

# Evaluation of Optimum Condition for Designing High-Performance Electro-Driven Polymer Hydrogel Systems

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**ABSTRACT:** This study investigated a parameter that determines an optimum condition of the content of the ionic group and the concentration of outer solution for high-performance electro-driven polymer hydrogel membranes. The optimum condition for quick bending was determined by a simple method that identified the initial conditions based on Donnan equilibrium theory. Since the bending behavior depends on the initial conditions of the ionic group content and the concentration of the outer solution, it can be predicted by the ratio of the ionic concentrations at the membrane–solution interface; the inverse of the Donnan ratio ( $1/K$ ) at the initial condition. The bending rate of the membranes showed a maximum value at around  $1/K = 0.15$ . The relationship between several interrelated control factors and the bending dynamics of the gel membranes was established by using the initial system parameters alone.  $1/K$  is the effective simple parameter to determine the optimum condition of the content of the ionic group and the concentration of the outer solution for high-performance membranes. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 111–118, 2000

**Key words:** polymer hydrogel membrane; bending, optimum condition; electric field; Donnan equilibrium theory

## INTRODUCTION

Membranes of ionic polymer hydrogel have been known to be bent in an electric field.<sup>1–6</sup> These materials have been attracting much attention in medical and mechanical engineering fields. In the application of these materials to active catheter, micromachine and micromanipulator, quick response in bending is required to obtain high performance of those membranes. Response speed of the membranes depends on many factors that can be classified mainly into two categories: (A) molecular design and (B) operating conditions. Molecular design includes ionic group content, thickness, shape, and strength of the membrane. On the other hand, operating conditions include intensity and function in an applied electric field

and ionic species in outer electrolyte solution (type and concentration). Some studies have been reported on both the bending behavior of the gel membranes in an electric field and the bending mechanism. Shiga and Kurauchi<sup>2</sup> showed the bending of the poly(acrylic acid) gel membrane in an electric field and pointed out that this phenomenon occurred by the osmotic pressure caused by the ion concentration difference between the inside and the outside of a gel. Choi et al.<sup>4</sup> observed the bending phenomena of the neutral and anionic polymer gels in various salt solutions. They showed the effect of salts on the bending pattern in the copolymer gel of AMPSA/BMA and the AAm gel. Doi et al.<sup>7</sup> calculated the swelling behavior in two situations, one in which the gel was placed into contact with one electrode, and the other in which the gel was placed between the electrodes without contacting either. The bending behavior has not been clarified yet because of many interrelated control factors and uncertainty

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of the bending mechanism. Therefore, it is an important subject to clarify systematically the effect of those controlling factors on the bending behavior of the gel membranes and to provide the guidelines of both the molecular design and the operating conditions for controlling the bending.

The ionic polymer hydrogel membranes with a variety of ionic group contents were synthesized. The bending behavior of the electro-driven ionic polymer hydrogel membranes was investigated in electrolyte solutions with various concentrations. The bending behavior of the membranes was elucidated by means of the molecular design (ionic group content of the membrane) and the operating conditions (type and concentration of ions in outer solution and intensity of the applied electric field). An effective simple method that determined an optimum condition of the bending behavior was proposed.

## EXPERIMENTAL

### Preparation of PVA-PAMPS Interpenetrating Network

Low mechanical strength of ionic polymer hydrogel membranes is a serious problem in the applications of the material to active catheters, micromachines, micromanipulators, and so on. Introduction of a poly(vinyl alcohol) (PVA) network in the ionic hydrogel membrane through forming its interpenetrating network is an effective way to improve the mechanical strength of the membrane. The ionic polymer hydrogel membranes with PVA-interpenetrating network [poly(vinyl alcohol)-poly(2-acrylamide-2-methylpropane sulfonic acid); PVA-PAMPS] were prepared by the following way. 2-Acrylamido-2-methylpropane sulfonic acid (AMPS; 3.11–9.33 g, which corresponds to 0.5–1.5M of concentration of ionic group  $C_M$ ), 0.231 g of *N,N'*-methylene-bis-acrylamide (BIS, crosslinker), 0.411 g of ammonium peroxydisulfate (AP, initiator), and 1.25 g of poly(vinyl alcohol) (PVA, polymerization degree 2000 and saponification 99.9%) were dissolved in a 30-mL mixture of distilled water and dimethyl sulfoxide (DMSO; 10.0 g). The solution was poured between two glass plates, with spacers of a known thickness, and the plates were covered with poly(vinylidene chloride) film. The glass plates filled with the pregel solution were frozen at 258 K for 6 h. Subsequently, the solution was thawed at

room temperature for 1 h. The freezing–thawing cycle was repeated four times to form a PVA network. Then, the free radical polymerization of AMPS was carried out at 333 K for 6 h to form a PAMPS network. The synthesized PVA-PAMPS gel membranes were washed with distilled water several times and then immersed in a  $\text{Na}_2\text{SO}_4$  aqueous solution until they reached equilibrium.

