

Charge Mosaic Membranes Prepared from Laminated Structure of Charged Gel Layers: Effect of Membrane Structure on the Salt Permselectivity

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A charge mosaic membrane has high permselectivity for electrolytes. This property is desired for purification of biochemical materials and food additives. There have been many reports of attempts to prepare such membranes. However, it is difficult to make charge mosaic membranes for practical applications. We here report on the preparation of charge mosaic membranes prepared from laminated structure of charged-poly(vinyl alcohol) membranes. The membranes were prepared by stacking negatively-charged membranes and positively-charged membranes alternately and by cutting the stack of the charged layers. Permeation experiments were performed in a dialysis system consisting of the membrane and mixed solutions of KCl and sucrose. Although the salt flux through the membrane is 10 times less than that through a charge mosaic membrane, Desalton (Tosoh Co., Ltd.) which was prepared using micro-phase separation, the permselectivity for salt of our membrane is 20 times higher than Desalton.

Key words: charge mosaic membrane, permselectivity, laminated structure, gel, desalination

1. INTRODUCTION

A charge mosaic membrane consists of anion- and cation-exchange regions arranged in parallel each other. Each charged region provides a continuous pathway from one membrane surface to the other. In the phenomenological theory proposed by Sollner [1], anions and cations can permeate through their respective countercharge regions in the membrane, resulting in circulating currents between individual ion-exchange regions. Hence, a charge mosaic membrane shows negative osmosis and much more efficient electrolyte transport than nonelectrolyte transport. These properties are desired for desalination of water or purification of biochemical materials or food additives. The existence of the circulating currents in the membrane was predicted theoretically by Kedem and Katchalsky [2] and investigated experimentally by Weinstein et al. [3]. The transport behaviors of the membrane can be explained using the battery model for the circulating currents. The theory shows that a charge mosaic membrane has higher permselectivity for salts in the case that: (1) each charged domain pass through the membrane perpendicularly; (2) it has short distance between the cation- and anion-exchange regions; (3) the charge density in the anionic and cationic domains is similar and as high as possible.

Various techniques have been developed for preparing

charge mosaic membranes. Fujimoto and coworkers succeeded in fabricating a charge mosaic membrane which has a microphase-separated structure (domain size about 50nm) containing striped regions of positive and negative charges provided by a pentablock copolymer [4-7]. Desalton (Tosoh Co., Ltd., Tokyo) is the commercial name for the membrane. There have been many preparation methods for charge mosaic membranes: a polymer blend with a modulated structure [8], an epitaxial process of phase growth [9-12], laser-induced surface graft polymerization [13] and microsphere gel [14]. However, it is difficult to make charge mosaic membranes for practical applications.

In this study, we report on the preparation of charge mosaic membranes prepared from laminated structure of charged-poly(vinyl alcohol) membranes.

2. EXPERIMENTAL

2.1. Samples

Aqueous solutions of a mixture of PVA[poly(vinyl alcohol), Aldrich] and AP-2[Kuraray CO. Ltd.] were cast for negatively-charged membranes, and those of PVA and PAAm[poly(allylamine), Nittobo Industries Inc.] were cast for positively-charged membranes. The volume fraction of PVA and AP-2 or PAAm was changed to control the charge densities of the charged membranes. AP-2 is a kind of PVA which contains 2 mol% of

2-acrylamido-2-methylpropane sulfonic acid groups as a copolymer, and hence provided negatively-charged sites. Charge mosaic membranes were prepared as follows: after swelling the charged PVA membranes in ion-exchanged water, we stacked negatively-charged membranes and positively-charged membranes alternately and past them with PVA aqueous solution as binder. After drying the stack of the membranes for 6 h. in a vacuum oven, charge mosaic membranes were obtained by cutting the stack by using a cutting machine (Maruto, CO. MC-120). The membranes were annealed at 160 °C for 20 min. and crosslinked in a glutaraldehyde solution.

