

Transport Properties of Ions through pH Memorizable Charged Membranes Prepared from Poly (vinyl alcohol)

Mitsuru Higa, Tomoichi Watabe 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 the design and preparation of a novel pH-memorizable charged membrane whose charge density has two values when it is immersed into low-pH and high-pH solutions. The membrane can memorize the values even after immersing it into a salt solution of intermediate pH. The membrane was prepared from an aqueous solution of poly(vinyl alcohol) which contains 1 mol% of itaconic acid groups as copolymer component. The membrane potential after treating the membrane with HCl solution of pH 1 has more than 8 mV higher value than that after treating it with NaOH solution of pH 13 for more than 400h even in a salt solution of pH=5.5. The permeability of Cl⁻ ion after the low-pH treatment is about 20 times larger than that after the high-pH treatment. The membrane maintains the high-permeability of anions even in the solution of pH=5.5. This indicates that the membrane can memorize pH states of solutions.

Key words: Memory effect, pH, gel, membrane potential, Ionic permeability, Charge density

1. INTRODUCTION

There are many potential applications of 'intelligent' hydrogel systems in many fields. Many of the hydrogels undergo abrupt changes in volume in response to external stimuli such as pH [1-4], temperature [5-13] electric fields [14-16] and light [17-19], so that the permeability of certain solutes through the gels can be controlled by these stimuli. For some applications, it would be very useful to have a charged membrane whose charge density has two values when it is immersed into low-pH and high-pH solutions, and can retain the values for long time period after immersing it into a salt solution of pH=5.5 as shown in Fig.1. Here we report such a novel pH-memorizable charged membrane.

2. EXPERIMENTAL

2.1 Sample preparation

A pH-memorizable charged membrane was prepared by casting an aqueous solution of IT-1 polymer [Kuraray CO. Ltd.] which contains 1 mol% of itaconic acid as copolymer component as shown in Fig.2, and by crosslinking it in a glutaraldehyde solution.

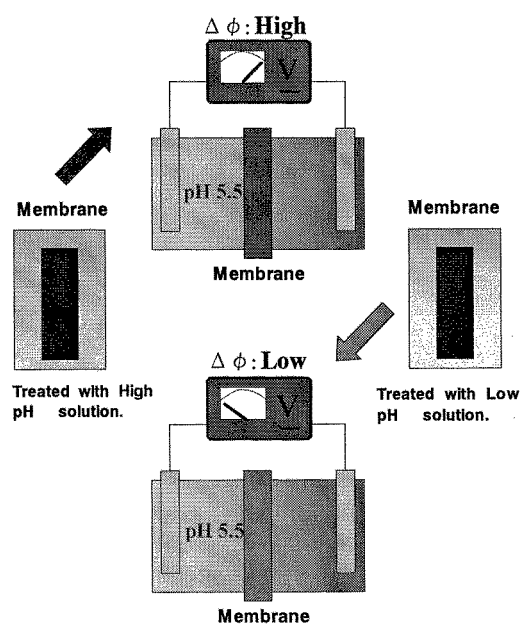


Fig.1 Schematic diagram of membrane potential changes of a novel pH-memorizable charged membrane. After immersing the sample membrane into treatment solutions with different pH, the membrane has different values of the membrane potential, and retains the values for long time period even in a salt solution of pH=5.5.

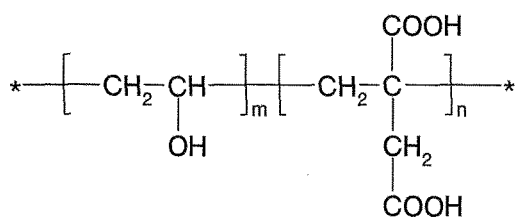


Fig. 2 Chemical structure of IT-1 polymer. Mole fraction of itaconic acid groups to vinyl alcohol groups is 1 mol %.