### Apparatus

The electrolytic cell shown in Figure 1 was used to investigate the bending behavior of PVA-PAMPS gel membrane. The membrane (20 mm long and 5 mm wide) was suspended at the center between a pair of Pt-electrodes in the cell filled with a  $\text{Na}_2\text{SO}_4$  aqueous solution. The membrane was equilibrated in the  $\text{Na}_2\text{SO}_4$  aqueous solution (1–2 valent electrolyte solution) before the bending experiment. The time course of bending angle of the membrane was measured through monitoring the bending behavior by a video camera. The bending angle  $\theta$  of the membrane was calculated by the following equation.

$$\theta = 2 \tan^{-1} \left( \frac{y}{x} \right) \quad (1)$$

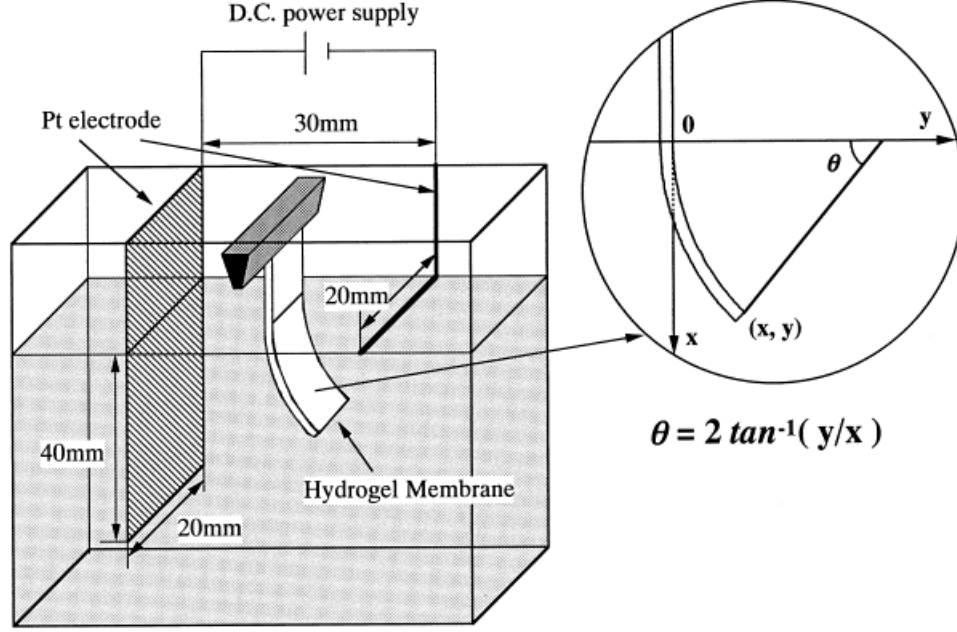
where  $x$  and  $y$  are the position of the free end of the membrane on the  $x$ – $y$  coordinate shown in Figure 1.

## DONNAN EQUILIBRIUM THEORY

The concentrations of ions in the membrane and in the outer solution are related by eq. (2), based on Donnan equilibrium theory.<sup>8</sup>

$$\frac{C_{ig}}{C_{is}} = \exp \left( -z_i \frac{F\Delta\phi}{RT} \right) = K^{z_i} \quad (2)$$

where  $K$ ,  $\Delta\phi$ ,  $F$ ,  $R$ ,  $T$ , and  $z$  denote Donnan ratio, Donnan potential, Faraday constant, gas constant, absolute temperature, and valence of ion, respectively.  $C_{ig}$  and  $C_{is}$  denote the concentrations of ions in the gel membrane ( $g$ ) and in the outer solution ( $s$ ). The subscript  $i$  means the species of ion [ $i = \text{A}$  (counter ion),  $\text{B}$  (co-ion),  $\text{H}$  (proton),  $\text{OH}$  (hydroxide ion)]. The electrically neutral condition should be satisfied simultaneously in both phases (in the gel membrane and



