

Preparation of Macroreticular Anion Exchange Membrane and its Behavior Relating to Organic Fouling

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Synopsis

Base membranes were prepared by coating a monomer mixture consisting of styrene-divinylbenzene-polybutadiene-*t*-amyl alcohol onto a polypropylene cloth and subsequently by polymerizing the monomers. The resultant base membranes were chloromethylated and then quaternized. Thus, macroreticular anion exchange membranes were prepared and their properties were investigated. Furthermore, the organic fouling of the membranes was studied by using Na dodecylbenzenesulfonate as a foulant. The resistibility of the membranes was dependent on the balance between the porosity of the membranes and the foulant quantity.

INTRODUCTION

A serious drawback in practical use of anion exchange resins of gel type is the fact that they are easily stained by anionic organic substances in brackish water,¹⁻⁴ and macroreticular anion exchange resins have therefore been prepared to get rid of organic fouling.⁵⁻⁷ Similarly, organic fouling of anion exchange membranes has also been one of the most serious problems in electro-dialytic desalination of brackish water,⁸⁻¹¹ and porous anion exchange membranes have been prepared in order to overcome the organic fouling in this process.¹²⁻¹⁴ Hodgdon and Alexander¹⁴ have prepared macroreticular anion exchange membranes as follows: the base membranes were first prepared by bulk polymerization of styrene(St)-divinylbenzene (DVB) in the presence of a solvent good for the monomers but poor for the resultant polymer, between glass plates by using a synthetic fabric both as spacer and reinforcing material; the resultant base membranes were chloromethylated and subsequently quaternized with trimethylamine.

This paper is concerned with the preparation of a macroreticular anion exchange membrane and its behavior relating to organic fouling by sodium dodecylbenzenesulfonate (Na-DBS) as model of the anionic organic substances.

EXPERIMENTAL

Preparation of Macroreticular Anion Exchange Membranes

All the reagents used were of commercial grade. The monomer mixtures, with the recipes shown in Table I, were coated onto a polypropylene cloth as

reinforcing material, and the resultant composites were wrapped with cellophane film and heated at 80°C for 10 hr in order to polymerize the monomers by the use of benzoyl peroxide as polymerization initiator. The resultant base membranes were chloromethylated with chloromethyl methyl ether containing stannic chloride as a catalyst (2–3% by volume) at 25°C for 5 hr and subsequently quaternized with an aqueous solution of trimethylamine (15%) at room temperature for 24 hr.

Measurements

Alternating current electric resistance, water content, and anion exchange capacity of the anion exchange membrane were measured by the ordinary methods.¹⁵ The electric resistance at 1000 Hz was measured in a 0.5*N* NaCl solution at 25°C. The concentration of the fixed anion exchange group was shown as the quotient of anion exchange capacity/water content. Transport number was calculated by the use of the Nernst equation from the membrane potential measured at 25°C in the following system: 0.5*N* NaCl solution/membrane/2.5*N* NaCl solution. Diffusion coefficient of the membrane for NaCl was determined by the use of Fick's law from the diffusion rate of NaCl through the membrane, determined at 25°C with stirring in the following system: water (120 ml)/membrane/4*N* NaCl solution (300 ml). The stirring rate was kept at 1500 rpm in order to eliminate the influence of the diffusion boundary layers at the membrane/solution surfaces.

The fouling curve, in other words, the change in voltage across the membrane (V_m), was measured at 25°C by the aid of the apparatus shown in Figure 1. The volumes of the solutions in both the anode and cathode compartments were 120 ml each. The change in the concentration of Na-DBS in the cathode compartment was measured with stirring (1500 rpm) as follows: an aliquot of the solution (5 ml) was taken out of the compartment at definite time intervals and the amount of Na-DBS was determined by means of UV spectroscopy ($\lambda_{\max} = 220 \text{ m}\mu$).

The changes in the pH values of the solutions in the anode and cathode compartments were measured with stirring (1500 rpm) at 25°C with the aid of a pH meter by use of the apparatus shown in Figure 1.

