EFFECT OF POLYION COMPOSITION ON SOLUTE REJECTION BY DYNAMIC POLYION COMPLEX MEMBRANES

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Dynamic polyion complex membrane (PIC-DM) was formed by depositing a mixture of two oppositely charged polyions, sodium polyacrylate and polyethylene imine. The effect of composition on solute rejection by the PIC-DM formed was investigated.

The rejection curve of the PIC-DM shifted to the higher-molecular weight side with increase of the charge amount of excess polyion in the mixture. The membrane structure evaluated from the solute rejection property was analyzed successfully by dual pore sizes model. The pore sizes and their number fractions were related to the ratio of charge of the polyions.

Introduction

Dynamic membranes are formed on porous support by filtering solution containing membrane-forming material. Examples of membrane materials reported so far are Zr(IV)-polyacrylic acid[10,11] for reverse osmosis use, hydrous Zr(IV) oxide[5] and oval-bumin[7] for ultrafiltration use. Solute rejection by the dynamic membrane varied significantly with the membrane-forming materials and the membrane formation procedure. However, few studies in which the membrane performance was studied in terms of the relation between the properties of membrane-forming material and the structure of the dynamic membrane have been published.

In the previous studies,[12,13] dynamic polyion complex membranes (PIC-DM) were prepared by two methods: forming the membrane by filtering a solution containing two oppositely-charged polyions on a porous ceramic tube (simultaneous deposition method), and forming the membrane layer-wise by attaching a polyion dynamically to a dynamic membrane of oppositely charged polyion which was formed on a ceramic tube beforehand (sequential deposition method). It was demonstrated that membranes formed by these two methods showed a large difference in solute rejection properties. This difference was explained in terms of the PIC formation process during the membrane formation.

Dynamic PIC membranes formed by the simultaneous deposition method were given charges of different amount by varying the polyion composition of the membrane-forming solution. In the present study, the effect of polyion composition on solute rejection of the PIC-DM formed by the simultaneous deposition method was investigated. The structure of the PIC-DM was analyzed with a model, assuming that membrane pores were of two different sizes.

1. Experimental

1.1 Apparatus

The apparatus was the same as described in the previous paper.[12] The membrane module has one porous ceramic tube and an effective membrane area of 74.5 cm².

Operating pressure, liquid linear velocity in the module, and temperature were kept at 0.49 MPa, 2.07 m·s^{-1}, and 298 K, respectively.

1.2 Materials

The polyions used were sodium polyacrylate (SPA, linear polymer, average $M_W = 3 \times 10^6$) as the polyanion and polyethylene imine (PEI, branched polymer, average $M_W = 1 \times 10^5$) as the polycation. Both polyions are weak polyelectrolytes.

Charge density of the polyion was measured by colloid titration.[8] **Figure 1** shows the dependence of charge density of the polyions on solution pH. For titrating PEI solution, N/400 potassium polyvinyl sulfate (PVSK) was used as titrant and toluidine blue as indicator. For titrating SPA solution, an excess of N/200 methylglycol chitosan was added on the SPA solution to form precipitate, and the excess was titrated by N/400 PVSK.

To obtain information about the conformational properties of the polyions, kinematic viscosities of the solution, which are related to the size of solute molecule, were measured with a capillary viscometer. The results are shown in **Fig. 2**. The kinematic viscosity of the SPA solution was larger and much more sensitive to both ionic strength and pH than that of the PEI solution. This was due to the difference in molecular weight and molecular structure of the polyions.

1.3 Membrane formation procedure

Dynamic PIC membranes were formed by circulating a solution containing SPA, PEI and 50 mol·m^{-3} NaCl of pH 6.0 for 60 minutes, letting both SPA and PEI molecules deposit on the ceramic tube simultaneously. The permeate and the concentrate were returned to the feed tank to maintain constant concentration of the polyions in the tank. The composition of polyion of the solution was represented by weight fraction of PEI.

$$X_C = C_C \cdot V / (C_C \cdot V + C_A \cdot V) \tag{1}$$

where C_C and C_A are concentrations of PEI and SPA, respectively, and V is working volume. The total concentration of the polyions mixture, $(C_C \cdot V + C_A \cdot V)/V$, was kept constant to be 0.1 kg·m^{-3}. The amount ratio of charges of PEI to those of SPA in the solution was calculated by Eq. (2):

$$Q = Z_C \cdot C_C / Z_A \cdot C_A \tag{2}$$

where Z_C and Z_A are charge densities of PEI and SPA, respectively. The value of charge density was obtained from the data shown in Fig. 1.

