

inferred from the difference between the flux data for the HDEHP/*n*-heptane-Ni system (see Fig. 3), further information might be drawn from the difference in the interfacial tension.

In conclusion, we found that the present continuous regeneration is useful in prolonging the lifetime of SLMs, which utilize the buoyancy of membrane liquid. Thus the application of the present regeneration method to a multi-fibers module has been undertaken.

Nomenclature

J	= permeation flux of metal ion	[kmol/m ² ·s]
t	= operation time	[min] or [h]
u_s	= shell-side flow velocity	[cm/s]
u_t	= tube-side flow velocity	[cm/s]
[]	= concentration of ion	[mol/dm ³]

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DYNAMIC FORMATION OF POLYION AND POLYION COMPLEX MEMBRANES, AND THEIR SOLUTE REJECTION

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In recent years, the formation of dynamic membranes for ultrafiltration use have been reported.^{3,5)} Polyion is one of the candidates for membrane material because of its conformational versatility.¹⁾ There are some studies concerning solid membranes of polyion complex (PIC) prepared by the casting method, but only a few studies of dynamic polyion and PIC membranes have been reported.²⁾

In this work, two dynamic polyion membranes and two types of dynamic PIC membranes were formed and their solute rejections were investigated.

1. Experimental

1.1 Apparatus

Figure 1 shows the cross section of the module (TDK Corp., Dynaceram DC-0005) used and a schematic diagram of the experimental setup. The module has one porous ceramic tube (O.D. = 5 mm, I.D. = ca. 2 mm, length = 500 mm) and an effective membrane area of 74.5 cm². The mean pore size of the surface layer of the tube is 50 nm. Operating pressure, liquid

linear velocity, and temperature were kept at 0.49 MPa, 2.07 m·s⁻¹, and 298 K, respectively.

1.2 Membrane formation procedure

Polyions used were sodium polyacrylate (SPA, linear polymer, average $M_w = 3 \times 10^6$) for polyanion and polyethylene imine (PEI, branched polymer, average $M_w = 1 \times 10^5$) for polycation.

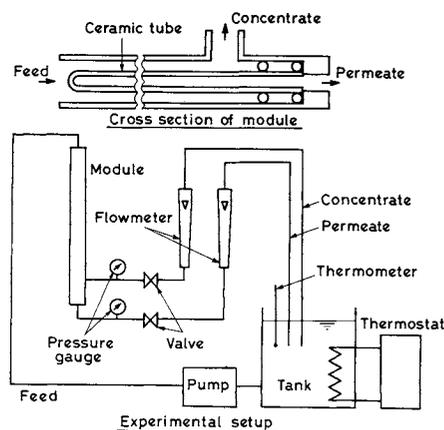


Fig. 1. Cross section of module used and schematic diagram of experimental setup.

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1) Dynamic polyion membranes Two dynamic polyion membranes of SPA and PEI were formed by circulating a solution containing $50 \text{ g} \cdot \text{m}^{-3}$ polyion and $0.05 \text{ mol} \cdot \text{dm}^{-3}$ NaCl for 60 minutes. To make a compact deposit layer of polyion, pH of solution was adjusted to 2.5 for the case of SPA and 8.9 for PEI.

2) Dynamic PIC membranes Two types of membranes were formed. i) PIC(I) membrane was a membrane formed by circulating a solution containing $50 \text{ g} \cdot \text{m}^{-3}$ SPA, $50 \text{ g} \cdot \text{m}^{-3}$ PEI and $0.05 \text{ mol} \cdot \text{dm}^{-3}$ NaCl for 120 minutes. ii) PIC(II) membrane was a membrane formed layerwise as follows. PEI was attached dynamically onto the surface of the SPA membrane mentioned above by circulating a solution containing $50 \text{ g} \cdot \text{m}^{-3}$ PEI of pH 2.5 for 60 minutes.

After formation of the membrane, the solution was replaced by deionized water and pH was adjusted to 6.0.

1.3 Solute separation experiment

Solutes used were glucose, raffinose, polyethylene glycols and dextrans of various molecular weights. Solute concentration and pH of solution were kept at $200 \text{ g} \cdot \text{m}^{-3}$ and 6.0, respectively. Rejection of the membrane was evaluated by the observed rejection calculated by Eq. (1).

$$R_{\text{obs}} = 1 - C_p/C_b \quad (1)$$

where C_b and C_p are solute concentrations of feed solution and permeate, respectively. Solute concentration was measured by a total organic carbon analyzer (Shimadzu TOC-500).

2. Results and Discussion

2.1 Membrane formation

Figure 2 shows the changes of flux J_v and self-rejection R_{obs} with time during the formation of four membranes. In the formation of the PIC(II) membrane, the beginning of PEI attachment is designated as $t=0$ in the figure. For all membranes, the fluxes decreased first and reached constant value within 60 minutes, and final rejections above 0.9 were obtained. These results showed that self-rejecting dynamic membranes were formed for all membranes tested.

