

Permselectivity of Anions through Gel Membranes Prepared from N-isopropylacrylamide and Poly(vinyl alcohol)

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We made a hydrogel membrane that has permselectivity between nitrate and fluoride ions. The membrane was prepared by *in situ* polymerization of N-isopropylacrylamide in a poly(vinyl alcohol)(PVA) solution and by crosslinking them with a glutaraldehyde(GA) solutions, changing PVA content, C_{PVA} , and GA concentration, C_{GA} , in order to investigate the effect of hydrophilicity of the membrane on the permeability of nitrate and fluoride ions. The permeation experiment in a dialysis system consisting of the membrane and mixed salt solutions shows that the permeability coefficient of fluoride ions, P_F , is higher than that of nitrate ions, P_{NO_3} , when C_{PVA} is low. On the other hand, P_{NO_3} is higher than P_F when C_{PVA} is high because the hydrophilicity of the membrane decreases with C_{PVA} . Both P_{NO_3} and P_F decrease with increasing C_{GA} because the hydrophilicity of the membrane decreases with increasing C_{GA} . These results indicate that the permselectivity of anions with same sign and same valence through a membrane can be controlled by changing the hydrophilicity of the membrane.

Key words : Membrane, permselectivity, N-isopropylacrylamide, hydrophilicity, Temperature-responsive

1. INTRODUCTION

Excessive fluoride content in water causes a multiplicity of ill effects for a human being e.g. fluorosis, osteoporosis, arthritis, hip fractures, cancer, infertility, thyroid disorder, brain damage and alzheimer disease etc. [1]. Nitrate ions also affect our health e.g. methemoglobinemias, blue baby syndrome and cancer [2]. The concentration of fluoride and nitrate ions in ground water increases recently because of ground water mining and heavy usage of nitrogen fertilizers in agriculture, respectively. Thus, removal of these ions from ground water is needed for improving the quality of drinking water. One of the methods to remove ions is membrane separation. Hence, development of a membrane that has high permselectivity between these ions is needed for improving the quality of drinking water.

In general, the permeability coefficient, P_i , through a membrane is given from the diffusion coefficient, D_i , and the solubility coefficient, S_i , in the membrane as:

$$P_i = D_i \times S_i \quad (1)$$

D_i is a function of ionic mobility in water and membrane water content, and S_i depends on chemical affinity difference between ions and membrane matrix.

The permselectivity due to the diffusion coefficient depends on the crosslinking degree of a membrane [3-6]. For example, the permselectivity between calcium and sodium ions through an ion-exchange membrane depends on the degree of crosslinking [7]. However, this method will induce the increase of the electric resistance of the membrane.

The other way to control the permselectivity is changing the solubility coefficient of ions. Sata et al. have tried to control the solubility coefficient of anion-exchange membranes by coating polyanion on the membrane surfaces. The permeability of chloride ions decreases by electric repulsion between the polyanion and ions [8]. Sata et al. [9-11] also have tried to control the solubility coefficient by changing the hydrophilicity of anion exchange groups in a membrane to control permselectivity between anions with the same sign and the same valence. Gibbs hydration energy of fluoride

ions is larger than that of nitrate ions [12]. Hence, the hydrophilicity of fluoride ions is higher than that of nitrate ions. This indicates that the permselectivity between these two anions can be controlled by changing the hydrophilicity of the membrane. Poly (N-isopropylacrylamide) (PNIPAAm) is well known as a temperature-responsive polymer that has a lower critical solution temperature (LCST) at 32 °C and changes its hydrophilicity as a function of the temperature [13-16]. Thus, the hydrophilicity of a membrane prepared from PNIPAAm and poly(vinyl alcohol) (PVA) will be controlled by changing both PNIPAAm/PVA ratio and the temperature because the hydrophilicity of PNIPAAm will be higher than that of PVA at temperatures below the LCST, but lower at temperatures above the LCST.