2.2. Measurement of membrane water content

The water content was measured as follows: the membrane, weighted in the dry state, was immersed in an ion-exchanged water for 3 days. The membrane was removed from the water, tapped with filter paper to remove excess water on the membrane surface, and was weighted in the wet state. The water content is given from the weights in the wet state, W_w , and in the dry state, W_d , as:

$$H = \frac{W_w - W_d}{(W_w - W_d) + W_d / 1.3} \quad (1)$$

where 1.0 and 1.3 are the densities of water and PVA.

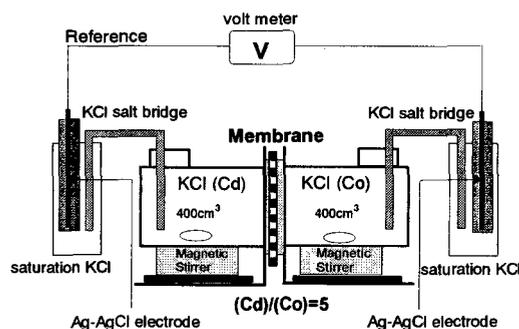


Fig. 1 Apparatus for membrane potential measurement.

2.3. Determination of the membrane charge density

Membrane potentials $\Delta\phi$ were measured using an apparatus shown in Figure 1 as a function of the KCl concentration of the chambers. From the measured membrane potential, the membrane charge density C_x was calculated in terms of [15,16],

$$\Delta\phi = -\frac{RT}{F} \ln \left(r \cdot \frac{\sqrt{C_x^2 + (2C_o)^2} - C_x}{\sqrt{C_x^2 + (2rC_o)^2} - C_x} \right) - \frac{RT}{F} W \ln \left(\frac{\sqrt{C_x^2 + (2rC_o)^2} - C_x W}{\sqrt{C_x^2 + (2C_o)^2} - C_x W} \right) \quad (2)$$

where $W = (\omega_K - \omega_{Cl}) / (\omega_K + \omega_{Cl})$; ω_K and ω_{Cl}

are the K^+ and Cl^- ion mobilities in a membrane, respectively; F , R and T are the Faraday constant, the gas

constant and the absolute temperature, respectively. C_o is the KCl concentration on the low-concentration chamber; r is the concentration ratio between the high- and the low-concentration chambers. Parameters W and C_x were adjusted so that the left-hand side of Eqn. (2) fits the experimental data of $\Delta\phi$ at various KCl concentration.

2.4. Measurement of the domain size

A charge mosaic membranes were soaked in an acid dye solution (Suminal Fast Blue R, Sumitomo Chemical Co.) for 6 h. Since the dye colored only the positively-charged layers dark blue, the thickness of the domain size between the charged layer of the membrane can be measured with a microscope.

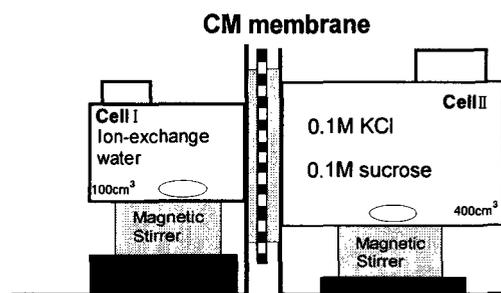


Fig. 2 Apparatus for permeation experiment. One chamber of the cell was filled with a mixed solution of 0.1M KCl and 0.1M sucrose and the other was filled with an ion-exchanged water. The volume of the chambers at the low- and the high-concentration sides were 100 cm³ and 400 cm³, respectively. The effective membrane area of the cell is 2.54 cm².

2.5. Permeation Experiments

Permeation experiments were performed with magnetic stirring, using an apparatus shown in Figure 2. The solution in the chamber at the low-concentration side was sampled to measure the concentration of K^+ ions by a conductivity meter (HORIBA Ltd., ES-12). The concentration of sucrose was also measured by using a UV-VIS detector (MILTON ROY CO., SPECTRONIC 20D).

