

SALT SEPARATION BY CHARGED MEMBRANESJan SCHAUER^a and Takaomi KOBAYASHI^b^a *Institute of Macromolecular Chemistry,**Academy of Sciences of the Czech Republic, 162 06 Prague 6, The Czech Republic*^b *Department of Chemistry,**Nagaoka University of Technology, Kamitomioka, Nagaoka, Niigata 940-21, Japan*

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Two negatively charged membranes made from poly(acrylonitrile-*co*-sodium styrenesulfonate) having ion exchange capacity of 0.058 and 0.15 meq/g dry matter were tested in ultrafiltration of aqueous solutions of dextrans and low-molecular-weight electrolytes. The former membrane, though permeable to bulky dextrans (molecular weight cut-off approximately 500 000), fairly retained small electrolytes. The latter, extremely hydrophilic membrane showed little resistance to the feed solution and no retention of solutes was observed. The influence of the feed concentration, electrolyte type, and operating pressure on the solute retention was determined.

Ultrafiltration membranes are defined¹ as the membranes with pore sizes smaller than 0.01 μm and molecular weight cut-off higher than 1 000. Typical ultrafiltration membranes separate solute molecules by sieving mechanism. While this holds for uncharged membranes, membranes from polymers having ionic groups show electric repulsion to solutes having charge of the same sign. Therefore charged membranes can show specific separation ability. In this work, poly(acrylonitrile-*co*-sodium styrenesulfonate) was synthesized; the membranes prepared from the polymer were tested for permeation and separation of low-molecular-weight salts and uncharged macromolecular solutes.

EXPERIMENTAL

Poly(acrylonitrile-*co*-sodium styrenesulfonate) (PAN-*co*-SSS) was synthesized by radical copolymerization of acrylonitrile and sodium styrenesulfonate. Details of the synthesis are described elsewhere².

The membranes were prepared by casting a DMSO solution, which was 9% in PAN-*co*-SSS and 1% in poly(ethylene glycol) ($M_w = 2 \cdot 10^4$), on a glass plate, coagulation in water, and washing the membranes with water to remove poly(ethylene glycol) and DMSO.

Ion exchange capacity of the membranes, as determined by titration, was 0.058 or 0.15 meq/g of dry polymer.

The ultrafiltration experiments were carried out in a stirred cell (Amicon Model 8050). The permeation measurements were carried out with distilled water, aqueous solutions of NaCl, Na₂SO₄, MgCl₂, MgSO₄, and Na₃PO₄ of concentrations 0.005 – 0.1 g/l, and 0.1 wt.% aqueous solutions of Dextran T10 ($M_w = 9\,900$, $M_n = 5\,700$), Dextran T40 ($M_w = 35\,600$, $M_n = 19\,800$), Dextran T

($M_w = 74\ 300$, $M_n = 36\ 300$), and Dextran T500 ($M_w = 486\ 000$, $M_n = 197\ 700$) (all Pharmacia Chemicals). The dextran concentrations were determined with a differential refractometer (Waters R4), the salt concentrations by conductivity measurements.

The water content of the membrane is defined as $S = (W_s - W_o)/W_o$, where W_o and W_s represent the weights of the dry and swollen membranes, respectively.

RESULTS AND DISCUSSION

The characteristics of the membranes are shown in Table I. Membrane 1, with the higher ion exchange capacity, was very hydrophilic and showed extremely high fluxes but no retention of dextrans and salts was observed. Membrane 2 of the lower ion exchange capacity was somewhat less hydrophilic. Its fluxes were by an order lower. SEM micrographs of a cross-section of Membrane 2 are shown in Fig. 1: a sponge-structured polymer with interconnected micropores forms the skin layer and separates finger-like pores in the sublayer as well. The retentions of high-molecular-weight dex-

TABLE I
Characteristics of the poly(acrylonitrile-*co*-sodiumstyrenesulfonate) membranes

Membrane	Ion exchange capacity ^a meq/g	Thickness ^b μm	H ₂ O content %	Flux ^c cm ³ /cm ² s
1	0.15	100	2 400	0.081
2	0.058	100	500	0.0085

^a Dry matter; ^b wet membrane; ^c at 0.1 MPa, feed – distilled water.

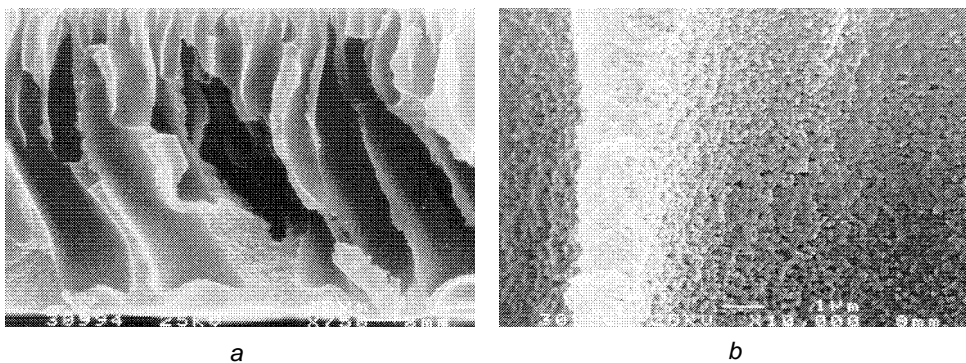


FIG. 1

SEM micrographs of Membrane 2. *a* Cross-section; *b* detail of the cross-section

trans by this membrane are shown in Fig. 2. It can be seen that the membrane has a very high molecular-weight cut-off for uncharged molecules of above 500 000.

