

Effect of preparation conditions on transport properties of temperature-responsive charged membranes

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A membrane whose charge density changes in response to the temperature changes can control transport modes of specific ions. We prepared the temperature-responsive charged membrane from poly(vinyl alcohol)(PVA), polyanion and *in situ* polymer of N-isopropylacrylamide and PVA. In order to obtain the membranes with high temperature-response in the charge density, we examined the relationship between the preparation conditions and the membrane properties. Temperature-response in the charge density, rCx , depended on both r_p , which is the division of the polyanion content by the *in situ* polymer content, and glutaraldehyde concentration, C_g . rCx had a maximum value when r_p was 0.10 and C_g was 0.025vol%. Under these conditions, the value of the charge density at 50°C was 0.2 mol dm⁻³ and 9 times larger than that at 10°C. Key words : Temperature-responsive, Membrane, Transport mode, N-isopropylacrylamide, Charge density

1. INTRODUCTION

There are many studies on hydrogels, which change their volume in response to external stimuli such as pH [1-4], temperature [5-13], electric fields [14-16] and light [17-19]. The gels have potentials in applications for drug delivery, micro chemical chip because the volume change of the gel in response to external stimuli has been utilized to control permeability of solutes through the gel membrane. For some applications, such as 'intelligent' drug delivery system, it is needed to control not only the permeability but also the transport modes (*uphill* and *downhill* transport) of specific ions in response to external stimuli. It has been reported that the transport modes of specific ions through the charged membrane depend on the membrane charge density as shown in Fig.1 [20, 21]. When the charge density is lower than the concentration of the solution in the chambers, ions are transported along with their concentration gradient (*downhill* transport). On the other hand, specific ions are transported against their concentration gradient (*uphill* transport) when the charge density is higher than the concentration in the chambers. For the applications mentioned above, a membrane having high temperature-response in the charge density and high value of the charge density is needed for controlling the transport modes of ions.

The aim of this study is to examine the effect of the preparation conditions: the polyanion content and the crosslinking conditions, on the temperature-response in the charge density.

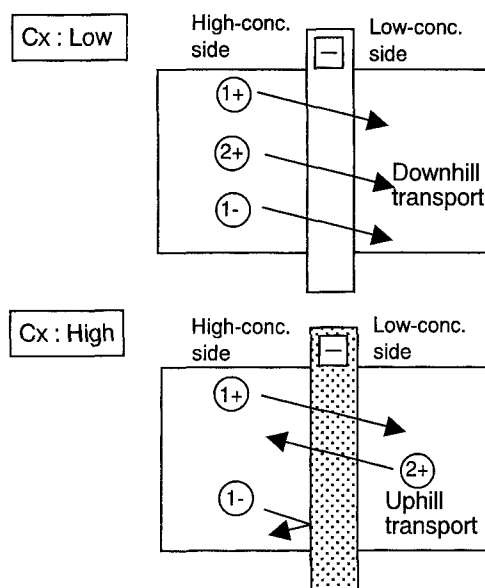


Fig.1 Control of ionic transport modes in response to charge density changes of a charged membrane.

2. EXPERIMENTAL

2.1. Sample membranes.

Temperature-responsive charged membranes were obtained by *in situ* polymerization of N-isopropylacrylamide [NIPAAm, Wako Pure Chemical Industries, Ltd.] in a poly(vinyl alcohol)[PVA, Aldrich] solution and by casting the mixture of dimethyl sulfoxide solution of the polymer obtained (*in situ* polymer), PVA and a polyanion, which contains sulfonic groups and hydroxyl groups. These membranes were annealed at 160°C for 20min and crosslinked in a glutaraldehyde solution at various concentrations at 25°C for 1 day.

2.2. Measurement of the water content.

The water content was measured as follows: the membrane, weighted in the dry state was immersed in an ion-exchanged water at a desired temperature for 6 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 as:

$$H = \frac{(W_w - W_d)/1.0}{(W_w - W_d)/1.0 + W_d/1.3} \quad (1)$$

where W_d and W_w are the weight in the dry state and that in the wet state, respectively, and 1.0 and 1.3 are the densities of water and the polymer, respectively. The water contents of the membranes were measured at 10°C and 50°C.