After formation of the membrane, the membrane-forming solution was replaced by deionized water to rinse the membrane and the change in volume flux was examined. Solute separation experiments were carried out after a constant water flux was obtained.
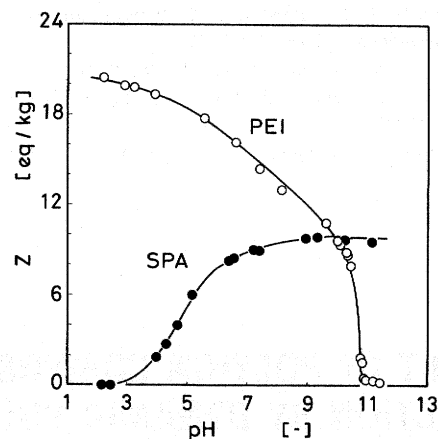

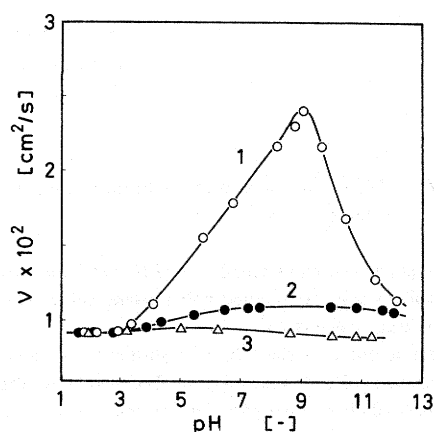**Fig. 1.** Dependence of charge density of polyion on solution pH

Fig. 2. Dependence of kinematic viscosity on solution pH
1. SPA 0.2 kg·m^{-3}, $C_S = 0$ mol·m^{-3}; 2. SPA 0.2 kg·m^{-3}, $C_S = 50$ mol·m^{-3}; 3. PEI 0.2 kg·m^{-3}, $C_S = 0$ mol·m^{-3}

Table 1. Molecular weights, diffusivities and radii of the solutes

Solute	M_W [—]	D [cm^2·s^{-1}]	Ref.	R_s [nm]	Ref.
Glucose	180	6.9×10^{-6}	4)	0.36*	
Raffinose	504	4.2×10^{-6}	4)	0.58*	
PEG #1500	1500	2.3×10^{-6}	4)	1.07*	
PEG #4000	3000	1.9×10^{-6}	6)	1.29*	
PEG #7000	6500	1.4×10^{-6}	6)	1.75*	
PEG #20000	2×10^4	1.0×10^{-6}	6)	2.45*	
Dextran	4×10^4	8.0×10^{-7}	6)	4.47	2)
Dextran	7×10^4	5.8×10^{-7}	7)	5.81	2)
Dextran	15×10^4	5.4×10^{-7}	7)	8.31	2)
Dextran	25×10^4	5.2×10^{-7}	7)	10.6	2)

* Calculated by Stokes-Einstein equation.

1.4 Solute separation experiment

Solutes used were glucose, raffinose, polyethylene glycols and dextrans of various molecular weights. **Table 1** shows their molecular weights, diffusivities and molecular radii. Values of molecular radii, R_s, were estimated by the Stokes-Einstein equation.

$$R_S = \kappa \cdot T/(6 \cdot \pi \cdot \mu \cdot D) \qquad (3)$$

Solute concentration and pH of the feed solution were kept at $0.2\,\mathrm{kg \cdot m^{-3}}$ and 6.0, respectively. Solute concentrations of the feed solution and the permeate were measured by a total organic carbon (TOC) analyzer (Shimadzu, TOC-500). These solutes were not rejected by the ceramic tube itself, but when the PIC-DM was formed they were rejected.