3. RESULTS AND DISCUSSION

In order to make a charge mosaic membrane with high permselectivity for salts, the membranes should have the same charge density in the negatively and positively charged domains. Hence, we obtained the charged density of negatively- and positively-charged PVA membranes as a function of the polyanion content, C_{pa} , and the polycation content, C_{pc} , respectively, to estimate the best value of the polyelectrolyte content in the two charged membranes. The experiments, whose results are not described here, revealed that $C_{pa}=60\text{mass}\%$ for negatively-charged layers of and $C_{pc}=8\text{mass}\%$ for positively-charged ones are the best polyelectrolyte contents for preparing a charge mosaic membrane.

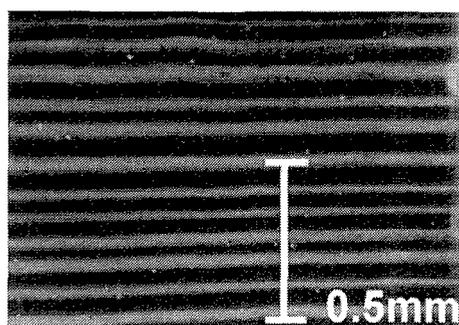


Fig. 3 A photograph of the charge mosaic membrane CM-1. The light parts correspond to the cation-exchange domains, the dark parts to anion-exchange domains.

Fig. 3 shows a photograph of the charge mosaic membrane CM-1. The distance between the ion-exchange domains is ca. $42 \mu\text{m}$. The distance is about 2,100 times larger than that of a charge mosaic membrane prepared by microphase separation method [4-7].

Fig. 4 shows the membrane potential of the charge mosaic membranes obtained as well as a negatively- and a positively-charged membranes. When the KCl concentration is low, the potentials of a cation-exchange membrane and an anion-exchange one are about 40mV and -40mV , respectively. The potential of the charge mosaic membranes are about 0mV and -10mV for CM-1 and CM-2, respectively. This means that: the charge density of the two charged layers in both CM-1 and CM-2 membranes has the same values each other; and the total domain area of the positively-charged layers in CM-2 are slightly larger than that of the negatively-charged layers.

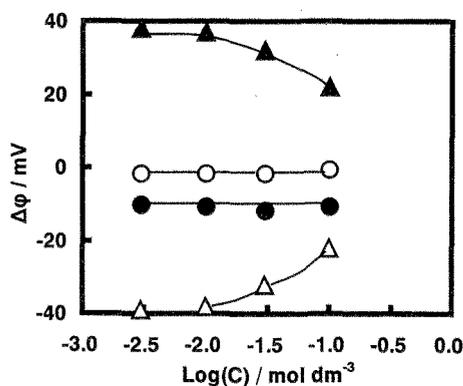


Fig. 4 The membrane potential of the charge mosaic membranes obtained in this study, and a negatively- and a positively-charged membranes.

(○) and (●) are the data for CM-1 and CM-2, respectively; (▲) and (△) are those for a negatively- and positively charged membranes, respectively.

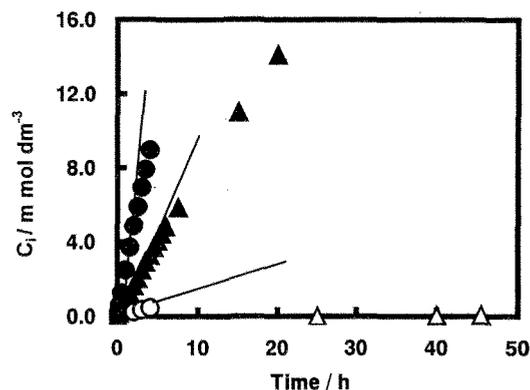


Fig. 5 Time-concentration curves of KCl and sucrose through membrane CM-1 and CM-2.

