, although the flux value fluctuates a little. This probably resulted from some unstable structure of the membrane. In the following experiments, the membranes which were exposed at high pressure for a certain period of time (50 h) were employed.

The pressure dependence of the flux is shown in Figure 4 on some membranes from the casting solutions of different PVA concentration. The flux did not show hysteresis by pressure, suggesting that the compaction is reversible against pressure and is reproducible on repetitive operation. This property is considered to be originated from the elasticity of the hydrogel. The flux decreased with increasing the PVA concentration of the casting solution. The flux of the membrane prepared from the aqueous solution of high PVA concentration attained the saturation of the flux more readily than that of the membrane from low PVA concentration. These resulted from the difference in network density or the water content of PVA-hydrogel membrane (Table I).

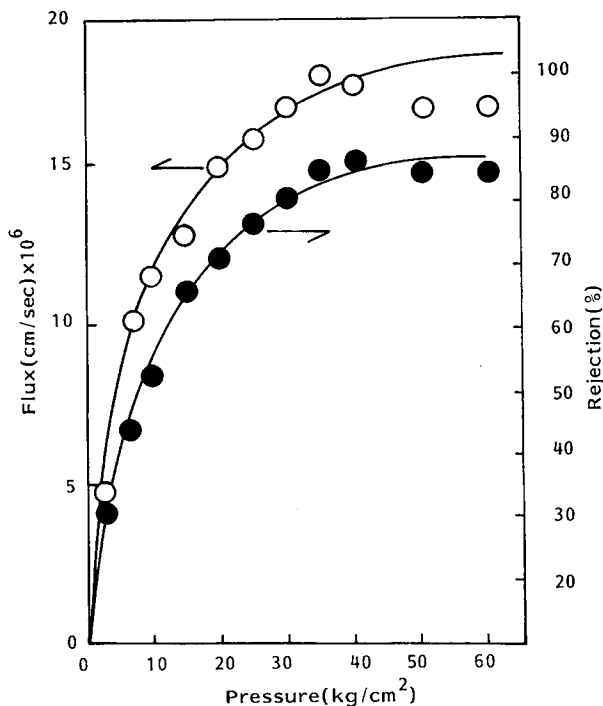


Fig. 4. Pressure dependence of flux (○) and rejection (●). Feed: 1% aqueous solution of PEG400.

In view of membrane function, the membrane that was prepared from low PVA concentration is more useful because of its high water permeability. However, the smaller the PVA concentration of casting solution, the poorer the mechanical strength of the membrane: that is, the membrane deterioration is remarkable (Table I). Subsequent measurements were carried out with the membrane 2, which was prepared from 10 wt % aqueous solution of PVA unless otherwise specified, since the deterioration of the membrane scarcely takes place after the pretreatment. The higher the polymer content of the gel membrane, the lower the flux value, and also the flux shows that the compaction proceeds remarkably on all hydrogel membranes.

Pressure Dependence of Rejection Values on Poly(ethylene Glycol)

The pressure dependence of flux and rejection is shown in Figure 5, employing poly(ethylene glycol), whose degree of polymerization is 400 and is abbreviated as PEG400, as a solute. The rejection value R_j increased with applied pressure together with the increase of the flux value. The flux in Figure 6 indicated nearly the same value to that of water in Figure 4, suggesting the flux-pressure curve in Figure 5 results mainly from the compaction of the membrane and not from the formation of the concentration polarization layer on the membrane surface. In the case of 1 wt % PEG400 aqueous solution, the rejection could be controlled from ca. 30% to ca. 85% by changing the operating pressure from 5 kg/cm² to 60 kg/cm². Baker reported that the