Rejection of the membrane was evaluated by the observed rejection, R_{obs}, and by the true rejection, R.

$$R_{obs} = 1 - C_P/C_B \qquad (4)$$

$$R = 1 - C_P/C_M \qquad (5)$$

where C_B, C_P and C_M are solute concentration in feed solution, in permeate and at membrane surface, respectively. The value of C_M is estimated by the concentration polarization equation.[4]

$$(C_M - C_P)/(C_B - C_P) = \exp(J_V/k) \qquad (6)$$

The value of mass transfer coefficient, k, was estimated using the Deissler correlation[4] since the flow in the module was turbulent at a Reynolds number of 5700.

$$N_{sh} = 0.023 \cdot N_{Re}^{0.875} \cdot N_{Sc}^{0.25} \qquad (7)$$

The viscosity of water, $0.089\,\mathrm{g \cdot cm^{-1} \cdot s^{-1}}$, was used in the calculations above because the solutions were dilute.

2. Results and Discussion

2.1 Membrane formation

Figure 3 shows the changes of fluxes and self-rejections with time during membrane formation. For all the membranes, fluxes decreased rapidly within the first few minutes and reached a constant value within 60 minutes. Self-rejections above 0.9 were obtained at 5 minutes and final rejections above 0.95 were obtained. These results showed that self-rejecting dynamic membranes were formed for all the polyion compositions tested.

When the membrane-forming solution was replaced by deionized water, the water flux changed and reached a constant value. **Table 2** shows the differences in flux before and after the solution replacement. Fluxes of the membranes of $X_C = 0.31$ and 0.5 were little changed, but, those of the membranes of $X_C = 0.2$ and 0.8 approximately doubled. The flux change was explained by the lowered ionic strength, which resulted in less suppression of interaction between the excess charges of the membrane. In turn, the membrane became more porous by the repulsion force of the excess charges.

2.2 Solute rejection

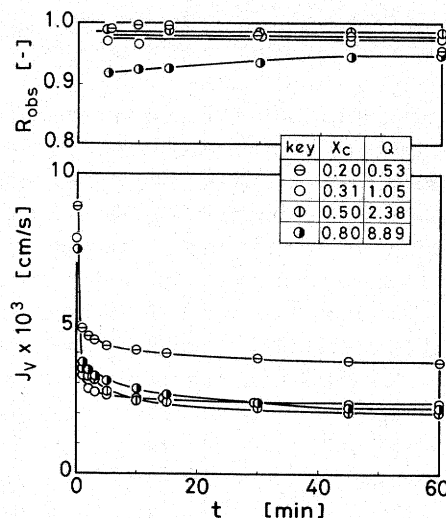**Figure 4** shows the solute rejections and fluxes of

Fig. 3. Time course changes of flux and self-rejection during membrane formation

Table 2. Comparison of water flux before and after solution replacement by deionized water

Membrane		Flux, J_V [cm·s^{-1}]***	
X_C [—]	Q [—]	before*	after**
0.20	0.58	3.8×10^{-3}	6.1×10^{-3}
0.31	1.05	2.2×10^{-3}	2.0×10^{-3}
0.50	2.38	2.0×10^{-3}	2.4×10^{-3}
0.80	8.89	2.1×10^{-3}	3.6×10^{-3}

* before: before solution replacement; circulating solution contained polyions and 50 mol·m^{-3} NaCl.
** after: after solution replacement; circulating solution was deionized water.
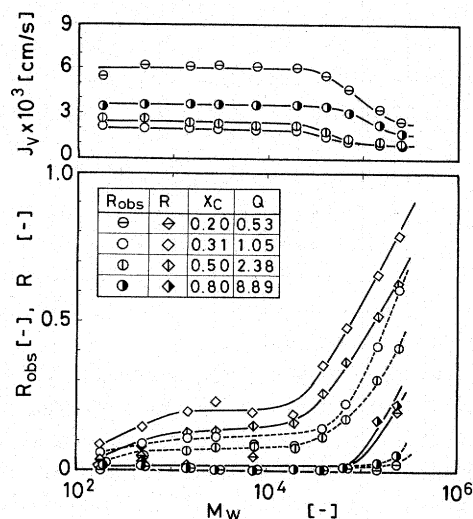*** applied pressure: 0.49 MPa.