(●) and (○) are the data for KCl and sucrose through CM-1, respectively; (▲) and (△) are those through CM-2, respectively.

Table I : Characteristics of charge mosaic membranes obtained in this study: water content, H , membrane thickness, d , permeability coefficient of KCl, and sucrose, P_{KCl} and P_{suc} , respectively, and permselectivity between KCl and sucrose, α .

Sample	H [-]	d [μm]	P_{KCl} [cm^2/s]	P_{suc} [cm^2/s]	α [-]
CM-1	0.60	220	5.9×10^{-10}	2.1×10^{-11}	28
CM-2	0.39	180	1.6×10^{-10}	1.3×10^{-13}	1200

Fig. 5 shows time-concentration curves of KCl and sucrose through membrane CM-1 and CM-2. The permeability coefficient of KCl, P_{KCl} , and that of sucrose, P_{suc} , were obtained from the slope of the curves. Permselectivity between KCl and sucrose, $\alpha \equiv P_{KCl}/P_{suc}$, was obtained from the ratio of the coefficients. The permeability coefficient of CM-1 and CM-2 were also obtained from the permeation experiment and were listed in Table I as well as the water content and membrane thickness. The water content of membrane CM-2 is much smaller than that of membrane CM-1 because membrane CM-2 was crosslinked by glutaraldehyde. The values of both P_{KCl} and P_{suc} decrease with decreasing water content. P_{suc} decreases more rapidly than P_{KCl} does. Hence, the permselectivity increases with decreasing of the water content, and CM-2 has higher permselectivity for salt. In order to compare the charge mosaic membrane obtained in this study with the membrane prepared by the other methods, the characteristics of these membranes were listed in Table II. Desalton was prepared using a microphase separation of pentablock copolymers so that it has very small domain size in the alternating regions of positive and negative charges. This small domain size gives the membrane much higher salt flux than the other charge mosaic membranes. CM-3 was

Table II : Characteristics of charge mosaic membranes: domain size of the charged layers, r_d , membrane thickness, d , flux of KCl, J_{KCl} and sucrose, J_{suc} , permselectivity between KCl and sucrose, α .

Membrane	r_d	d	J_{KCl}	J_{suc}	α
CM-1	42000	220	2.7×10^{-8}	9.4×10^{-10}	28
CM-2	42000	180	9.0×10^{-9}	7.3×10^{-12}	1200
CM-3	1500	1	2.0×10^{-8}	1.2×10^{-9}	17
Desalton	20	300	9.9×10^{-8}	1.6×10^{-9}	60

prepared using an epitaxial process of phase growth [12]; hence, the thickness of the membrane is over 100 times less than that of the other membranes. Although the salt flux of CM-2 is less than that of CM-3 and Desalton, the permselectivity of CM-2 is 20 times higher than that of Desalton because of the lower flux of sucrose through CM-2. From the theoretical point of view, the less domain size a charge mosaic membrane has, the higher permselectivity for salt it has. Although the domain size of CM-2 is over 2000 times larger than that of Desalton, the permselectivity of CM-2 is 20 times higher than that of Desalton. Such a high permselectivity of CM-2 probably comes from the difference of membrane charge structure between CM-2 and Desalton: (1) CM-2 has almost 100% of the effective membrane area while Desalton has less than 50% of the area because it has over 50% of non-permeable regions; (2) all of the charged domains of CM-2 have a continuous pathway from one membrane surface to the other.

4. CONCLUSION

In this study, charge mosaic membranes were prepared from laminated structure of negatively charged- and positively charged poly(vinyl alcohol) membranes. The domain size between the charged layers of the membranes is over 2000 times larger than a charge mosaic membrane, Desalton which was prepared using micro-phase separation. Although the salt flux through the membrane obtained in this study is 10 times less than that through Desalton, the permselectivity for salt of the membrane is 20 times higher than that of Desalton.

5. ACKNOWLEDGMENT

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