2.3. Measurement of the membrane charge density.

In order to examine temperature-response in the charge density, membrane potential, $\Delta\phi$, was measured using an apparatus shown in Fig. 2 as a function of the KCl concentration of the chambers. From the measured membrane potential, the charge density C_x was calculated in terms of [22, 23]:

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

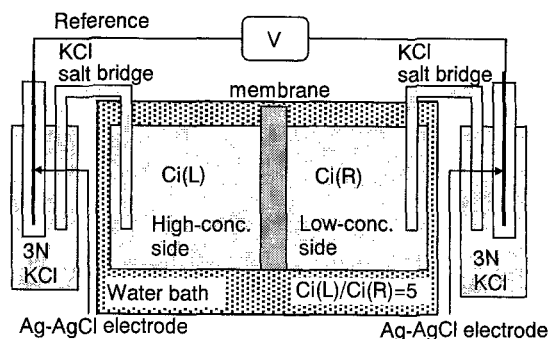


Fig.2 Apparatus of membrane potential measurements.

where $W = (\omega_K - \omega_{Cl})/(\omega_K + \omega_{Cl})$; ω_K and ω_{Cl} are the K^+ and Cl^- ion mobilities in the 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 concentrations.

3. RESULTS AND DISCUSSION

3.1 The effect of polymer content on the temperature-response in the charge density.

Fig. 3 shows the water content, H , of the temperature-responsive charged membranes as a function of r_p , where r_p is defined as the division of the polyanion content by *in situ* polymer content. The water content at 10°C was higher than that at 50°C. When the temperature is lower than the lower critical solution temperature (LCST) of polyNIPAAm chains in the *in situ* polymer, the polyNIPAAm chains are hydrophilic so that the membrane has high water contents. On the other hand, the polyNIPAAm chains become hydrophobic at the temperatures above the LCST, so that the water content decreases. The water content at 50°C increased with increasing r_p because the amount of the charged groups in the membrane increased with r_p . On the contrary, the water content at 10°C decreased with increasing r_p because the amount of physical crosslinking increased with hydroxyl groups which increase with r_p .

Figure 4 shows the relationship between the charge density and r_p . The charge density at 50°C was greater than that at 10°C for all the values of r_p . The charge

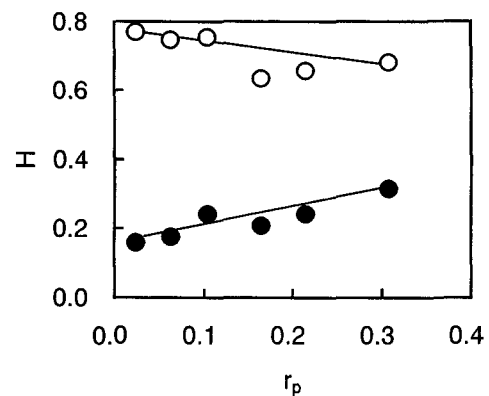


Fig.3 The water content, H , vs. the polymer ratio, r_p . ○:10°C, ●:50°C. PVA content, 15wt%; crosslinking condition, 0.025vol% glutaraldehyde.

density is proportional to the division of the ion-exchange capacity by the water content. The water content decreased with increasing the temperature as shown in Fig.3 while the temperature-response in the ion-exchange capacity, whose results are not shown here, was independent of the temperature changes. Hence, the charge density increases with increasing temperature. The charge density increased with increasing r_p at 10°C because the ion-exchange capacity of the membrane increased with increasing r_p . The charge density at 50°C had a maximum value when r_p was 0.21 and decreased when r_p was higher than 0.21 because the effect of the water content increase on the charge density decrease was greater than that of the ion-exchange capacity increase as r_p increased.

Figure 5 shows the temperature-response in the charge density, rCx , which is defined as the ratio of the charge density at 50°C and at 10°C, as a function of r_p . rCx increased with r_p because the increase of charge density at 50°C was greater than that at 10°C as shown in Fig.4. rCx had a maximum value when r_p was 0.10 and decreased because the increase ratio of the charge density at 50°C with r_p was less than that at 10°C when r_p was higher than 0.10.

3.2 The effect of glutaraldehyde concentration on the temperature-response in the charge density.

Figure 6 shows the charge density as a function of glutaraldehyde concentration, C_g . The values of the charge density both at 10°C and 50°C increased with C_g because the degree of crosslinking increased with C_g so

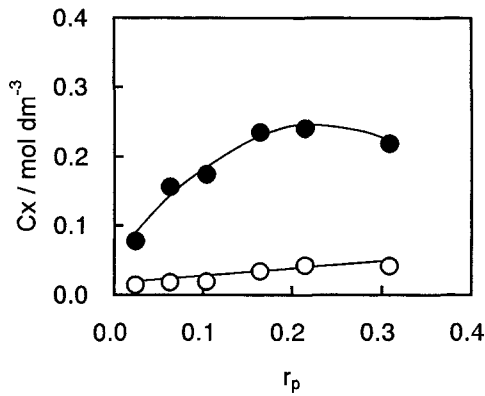


Fig.4 The charge density, C_x , vs. the polymer ratio, r_p .
○:10°C, ●:50°C.
PVA content, 15wt%; crosslinking condition, 0.025vol% glutaraldehyde.

