# Effect of Ions on the Dynamic Behavior of an Electrodriven Ionic Polymer Hydrogel Membrane

**M. HOMMA, Y. SEIDA, Y. NAKANO**

Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Midori, Yokohama, Kanagawa 226-8502, Japan

**ABSTRACT:** The bending mechanism of an electrodriven ionic polymer hydrogel membrane was investigated in terms of the concentration of ionic groups and the valence of ionic species within the hydrogel membrane. It was elucidated that the distribution of the ionic concentration played an important role in the bending behavior of the membrane. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 76–80, 2001

## INTRODUCTION

The membranes of ionic polymer hydrogels in an electrolyte aqueous solution show bending in an electric field. Several researchers have investigated the bending behavior of the ionic hydrogel membrane.[1–4] Shiga and Kurauchi pointed out that the bending phenomenon took place because of the osmotic pressure caused by the difference in the ionic concentration between the inside and the outside of the gel.[3] However, there have been few reports on the bending mechanism analyzed experimentally from a viewpoint of ionic transport.

Ionic polymer hydrogel membranes with various concentrations of ionic groups were synthesized. The bending behavior of the electrodriven ionic polymer hydrogel membranes was investigated in electrolyte solutions with various valences of counter ion. The objective of this study was to elucidate the bending mechanism of the ionic hydrogel membrane based on the ionic transport.

## EXPERIMENTAL

Poly(vinyl alcohol)–poly(2-acryamide-2-methylpropane sulfonic acid) (PVA–PAMPS) membranes were used as the ionic polymer hydrogel membranes in this study. The polymerization of PVA–PAMPS gel membranes were carried out according to a procedure previously described.[5] The synthesized PVA–PAMPS gel membranes were washed with a large amount of distilled water and then immersed in a $Na_2SO_4$ or $CuSO_4$ aqueous solution until they came to equilibrium with it. The bending behaviors of the PVA–PAMPS gel membranes were evaluated following the procedure described in a previous article.[5] The bending angle ($\theta$) of the membrane was calculated by the following equation.
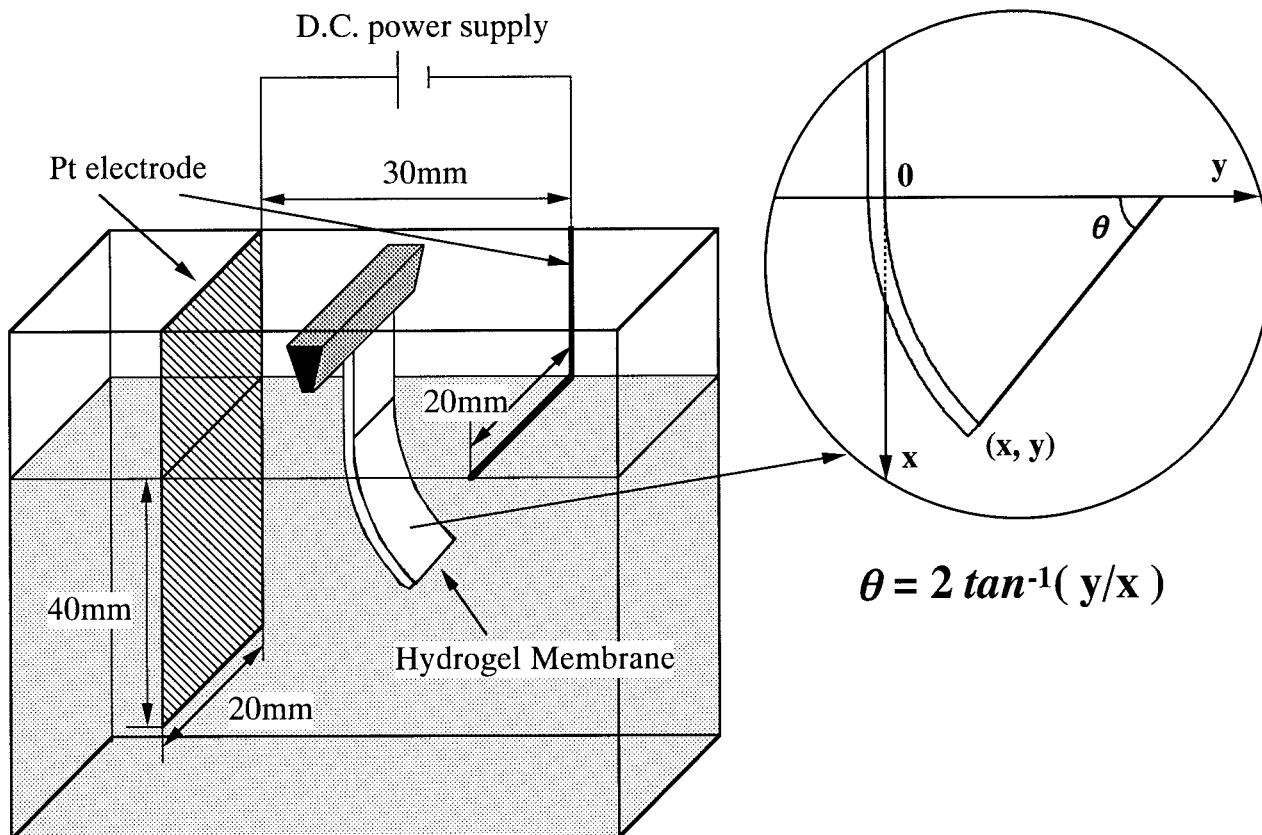
$$\theta = 2\tan^{-1}\left(\frac{y}{x}\right) \tag{1}$$