In this study, we prepare a temperature-responsive membrane by casting a polymer obtained by *in situ* polymerization of N-isopropylacrylamide in a poly(vinyl alcohol) (PVA) solution and by crosslinking a membrane obtained. The effect of PNIPAAm/PVA ratio on the permselectivity of nitrate and fluoride ions is investigated. We also examine the relationship between the permeability of these ions and glutaraldehyde concentration in the crosslinking process.

2. EXPERIMENTAL

2.1 Sample membranes.

Temperature-responsive membranes were prepared 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) and PVA. These membranes were annealed at 160°C for 20min and crosslinked in a glutaraldehyde aqueous solution 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:

$$H \equiv \frac{(W_w - W_d)/1.0}{(W_w - W_d)/1.0 + W_d/1.3} \quad (2)$$

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 content of the membranes was measured at 10°C and 50°C.

2.3 Permeation Experiment.

Permeation experiment was performed in a diffusion dialysis system consisting of the temperature-responsive membrane and mixed sodium nitrate and sodium fluoride solutions as shown in Figure 1 at 10°C and at 50°C. The chamber of cell I was filled with a mixed salt solution of 1.0×10^{-4} mol dm⁻³ sodium nitrate and 1.0×10^{-4} mol dm⁻³ sodium fluoride, and the chamber of cell II was filled with a mixed salt solution of 1.0×10^{-2} mol dm⁻³ sodium nitrate and 1.0×10^{-2} mol dm⁻³ sodium fluoride. The volumes of cell I and II were 100 cm³ and 400 cm³, respectively. The concentration changes with time of fluoride and nitrate ions in cell I were measured using an ion chromatograph (Hitachi Co. L-3710).

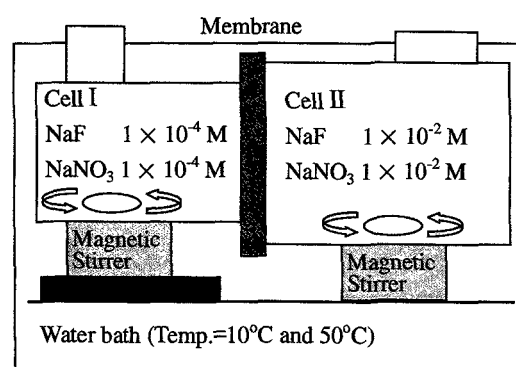


Fig.1 Apparatus for permeation experiment.

The permeability coefficient of the two anions, P_i , is calculated from the slope of the time-concentration curves using the following equation:

$$P_i = \frac{V_0 \cdot d \cdot \Delta C_i^I}{(C_{i,0}^{II} - C_{i,0}^I) \cdot S \cdot \Delta t} \quad (3)$$

where V_0 , d and S are the volume of cell I, the thickness and area of the membrane, respectively; $C_{i,0}^I$ and $C_{i,0}^{II}$ are the ionic concentration of cell I and cell II, respectively and $\Delta C_i^I / \Delta t$ is the initial concentration change at cell I.

The permselectivity between nitrate and fluoride ions is defined from the permeation coefficients of the two anions as:

$$\alpha \equiv \frac{P_{NO_3}}{P_F} \quad (4)$$

where P_{NO_3} and P_F are the permeation coefficient of nitrate and fluoride ions, respectively.

3. RESULTS AND DISCUSSION

3.1 The effect of PVA content on the permselectivity between nitrate and fluoride ions.

In order to investigate the effect of PVA content of the

membrane, C_{PVA} , on its hydrophilicity, we measured membrane water content, H , by changing C_{PVA} at a temperatures below the LCST of PNIPAAm (10°C) and above the LCST (50°C). Figure 2 shows H as a function of C_{PVA} . The value of H decreases with increasing C_{PVA} at 10°C . This indicates that the hydrophilicity of PNIPAAm chains is higher than that of PVA at temperatures below the LCST. On the other hand, the increase of H at 50°C with increasing C_{PVA} indicates that the hydrophilicity of PNIPAAm chains is lower than that of PVA at temperatures above the LCST. These results show that the hydrophilicity of the membrane can be controlled by changing both temperature and PVA/PNIPAAm ratio. The permselectivity between nitrate and fluoride ions through the membranes will depend on both C_{PVA} and temperature. Thus, we performed the permeation experiment using the membranes at 10°C and at 50°C .