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

the outer solution), as expressed by eqs. (3) and (4), respectively:

$$z_A C_{Ag} + C_{Hg} = -z_B C_{Bg} + C_{OHg} + C_M \quad (3)$$

$$z_A C_{As} + C_{Hs} = -z_B C_{Bs} + C_{OHs} \quad (4)$$

where  $C_M$  is the concentration of ionic group within the gel membrane suspended in the electrolyte solution. The chemical equilibrium relation of water is

$$K_W = C_{Hs} C_{OHs} = C_{Hg} C_{OHg} \quad (5)$$

pH in the outer solution is 7 in this system under study ( $C_{Hs} = C_{OHs}$ ). The Donnan ratio  $K$  in a membrane-electrolyte solution system is calculated by eq. (6), derived from eqs. (2), (3), and (5):

$$(-K^{z_A} + K^{z_B}) z_A z_B C_s + \left(K - \frac{1}{K}\right) C_{Hs} - C_M = 0 \quad (6)$$

If  $z_A = |z_B|$

$$\left(K^{z_A} - \frac{1}{K^{z_A}}\right) z_A C_s + \left(K - \frac{1}{K}\right) C_{Hs} - C_M = 0$$

where  $C_s$  is the concentration of outer electrolyte solution.

## RESULTS

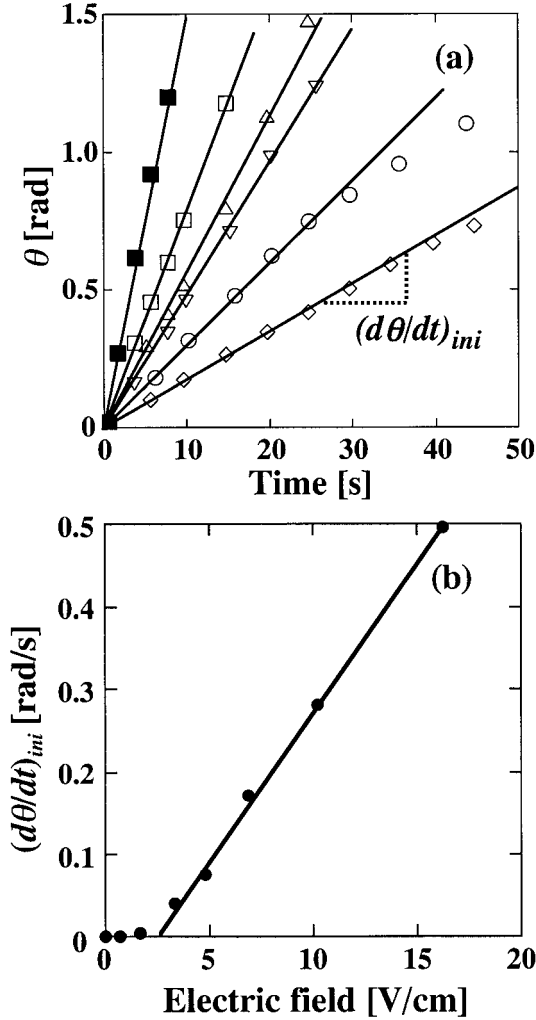
### Time Course of the Bending Angle

The time courses of the bending angle of the various membranes are plotted in Figure 2(a). The bending angle of all the membranes increased linearly with time in the initial stage. The bending rate  $(d\theta/dt)_{\text{ini}}$ , which was calculated from the initial slope of the time course, increased linearly with the intensity in the applied electric field beyond 2.5 V/cm [Fig. 2(b)]. The linearity of the time course of the bending was kept over a long period. This means that the bending behavior of the membrane is governed by the initial condition.

### Effect of the Thickness

The effect of the thickness of the membrane,  $\delta$  on the  $(d\theta/dt)_{\text{ini}}$  is shown in Figure 3.  $(d\theta/dt)_{\text{ini}}$  was correlated with  $\delta$  by the following equation:

$$\left(\frac{d\theta}{dt}\right)_{\text{int}} = \frac{a}{\delta^n} \quad (7)$$



**Figure 2** (a) Time courses of bending angle in the electric field of 10 V/3 cm: (○)  $C_M = 1.0M$ ,  $C_s = 0.002M$ ,  $\delta = 1.4$  mm; (■)  $C_M = 1.0M$ ,  $C_s = 0.01M$ ,  $\delta = 0.72$  mm; (□)  $C_M = 1.0M$ ,  $C_s = 0.01M$ ,  $\delta = 0.96$  mm; (◇)  $C_M = 1M$ ,  $C_s = 0.05M$ ,  $\delta = 1.1$  mm; (△)  $C_M = 0.5M$ ,  $C_s = 0.01M$ ,  $\delta = 1.0$  mm; (▽)  $C_M = 1.5M$ ,  $C_s = 0.01M$ ,  $\delta = 1.3$  mm. (b) Effect of the electric field on the initial bending rate:  $C_M = 0.5M$ ,  $C_s = 0.01M$ .

