

Permeation Properties of Glycol Chitosan–Mucopolysaccharide Complex Membranes

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Synopsis

The permeation properties of glycol chitosan–chondroitin sulfate C and glycol chitosan–heparin complex membranes have been studied. Discussion is devoted primarily to the desalination properties in reverse osmosis. Salt rejection and flux were dependent both on the composition of the membranes and the pH of the feed solutions. The results indicate that these complexes behave like polyampholytes. Minimum salt rejection occurs around the isoelectric point. Another characteristic of these membranes is a large pressure dependence of the salt rejection. This could be interpreted by assuming the compaction of these highly swollen membranes at high pressure.

INTRODUCTION

Since the early works of Bungenberg de Jong and co-workers on complex coacervation,¹ a number of works have been reported on the interaction between oppositely charged polyelectrolytes in aqueous media. A large part of such studies has been directed toward a better understanding of biologic systems, such as enzymatic processes, and of structure and properties of functional units, e.g., nucleoproteins and protein–polysaccharide complexes as two outstanding examples.

Recently, the polyelectrolyte complexes began to find their way into practical applications. Michaels and co-workers investigated various properties of a polyelectrolyte complex synthesized from sodium poly(styrene sulfonate) and poly(vinyl benzyl trimethylammonium chloride) and suggested its potential as a new material and referred to its characteristic physical and chemical properties.²⁻⁵ Considerable effort has been devoted to develop this material in the membrane field for separation and medical uses.^{6,7}

The structure and the composition of a polyelectrolyte complex would depend on a lot of factors such as the geometry and structure of the component polymers. This, therefore, may lead to a diversity of physical and chemical properties of these complexes. Furthermore, the interaction between oppositely charged polyelectrolytes involving weak polyelectrolyte should be affected by the pH of the surrounding solution because of the change in degree of dissociation. In this sense, it is of great interest to examine the properties of complexes involving weak electrolytes at various pH conditions. However, little has been reported about the properties of such complexes.

We have studied the effect of conformations and configurations of the component polymers on the interactions between oppositely charged polyelectrolytes

by using various polysaccharides and polypeptides.^{8,9} These complexes may afford particularly interesting materials for biomedical uses from the viewpoint of structural resemblance to various macromolecular complexes in the living system.

In this paper, we report the permeation properties of the membranes obtained from two polysaccharides bearing opposite charges. Glycol chitosan (GC) was chosen as the polycation component, and two mucopolysaccharides, chondroitin sulfate C (CSC) and heparin (Hep), as the polyanion component. GC is a copolymer of *N*-acetyl-D-glucosamine-6-glycol and D-glucosamine-6-glycol, and is prepared from *N*-acetyl-D-glucosamine (chitin) by de-*N*-acetylation after glycolation. Heparin is an alternating copolymer of L-iduronic acid, which is frequently O-sulfated at C 2, and D-glucosamine-*N*-sulfate with an additional O-sulfate group on C 6. CSC is an alternating copolymer of *N*-acetyl-D-galactosamine-6-sulfate and D-glucuronic acid.

EXPERIMENTAL

Materials

Glycol chitosan (Lot LM9931) was purchased from Wako Junyaku Co., Kyoto, and was used after dialysis followed by deionization through an ion exchange resin, Amberlite MB-1. The molecular weight of GC was 105,000 from the limiting viscosity number $[\eta]$ in 0.1*N* NaOH solution. The NH₂ content in GC was 0.62 per pyranose ring. Chondroitin sulfate C-Na (Lot V3P8090) and heparin-Na (Lot M4B1355) were purchased from Nakarai Chemicals Co., Kyoto, and were used after dialysis. The molecular weights of CSC and Hep determined from the limiting viscosity numbers $[\eta]$ in 0.15*M* sodium phosphate buffer containing 0.2*M* NaCl and in aqueous solution, respectively, were 45,000 and 10,200. The ratios of sulfonic group to carboxyl group of CSC and Hep were 1:1 and 2.1:1, respectively. The uronic acid contents of CSC and Hep were 31.2% and 38.5%, respectively, on a free acid basis.

