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Electrostatic Sieve Separation of Dextransulfate and Dextran by Negatively Charged Ultrafiltration Membranes

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Electrostatic sieve separation of dextransulfate (DS) and dextran (D), having similar molecular size, with negatively charged ultrafiltration membranes of poly(acrylonitrile-co-sodium styrenesulfonate) was carried out. The charged membrane has high rejection to DS with separation factor $\alpha_{D/DS}$ of approximately 25.

In the past decade, many high performance membranes have been developed.$^{1,2)}$ Among them, charged ultrafiltration membranes$^{3-8)}$ have been payed attractive attention to the separation and concentration because of electrostatic repulsion to ionic solute having same sign with the membrane.$^{3,4)}$ However, little is known concerning the separation of mixtures of macromolecular solutes by the electrostatic sieve separation of charged ultrafiltration membrane. In a typical ultrafiltration membrane having only mechanical sieve, it is impossible to separate the solute components having similar molecular size. Therefore, it is a challenging subject to evaluate the behavior of electrostatic sieve by charged ultrafiltration membranes.

In this communication, we prepared negatively charged ultrafiltration membranes of poly(acrylonitrile-co-sodium styrenesulfonate) P(AN-co-SSS)$^{9)}$ in order to develop a new membrane for electrostatic sieve separation. Preparation of the ultrafiltration membranes was followed by the phase inversion method previously reported;$^{5)}$ Dimethylsulfoxide solution containing 9 wt% of base polymer and 1 wt% of polyethylene glycol ($Mw=2x10^4$) was used. The membranes prepared were of about 100 μm thickness and 43mm diameter. The apparatus for ultrafiltration was similar to that previously used.$^{4,7)}$ Various molecular weight dextrans (Pharmacia) and dextransulfate (DS) having 1.6 mol% content of sodium sulfonate groups (Tokyo Kasei) were employed without further purification. The experimentally obtained rejection, R, is defined as $R=(C_b-C_p)/C_b$, where C_b and C_p denote the concentration of bulk and permeated solutes, respectively. The feed solution and the eluents were analyzed by GPC (type CCPD UV8000 of Toyo Soda Co. Ltd., with a 30 cm column of TSK_{gel} $G6000PW_{XL}$).

In order to examine charge effect of negatively charged ultrafiltration membrane on separation of D/DS mixture, the ultrafiltration membranes of P(AN-co-SSS) and polyacrylonitrile (PAN) having identical molecular cutoff property were used. As shown in Fig. 1, these membranes almost permeate both dextrans having 4×10^4 and 1×10^4 molecular weight. Fig. 2 shows GPC curves of feed solution before and after the permeation experiments. Here, the feed solution contained D and DS having 4×10^4 and 1×10^4 molecular weight, respectively. Total concentration of D and DS in feed solution was 0.1 wt% (D/DS=1/9 (w/w)). The GPC curve of the feed solution before permeation consists of two peaks for D and DS at the elution times of 11.1 and 12.5 min, respectively. After permeation through

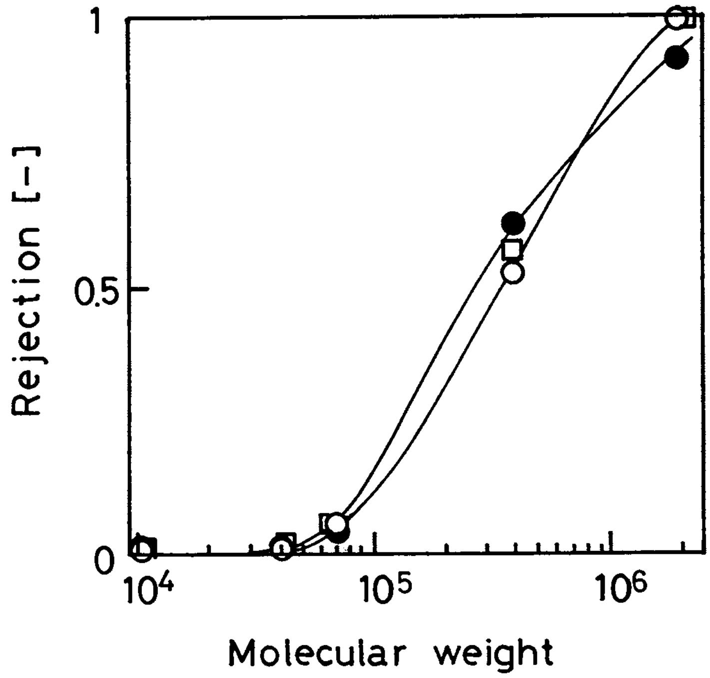

Fig. 1. Molecular cutoff curves of ultrafiltration membranes.
P(AN-co-SSS) having SSS groups for 0.058 (○) and 0.11 mmol/g (□), PAN (●).

