

Permselectivity of anions with same sign and same valence through temperature responsive anion-exchange membranes

Mitsuru Higa, Tomoko Yamakawa, Chika Miyamoto, Arifal,
Nobutaka Endo and Koji Matsusaki

Applied Medical Engineering Science,

Graduate School of Medicine, Yamaguchi University

Tokiwadai, 2-16-1, Ube City, 755-8611, Japan

Fax: +81-836-85-9201, e-mail: mhiga@yamaguchi-u.ac.jp

We describe design and preparation of temperature responsive anion-exchange membranes, which can control the permselectivity between anions with same sign and same valence in response to temperature changes. The membranes were prepared by casting dimethyl sulfoxide solution of mixed poly (vinyl alcohol)(PVA), poly(ally amine), and *in situ* polymer of PVA and N-isopropylacrylamide (NIPAAm). Poly(NIPAAm) chains in the membranes give the membranes high water content at temperatures below their lower critical solution temperature (LCST) (32 °C), and low water content at temperatures above the LCST. We performed permeation experiment in a dialysis system to investigate the permselectivity between fluoride and nitrate ions. The permselectivity, which is defined as the division of permeation coefficient of NO₃⁻ ion to that of F⁻ ion, increases at 50 °C, but decreases at 15 °C with increasing poly(NIPAAm) content because of the change of membrane hydrophilicity. This indicates that the permselectivity between the ions through the membrane can be controlled by changing the temperature and the poly(NIPAAm) content.

Key words: Anion-exchange membrane, N-isopropylacrylamide, Hydrophilicity, Temperature response Permselectivity

1. INTRODUCTION

Ion exchange membranes have been widely used in many industrial fields such as wastewater treatment and water purification because of their high selectivity between cations and anions. One of the unsolved problems in separation processes using the membranes is a lack of permselectivity between ions having same sign and same valence.

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

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

D_i is a function of ionic mobility in water and membrane water content; hence, the permselectivity due to the diffusion coefficient depends on the network structure of the membrane [1-4]. For example, the permselectivity between calcium and sodium ions through an ion-exchange membrane depends on the degree of crosslinking [5]. However, this method will induce the

increase of the electric resistance of the membrane. The other way to control the permselectivity is changing the partition coefficient of ions in the membrane. K_i depends on chemical affinity difference between ions and membrane matrix. The value of K_i can be changed, for example, by coating polyanion on the membrane surfaces [6], and changing the hydrophilicity of anion exchange groups [7-9]. The other way to control the partition coefficient of ions is changing the hydrophilicity of membrane matrix. 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 temperature [10-13]. Thus, the hydrophilicity of membrane matrix containing PNIPAAm will be controlled by changing both PNIPAAm content and the temperature. Yamakawa et al. [14] have prepared a temperature-responsive non-charged membrane from *in situ* polymer of poly(vinyl alcohol) (PVA) and PNIPAAm.

The permselectivity between nitrate and fluoride ions is a function of both PNIPAAm/PVA ratio and the temperature. In this paper, temperature-responsive anion-exchange membranes are prepared from poly(vinyl alcohol)(PVA), polycation, and *in situ* polymer of PVA and PNIPAAm to obtain a membrane having much higher selectivity for anions.

2. EXPERIMENTAL

2.1 Sample membranes.

Temperature-responsive anion-exchange membranes were prepared by casting a mixture of dimethyl sulfoxide (DMSO) solution of a poly(vinyl alcohol) [PVA, Aldrich], poly(allylamine)[PAAm, Nittobo Industries Inc.] and an *in situ* polymer of N-isopropylacrylamide [NIPAAm, Wako Pure Chemical Industries, Ltd.] and PVA. These membranes were annealed at 160 °C for 20 min and cross-linked in a mixture of 0.01 vol % glutaraldehyde, 0.1 mol dm⁻³ HCl, 2 mol dm⁻³ NaCl aqueous solution at 25 °C for 24 h.

2.2 Measurement of the water content.

The water content was measured as follows: the membrane, weighted in the dry state was immersed in 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 in the wet state, respectively, and 1.0 and 1.3 are the densities of water and the polymer, respectively. The water content was measured at 15 and 50 °C.