Preparation of Membranes

Casting. Separate 1.0–1.5 wt % aqueous solutions were prepared for GC, CSC, and Hep. Mixtures were prepared by slow dropwise addition of an aqueous solution of CSC or Hep to the GC solution with stirring. The final pH values of the mixtures were in the range of about 6.5 to 8.5. The solutions having desired concentration ratios were spread on glass plates to uniform thickness and dried in vacuo at temperatures between 25°C and 30°C for two days. The relative proportions of the two components are quoted as the mole concentration of amino group to that of sulfonic group.

Crosslinking. In order to stabilize the membrane for permeation measurements over wide pH ranges, the dried membrane was crosslinked by immersing in a 20% solution of epichlorohydrin in ethanol at 70°C for 7 hr. The dry membranes thus prepared had thicknesses between 12 μ and 19 μ . For comparison with complex membranes, GC membrane was prepared by a similar method in the absence of acidic component. The water contents of the water-swollen membranes at atmospheric pressure and at room temperature were about 50% for GC-CSC, 55% for GC-Hep, and 40% for GC membranes, respectively.

Reverse Osmosis Measurement

The reverse osmosis (RO) measurements were made using a RO test loop for membranes equipped with three cells of 40 mm diameter made by Tama Seiki Ind. Co. Ltd. The membranes were supported by a Millipore filter VSWP 04700 and a sintered stainless steel disk. The reverse osmosis measurements were continued on each membrane until the water flux and the salt rejection were stabilized. The salt (or solute) rejection, R_s , is given by

$$R_s = 1 - (C_e/C_f) \quad (1)$$

where C_f is the concentration of the salt in the feed solution and C_e is the concentration of the salt in the effluent. The concentrations of the salt in aqueous solutions were determined by conductivity measurement. A Toshiba-Beckman total carbon analyzer (Model 102) was used to measure the concentration of the organic solutes. The accuracy of the analysis was ± 1 ppm in terms of carbon content.

RESULTS AND DISCUSSION

Both GC-CSC and GC-Hep membranes have three types of ionic groups, i.e., a strong acidic group ($-\text{SO}_3\text{H}$), a weak acidic group ($-\text{COOH}$), and a weak basic group ($-\text{NH}_2$). Therefore, the permeation properties of these membranes

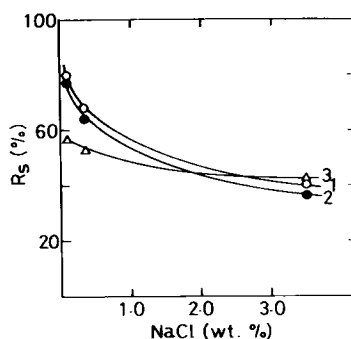


Fig. 1. Salt rejection plotted vs. concentration of salt in feed solution for GC-CSC membranes of (○) 48:52, (●) 51:49, and (△) 70:30 concentration ratio. Test conditions: 25°C, 80 atm, and pH 5.80.

would largely be dependent on the composition. Figure 1 shows the dependence of the salt concentration of feed solution on the rejection R_s for various GC-CSC membranes having different compositions. The salt rejection increases with decreasing feed concentration which is one of the characteristics of charged membranes. However, the relationship is dependent on the composition of the membrane.

The salt rejection and the flux at pH 5.80 for various GC-CSC membranes and for GC membrane as functions of operating pressure are shown in Figure 2. Marked composition dependences are observed. With respect to the flux, no thickness correction was made because of the difficulty of measuring the thickness of the membranes under high pressures.