RESULTS AND DISCUSSION

In this study, polybutadiene was added to the monomer mixture in order to make it easy to coat the monomer mixture onto the reinforcing material. This also made it possible to use the previously reported process for the "paste method," a semicontinuous process.¹⁶

Figure 2 shows the relation between the *t*-amyl alcohol (*t*-AmOH)/(St+DVB) value and the water content, the anion exchange capacity, and the concentration of the fixed anion exchange group. The increase in the water content with increase in the *t*-AmOH/(St+DVB) value could be considered to show that the resultant anion exchange membranes became more porous. On the other hand, the anion exchange capacity decreased with increase in the *t*-AmOH/(St+DVB) value. Accordingly, the tendency of the concentration of the fixed anion exchange group was reasonably understandable.

Figure 3 shows the relations between the *t*-AmOH/(St+DVB) value and

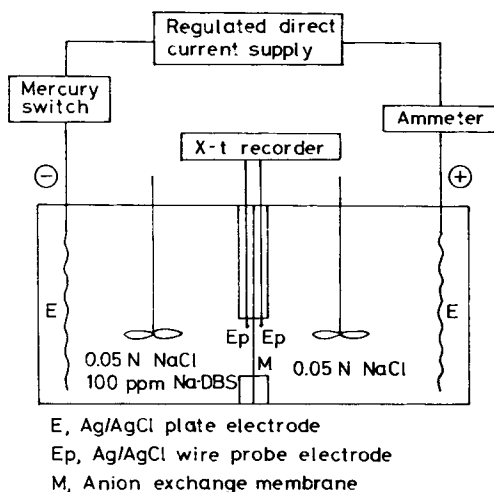


Fig. 1. The apparatus: effective area of the membrane, 10 cm².

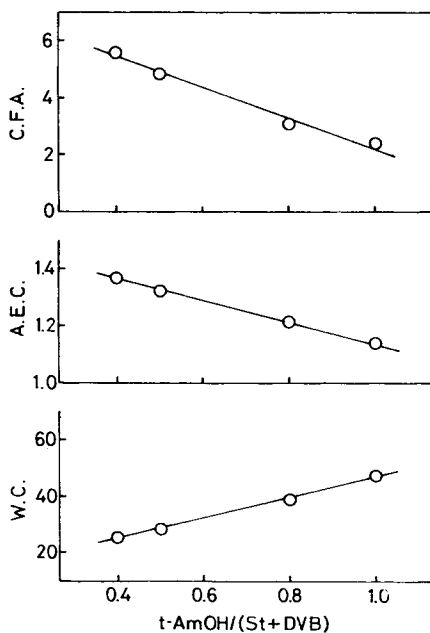


Fig. 2. Water content W.C. (g H₂O/g dry membrane), anion exchange capacity A.E.C. (meq/g dry membrane), and concentration of fixed anion exchange group, C.F.A. (meq/g H₂O).

the electric resistance, the transport number, and the diffusion coefficient of the membrane for NaCl. The membranes became more porous with increase in the $t\text{-AmOH}/(\text{St}+\text{DVB})$ value, so the tendency of the electric resistance could be easily understood. The increase in the diffusion coefficient and the decrease in the transport number with increase in the $t\text{-AmOH}/(\text{St}+\text{DVB})$ value could be explained in terms of the decrease in the concentration of the fixed anion exchange group: decrease in the concentration of the fixed anion exchange group results in an increase in the NaCl concentration in the mem-

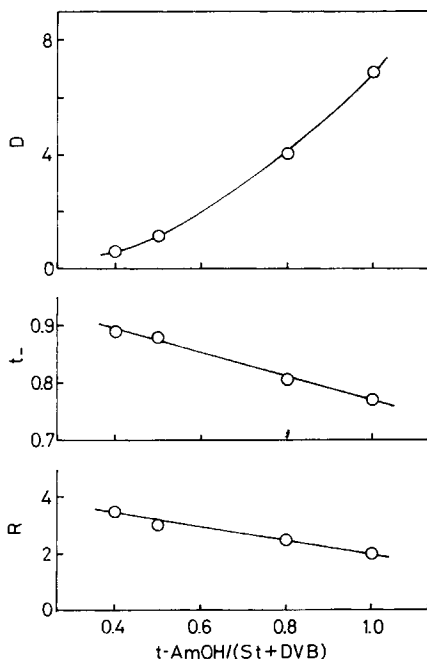


Fig. 3. Alternating current electric resistance R (ohm-cm²), transport number t , and diffusion coefficient for NaCl, D (cm²/hr).