2.3 Measurement of the partition coefficient of ions.

The membrane, weighed in the dry state, W_d , was immersed in C_i ($= 0.5$) mol dm⁻³ mixed NaF and NaNO₃ solution at 15 and 50 °C for 1 h, then in 1.0×10^{-4} mixed NaF and NaNO₃ solution for 3 h. After being weighted in the wet state, W_w , the membrane was immersed in V ($= 30$) mL of 0.01N Na₂SO₄ solution for 3 h. The concentration of F⁻ and NO₃⁻ ions in the Na₂SO₄ solution C_K , was measured by an ion chromatograph (Hitachi Co. L-3710). The partition coefficient, K_i is defined as the division of the ionic concentration in the membrane and in the solution as:

$$K_i = \frac{30C_K}{(W_w - W_d)C_i} \quad (3)$$

2.3 Determination of the Charge Density.

The charge density was estimated from membrane

potential data [15]. The potential was measured at various temperatures, using an acrylic plastic cell of two parts separated by the membrane. One chamber of the cell was filled with KCl solutions of various concentrations (0.01, 0.03, 0.1M), C_o . The other chamber was filled with KCl solutions whose concentration was 5 times higher than those in the first chamber ($r=5$). From the measured membrane potentials, $\Delta\phi$, the charge density, C_x , was calculated in terms of

$$\Delta\phi = -\frac{RT}{F} \ln \left(r \cdot \frac{\sqrt{C_x^2 + (2C_o)^2} - C_x}{\sqrt{C_x^2 + (2rC_o)^2} - C_x} \right) - \frac{RT}{F} W \ln \left(\frac{\sqrt{C_x^2 + (2rC_o)^2} - C_x W}{\sqrt{C_x^2 + (2C_o)^2} - C_x W} \right) \quad (4)$$

where $W = (\omega_K - \omega_{Cl})/(\omega_K + \omega_{Cl})$, and ω_K and ω_{Cl} are the K⁺ and Cl⁻ mobilities in a gel membrane, respectively; F , R and T are the Faraday constant, the gas constant and the absolute temperature, respectively. Parameters W and C_x were adjusted so that the left-hand side of equation (4) fits the experimental data of $\Delta\phi$ at various KCl concentrations.

2.4 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 at 15 and 50 °C. The chamber of cell I was filled with a mixed salt solution of 1.0×10^{-4} mol dm⁻³ sodium nitrate, 1.0×10^{-4} mol dm⁻³ sodium fluoride, and 1.0×10^{-4} mol dm⁻³ sodium sulphate 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 of fluoride and nitrate ions in cell I were measured using an ion chromatograph (Hitachi Co. L-3710). The permeability coefficient of the two anions, P_i , is calculated from the slope of the time-concentration curves using the following equation:

$$P_i = \frac{V_o \cdot d \cdot \Delta C_i^I}{(C_{i,0}^{II} - C_{i,0}^I) \cdot S \cdot \Delta t} \quad (5)$$

where V_o , 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.

3. RESULTS AND DISCUSSION

3.1 The effect of PNIPAAm content on the water content.

In order to investigate the effect of PNIPAAm content in the membrane, C_{NIPAAm} , on its hydrophilicity, the water

content, H , measured by changing C_{NIPA} at temperatures below the LCST of PNIPAAm (15 °C) and above the LCST (50 °C) is shown in Figure 1. The value of H increases with increasing C_{NIPA} at 15 °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_{NIPA} 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 the PVA/PNIPAAm ratio.

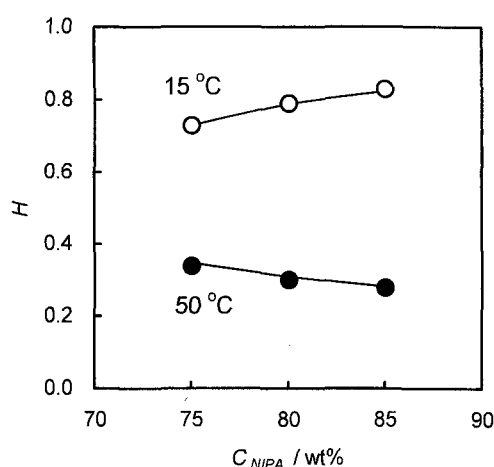


Fig.1 The water content, H , of the temperature-responsive anion-exchange membranes as a function of NIPAAm content, C_{NIPA} .

3.2 The effect of PNIPAAm content on the charge density

Figure 2 shows the charge density as a function of C_{NIPA} . The charge density at 50 °C is larger than that at 15 °C. The charge density of an ion-exchange membrane is defined as the division of the ion-exchange capacity of the membrane by its water content. The water content at 50 °C is lower than that at 15 °C as shown in Figure 1 while the ion-exchange capacity is almost independent of temperature. Hence, the charge density at 50 °C has higher values than at 15 °C. This indicates that the membranes have higher permselectivity between anions and cations at 50 °C than at 15 °C. The charge density at 50 °C increases with C_{NIPA} because of the decrease of the water content.