The composition dependence on salt rejection can be seen more clearly in a plot of R_s at 60 atm against the composition (Fig. 3). At about 0.65 GC fraction,

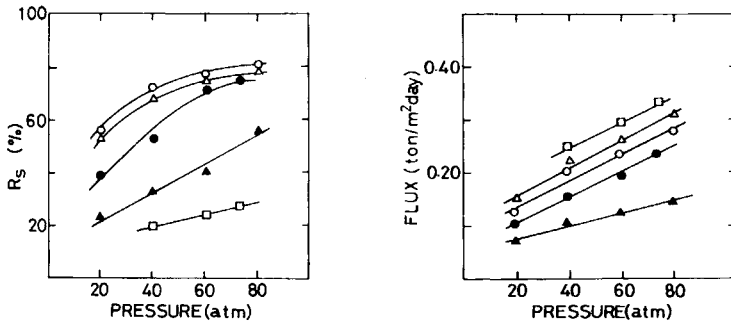


Fig. 2. Salt rejection and flux vs. operating pressure for GC-CSC membranes of (○) 48:52, (Δ) 51:49, (□) 65:35, and (▲) 70:30 concentration ratio and for GC membrane (●). Test conditions: 25°C, pH 5.80, and 0.10 wt % NaCl.

the plot exhibits a trough. This fact may suggest that this GC fraction is close to the isoelectric composition at pH 5.80. With respect to the membrane GC(0.65)-CSC(0.35), potentiometric titration was carried out to obtain an accurate value of the isoelectric point. However, it was not possible to detect the value, because the pK value ($=6.0$) of the amino residue in GC is not sufficiently far from that of the carboxyl residue in CSC ($=4.5$). In a previous work,⁸ we reported the complex formation between GC and various acidic mucopolysaccharides as functions of pH using turbidimetric and potentiometric measurements, and found that the experimental composition of the GC-CSC complex deviated from the stoichiometric composition calculated from the degree of dissociation of individual ionizable groups at the given pH in the pH range studied (Fig. 4).

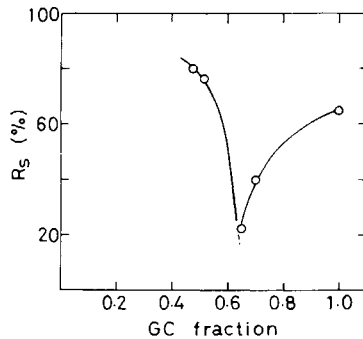


Fig. 3. Salt rejection plotted vs. GC fraction in membrane. Test conditions: 25°C, 60 atm, pH 5.80, and 0.10 wt % NaCl.

The fact that the isoelectric composition obtained from the reverse osmosis measurements is close to the complex composition obtained from the turbidimetric measurements is noteworthy from the viewpoint of the predictability of permeation properties of membranes from the turbidimetric measurements. The deviations from the calculated stoichiometric composition at given pH's may mainly result from the induced ionization of uncharged groups by oppositely charged groups. However, even at the region where the net charge is close to zero, there may be many charged groups on the complex because of the geometric hindrance brought about by the bulky pyranose ring, as we have suggested in the previous paper. As a result, the salt rejection may not be zero at any com-

position. Anyway, these results show that the principle of the salt rejection of these membranes is ionic in nature. Both the interaction between fixed charges and mobile coions of salt solutions, often referred to as Donnan exclusion, and the interaction between the oppositely charged segments in the complex are responsible for the salt rejection, as is shown in the equilibrium of a polyampholyte molecule with small ions.

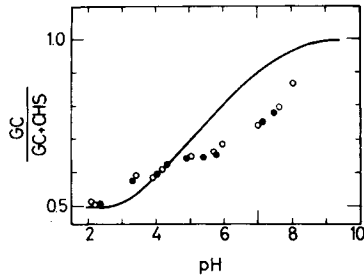


Fig. 4. GC fraction in GC-CS complex plotted vs. pH for GC-CSC (O) and GC-CSA (●) systems.⁸ Solid curve denotes the relation when complex formation is performed stoichiometrically.

Another characteristic of the permeation properties of a GC-CSC membrane is the dependence of the salt rejection on the operating pressure (see Fig. 2). This would be due to the compaction of these highly swollen membranes (water content at atmospheric pressure is ca. 50%) at high pressure. This effect will result in an increased charge density in the membrane, and, consequently, in an increased salt rejection. Similar permeation properties were found on GC-Hep membranes (Fig. 5).