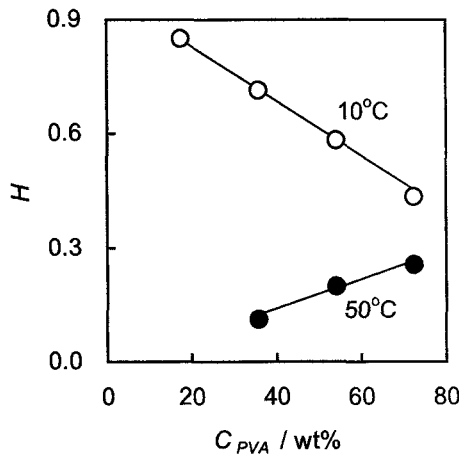


Fig.2 The water content, H , as a function of PVA content, C_{PVA} .
Glutaraldehyde concentration, 0.01 vol%.

Figure 3 shows one example of the permeation experiments at 10°C . We calculated the permeability coefficient, P_i , from the slope of the time-concentration curves in the permeation experiments.

Figure 4 shows P_i obtained from the time-concentration curves at 10°C and 50°C as a function of C_{PVA} . At the low temperature, the permeability coefficient of both fluoride ions, P_F , and nitrate ions, P_{NO_3} , decrease with increasing C_{PVA} while that of the two anions increase with C_{PVA} at the high temperature. The dependence of P_i on C_{PVA} in Figure 4 is due mainly to the water content change with C_{PVA} shown in Figure 2. Mackie and Meares [17] give ionic mobility in a water-swollen membrane, $\bar{\omega}_i$, as a function of its water content and ionic mobility in aqueous solution, ω_i , as:

$$\bar{\omega}_i = \frac{H^3}{(2-H)^2} \omega_i \quad (5)$$

The equation indicates that ionic mobility in a water-swollen membrane decreases with decreasing water content. Figure 2 shows that the water content of the membranes increases with C_{PVA} at 10°C , but decreases at 50°C . Hence, the permeability coefficient of both these anions decreases at 10°C , but increases at 50°C .

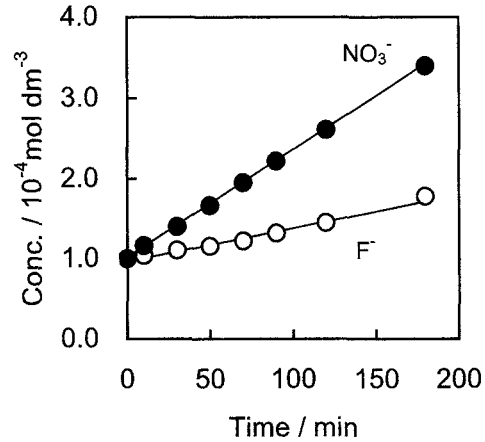


Fig.3 Time-concentration curves through the temperature-responsive membrane at 10°C .
 C_{PVA} , 54wt%; Glutaraldehyde concentration, 0.01 vol%.

