STRUCTURE AND PROPERTIES OF CHARGED ULTRAFILTRATION MEMBRANES MADE OF SULFONATED POLYSULFONE

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Negatively charged ultrafiltration membranes were prepared from Na-form sulfonated polysulfone (SPS), which was made by sulfonation of polysulfone using SO_3-triethyl phosphate complex. Two kinds of SPS, having charge densities of 1.60 and 0.776 meq/g, were obtained. Casting conditions were optimized by varying polymer concentration, evaporation temperature and casting period. This membrane showed less fouling when ovalbumin was negatively charged at high pH. Tubular membranes were used to get reflection coefficient and solute permeability with PEG #600 to #6,000. Using these values and pure water permeability, pore radius and $A_k/\Delta X$ were calculated on the basis of the steric hindrance pore model. The radius was 18.7 Å and 24.0 Å for the high and the low charge density membrane, M1 and M2, respectively. $A_k/\Delta X$ calculated from water and solute permeabilities coincided well for M1, but not for M2. This may be due to the hydrophobicity of the latter.

Introduction

Although there are many commercial ultrafiltration membranes sold in the market, none is claimed to offer the effect and merit of bearing a charge. This charge effect may perhaps be used in the recovery of electrophoretic paint by ultrafiltration, but so far no results have not been reported.

Since the charged ultrafiltration membrane has three variables, namely sign and density of the charge attached to the membrane matrix, and pore size, it can be considered to have more flexibility than the uncharged membrane for practical application. It has already been predicted that the charged membrane can expel solute and colloidal particles that bear charges of the same sign, so that the membrane can be protected from fouling by gel layer formation on the membrane surface.[5] But this fact has not been proved yet. Data of adverse results have been published recently.[9]

In this investigation sulfonated polysulfone (SPS) was selected as the charged membrane material. SPS has already been used for reverse osmosis and ultrafiltration membranes. Friedrich[4] reported the various manufacturing conditions that resulted in membranes of various natures. The material used in this case is the H-form of SPS. Koyama[6] made reverse osmosis membranes also from H-form SPS and tried to find the best conditions for obtaining membranes that show high rejection of NaCl. Patents[2,3,11] of Rhone-Poulenc of France claim manufacturing methods to make ultrafiltration membranes by using H-form

SPS.

Here Na-form SPS was used. This required the use of new conditions to make ultrafiltration membranes, since the solubilities of H- and Na-forms are different. Natures of membranes obtained by our method, reported in this paper, were determined by using the experimental and analytical method previously developed.[7,8]

1. Membranes

1.1 Preparation of sulfonated polysulfone

Polysulfone (P 1700, Union Carbide) was sulfonated by following the method developed by Noshay.[10] But the original method had to be altered in our case. Procedure of a sulfonation is shown in **Fig. 1**. Charge density can be varied by changing the amount of SO_3/TEP complex to polysulfone. Charge densities obtained were 1.60 and 0.776 meq/g, as measured by the acid-base titration method.

1.2 Casting procedure

Flat sheet membranes were cast from solutions of SPS/N-methyl-2 pyrrolidone/$LiNO_3$, whose weight ratio ranged from 1/4/0.2 to 1/5/0.2. Evaporation of the solvent was done in an air oven at temperatures from 45 to 65°C with an evaporation period from 45 to 60 min. The final gelation was done in ice-cold water.

Tubular membranes were made under conditions shown in **Table 1**. Membranes were cast inside a glass tube (I.D. 1.26 cm) and the solvent was evaporated by flowing hot air. After gelation, membranes were withdrawn from the glass tube and put into supporting tubes made of porous polyolefin. The membrane designated as M1 has a charge density of 1.60 meq/g; that of M2 is 0.776 meq/g.

Polysulfone(PSF)   Ethylenedichloride(EDC) C_2H_5O
                                               $C_2H_5O-P-O\cdot EDC, 2SO_3\cdot EDC$
                    ClH_2C-CH_2Cl C_2H_5O 70ml, 9.5ml, 70ml
50gr   340ml   (TEP)
                                                19.2ml

                                        Mix on Ice Bath
                                               C_2H_5O
                    Dissolve $C_2H_5O\ P-O-SO_3$
                                               $C_2H_5O-SO_3$
                    Simultaneous   (2/1 SO_3/ TEP Complex)
                    Titration