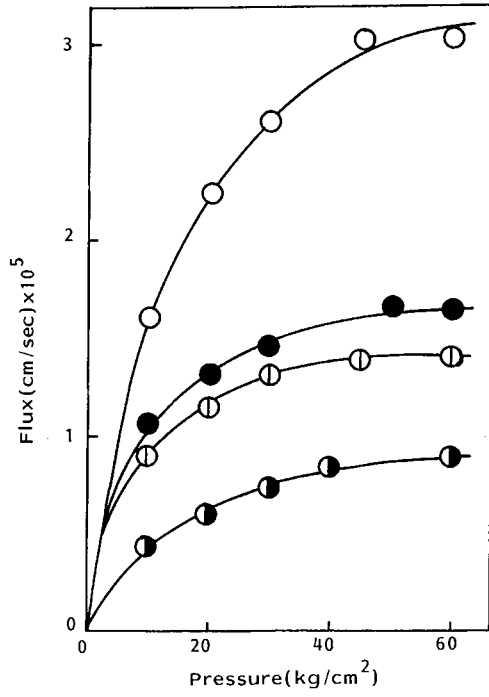


Fig. 5. Effect of PVA concentration in casting solution on water flux: (○) 7.5 wt %; (●) 10 wt %; (◐) 12 wt %; (◑) 20 wt %.

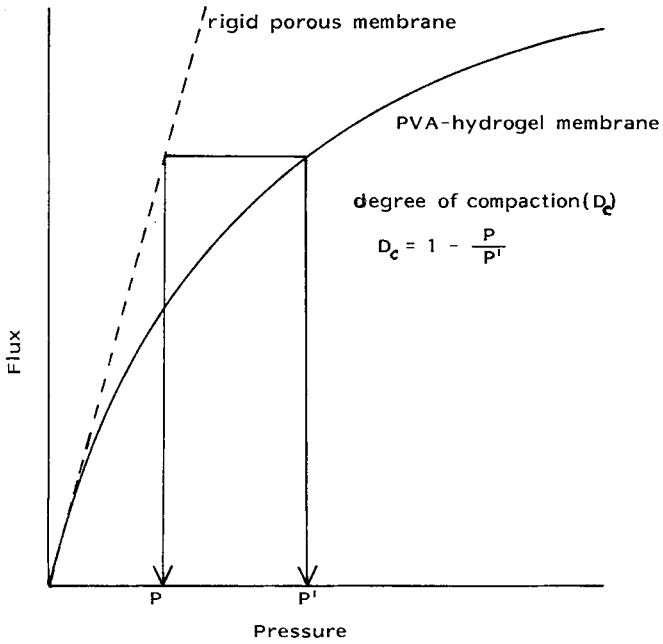


Fig. 6. Estimation of degree of compaction.

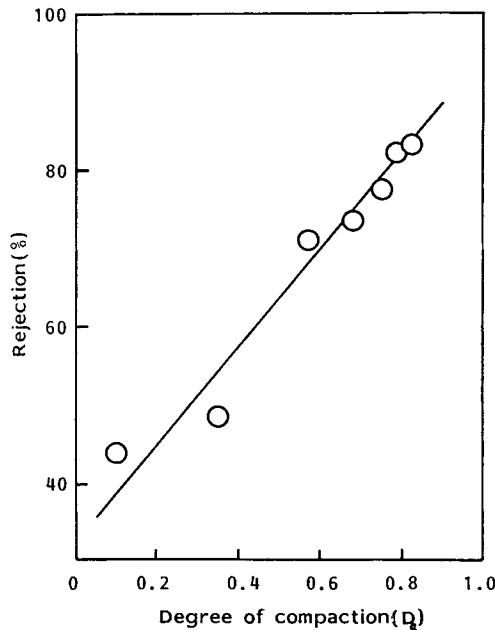


Fig. 7. Dependence of rejection on the degree of compaction. Solute is PEG400.

rejection changes by operating pressure on the commercial cellulose acetate membranes, too.¹⁷ However, from the point of the wide range of control of separability by the use of the reversible compaction of the membrane, this PVA-hydrogel membrane is highly specific.

In order to understand the effect of the compaction in more detail, the degree of compaction D_c was defined and was estimated as shown in Figure 6. As can reasonably be accepted that the interstices of polymer networks in gel membrane reduce by compaction, the broken line with a slope at pressure = 0 is the flux-pressure curve may be considered to be a flux-pressure curve in which no compaction occurs by operating pressure. The difference between the line and the curve can, therefore, be used as a measure of compaction of the membrane as long as solute does not affect the flux reduction.