After formation of the membrane, pH was shifted gradually and finally adjusted to 6.0. Figure 3 shows the flux changes of the four membranes during the pH adjustment. The flux of the PEI membrane scarcely changed. On the contrary, fluxes of the other three membranes decreased with increasing pH. These flux changes were considered to be caused by the increase of the dissociation degree of SPA molecule. The flux reduction of the SPA membrane was possibly due to the conformational change of SPA molecule by which interpenetration of polymer chains had occurred in the deposit layer. In the case of the two PIC mem-

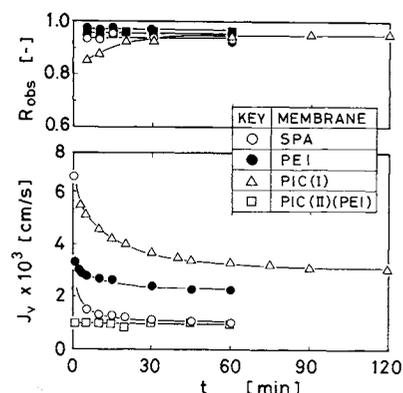


Fig. 2. Change of flux and rejection during membrane formation.

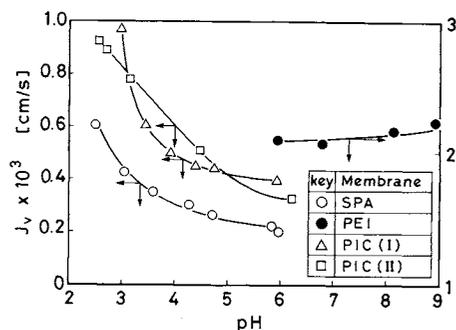


Fig. 3. Change of flux during pH adjustment.

branes, it is considered that the increase in dissociation degree resulted in the formation of PIC, which carries regions of hydrophobic nature,⁴⁾ and the flux decreased due to the hydrophobic PIC-water interaction.

After the adjustment of pH to 6.0, the solution was replaced by deionized water and the membrane fluxes were examined. The flux of the SPA membrane increased about two times by the solution replacement. This change was considered to be due to the further conformational change of SPA resulting from the lowering of ionic strength of the solution. The fluxes for the two PIC membranes did not change.

2.2 Solute rejection

Figure 4 shows solute rejections and fluxes. Solute rejection of the SPA membrane increased with molecular weight of solute above 1×10^4 . The rejection curve of the PEI membrane was slightly shifted to the lower-molecular weight side compared to that of the SPA membrane and showed a small shoulder around the molecular weight of 1500. Flux of the PEI membrane decreased gradually with increasing molecular weight above 1×10^4 . This may be caused by the formation of dextran gel layer.

The rejection properties of the two PIC membranes were different from those of polyion membranes. The rejection curve of the PIC(I) membrane was shifted to the higher-molecular weight side. The PIC(II) mem-

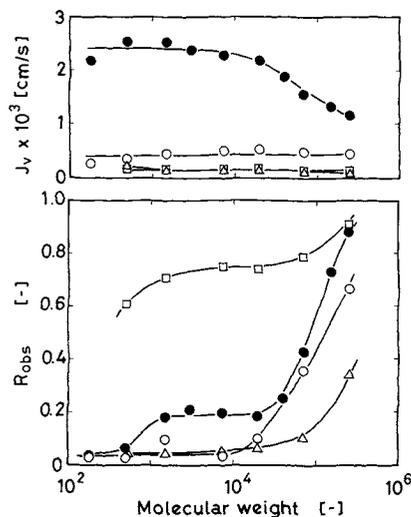


Fig. 4. Solute rejections of dynamically formed membranes (symbols are the same as those in Fig. 3).

brane rejected the solute of molecular weight above 1500, the observed rejection being 0.75 or more.

These solute rejection properties of the PIC membranes can be explained by considering the pattern of PIC formation. In the PIC(I) membrane, PIC is considered to be formed uniformly throughout the membrane. When PIC is formed, an agglomerate of dense polymer segments is formed and at the same time a region of thin polymer segments appears around the agglomerate. The PIC(I) membrane, therefore, is considered to have larger apparent pore size than that of the SPA membrane. On the contrary, in the PIC(II) membrane PIC is considered to be

formed layerwise along the contact plane of a SPA-rich lower layer and a PEI-rich upper layer. The PIC agglomerates were concentrated in the vicinity of the contact plane like a skin layer of solid ultrafiltration membranes. Hence, the effective pore size of dynamic PIC(II) membrane became smaller. From the above results, it is concluded that dynamic PIC membranes of different rejection properties can be prepared by the formation procedure of PIC.

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Nomenclature

C_b	= solute concentration of feed solution	[g · m ⁻³]
C_p	= solute concentration of permeate	[g · m ⁻³]
J_v	= flux	[cm · s ⁻¹]
M_w	= molecular weight	[-]
R_{obs}	= observed rejection	[-]
t	= time	[min]

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