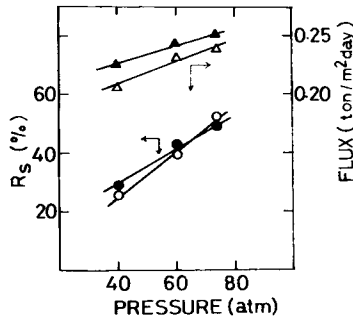


Fig. 5. Salt rejection and flux vs. operating pressure for (●, ▲) 66:34, and (○, Δ) 62:38 GC-Hep membranes. Test conditions: 25°C, pH 5.80, and 0.10 wt % NaCl.

As mentioned before, these membranes have a strong acidic group and two weak ionic groups. Therefore, the permeation properties of these membranes would also depend on the pH of the feed solution as well as on the composition of the membranes. In Figure 6, the salt rejection and the flux are plotted against the pH of the feed solution for GC-Hep membranes and a GC membrane. With the GC membrane having a weak basic group ($-NH_2$), both the salt rejection and flux decrease with increasing pH value of the feed solution as a result of change in the degree of ionization of $-NH_2$ groups in the membrane. With respect to GC-Hep membranes, both the salt rejection and flux were found to be dependent on pH and to give a minimum at around pH 6, a pH presumed to be the isoelectric point. Similar results were reported for ionic block copolymers by Kamachi et al.^{10,11}

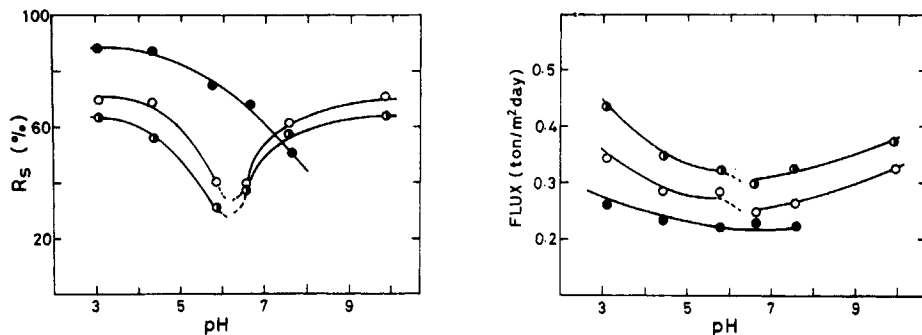


Fig. 6. Salt rejection and flux vs. pH of feed salt solution for (○) 66:34 and (◐) 62:38 GC-Hep membranes and for GC membrane (●). Test conditions: 74 atm, 25°C, and 0.10 wt % NaCl.

As is shown in Figure 7, GC-CSC membranes exhibit similar permeation property. The test conditions (0.2N NaCl at 84 atm) were selected to compare the results with the results of Yasuda et al.^{12,13} for ionic membranes. They found that, for ionic membranes, irrespective of the kind of charge, the chemical nature of the polymer and the film morphology, the salt rejection R_s , and the water permeability K_1 are related by

$$K_1 = A \exp(-BR_s) \quad (2)$$

where A and B are constants. However, the obtained results for GC-CSC membranes, as well as for GC-Hep membranes and GC membrane, are in disagreement with the relationship, that is, minimum flux is obtained around at minimum salt rejection. It is known that crosslinked polyelectrolyte gels exhibit contractile properties owing to the change in the ionization state of the system. The pH change, therefore, would cause change in thickness of the membrane. This may be one of the reasons of such differences in the flux-versus-salt rejection relationships.