In Figure 7, the relationship between the R_j value and the degree of compaction was shown. R_j value seems to be proportional to the degree of compaction in the pressure range observed.

The dependence of the rejection of PEG400 on the PVA content of the gel membrane is shown in Figure 8. PEG400 1% aqueous solution was used as a feed solution. The membranes in Table I were used. The R_j value increased with PVA concentration of the casting solution, and this tendency was small at high pressure. The increase of the R_j value may result from the increase of membrane density. Because the membrane prepared from an aqueous solution of low PVA concentration is greatly compacted at high pressure, the membrane becomes dense, making the permeation properties close to the membrane prepared from high concentration PVA aqueous solution. These results together with those in Figure 5 and Figure 7 show that the increase of

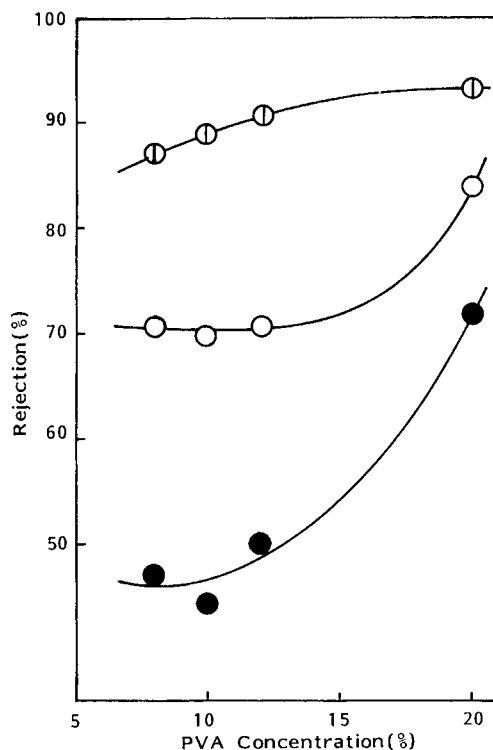


Fig. 8. Dependence of rejection on the PVA concentration of the casting solution. Solute is PEG400. (●) 10 kg/cm²; (○) 30 kg/cm²; (⊙) 60 kg/cm².

polymer content or that of the degree of compaction decreases the size of the interstices through which the permeate passes.

In general, in the rigid membranes such as cellulose acetate membranes, which have a dense active layer, it is known that both flux and the R_j value decrease by increasing permeant concentration polarization.¹⁸ This phenomenon is known to result from a concentration polarization or gel polarization layer that is formed by rejected solutes accumulated on the membrane surface. It is reported that this layer acts in series with the underlying membrane to form a barrier to the flux and to the permeation of low molecular weight solutes.^{19,20} The same phenomenon can also be observed in the PVA-hydrogel membrane. However, the phenomenon may be expected to be different from the dense membrane.

In Figure 9, the effects of permeant concentration on the flux and R_j value were shown at various pressures. The R_j value decreased slightly with the PEG concentration [Fig. 9(a)]. The rejection decreased with the feed concentration. This can be explained on the ground of the thickness or the concentration of the polarization layer. In the case at the pressure of 60 kg/cm², the rejection attained constant value with PEG aqueous solution over 8 wt %. At pressure 30 and 10 kg/cm², a similar tendency was observed. This suggests that the polarization layer attains steady state. In the case at high pressure, the polarization layer is liable to arise because of the high rejection. This