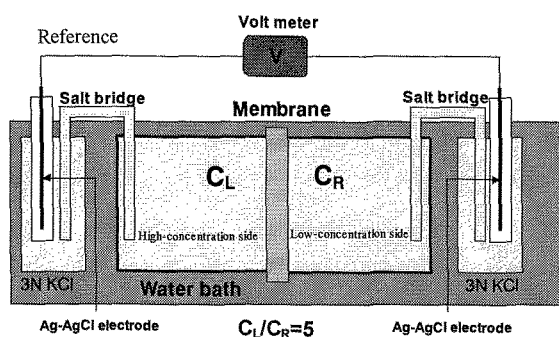


Fig. 3 Apparatus for membrane potential measurement. The membrane potential was measured using KCl solutions of pH=5.5.

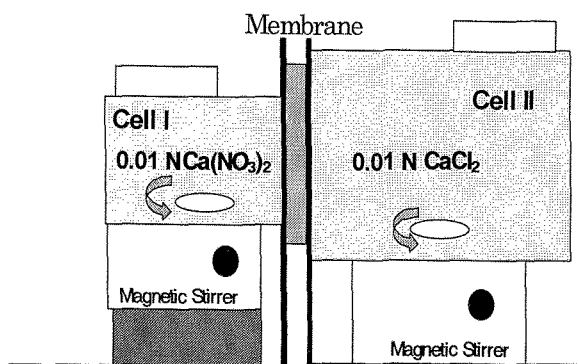


Fig. 4 Apparatus for permeation experiment. The volume of the chambers at the cells I and II were 100cm³ and 400 cm³, respectively. The effective membrane area of the cell is 7.04cm².

2.2 pH treatments

Before measuring the membrane potential and the permeation of ions and urea, the membrane was treated with the two solutions of different pH: a NaOH solution of pH=13 (high-pH treatment), and a HCl solution of pH=1 (low-pH treatment).

2.3 Membrane potential measurement

The membrane potential of the pH-memorizable charged membrane was measured at 25°C using an acrylic plastic cell of two parts separated by the membrane as shown in Fig.3. One chamber of the cell was filled with KCl solutions of various concentrations of pH=5.5. The other chamber was filled with KCl solutions whose concentrations were 5 times higher than those in the first chamber.

2.4 Permeation measurement

Permeation of ions and urea through the membrane at 25°C was measured in a dialysis system consisting of the membrane and two cells: cell I and cell II which contain 0.01N CaCl₂ and 0.01N Ca(NO₃)₂, respectively. The concentration change of Cl⁻ ion and urea in cell I was measured by an ion selective electrode and HPLC, respectively.

3. RESULTS AND DISCUSSION

3.1 Membrane potentials after the pH treatments

Fig. 5 shows the membrane potential through the membrane as a function of immersing time, t . When $t=48\text{h}$, the potential after the high-pH and the low-pH treatments are 28mV and 4.0mV, respectively. Although the potential difference between the two treatments decreases with time, the difference is still more than 8mV when $t>400\text{h}$. This indicates that the pH-memorizable charged membrane can memorize pH states of the treatment solutions for long time period. The Teorell-Meyer-Sievers theory shows that the higher values of the membrane potential a membrane has, the

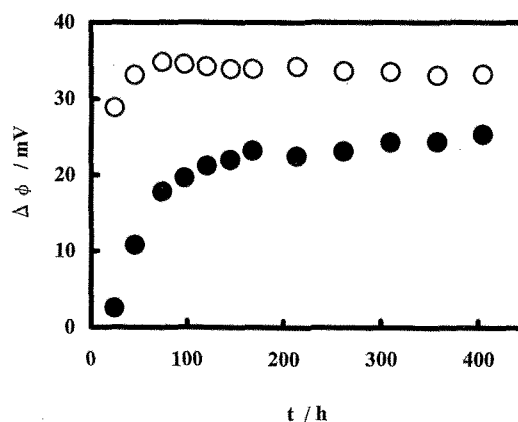


Fig. 5 Membrane potential, $\Delta\phi$, of membrane M-1 vs. immersing time, t . The membrane was immersed in KCl solution of pH=5.5 during the measurements. The open and solid circles are the data after the high-pH and low-pH treatment, respectively.