where  $a$  and  $n$  are fitting parameters. In this experimental result,  $n$  is equal to 1.7. As  $(d\theta/dt)_{ini}$  depends on  $\delta$  remarkably, the value of  $(d\theta/dt)_{ini}$  should be corrected for the thickness to compare  $(d\theta/dt)_{ini}$  for the membranes that differ from one another in thickness. The corrected  $(d\theta/dt)_{ini}$  value for 1-mm thickness was used.

#### Effect of $C_s$ and $C_M$

The relationship between  $C_s$  and  $(d\theta/dt)_{ini}$  of the membranes for a series of  $C_M$  is shown in Figure

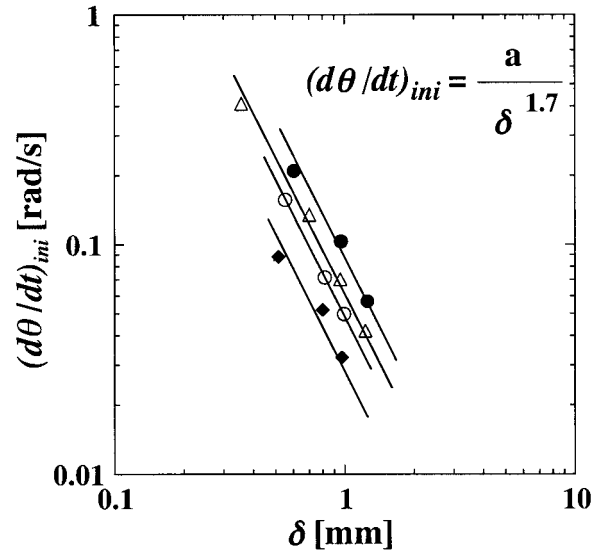
4(a). Each membrane had a maximum  $(d\theta/dt)_{ini}$  at a specified  $C_s$ .  $C_s$  at the maximum  $(d\theta/dt)_{ini}$  shifted to higher  $C_s$  region with increasing  $C_M$ . Figure 4(b) shows the swelling curve of the membranes. It was found that the membranes show the maximum  $(d\theta/dt)_{ini}$  at the swelling ratio  $V/V_0$  of 0.75 from Figures 4(a,b).

#### DISCUSSION

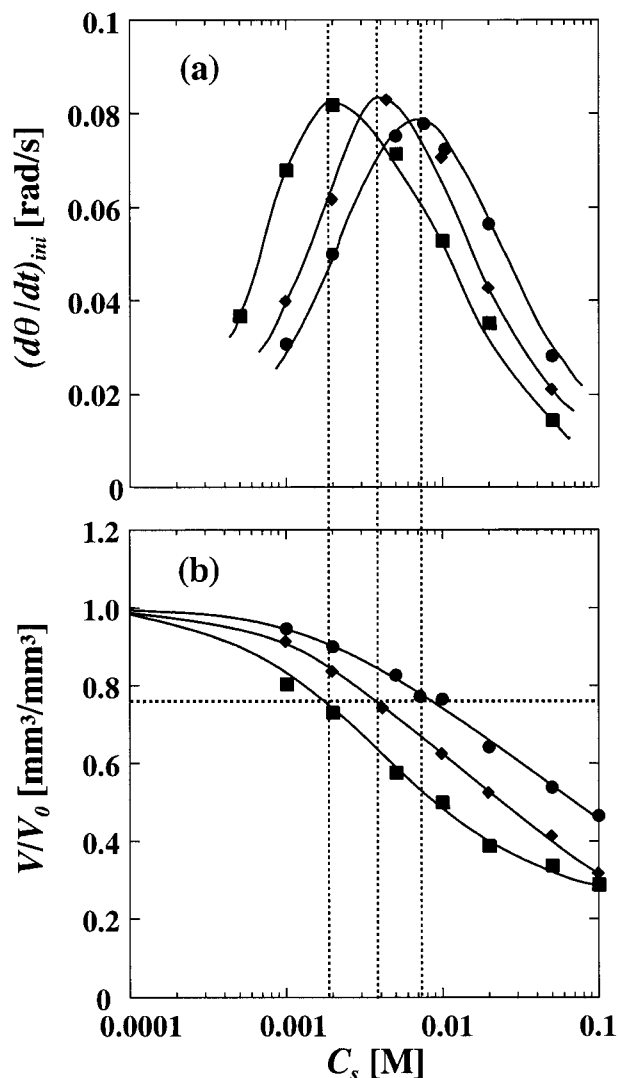
The swelling behavior of the ionic hydrogel membrane depends on the osmotic pressure. The swelling pressure due to the ions  $\Delta\pi$  can be expressed by the difference between the osmotic pressures due to the solute in the membrane and in the outer solution, as follows:

$$\Delta\pi = RT \sum_i (C_{ig} - C_{is}) \quad (8)$$

In an electric field,  $C_{ig}$  and  $C_{is}$  at the membrane–solution interface change with elapse of time due to ionic transport through the gel membrane. As mentioned in the section 4.1, the results in Figure 2(a) indicated that the bending behavior of the membranes depended for a long period on the initial condition of  $C_{ig}$  and  $C_{is}$ .  $C_{ig}$  and  $C_{is}$  were



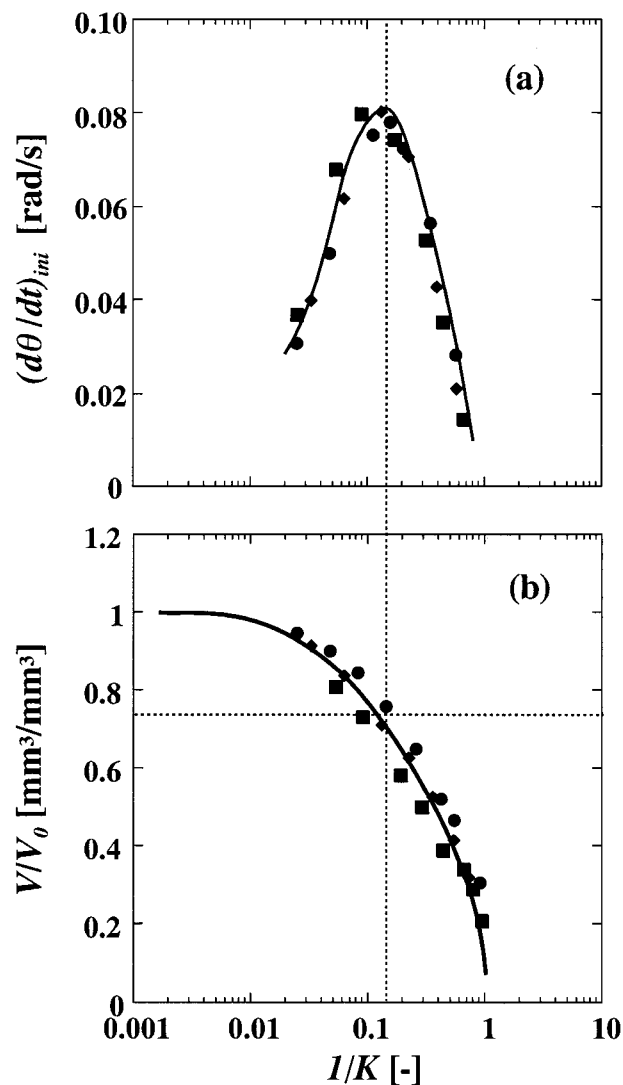
**Figure 3** Relationship between thickness;  $\delta$  of the membrane and initial bending rate;  $(d\theta/dt)_{ini}$  in the electric field of 10 V/3 cm: (●)  $C_M = 0.5M$ ,  $C_s = 0.005M$ ; (○)  $C_M = 0.5M$ ,  $C_s = 0.01M$ ; (△)  $C_M = 1.5M$ ,  $C_s = 0.01M$ ; (◆)  $C_M = 0.5M$ ,  $C_s = 0.02M$ .