                    Reaction under vigorous agitation
                            30°C 1hr

                            CH_3 O
                                          ‖
                    —⬡-C-⬡-O-⬡-S-⬡-O— Sulfonated Polysulfone-H
                            CH_3 SO_3 O   (SPS-H)

                    ├—$(CH_3)_2CHOH$(IPA) 180ml
                    ├— $NaOCH_3$ 100ml

                            CH_3 O
                                          ‖
                    —⬡-C-⬡-O-⬡-S-⬡-O— Sulfonated Polysulfone-Na
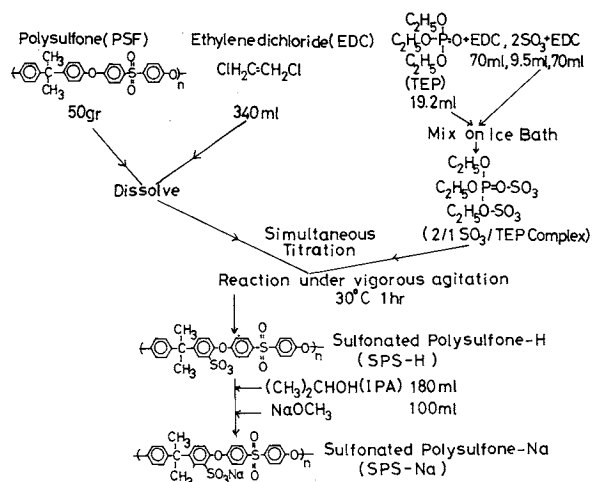 CH_3 SO_3Na O   (SPS-Na)

Fig. 1. Procedure of SPS synthesis by sulfonating PSF.

Table 1. Casting conditions of tubular membranes and their characteristics

Membrane No.	M1	M2
Solvent	NMP	
Swelling agent	LiNO$_3$	
Charge density [meq/g]	1.6	0.776
SPS/NMP/LiNO$_3$ [wt. ratio]	1/5/0.2	1/7.5/0.35
Solvent evap. temp. [°C]	60	60
Solvent evap. period [min]	30	20
Gelling condition	4°C ice bath	
Pure water permeability		
$L_p \times 10^3$ [cm/(s·MPa)]	1.1	0.8

2. Experimental

2.1 Test of flat sheet membrane

Flat sheet membranes were tested using a batch-type cell, Ulvac Service Co., MC-2, whose volume is about 5 ml. This cell was used to measure characteristics of various membranes quickly and to find the best casting condition. Molecular weight cut-off values were measured using polyethylene glycol of various molecular weights from 400 to 20,000 supplied by Wako Pure Chemical Co. This cell was also used to investigate the effect of a charge on the plugging characteristics of membranes using ovalbumin at different pH values.

2.2 Characterization of tubular membranes

After finding the best casting condition, membranes were cast in tubular form and tested by the same ultrafiltration apparatus used previously.[7] In this type of cell the effect of concentration polarization can be corrected and true membrane nature can be obtained precisely. Here again polyethylene glycol of various molecular weights was used to determine the molecular weight cut-off of membranes: PEG #600 (M.W., 600), PEG #1,000 (M.W., 1,000), PEG #1,540 (M.W., 1,500), PEG #4,000 (M.W., 3,000) and PEG #6,000 (M.W., 7,500). Testing con-

ditions were as follows: temperature, 25°C; flow rate, 1.7–9.0 l/min; pressure, 0.1–0.8 MPa. Concentrations were below 500 ppm to prevent gel layer formation on the membranes.

3. Results and Discussion

3.1 The characteristics of membranes cast under various conditions

Table 2 shows the characteristics of membranes cast under various conditions, where gap width means the clearance between a glass plate and a casting blade. It is seen from the table that the evaporation temperature of solvent should be higher than 65°C, and that conditions designated as F are best in this experimental range.

Changes of molecular weight cut-off are shown in Figs. 2 and 3, where effects of polymer concentration and evaporation period are shown. Higher polymer concentration and longer evaporation period shift the cut-off value to lower molecular weight, and give tighter membranes.