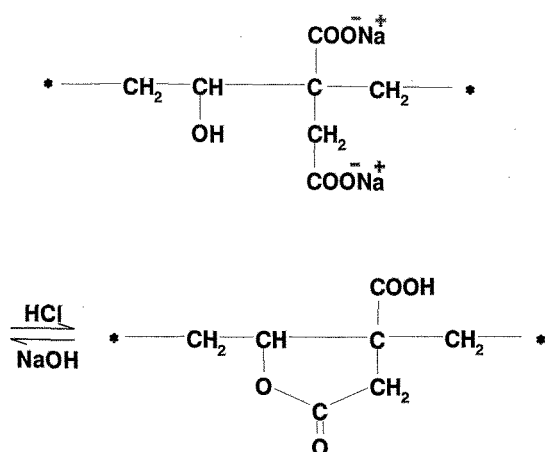
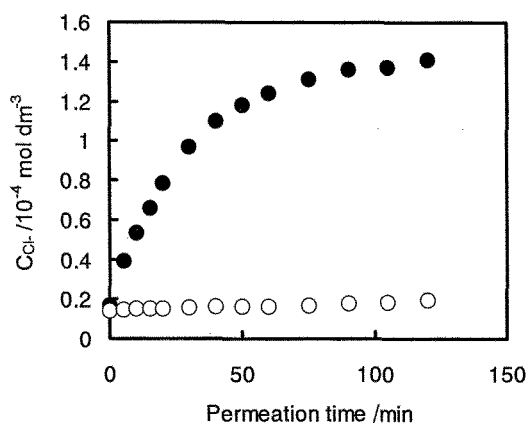


Fig. 6 The formation of lactone rings in the polymer chain.



higher charge density it has. Hence, the membrane after the high-pH treatment has higher charge density than that after the low-pH treatment.

Fig. 7 The Cl⁻ ion concentration change with time in mixed KCl and KNO₃ solutions of pH=5.5. Open and solid circles are the data after the high- and the low-pH treatments, respectively

The mechanism of the pH memory effect will be explained as follows: After the high-pH treatment, the carboxyl groups in the membrane dissociate; hence, the membrane has higher charge density as shown in Fig. 6. After the low-pH treatment, sodium ions in the membrane are exchanged for hydrogen ions in the solution. And then hydroxyl groups and carboxyl groups forms lactone rings. Therefore, the charge density decreases. The lactone rings will exist quasi-stably even in a salt solution of intermediate pH.

Table 1 Permeability coefficient of Cl⁻ ions and urea after the low-pH and high-pH treatments, $P(L)$ and $P(H)$, respectively and the ratio of the permeability coefficients, r_p .

solutes	$P(L)$ ¹⁾	$P(H)$ ¹⁾	r_p ²⁾
Cl ⁻	19	0.83	23
Urea	4.0	2.5	1.6

1) [$\times 10^{-8} \text{m}^2 \text{s}^{-1}$]. Immersing time=24h.

2) $r_p = P(L)/P(H)$

3.2 Ionic permeation change through the pH-memorizable charged membrane after the pH treatments

It is well known that ionic permeability through a charged membrane depends on its charge density [20-23]. We measured ionic permeation in a dialysis system consisting of the membrane and mixed KCl and KNO₃ solutions of pH=5.5 after the two different pH treatments. Fig. 7 shows the time-concentration curves of Cl⁻ ion at the cell I of the system shown in Fig.4. The permeability coefficient of Cl⁻ ion was calculated from the slope of the time-concentration curves and listed in Table 1. The permeability coefficient of urea was also calculated from the slope of its time-concentration curves, whose data are not shown here. The permeability of Cl⁻ ion after the low-pH treatment is about 20 times larger than that after the high-pH treatment while that of urea has almost same values between the treatments [24]. The reason why the permeability difference of the anion between the two treatments occurs even in the permeation experiment using salt solutions of pH=5.5 is that: after the high-pH treatment, the membrane has high values of the charge density as a negatively-charged membrane so that the permeation of anions through the membrane is low. The value of the charge density does not change even in a salt solution of pH=5.5. Therefore, the membrane maintained the low permeability state for anions. After the low-pH treatment, the charge density decreases; hence, the permeation of anions through the membrane has a high value. The permeation of non-charged solutes does not depend on the pH treatments because its permeation is independent of the value of membrane charge density; hence, the ratio of permeability coefficient of urea is almost equal to unity. These results show that the pH-memorizable charged membrane can control the permeability of only anions in response to the pH of the treatment solutions and maintain the state of the permeability for long time period even in a salt solution of pH=5.5.