While the membrane is freely permeable to (most) uncharged molecules, it retains to some extent small ionic compounds. The retention of ionic compounds is strongly dependent on the feed concentration: while increasing the feed concentration the retention decreases (Fig. 3), which is a characteristic feature of the charged membrane. Yaroshchuk and Staude³ derived the following equation from the Donnan equation for negatively charged membranes and fixed charge concentrations much higher than those of the feed solutions:

$$\frac{1}{v_-} (1 - R) = \left[v_+ z_+ \frac{c_0}{c_x} \right]^{z_- / z_+}, \quad (1)$$

where R is retention, c_0 is the feed electrolyte concentration, z_- , z_+ , v_+ , v_- are the charges and stoichiometric coefficients of the ions, and c_x is the fixed charge concentration in the membrane. If c_x does not vary with c_0 , the plot of $\log(1 - R)$ versus $\log c_0$ is linear, and the slope is governed by the valence type of the electrolyte. Ideally, the slope should be equal to 0.5 for MgCl_2 , 1 for NaCl and MgSO_4 , 2 for Na_2SO_4 , and 3 for Na_3PO_4 . In Fig. 4, the experimental results are plotted in this manner for a series of salt solutions.

The results indicate that: (i) all the obtained plots always give a reasonable straight line in accord with Eq. (1); (ii) the slopes for MgCl_2 , NaCl , MgSO_4 , Na_2SO_4 , and Na_3PO_4 are 0.060, 0.11, 0.14, 0.20, and 0.28, respectively; hence, they follow the same

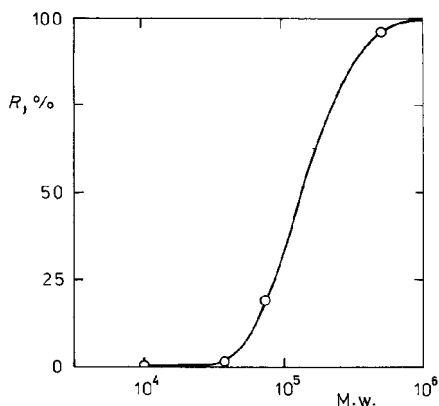


FIG. 2

Dependence of retention on molecular weight of dextrans for Membrane 2; (0.1 wt.% aqueous solution, 0.1 MPa)

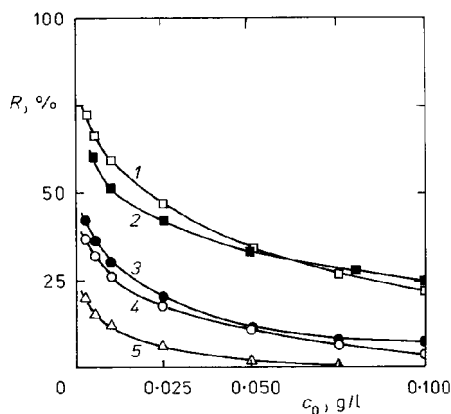


FIG. 3

Dependence of retention on concentration of salt in feed solution (0.1 MPa) for Membrane 2. 1 Na_3PO_4 , 2 Na_2SO_4 , 3 MgSO_4 , 4 NaCl , 5 MgCl_2

order as predicted theoretically; (iii) however, the absolute values of these slopes are much smaller than it follows from Eq. (1). It is clear that the membrane rejects small ions by the Donnan mechanism, but its behaviour shows deviations from a simple model.

It is well known that the retention of solutes by homogeneous reverse osmosis membranes increases with an increase in operating pressure. This can be explained by means of the solution-diffusion model⁴. An increased retention associated with an increase in operating pressure was also observed in separation of charged solutes by charged membranes^{5,6} and this phenomenon was explained by the charged capillary model⁷. However, the membranes tested in this work (less hydrophilic, type 2), showed an entirely opposite behaviour (Fig. 5): maximum retentions were attained at low operating pressures. As these membranes showed a considerably higher rate of water permeation through the pores, the explanation is probably to be found in electrokinetic phenomena.

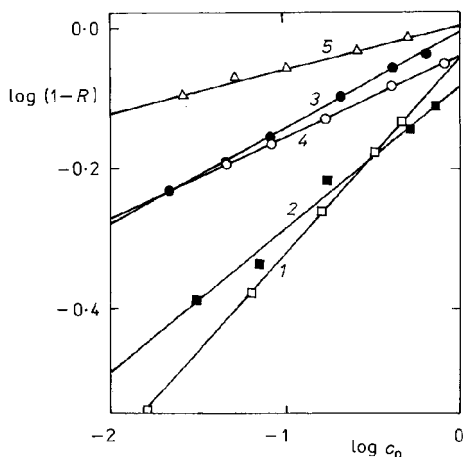


FIG. 4

Plot of $\log(1-R)$ vs \log of feed concentration, c_0 , in mmol/l at 0.1 MPa for Membrane 2. For curves 1–5 see the legend to Fig. 3

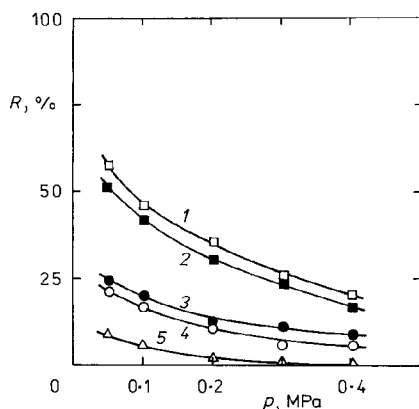


FIG. 5

Dependence of retention on operating pressure for Membrane 2. Feed concentration 0.025 g/l. For curves 1–5 see the legend to Fig. 3

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