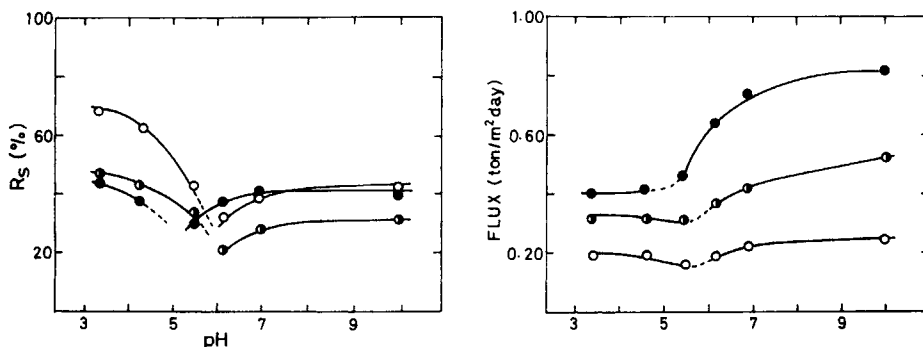


Fig. 7. Salt rejection and flux vs. pH of feed salt solution for (○) 83:17, (◐) 77:23, and (●) 59:41 GC-CSC membranes. Test conditions: 84 atm, 25°C, and 1.15 wt % NaCl.

The isoelectric point estimated from Figure 7 for various GC-CSC membranes at high NaCl concentration deviates from that obtained from turbidimetric measurements (Fig. 4), in spite of the good agreement for systems at low NaCl concentration (Fig. 3). This may be caused by the difference in ionic strength of the feed solution. The interaction between acidic groups and basic groups

TABLE I
Organic Solute Separation Properties of Complex Membranes^a

Membrane type	Solute retention, %		
	Urea	Glucose	Sucrose
GC(0.65)–CSC(0.35)	3.2	54.5	73.0
GC(0.62)–Hep(0.38)	5.5	55.0	68.0
GC(0.66)–Hep(0.34)	5.5	57.5	65.5

^a Test conditions: 74 atm, 0.25 wt % solute.

in the membrane would largely be affected by the ion-shielding activity of the electrolytes in the solution, especially at high ionic strength.

Polyelectrolyte complex membranes were evaluated as ultrafiltration membranes. Typical performance data on organic solute retention for some GC–CSC and GC–Hep membranes are shown in Table I. The result that % solute retention of all the membranes increases with increasing molecular weight of solute suggests the distribution of the pore size of the membranes. However, the permeation property would depend on the pressure, because considerable compaction would occur at high pressure.

References

1. H. G. Bungenberg de Jong, *Colloid Science*, Vol. 2, H. R. Kruyt, Ed., Elsevier, Amsterdam, 1949.
2. A. S. Michaels, *Ind. Eng. Chem.*, **57**, 32 (1965).
3. A. S. Michaels and R. G. Miekka, *J. Phys. Chem.*, **65**, 1765 (1961).
4. A. S. Michaels, G. L. Falkenstein, and N. S. Schneider, *J. Phys. Chem.*, **69**, 1456 (1965).
5. A. S. Michaels and H. J. Bixler, Eds., *Kirk–Othmer Encyclopedia of Chemical Technology*, 2nd ed., Vol. 16, Interscience, New York, 1968, p. 117.
6. A. Rembaum, *Appl. Polym. Symp.*, **22**, 299 (1973).
7. M. K. Vogel, R. A. Cross, and H. J. Bixler, *J. Macromol. Sci. Chem.*, **A4**(3), 675 (1970).
8. A. Nakajima and K. Shinoda, *J. Colloid Interfac. Sci.*, to be published.
9. A. Nakajima, K. Shinoda, T. Hayashi and H. Sato, *Polym. J.*, **7**, 550 (1975).
10. M. Kamachi, M. Kurihara, and J. K. Stille, *Macromolecules*, **5**, 161 (1972).
11. M. Kurihara, M. Kamachi, and J. K. Stille, *J. Polym. Sci.*, **11**, 587 (1973).
12. H. Yasuda, C. E. Lamaze, and A. S. Schindler, *J. Polym. Sci.*, **9**, 1579 (1971).
13. H. Yasuda and A. S. Schindler, *Reverse Osmosis Membrane Research*, H. K. Lonsdale and H. E. Podall, Eds., Plenum Press, New York, 1972.

Received December 30, 1975

Revised April 6, 1976