where $x$ and $y$ are the position of the free end of the membrane on the $x$–$y$ coordinate shown in Figure 1.

## RESULTS AND DISCUSSION

Figure 2 shows the effect of the amount of ionic groups on the bending rate. The value of the bend-
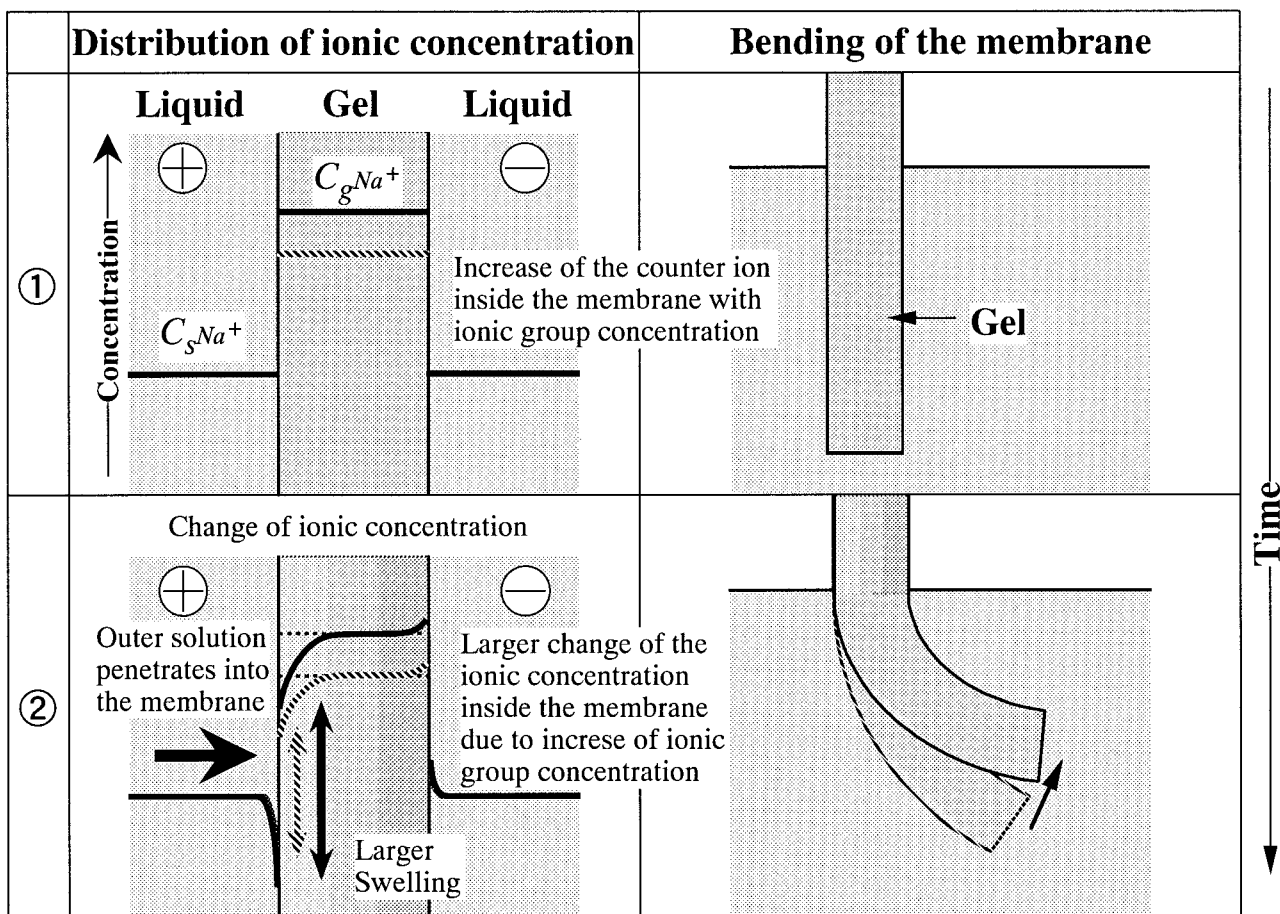
---