3.3 The selectivity in the partition coefficients as a function of PNIPAAm content

Figure 3 shows the selectivity in the partition coefficients, K_{NO_3}/K_F , as a function of C_{NIPA} . K_{NO_3}/K_F at 50 °C is larger than unity, but less than unity at 15 °C. This indicates that at 50 °C, the selectivity for NO_3^- ions

through the membrane is larger than that for F^- ions, and *vice versa* at 15 °C. The reason of the difference in K_{NO_3}/K_F between the two temperatures will be explained as follows: The Gibbs free energy for hydration and stokes radius are -270 kJ mol^{-1} and 1.29 \AA for a nitrate ion, and -434 kJ mol^{-1} and 1.66 \AA for a fluoride ion, respectively [16]; hence, a fluoride ion is more hydrophilic than a nitrate ion. From the results in Figure 2, the hydrophilicity of PNIPAAm chains is lower than that of PVA at temperatures above the LCST, but higher at temperatures below the LCST. Therefore, the low membrane hydrophilicity at 50 °C gives the high partition coefficient for hydrophobic NO_3^- ions. On the other hand, at 15 °C, the high membrane hydrophilicity gives the high partition coefficient for hydrophilic F^- ions. K_{NO_3}/K_F increases with C_{NIPA} at 50 °C, but decreases at 15 °C. This is due that the membrane hydrophilicity decreases with C_{NIPA} at 50 °C, but increases at 15 °C.

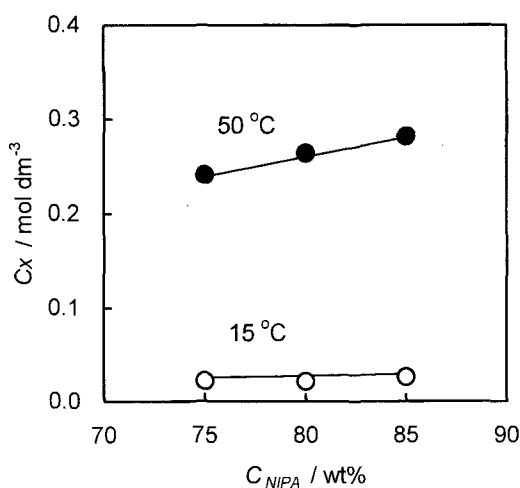


Fig.2 The charge density, C_x , of the temperature-responsive anion-exchange membranes as a function of PNIPAAm content, C_{NIPA} .

3.4 The permselectivity between NO_3^- and F^- ions as a function of PNIPAAm content

In order to examine the dependence of the partition coefficient ratio on the permselectivity, we performed the permeation experiment using the membranes at 15 and 50 °C.

Figure 4 shows the permselectivity between nitrate and fluoride ions, P_{NO_3}/P_F , as a function of C_{NIPA} . The permselectivity increases at 50 °C, but decreases at 10 °C with increasing C_{NIPA} . This means that the more PNIPAAm content does the membrane have, the more selectivity for nitrate ions it has because the decrease of the hydrophilicity with increasing C_{NIPA} gives the increase of the partition coefficient of nitrate ions as shown in Figure 3. The value of

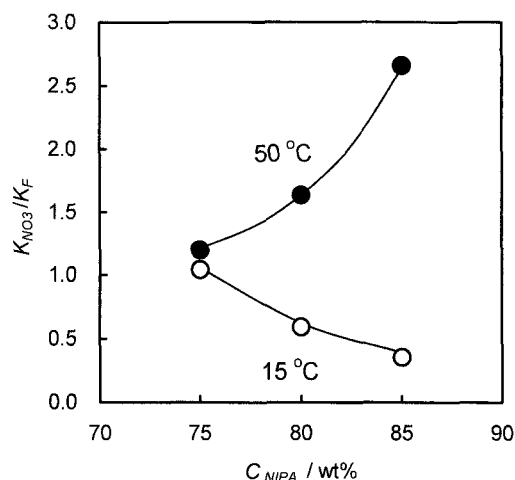


Fig.3 The Solubility coefficient ratio, K_{NO_3}/K_{F^-} , in the temperature-responsive anion exchange membranes as a function of NIPAAm content, C_{NIPAAm} .

the selectivity at 15 °C changes with C_{NIPAAm} more steeply than at 50 °C. This means that the hydrophilicity of PNIPAAm chains at 15 °C is higher than that of PVA. Under the conditions that at temperatures below the LCST and when $C_{NIPAAm} = 80\text{wt}\%$, the selectivity is less than unity. This indicates that the permeability of fluoride ions is higher than that of nitrate ions under the conditions.