4. CONCLUSIONS

We prepared a novel pH-memorizable charged membrane by casting an aqueous solution of poly(vinyl alcohol) which contains 1 mol% of itaconic acid groups as copolymer component, and by crosslinking it in a glutaraldehyde solution. The charge density of the membrane has two values when it is immersed into low-pH and high-pH solutions, and can retain the values even after immersing it into a salt solution of pH=5.5. The change of the charge density affects on membrane transport properties of ions: the permeability coefficient of Cl⁻ ion after low-pH treatment is more than 20 times higher than that after high-pH treatment. This function of the membrane will be applied to ionic devices such as chemical valves in chemical chips.

5. ACKNOWLEDGMENT

This work was supported by the Grant-in-Aid for Scientific Research on Priority Areas (A), No. 13022245, Grant-in-Aid for Scientific Research (C), No. 13640581, of the Ministry of Education, Culture, Sports, Science, Technology, the Salt Science Research Foundation, No.0212, Tateisi Science and Technology Foundation, No. 1031017 and Electric Technology Research Foundation of Chugoku, No. 89.

6. REFERENCES

- [1] T. Tanaka, *Phys. Rev. Lett.* **40**, 820 (1978).
- [2] T. Tanaka, *et al. Phys. Rev. Lett.* **45**, 1636 (1980).
- [3] R. A. Siegel, B. A. Firestone, *Macromolecules* **21**, 3254 (1988).
- [4] Y. Hirokawa, T. Tanaka, *J. Chem. Phys.* **81**, 6379 (1984).
- [5] A. S. Hoffman, *J. Controlled Release* **6**, 297 (1987).
- [6] Y. H. Bae, T. Okano, R. Hsu, S. W. Kim, *Makromol. Chem., Rapid Commun.* **8**, 481 (1987).
- [7] T. Okano, Y. H. Bae, H. Jacobs, S. W. Kim, *J. Controlled Release* **11**, 255 (1990).
- [8] L.-C. Dong, A. S. Hoffman, *J. Controlled Release* **15**, 141 (1991).
- [9] G. Chen, A. S. Hoffman, *Nature* **373**, 49 (1995).
- [10] R. Yoshida, *et al. Nature* **374**, 240 (1995).
- [11] T. Aoki, *et al. Macromolecules* **27**, 947 (1994).
- [12] M. J. Snowden, B. Z. Chowdhry, B. Vincent, G. E. Morris, *J. Chem. Soc., Faraday Trans.*, **92**, 5013 (1996).
- [13] H. Feil, Y. H. Bae, J. Feijen, S. W. Kim, *J. Membrane Sci.* **64**, 283 (1991).
- [14] T. Tanaka, I. Nishio, S.-T. Sun, S. Ueno-Nishio, *Science* **218**, 467 (1982).
- [15] I. C. Kwon, Y. H. Bae, S. W. Kim, *Nature* **354**, 291 (1991).
- [16] Y. Osada, H. Okuzaki, H. Hori, *Nature* **355**, 242 (1992).
- [17] K. Ishihara, N. Hamada, S. Kato, I. Shinohara, *J. Polym. Sci. Polym. Chem.* **22**, 881 (1984).
- [18] A. Suzuki, T. Tanaka *Nature* **346**, 345 (1990).
- [19] A. Suzuki, T. Ishii, Y. Maruyama, *J. Appl. Phys.* **80**, 131 (1996).
- [20] M. Higa, A. Tanioka, K. Miyasaka, *J. Membr. Sci.*, **49**, 145 (1990).
- [21] M. Higa, A. Kira, *J. Phys. Chem.* **96**, 9518 (1992).
- [22] M. Higa A. Tanioka and K. Misayaka, *J. Membr. Sci.*, **37**, 251 (1988).
- [23] M. Higa, A. Kira, A. Tanioka and K. Miyasaka, *J. Chem. Soc. Faraday Trans.*, **89**, 3433 (1993).
- [24] M. Higa *et al.* 38th Macromolecular IUPAC Symposium, 753, (2000).

(Received October 13, 2003; Accepted April 9, 2004)