**Figure 1**    Schematic diagram of electrolytic cell for measuring the bending behavior of the membrane.

ing rate was corrected for the membrane thickness as described in a previous article.[5] The bending rate of the membrane increased with the concentration of ionic group below $1M$ AMPS. Figure 3 shows the schematic diagram of the relationship between the distribution of ionic concentration both in the membrane and in the outer solution and the bending of the membrane. At equilibrium, the concentration of counter ion in the membrane was higher than that in the outer solution because of Donnan equilibrium. In the applied electric field, the ionic concentration inside the membrane on the anode side decreased because of the transport of cation toward the cathode. The anode side of the membrane swelled because of the increase of the osmotic pressure derived from the difference in the ionic concentration at the membrane–solution interface on the anode side. The concentration of the counter ion in the membrane increased with the concentration of the ionic group even for the same concentration of the outer solution. The bending rate of
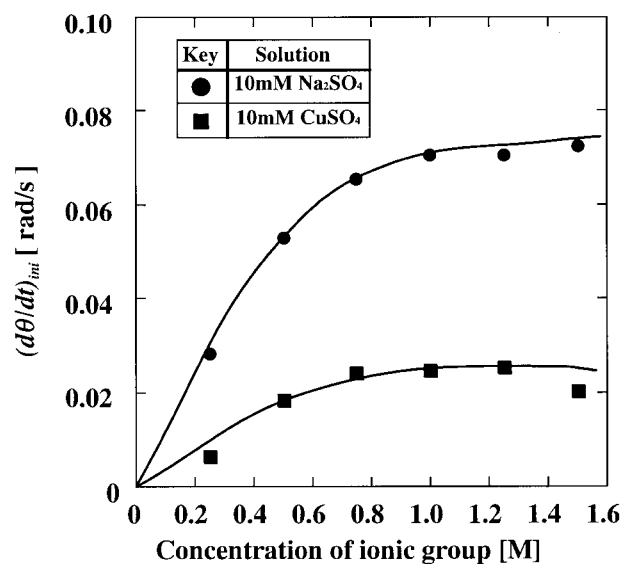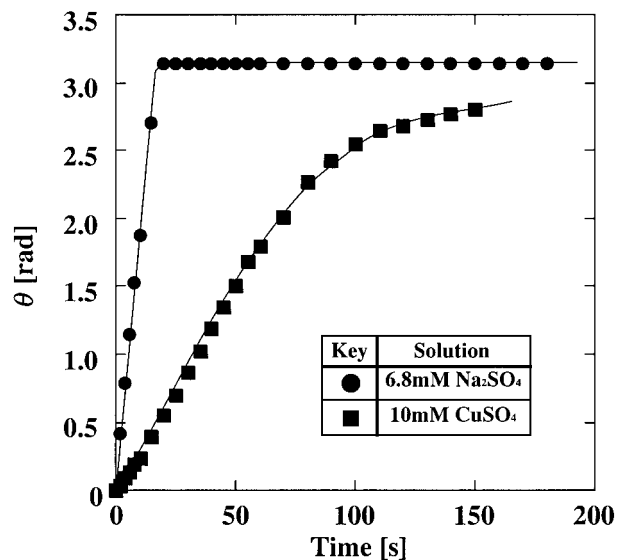