3.2 The effect of a charge against gel layer formation

The membrane, F, and ovalbumin (M.W., 45,000) were used to learn the effect of a charge on gel layer formation by changing pH. The isoelectric point of ovalbumin is pH 4.5, it is negatively charged at high pH and positively charged at low pH. The membrane has a negative charge and is expected to reject ovalbumin at high pH. Ovalbumin solution of 10,000 ppm is adjusted to pH 11.64 and 3.31, respectively, and used. Decreases of flux through the membrane with time are shown in Fig. 4, where it is seen that the decrease rate of flux is lower for pH 11.64 than for pH 3.31. After 60 min gel layer formation for pH 3.31 solution ceased, while it continued for the higher pH. Membranes were washed with pure water after finishing the experiment. The flux of the membrane used with high pH solution recovered to the initial value, but that with low pH solution could not be recovered by simple washing with water. The membrane was plugged and showed lower molecular cut-off value, as is shown in Fig. 5. This plugged membrane can be made to recover after immersing in NaOH solution of pH 11.0 for 3 hr. These facts show that the membrane charge works effectively to prevent gel layer formation of solute having the same charge and to prevent it from plugging the membrane.

3.3 Results with tubular membrane

The effect of concentration polarization can be corrected by using correct mass transfer coefficients near the membrane surface, which can be experimentally obtained by the velocity variation method.[7] In this investigation mass transfer coefficients obtained could be expressed by Deissler's correlation as before. The true rejection value, R, is given as

Table 2. Membranes made under various conditions and their characteristics

	A	B	C	D	E	F
Conc. of polymer [wt.%]	20	20	20	20	16.7	16.7
Solvent evap. temp. [°C]	65	55	45	65	65	65
Solvent evap. period [min]	60	60	60	45	60	45
Gap width [μm]	480	260–480	260–480	390	390	260
Memb. thickness [μm]	180	—	—	130	100	130
Pure water permeability $L_p \times 10^3$ [cm/(s·MPa)]	0.73	—	—	0.80	0.78	2.16
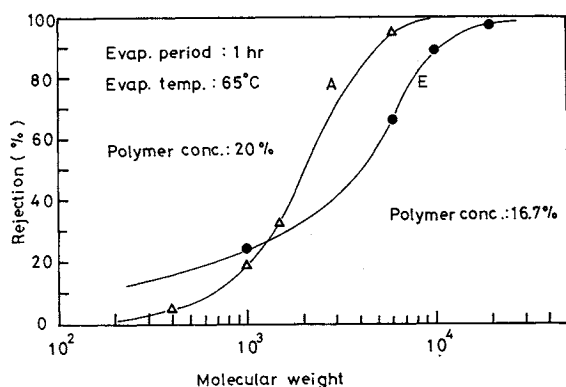
Fig. 2. Effect of polymer concentration on molecular weight cut-off.
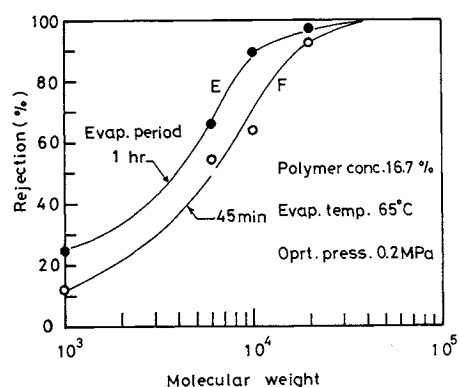
Fig. 3. Effect of solvent evaporation period on molecular weight cut-off.
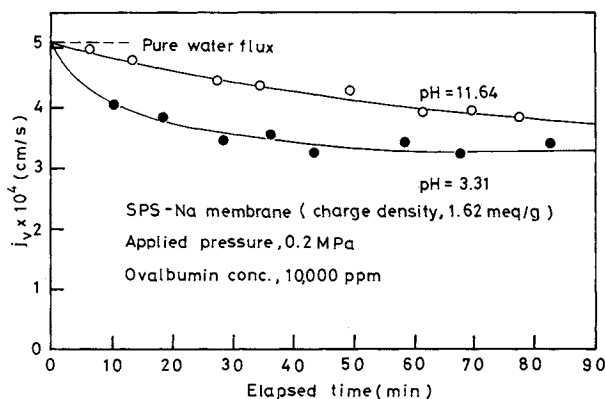
Fig. 4. Effect of pH of ovalbumin solution on flux decrease; operating pressure 0.2 MPa, ovalbumin concentration 10,000 ppm, membrane charge density 1.62 meq/g.
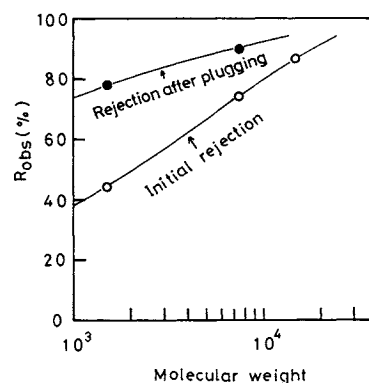