Fig. 4. Effect of polyion composition on solute rejection of dynamic PIC membrane formed by simultaneous deposition method

the PIC-DMs. True rejection of the membrane of $X_C = 0.31$ increased with molecular weight of solute above 2×10^4. Cut-off molecular weight, defined by the true rejection at 0.9, of the membrane was esti-

mated to be about 3×10^5. This value was larger than that of reported dynamic membranes of hydrous Zr(IV) oxide[5] and ovalbumin.[7]

As excess charges of the PIC-DM increased, i.e., as the value of Q became larger or smaller than unity, the rejection curve shifted to the higher-molecular weight side. This was due to the repulsion force by the excess charge in the membrane, which enlarged the space for the passage of solute and solvent molecules. Although the amount of charge of the excess polyion was about twice that of the other in the membranes of both $X_C = 0.2$ (SPA-rich membrane) and $X_C = 0.5$ (PEI-rich one), the rejection curve of the SPA-rich membrane shifted more to the higher-molecular weight side than that of the PEI-rich membrane. Thus, the effect of the excess charge of polyions on solute rejection of the PIC-DM was more pronounced in the SPA-rich membrane than that in the PEI-rich membrane. This was due to the fact that the SPA molecule expanded more than the PEI molecule, as shown in Fig. 2.

The rejection curves of the membranes of $X_C = 0.5$ and 0.31 showed a shoulder at a molecular weight of about 1500. This suggests that the membranes had two kinds of passages for solute: one of them contributing to the rejection of the smaller solute of molecular weight more than 1500, the other contributing to the rejection of the larger solute of molecular weight more than 10,000. The fact that the height of the shoulder in the rejection curve is low suggests that the flux through the passages of smaller size is less than that through the larger ones.

On the other hand, flux, J_V, for each membrane was almost constant for solutes of molecular weight less than 10,000 and decreased gradually with increasing molecular weight above 10,000. This may be caused by the formation of a dextran gel layer or plugging of the passages by dextran molecules.[3] The fluxes increased with increase of the excess charges. The fluxes of the PIC-DMs ranged from 2×10^{-3} to 6×10^{-3} cm·s^{-1}. These values were comparable to those of dynamic membranes formed with Zr(IV), Fe(III)[5] and ovalbumin.[7]

2.3 Structure of dynamic PIC membrane

Dynamic PIC membrane by the simultaneous deposition method is considered to be formed as follows. First, polyion complex is formed in the feed solution by contacting SPA and PEI molecules before depositing onto the ceramic tube, because both polyions are dissociated at pH 6.0. Then, microagglomerates of some PICs are formed in the solution. The PIC microagglomerates deposit on the ceramic tube, resulting in a dynamic membrane. Therefore, the structure of the PIC membrane is characterized by the size and structure of the PIC microagglomerate. Factors affecting the properties of the agglomerate

are charge, molecular weight, molecular structure of polyions, pH, and ionic strength of solution.

The composition of the PIC microagglomerate is thought to depend on the composition of polyions in the solution. The charge of the agglomerate changes from negative to positive according to their polyion composition and pH of the solution. When SPA and PEI molecules have the same amount of charge, the charges of both polyions are neutralized and the PIC agglomerate has a closely packed form because of its hydrophobic nature.[9] As excess charge increases, regions of thin polymer segments appear around the excess charge in the agglomerate and porous space among the agglomerates is enlarged by the repulsive force of their surface charge. Hence the structure of the membrane becomes more porous as the excess charge increases.

When solute and solvent molecules pass through the dynamic PIC membrane, each molecule will pass through two different paths, that is, openings in the agglomerate and porous spaces among the agglomerates.