**Figure 2**    Relationship between the concentration of the ionic group and the bending rate of the membrane (10/3.0 V/cm electric field).

| **Distribution of ionic concentration** | | | **Bending of the membrane** |
|---|---|---|---|
| **Liquid** **Gel** **Liquid** | | | |
| ① $C_gNa^+$ $C_sNa^+$ | Increase of the counter ion inside the membrane with ionic group concentration | | Gel |
| ② Change of ionic concentration Outer solution penetrates into the membrane Larger Swelling | Larger change of the ionic concentration inside the membrane due to increse of ionic group concentration | | |

**Figure 3** Schematic diagram of the bending mechanism of the ionic hydrogel membrane

the membrane increased with the difference in the counter ionic concentration at the membrane–solution interface below 1$M$ AMPS because the osmotic pressure changed drastically in the electric field. The bending rate of the membrane, however, did not increase above 1$M$ AMPS because the free mobile ions did not increase because of the counter ionic condensation. As a result, the osmotic pressure did not change largely. The distribution of the ionic concentration in the membrane due to ionic transport played an important role in the bending rate.

Figure 4 shows the time course of $\theta$ of the membranes in $Na_2SO_4$ and $CuSO_4$ aqueous solutions. The concentration of outer solution with each valence of counter ion ($Na^+$ and $Cu^{2+}$) was regulated for the equivalent conductivity to show the difference of the bending behavior based on the valences of counter ion. Despite the equivalent conductivity of electrolyte solutions, the