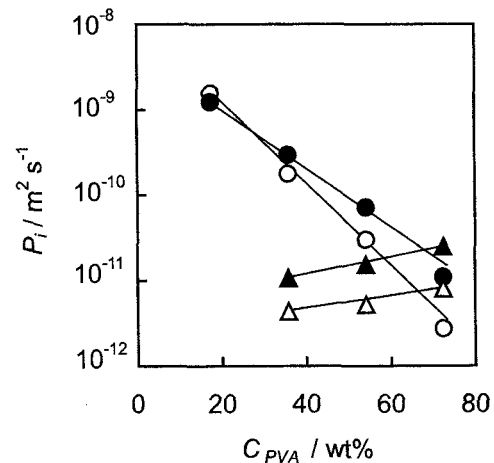


Fig.4 Permeability coefficient of anions, P_i , vs. PVA content, C_{PVA} .
Glutaraldehyde concentration, 0.01 vol%.
●: NO_3^- ion at 10°C , ○: F^- ion at 10°C ,
▲: NO_3^- ion at 50°C , △: F^- ion at 50°C .

Figure 5 shows the permselectivity between nitrate and fluoride ions, α , as a function of C_{PVA} . The permselectivity both at 10°C and at 50°C increases with C_{PVA} . This means that the more PVA content does the

membrane have, the more selectivity for nitrate ions it has because the decrease of the hydrophilicity of the membrane with increasing C_{PVA} gives the increase of the solubility of nitrate ions into the membrane. The value of the selectivity at 10°C changes with C_{PVA} more steeply than at 50°C. This means that the hydrophilicity of PNIPAAm chains at 10°C is higher than that of PVA. There have been many reports on ion-exchange membranes that have permselectivity for nitrate ions or for fluoride ions [9]; however, there is no report on a membrane that can control permselectivity between these ions changing its polymer content. Under the conditions that at a temperature below the LCST and when $C_{PVA} = 18\text{wt}\%$, the value of the selectivity is less than unity. This indicates that the permeability of fluoride ions is higher than that of nitrate ions under the conditions.

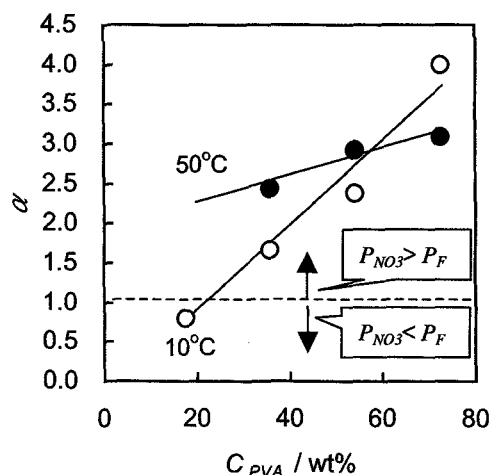


Fig.5 The permselectivity between nitrate and fluoride ions, α , as a function of PVA content, C_{PVA} . Glutaraldehyde concentration, 0.01 vol%.

3.2 The effect of glutaraldehyde concentration in the crosslinking process on the permselectivity between nitrate and fluoride ions.

We investigate the relationship between the permselectivity between fluoride ions and nitrate ions and the glutaraldehyde concentration, C_{GA} , in the crosslinking process. Both P_{NO_3} and P_F decrease with increasing C_{GA} although the water content, whose data does not shown here, is almost independent of C_{GA} . The steeper decrease of P_F than that of P_{NO_3} indicates that the hydrophilicity of the membrane decreases with increasing C_{GA} because the amount of hydroxyl groups in the membrane decreases with increasing C_{GA} .

4. CONCLUSIONS

We prepared the temperature-responsive membranes from PVA and N-isopropylacrylamide and measured permeability coefficient of nitrate and fluoride ions in a diffusion dialysis system. The membranes have permselectivity for fluoride ions under the conditions at temperatures below the LCST and $C_{PVA}=18\text{wt}\%$; and for nitrate ions under the other conditions. Both P_{NO_3} and P_F decrease with increasing the concentration of glutaraldehyde in the crosslinking process because the hydrophilicity of the membrane decreases by crosslinking reaction. These results indicate that the permselectivity between anions with same sign and same valence can be controlled by changing the hydrophilicity of membrane.

5. ACKNOWLEDGMENT

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6. REFERENCES

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