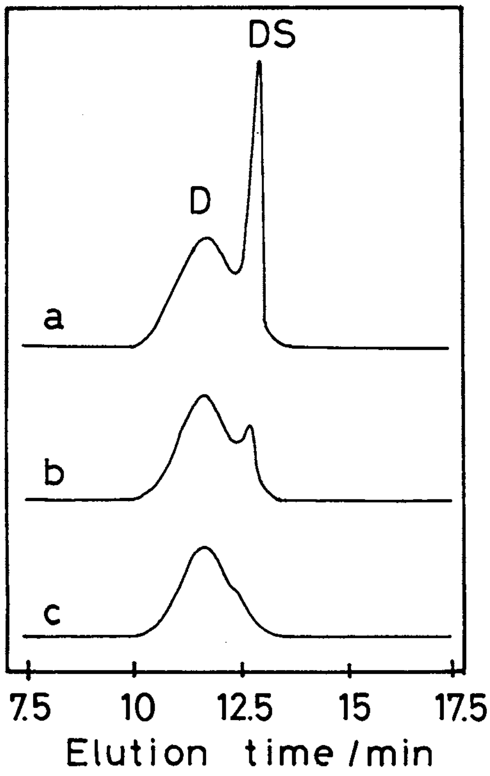

Fig. 2. GPC curves of feed solution of D/DS mixture (1/9 (w/w)) before (a) and after permeation through P(AN-co-SSS) membrane having SSS groups of (b) 0.058 and (c) 0.11 mmol/g, respectively.

Table 1. Separation of D/DS mixture by P(AN-co-SSS) membranes

Fixed charges mmol/g	Volume flux[a] m^3/m^2s	Rejection D	Rejection DS	Separation factor $\alpha_{D/DS}$
0.058	13.2×10^{-6}	0.03	0.85	7
0.11	7.8×10^{-6}	0.31	0.97	25

a)Measured by using 0.1 wt% of aqueous solution for the D/DS mixture.

the negatively charged ultrafiltration membrane, the peak of DS almost disappeared, while that of D was retained. The values of rejection for D and DS and those of separation factor,[1)] $\alpha_{D/DS}$, are shown in Table 1. The separation factor of P(AN-co-SSS) membrane having high content of SSS groups is approximately 25. In ultrafiltration membrane made of PAN[10)] having no charges, the GPC curve was the same as that of feed solution before permeation; all of the solutes permeate through the uncharged membrane without permselectivity. The separation factor obtained is almost unity.

To check the molecular size of D and DS at the permeation condition, reduced viscosity (η_{sp}/C) of 0.1 wt% of aqueous solution for D and DS was measured at 30 °C as 19 and 11, respectively. The data indicate that little is the different in the molecular size of D and DS; the molecular size of DS is slightly smaller than that of D. However, selective rejection of DS is only achieved by P(AN-co-SSS) membranes. The fact of the selective rejection is due to the electrostatic repulsion between the anionic solute and the negatively charged membrane as schematically shown in Fig. 3. Further study on the electrostatic sieve separation of macromolecular solutes with the negatively charged ultrafiltration membrane is

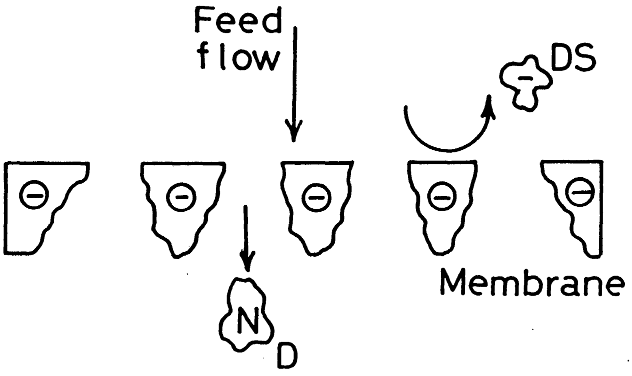

Fig. 3. Conceptual illustration of the charge effect of negatively charged ultrafiltration membrane on separation of D/DS mixture.

now progress and the details will be reported elsewhere.

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9) Copolymerization of acrylonitrile (AN) and sodium styrenesulfonate (SSS) was carried out in DMSO solution at 60 °C as follows; in reaction vessel of 500 mL capacity, 150 g of purified AN, 5.15 g of SSS and 435 mL of DMSO and 1.38 g of AIBN were introduced. Polymerization was carried out at 60 °C for 4 h in nitrogen flow. The mixture was poured into large quantity of aqueous methanol to precipitate copolymer (51% conversion). The content of SSS groups in the copolymer was determined from acid-base titration4) for 0.11 mmol/g. The copolymer having a low content of SSS groups (0.058 mmol/g) was prepared analogously from a mixture of 150 g of AN, 2.55 g of SSS, and 1.3 g of AIBN in 435 mL of DMSO (56.3% conversion). Acrylonitrile homopolymer (PAN) was prepared by photopolymerization according to literature.10)
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