4. CONCLUSIONS

We prepared temperature-responsive anion-exchange membranes from mixed poly (vinyl alcohol) (PVA), poly(allylamine), and *in situ* polymer of PVA and N-isopropylacrylamide (NIPAAm) and measured the water content, and the partition coefficient and permeability coefficient of nitrate and fluoride ions changing the temperature and the PNIPAAm content. The membranes have permselectivity for fluoride ions under the conditions at temperatures below the LCST and $C_{PVA}=80 \text{ wt } \%$, and for nitrate ions under the other conditions. These results indicate that the permselectivity between anions with same sign and same valence through the temperature-responsive anion-exchange membranes can be controlled by changing the hydrophilicity of the membrane.

5. ACKNOWLEDGMENT

This work was supported by the Salt Science Research Foundation, No. 0212.

6. REFERENCES

- [1] T. Sata, *J. Membr. Sci.*, **93**, 117 (1994).
- [2] M. Nishimura, M. Sugihara, M. Morioka, and M. Okita, *Kogyo Kagaku Zasshi*, **70**, 1040 (1967).
- [3] Y. Kosaka and H. Shimidzu, *Jpn. Pat.* 294, 387 (1961).

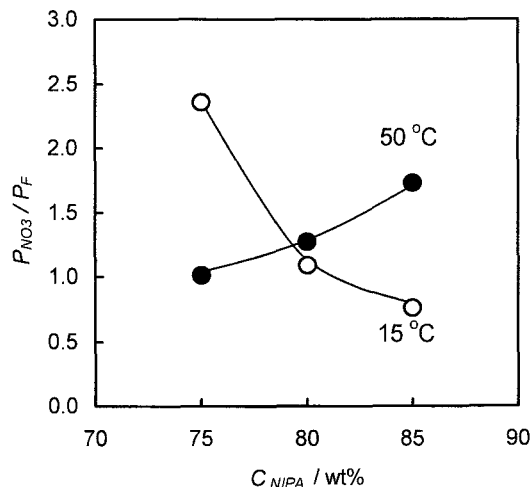


Fig.4 The permselectivity between nitrate and fluoride ions, P_{NO_3}/P_{F^-} , through the temperature-responsive anion exchange membranes as a function of NIPAAm content, C_{NIPAAm} .

- [4] T. Kawahara, H. Ihara and Y. Mizutani, *J. Appl. Polym. Sci.*, **33**, 1343 (1987).
- [5] T. Sata, T. Funakoshi and K. Akai, *Macromolecules*, **29**, 4029 (1996).
- [6] T. Sata, T. Yamaguchi, K. Matsusaki, *J. Membr. Sci.*, **100**, 229 (1995).
- [7] T. Sata, K. Teshima and T. Yamaguchi, *J. Polym. Sci. Part A: Polym. Chem.*, **34**, 1475 (1996).
- [8] M. Higa and Y. Tagami et al., *Trans. Mat. Res. Soc. J.*, **24**(2), 187 (1999).
- [9] T. Sata and K. Mine et al., *J. Chem. Soc., Faraday Trans.*, **94**(1), 147 (1998).
- [10] S. Kurihara, S. Sakamaki, S. Mogi, T. Ogata and T. Nonaka, *Polymer*, **37**, 1123 (1996).
- [11] G. Chen, A. S. Hoffman, *Nature*, **373**, 49 (1995).
- [12] T. Shimizu, M. Yamato, A. Kikuchi, T. Okano, *Biomaterials*, **24**(13), 2309 (2003).
- [13] H. Kanazawa, Y. Matsushima, T. Okano, *Source Adv. Chromatogr.*, **41**, 311 (2001).
- [14] T. Yamakawa, C. Miyamoto, S. Ishida, M. Higa and K. Matsusaki, *Trans. Mat. Res. Soc. J.*, **29**(6), 2599 (2004).
- [15] M. Higa and K. Akira, *J. Phys. Chem.*, **96**(23), 9518, (1992).
- [16] H. Ohotani, *Hydration of Ions*, Kyoritsu Shuppan, Tokyo, 30 (1992).

(Received December 24, 2004; Accepted April 15, 2005)