| Key | Solution |
|---|---|
| ● | 6.8mM Na₂SO₄ |
| ■ | 10mM CuSO₄ |

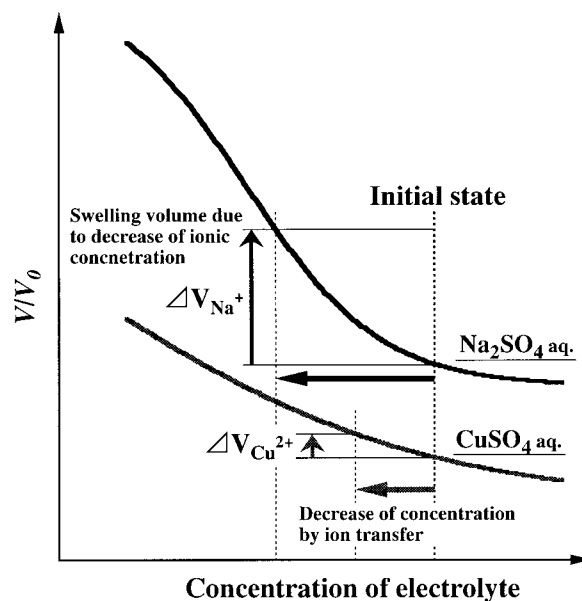**Figure 4** Time course of $\theta$ of the membrane (0.75$M$ AMPS, 10/3.0 V/cm electric field).
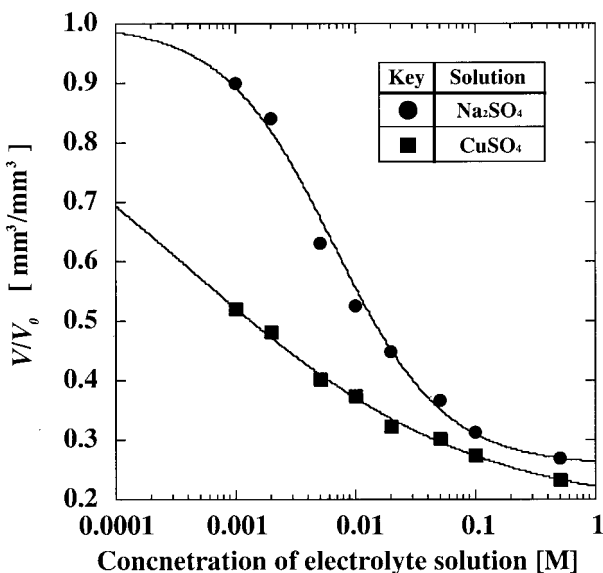
**Figure 5** Relationship between the concentration of the electrolyte solution and the swelling ratio of the membrane (0.75$M$ AMPS).

membrane in $Na_2SO_4$ solution bent more quickly than that in $CuSO_4$ solution. To explain the difference in the bending behavior caused by electrolyte species, the swelling curve of the membranes in each electrolyte solution was measured, as shown in Figure 5. The relationship between the change in ionic concentration in the membrane on the anode side and the change in swelling volume of the membrane is also depicted in Figures 5 and 6. The degree of change in swelling volume in $Na_2SO_4$ solution was much larger than that in $CuSO_4$ solution according to the decrease in ionic concentration in the membrane. When the membrane was placed in an electric field, the decrease in the amount of the univalent cation $Na^+$ in the membrane on the anode side was much larger than that of the bivalent cation $Cu^{2+}$ under the same current value. Therefore, the swelling volume caused by the decrease in the univalent cation became larger in comparison with the bivalent cation. Thus, the bending rate in $Na_2SO_4$ solution was much larger than in $CuSO_4$ solution, as shown in Figure 4. This showed that the bending behavior of the membrane depended on the change in swelling volume induced by the distribution of the ionic concentration in the membrane formed because of ionic transport.

To more clearly obtain evidence of the bending mechanism of the membrane, the bending

behavior of the membrane was investigated through a series of experiments in which the membrane immersed in 0.01$M$ $Na_2SO_4$ solution was transferred into $CuSO_4$ solution. Figure 7 shows the time course of $\theta$ of the membrane when the electric field was applied across the membrane under the previously mentioned conditions. The concentration of $Na^+$ in the membrane decreased, whereas $Cu^{2+}$ ions came from the outer solution and penetrated into the membrane to increase the concentration of $Cu^{2+}$ on the anode side of the membrane. In the case of 0.01$M$ $CuSO_4$ outer solution, the anode side of the membrane swelled, and the membrane bent to the cathode because the degree of decrease in $Na^+$ ionic concentration was larger than that of the increase in $Cu^{2+}$ ionic concentration. After a while, the anode side of the membrane shrunk, and the membrane bent to the anode because of the increase in $Cu^{2+}$ concentration. In the case of a higher concentration of 0.02$M$ $CuSO_4$ solution, the anode side of the membrane shrunk, and the membrane bent to the anode from the beginning because the degree of increase in $Cu^{2+}$ concentration was superior to that of the decrease in $Na^+$ concentration. Finally, at all concentrations of $CuSO_4$ solution, the anode side of the membrane swelled, and the membrane bent to the cathode because the distribution of $Cu^{2+}$ concentration instead of $Na^+$ was