brane phase when the membrane is soaked in NaCl solution, because the Donnan exclusion by the fixed anion exchange group for NaCl becomes less effective, which means that the NaCl becomes more permeable through the membrane. It is inevitable that the macroreticular anion exchange membrane has a smaller transport number and a larger diffusion coefficient than ordinary, tightly structured anion exchange membranes, and the outline of the results described above is approximately similar to that reported by Hodgdon and Alexander.¹⁴

Figure 4 shows the fouling curves of the anion exchange membranes by Na-DBS. Here, a relatively smaller current density (2 mA/cm²) was used so as to make it easy to elucidate the interaction between Na-DBS and the membranes. Clearly, the fouling curves were much affected by the t-AmOH/(St+DVB) value, and the more porous membrane was more resistant. Referring to the fact that tightly structured anion exchange membranes (for example, Neosepta AV-4T and Neosepta ACH-45T, manufactured by Tokuyama Soda Co., Ltd.) showed a rapid increase in V_m value,¹⁷ the shapes of the fouling curves shown in Figure 4 should be characteristic of macroreticular anion exchange membranes.

Figure 5 shows the change in the Na-DBS concentration in the cathode compartment with time. Membrane no. 4 was more resistant than membrane no. 1 but adsorbed more Na-DBS. Furthermore, although some amount of Na-DBS was adsorbed to membrane no. 4, it showed no increase in the V_m value. This means that the adsorption of Na-DBS will not always cause an increase in V_m value. Due to the fact that membrane no. 4 was more porous than membrane no. 1, the Na-DBS amount adsorbed to membrane no. 4 was more than that in

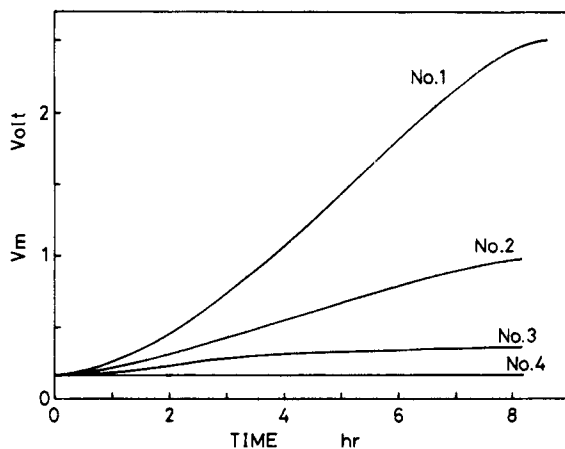


Fig. 4. Fouling curves of anion exchange membranes nos. 1-4 shown in Table I at 25°C; current density, 2 mA/cm².

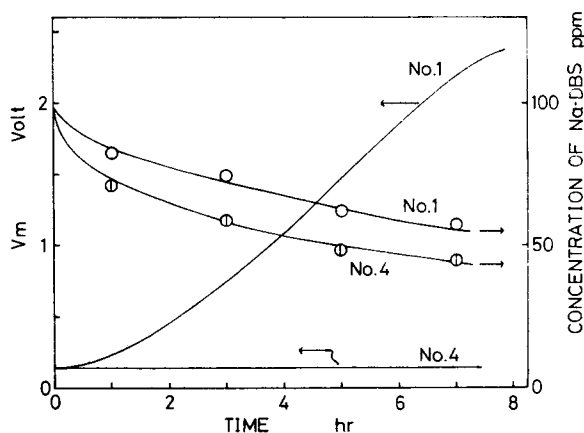


Fig. 5. Decrease in Na-DBS concentration in the cathode compartment at 25°C: membranes nos. 1 and 4 shown in Table I; current density, 2 mA/cm².

brane no. 4 was more than that in the case of membrane no. 1, but not enough to hinder transfer of the Cl anion through membrane no. 4. In the case of membrane no. 1, even when the adsorbed Na-DBS amount was less than that in the case of membrane no. 4, the adsorbed Na-DBS caused the hindrance of the transfer of the Cl anion, namely, an increase in V_m value. These results show that the adsorbed Na-DBS is increasingly accumulated in the membrane up to a limit in the amount of adsorbed Na-DBS (limit 1) without any increase in V_m value; and after exceeding this limit, the adsorbed Na-DBS should cause an increase in V_m value.