Fig. 5. Change of molecular weight cut-off value of PEG before and after plugging by ovalbumin.

$$\frac{R}{1-R} = \frac{R_{obs}}{1-R_{obs}} \cdot \exp(J_v/k) \tag{1}$$

where R_{obs} is the experimentally obtained rejection, J_v is the volume flux and k is the mass transfer coefficient. The relation between R and transport parameters, the reflection coefficient, σ, and the solute permeability, P, is given by the Spiegler-Kedem equation[12] as

$$R = \frac{\sigma(1-F)}{1-\sigma \cdot F} \tag{2}$$

where

$$F = \exp\left\{-\frac{(1-\sigma)}{P} \cdot J_v\right\} \tag{3}$$

Transport parameters, σ and P, were determined by the curve-fitting method by plotting R against $1/J_v$, as shown in **Fig. 6**. In this figure R values of M1 for PEG of different molecular weight are shown and solid lines represent Eqs. (2) and (3). As in the earlier report,[7] the experimental data fitted well with the Spiegler-Kedem equation. σ and P thus determined are shown in **Table 3**.

3.4 Analysis based on the steric hindrance pore model

Nakao[8] proposed the steric hindrance pore model, which fitted better with experimental data obtained by using cellulose acetate ultrafiltration membranes. Following this model σ and P are given as

$$\sigma = 1 - S_F\{1 + (16/9)q^2\} \tag{4}$$

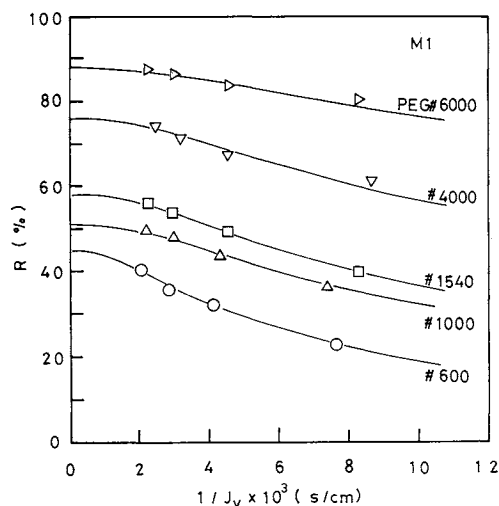$$P = D \cdot S_D \cdot (A_k/\Delta X) \tag{5}$$

Fig. 6. Plot of R vs. $1/J_v$ for different PEG by M1.

Table 3. Reflection coefficient and solute permeability for different solutes

| Solute | M1 | | M2 | |
	σ [—]	$P \times 10^4$ [cm/s]	σ [—]	$P \times 10^4$ [cm/s]
PEG #600	0.45	1.6	0.21	2.8
PEG #1000	0.51	0.81	0.25	2.1
PEG #1540	0.58	0.78	0.31	1.7
PEG #4000	0.76	0.46	0.51	0.94
PEG #6000	0.88	0.21	0.86	0.49

where

$$S_D = (1 - q)^2 \qquad (6)$$

$$S_F = 2(1 - q)^2 - (1 - q)^4 \qquad (7)$$

and

$$q = r_s/r_p \qquad (8)$$

As for $A_k/\Delta X$, this can also be obtained from pure water permeability, L_p, as

$$A_k/\Delta X = \frac{8\mu L_p}{r_p{}^2} \qquad (9)$$

From σ, pore radius, r_p, and q can be obtained by Eqs. (4) and (8) using Stokes radius of solute, r_s, which is obtained from diffusion coefficient. From P and q, $A_k/\Delta X$ is obtained by Eq. (5), which is also obtained from L_p by Eq. (9). These results are shown in **Table 4**. The average pore radius of M1 is 18.7 Å and that of M2 is 24.0 Å. Comparison of σ from Eq. (4) using this radius and that obtained from experimental data is shown in **Fig. 7**. It is seen that coincidence is generally good except in the high-molecular weight range. Since PEG is a linear polymer, it tends to give low rejection at high molecular weight compared to spherical molecules such as proteins,[1] and this could be the reason for the above results.