**Figure 6** Ionic mechanism of the bending behavior based on Figure 5.
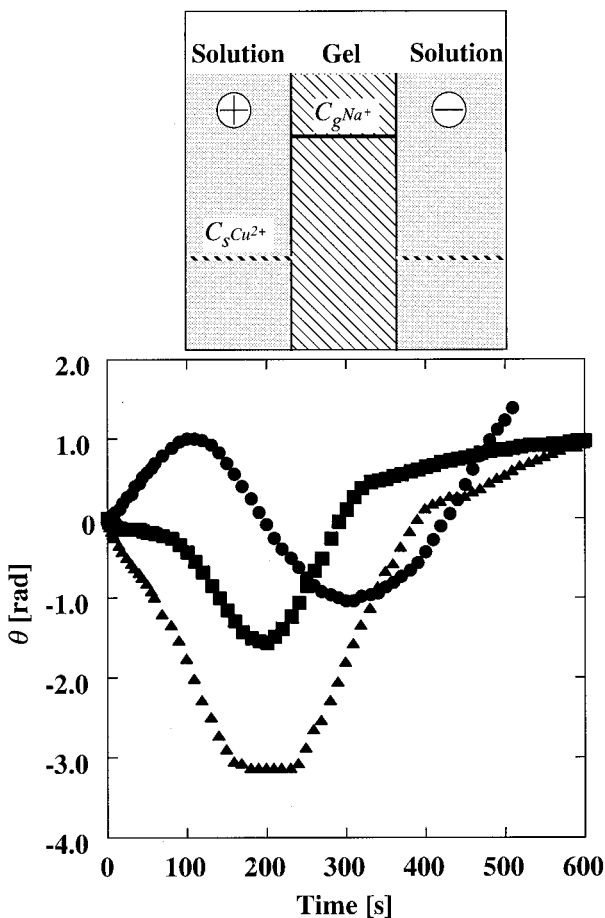
**Figure 7** Time course of $\theta$ of the membrane: (●) 0.01$M$ CuSO$_4$ aqueous outer solution, (■) 0.016$M$ CuSO$_4$ aqueous outer solution, and (▲) 0.02$M$ CuSO$_4$ aqueous outer solution (0.75$M$ AMPS, 10/3.0 V/cm electric field). The membranes were immersed in 0.01$M$ Na$_2$SO$_4$ aqueous solution at preparation.

formed through the membrane. As shown by these results, the bending mechanism was based on the distributions of ionic concentrations in the membrane caused by ionic transport.

## CONCLUSION

In this study, we clarified experimentally the bending mechanism (behavior) of an electro-driven ionic hydrogel membrane. It was found from an experiment with two different type (valence) cations (Na$^+$ and Cu$^{2+}$) that the bending behavior of the membrane depended on the distribution of the ion inside the membrane. It was indicated that the distribution of ionic concentration in the membrane played an important role in the bending phenomena of the membrane.

## REFERENCES

1. Yannas, I. V.; Grodzinsky, A. J. J Mechanochem Cell Motil 1973, 2, 113.
2. De Rossi, D.; Parrini, P.; Chiarelli, P.; Buzzigoli, G. Trans Am Soc Artif Int Organs 1985, 31, 60.
3. Shiga, T.; Kurauchi, T. J Appl Polym Sci 1990, 39, 2305.
4. Nakano, Y.; Seida, Y. Chem Eng Sci, submitted.
5. Homma, M.; Seida, Y.; Nakano, Y. J Appl Polym Sci 2000, 75, 111.