Since the Na-DBS amount in the case of membrane no. 4 was not enough to hinder the transfer of the Cl anion, it became an interesting question what would happen by adding more Na-DBS. Thus, a NaCl solution containing Na-DBS of 500 ppm was used in the cathode compartment. This amount of Na-DBS was clearly enough to be accumulated in membrane no. 4 over the limit and caused an increase in V_m value, as shown in Figure 6. Here, no Na-DBS was

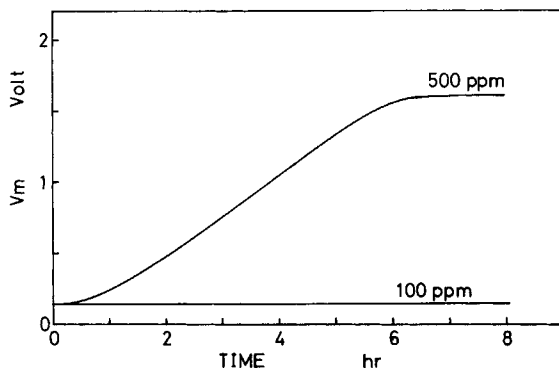


Fig. 6. Effect of Na-DBS concentration on the change in V_m value at 25°C: membrane no. 4 shown in Table I; current density, 2 mA/cm².

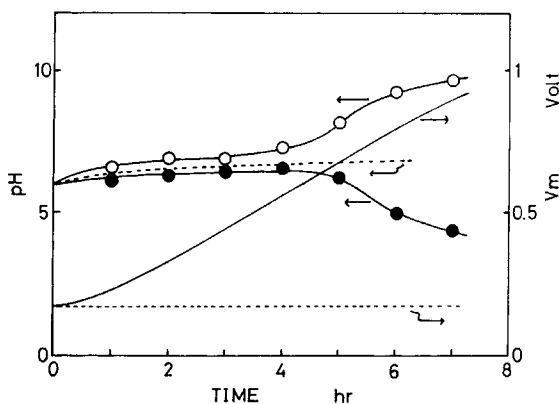


Fig. 7. Relation between change in the V_m value and pH changes of the solutions in both the anode and cathode compartments at 25°C: membrane no. 2 shown in Table I; dotted lines, no foulant; (O) anode compartment; (●) cathode compartment; current density, 2 mA/cm².

detected in the anode compartment even after supplying current for 7 hr; namely, no Na-DBS migrated through the membranes although the membranes were macroreticular.

The changes in the pH values of the solutions in both the anode and cathode compartments are shown in Figure 7. In the case of the control, no changes in pH and V_m values were observed. On the other hand, when the solution in the cathode compartment contained Na-DBS, an increase in V_m value with no pH change was observed for the first 4 hr, after which time distinct pH changes occurred. This shows that the accumulation of Na-DBS in the membrane caused an increase in V_m value, but no pH change. Therefore, there should be another limit of adsorbed Na-DBS amount (limit 2) over which the pH changes would be engendered. Summarily, Na-DBS was accumulated in the membrane with no increase in V_m value at first, and when its amount exceeded limit 1, the V_m value began to increase with no pH changes up to the limit 2. As soon as the adsorbed Na-DBS amount exceeded limit 2, the adsorbed Na-DBS apparently began to compose a multilayer on the membrane surface, while the V_m value increased. This means that a dielec-

tric layer was formed on the membrane surface. So, water splitting was engendered by the dielectric layer and pH changes of the solutions occurred. Probably, the formation of the multilayer is also the reason why no Na-DBS migrated through the macroreticular membranes.

As described above, the fouling phenomenon of macroreticular anion exchange membranes is dependent on the balance between the porosity of the membrane and the Na-DBS quantity in the solution, so the adsorbed Na-DBS amounts at limit 1 and limit 2 should be characteristic of each membrane, depending on the balance. Accordingly, in order to evaluate its practical applicability, the relation between membrane porosity and amount of organic foulant with various molecular shapes and sizes must further be investigated with regard to resistibility of the macroreticular anion exchange membrane to organic fouling.

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