$A_k/\Delta X$ values obtained are shown in **Fig. 8**, where

Table 4. r_p. and $A_k/\Delta X$

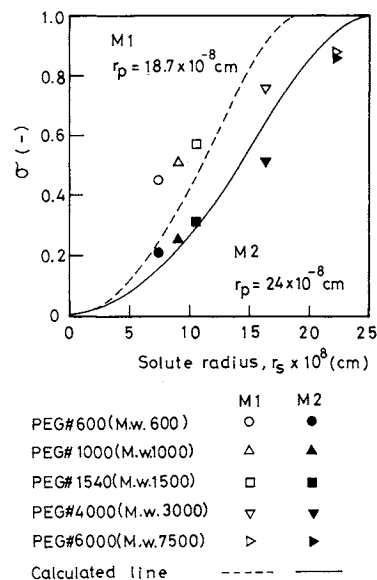| Solute | r_s [Å]* | M1 | | | M2 | |
		R_p [Å]	$A_k/\Delta X$ [cm^{-1}]		r_p [Å]	$A_k/\Delta X$ [cm^{-1}]
PEG #600	7.41	13.3	246		20.0	211
PEG #1000	9.06	15.2	183		22.2	217
PEG #1540	10.6	16.6	260		23.2	254
PEG #4000	16.3	21.7	496		27.4	382
PEG #6000	22.1	26.6	703		27.1	1380
Averaged value		$\bar{r}_p = 18.7$ Å			$\bar{r}_p = 24.0$ Å	

* See ref. 7.

Fig. 7. Relationship between reflection coefficient and Stokes radius based on steric hindrance model.
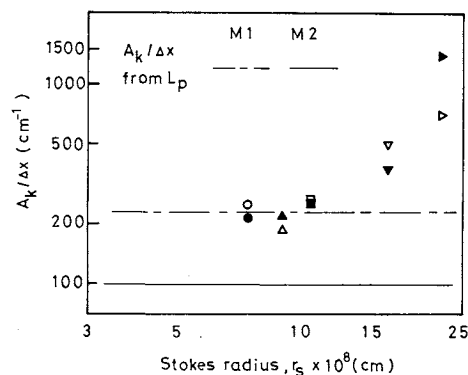

Fig. 8. Relationship between $A_k/\Delta X$ and Stokes radius base on steric hindrance pore model (keys are same as in Fig. 7).

it is seen that for M1 the values obtained by pure water and solutes pearmeabilities coincide well, whereas for M2 the values obtained by the pure water permeability are lower than those by the solute permeability. This result may show that M2 inherits a hydrophobic nature from the original polysulfone, while M1 becomes hydrophilic by sul-

fonation. This discussion should be extended to include many other membrane materials and be treated quantitatively on the basis of the hydrophobicity and hydrophilicity balance. Thus it is necessary to collect further experimental data using various ultrafiltration membranes.

Conclusion

To make the charged ultrafiltration membrane, polysulfone was sulfonated and sulfonated polysulfone having charge densities of 1.60 and 0.776 meq/g were obtained. The best casting condition was found for these materials by casting various flat sheet membranes. The charged membrane was also found to be effective in preventing plugging by ovalbumin bearing the same charge.

Tubular membranes were used to obtain precise transport parameters, using PEG of different molecular weights. The reflection coefficient and the solute permeability thus determined were used to estimate the pore radius based on the steric-hindrance pore model previously developed. The pore radius of membrane M1 was 18.7 Å and that of M2 was 24.0 Å. The coincidence of $A_k/\Delta X$ values obtained from water and solute permeability depends on the balance of hydrophobic and hydrophilic nature of the membrane.

Acknowledgment

Nomenclature

A_k = ratio of total cross-sectional pore area to effective membrane area [—]
D = diffusivity [cm²/s]
J_v = volume flux through a membrane [cm³/cm²·s]
k = mass transfer coefficient [cm/s]
L_p = pure water permeability [cm³/cm²·s·MPa]
P = solute permeability [cm/s]
ΔP = pressure difference [Pa]
q = ratio of solute radius to pore radius [—]
R = real rejection [—]
R_{obs} = experimentally observed rejection [—]
r_p = pore radius of gel layer [cm]
r_s = Stokes radius of solute
S_D, S_F = steric hindrance factors for diffusion and filtration flow, respectively [—]
ΔX = thickness of membrane [cm]

μ = viscosity [Pa·s]
σ = reflection coefficient [—]

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