Permeation through the membrane of dual pore sizes The structure of the dynamic PIC membrane is thought to be characterized by the pores of two sizes mentioned above. For simplicity, let the number densities of smaller pores of radius R_{P1} and the larger ones of radius R_{P2} be N_{P1} and N_{P2}, respectively. Solvent flow through each pore of the membrane is assumed to follow the Hagen-Poiseulle law.

$$J_{Vi} = N_{Pi} \cdot \pi \cdot R_{Pi}^4 \cdot P/(8 \cdot \mu \cdot L) \qquad (i = 1, 2) \quad (8)$$

The relationship between the solute concentrations at inlet and outlet of each pore is assumed to be given by Ferry's equation.[1]

$$J_{Si} = C_{Pi} \cdot J_{Vi} \quad (9)$$

$$C_{Pi} = C_M (1 - R_i) \quad (10)$$

$$R_i = [\lambda_i (\lambda_i - 2)]^2 \quad (11)$$

where

$$\lambda_i = \min[R_S/R_{Pi}, 1] \quad (12)$$

Permeation through unit area of the membrane is expressed as follows.

$$J_V = (N_{P1} \cdot J_{V1} + N_{P2} \cdot J_{V2})/(N_{P1} + N_{P2}) \quad (13)$$

$$J_S = (N_{P1} \cdot J_{S1} + N_{P2} \cdot J_{S2})/(N_{P1} + N_{P2}) \quad (14)$$

$$C_P = C_M \frac{\theta(1 - R_1) + (1 - R_2)}{\theta + 1} \quad (15)$$

$$R = (\theta \cdot R_1 + R_2)/(\theta + 1) \quad (16)$$

where

$$\theta = N_{P1} \cdot R_{P1}^4/(N_{P2} \cdot R_{P2}^4) = J_{V1}/J_{V2} \quad (17)$$

Smaller pores of R_{P1} contribute to the rejection of solutes having a molecular weight of about 1500 and almost reject solutes of molecular weight above 10,000. Larger pores of R_{P2} contribute only to the rejection of solutes having a molecular weight above 10,000. Parameter θ corresponds to height of the shoulder appearing in the rejection curve shown in Fig. 4. Parameters R_{P1}, R_{P2} and θ will increase with increase of excess charge of dynamic PIC membrane. Since the charge of the polyion was the only variable in the membranes tested, these parameters were a function of that charge. Values of the parameters were easily obtained by fitting the calculated values with experimental data, assuming the values of R_{P1}, R_{P2} and θ from the rejection of the solutes having a molecular weight of about 1500 and above 10,000, and the height of the shoulder in the rejection curve, respectively.

Figure 5 shows the estimated rejections of PIC-DMs based on the dual pore sizes model. The overall performance in terms of rejection of the PIC-DM is represented well by the model, although a small discrepancy is seen around the R_S value of 2 nm. **Figures 6 and 7** show the dependence of flux, J_V, and the parameters R_{P1}, R_{P2} and θ on the ratio of charges of PEI to SPA molecules. As the excess charge increased, the value of J_V, R_{P1} and R_{P2} increased but the value of θ decreased. That is, the PIC-DM turned more porous in structure as the excess charge increased. The dependence of these parameters on the ratio of charge of the polyions was stronger in the SPA-rich membrane than in the PEI-rich ones. These results coincide with the discussion above. The values of R_{P2} were about ten times those of R_{P1} in the PEI-rich membranes. Therefore, permeation through the larger pores was dominant. The overall membrane pores of widely distributed size, R_{P1} and R_{P2}, decreased the sharpness of the cut-off molecular size.