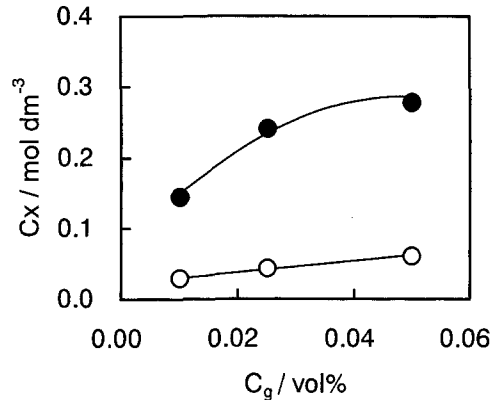


Fig. 6 The charge density, C_x , vs. the glutaraldehyde concentration, C_g .
○:10°C, ●:50°C.
PVA content, 15wt%; r_p , 0.21.

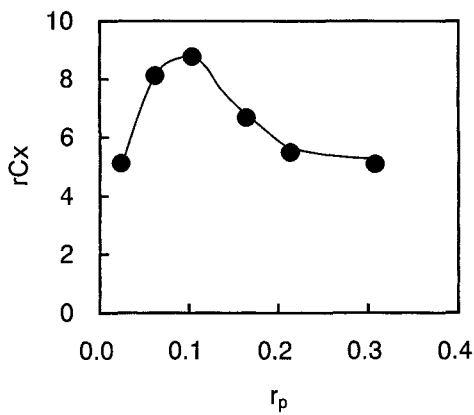


Fig.5 Temperature-response of the charge density, rCx , vs. the polymer ratio, r_p .
 $rCx=C_x(50^\circ C)/C_x(10^\circ C)$.

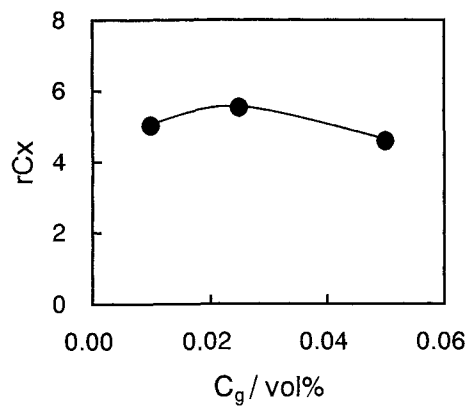


Fig.7 Temperature-response of the charge density, rCx , vs. the glutaraldehyde concentration, C_g .
 $rCx=C_x(50^\circ C)/C_x(10^\circ C)$.

that the water content decreased. On the other hand, the mechanical strength decreased with increasing C_g .

Figure 7 shows rCx as a function of C_g . rCx had a maximum value when C_g was 0.025vol%. When C_g was lower than 0.025vol%, the increase of the charge density at 50°C with C_g was greater than that at 10°C as shown in Fig.6 so that rCx increased with C_g . On the contrary, when C_g was higher than 0.025vol%, rCx decreased with increasing C_g because the increase of the charge density at 10°C was greater than that at 50°C. As a result, rCx had a maximum value when C_g was 0.025 vol%.

3.3 The effect of PVA concentration on the temperature-response in the charge density.

We prepared the membranes from PVA, polyanion and the *in situ* polymer. The mechanical strength of the membrane increases with the PVA content whereas the temperature-response in the charge density decreases with increasing PVA content. The temperature-response in the charge density depends on that in the water content, which decreases with increase of PVA content.

4. CONCLUSIONS

We prepared temperature-responsive charged membranes whose charge density increased with increasing temperatures. The ratio of the charge density at 50°C and at 10°C had a maximum value when the division of the polyanion content by the *in situ* polymer content was 0.10 and glutaraldehyde concentration was 0.025vol%. Under these conditions, the value of the charge density at 50°C was 0.2mol dm⁻³ and 9 times larger than that at 10°C. The computer simulations [21] predicted that a membrane having such a temperature-response in the charge density could control ionic transport modes by changing the temperature.

5. ACKNOWLEDGMENT

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