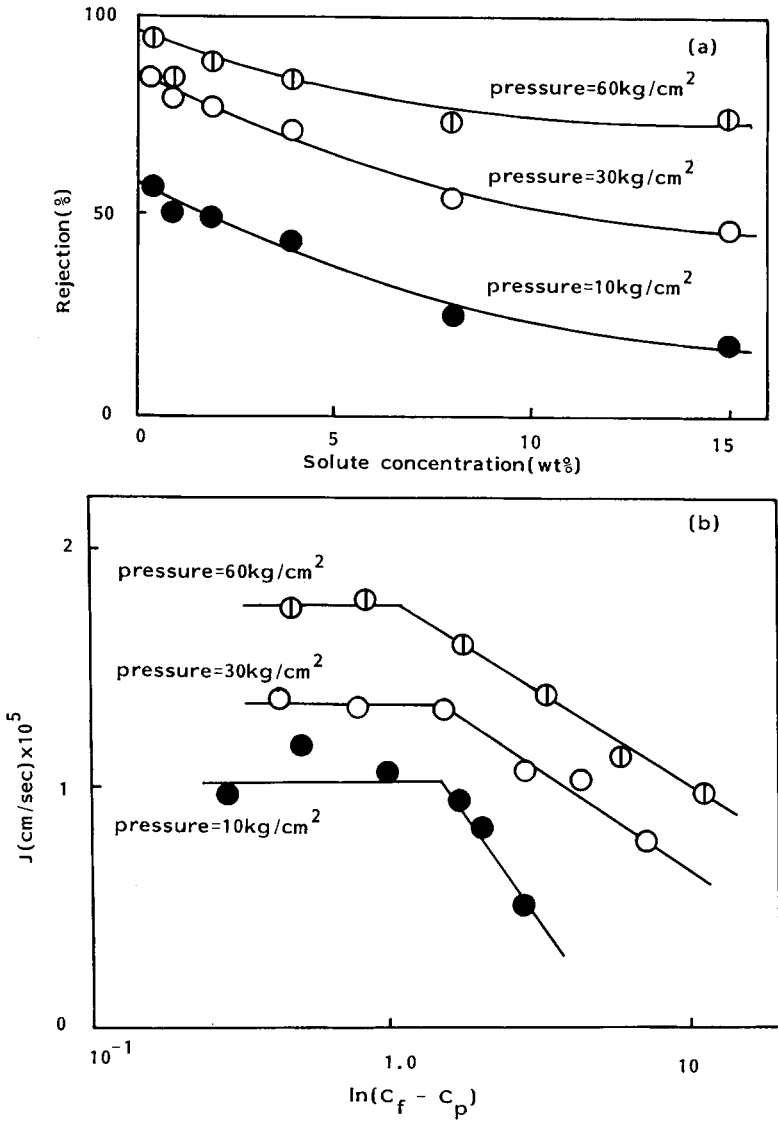


Fig. 9. Effect of feed concentration on the rejection (a) and flux (b). Solute is PEG400. (⊙) 60 kg/cm²; (○) 30 kg/cm²; (●) 10 kg/cm².

polarization layer was investigated on the basis of²¹

$$J = \frac{D}{\delta} \ln \frac{C_w - C_p}{C_f - C_p} \tag{2}$$

where J , δ , D , C_w , C_p , and C_f are the flux, the thickness of the polarization layer, the diffusion coefficient, the concentration on the membrane surface, the filtrate concentration, and the feed concentration, respectively. The results were shown in Figure 9(b). J remained constant when C_f is low, and then began to decrease with increasing C_f . The result suggests that the J

value is governed by intrinsic resistance of the membrane at low C_f , while, with increasing C_f , J began to be governed by the concentration polarization layer. The C_f value at the breaking point in Figure 9(b) changed from with ca. 3 wt % to ca. 1.2 wt % with the pressure increase. The C_f values are in agreement with the concentration suggested by Blatt et al., that is, the water-soluble linear chain polymer, whose principal chain is flexible, changes from sol into gel at its concentration range from 2 to 5 wt %.²²

CONCLUSION

The hydrogel membrane prepared by partially dehydrating repetitive freezing-thawing can be used for permeation. The membrane compacted at 60 kg/cm² shows reversible compaction by applied pressure. Pressure dependence of rejection value was investigated on PEG400 as a permeant. R_j value changed from 30 to 85% by increasing applied pressure from 2 to 60 kg/cm². The R_j value decreased with increasing solute concentration, suggesting the effect of concentration on the arising of polarization layer. Pressure dependence of the R_j value suggested the possible control of polymer fractionation by using the hydrogel membrane.

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Received September 1, 1988

Accepted September 14, 1988