Conclusion

Dynamic PIC membranes were formed by the simultaneous deposition method with changes in the polyion composition, and their solute rejections were measured. With increasing excess charge of the membrane, the rejection curve shifted to the higher-molecular weight side and the flux increased. The solute rejection of the membranes was analyzed successfully by the dual pore sizes model. The pore sizes and their number fractions were related to the ratio of charge amount of the polyions used.
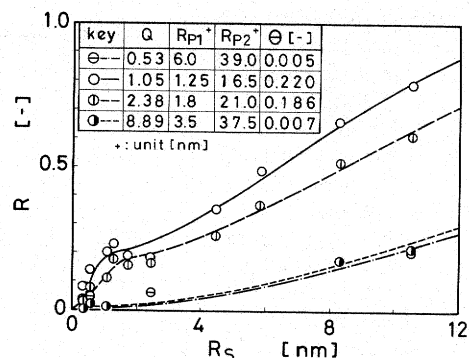
Fig. 5. Fitting results of calculated rejection curves by Eq. (16) to estimated true rejections

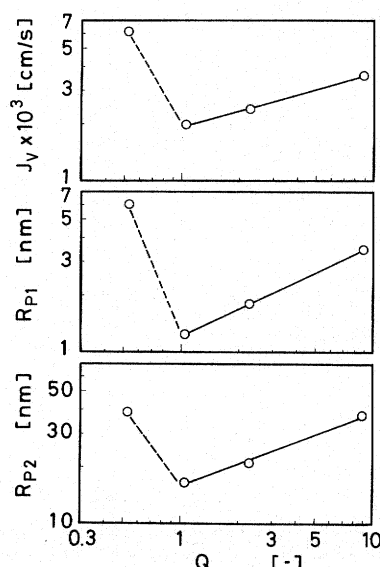| key	Q	R_{P1}^+	R_{P2}^+	θ [-]
$\ominus$--	0.53	6.0	39.0	0.005
O—	1.05	1.25	16.5	0.220
⊕--	2.38	1.8	21.0	0.186
⊙---	8.89	3.5	37.5	0.007

+ : unit [nm]

Fig. 6. Dependence of flux and pore sizes on ratio of charge amount of SPA to PEI
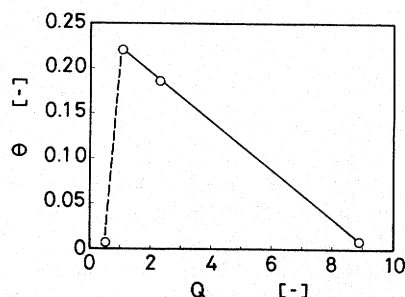
Fig. 7. Effect of ratio of charge amount of SPA to PEI on number fraction of pores

Nomenclature

C	= concentration of polyion	[kg·m^{-3}]
C_B	= solute concentration of feed	[kg·m^{-3}]
C_M	= solute concentration at membrane surface	[kg·m^{-3}]
C_P	= solute concentration of permeate	[kg·m^{-3}]
C_S	= concentration of sodium chloride	[mol·m^{-3}]
D	= diffusivity	[m^2·s^{-1}]
J_S	= solute flux	[mol·m^{-2}·s^{-1}]
J_V	= volume flux	[m^3·m^{-2}·s^{-1}]

k = mass transfer coefficient $[m^2 \cdot s^{-1}]$
L = length of pore $[m]$
M_W = molecular weight $[—]$
N_P = pore density $[m^{-2}]$
N_{Re} = Reynolds number $[—]$
N_{Sc} = Schmidt number $[—]$
N_{Sh} = Sherwood number $[—]$
P = pressure $[Pa]$
Q = ratio of charge amount of SPA to PEI $[—]$
R = true rejection $[—]$
R_{obs} = observed rejection $[—]$
R_P = pore radius $[m]$
R_S = solute radius $[m]$
T = absolute temperature $[K]$
t = time $[s]$
V = working volume $[m^3]$
X = weight fraction $[—]$
Z = charge density $[eq \cdot kg^{-1}]$

κ = Boltzmann's constant $[J \cdot K^{-1}]$
λ = dimensionless parameter ($= R_S/R_P$) $[—]$
θ = dimensionless parameter defined by Eq. (17) $[—]$
ν = kinematic viscosity $[m^2 \cdot s^{-1}]$
μ = viscosity $[Pa \cdot s]$

⟨Subscript⟩
A = polyanion ($=$ SPA)
C = polycation ($=$ PEI)

1, 2 = smaller and larger pores, respectively

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