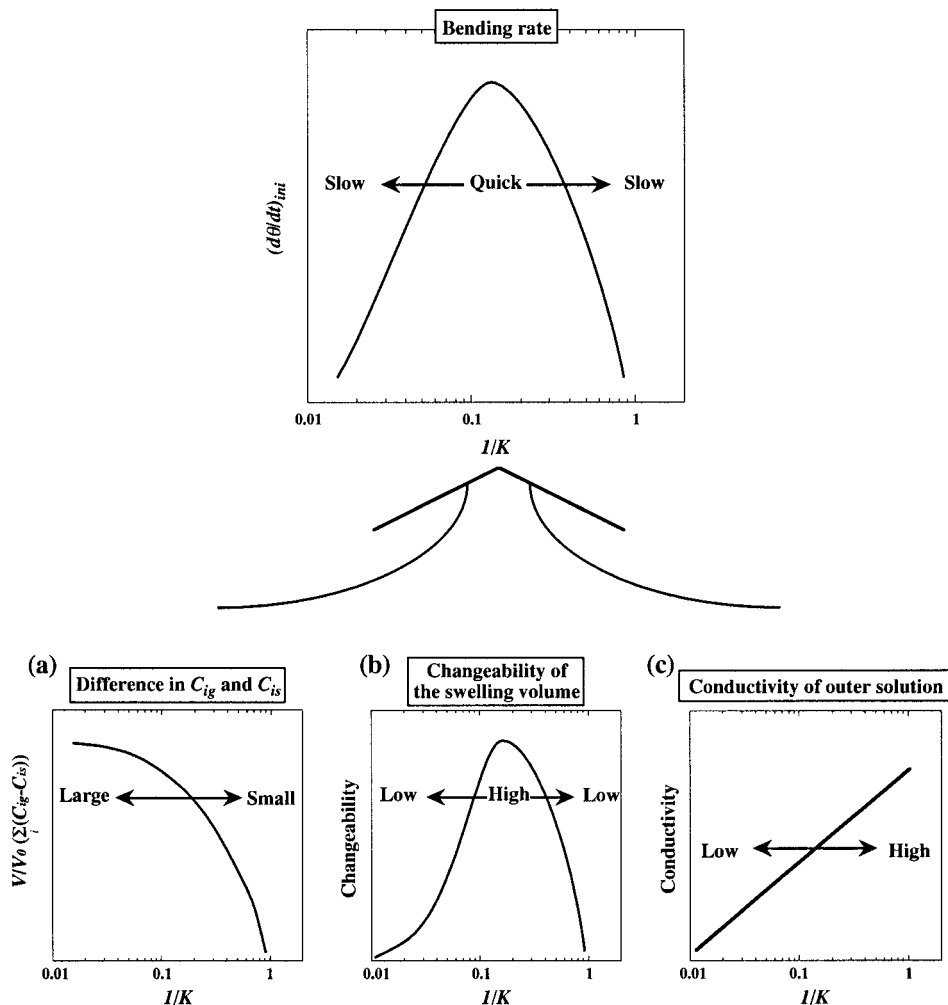
**Figure 4** Results of the bending rate and the swelling ratio of the membranes. (a) Relationship between the concentration of outer solution;  $C_s$  and the corrected bending rate;  $(d\theta/dt)_{ini}$  of the membranes in the electric field of 10 V/3 cm. (b) Swelling curves of the membranes: (■)  $C_M = 0.5M$ ; (◆)  $C_M = 1.0M$ ; (●)  $C_M = 1.5M$ .

related to  $C_s$  and  $C_M$  by Donnan equilibrium theory as shown in eqs. (2) and (6). Since  $(d\theta/dt)_{ini}$  was affected both by  $C_s$  and  $C_M$  as shown in Figure 4(a), we introduced the quantity  $C_s/C_M$  to elucidate the effect of these parameters on the bending behavior of the membranes under various conditions.  $C_s/C_M$  corresponds to the inverse of Donnan ratio ( $1/K$ ); the relative concentration of the outer solution to that of ionic group in the membrane. The values of  $1/K$  can be obtained

using eq. (6). The dependence of  $(d\theta/dt)_{ini}$  on  $1/K$  is shown in Figure 5(a) for the series of  $C_M$ . We assume the complete dissociation of the ionic group and neglect the counter ion condensation and chelate effect in the calculation of  $1/K$ . The  $C_M$  value at the preparation stage of the membrane was used in the calculation.  $(d\theta/dt)_{ini}$  for all the membranes can be correlated well with  $1/K$ , as shown by a single curve. There exists a maximum  $(d\theta/dt)_{ini}$  at around  $1/K = 0.15$  as shown in Figure 5(a). Figure 5(b) shows the relationship between  $1/K$  and  $V/V_0$ . It was found that



**Figure 5** (a) Relationship between  $1/K$  and the corrected bending rate;  $(d\theta/dt)_{ini}$  of the membranes in the electric field of 10 V/3 cm. (b) Relationship between  $1/K$  and the swelling ratio of the membranes;  $V/V_0$ : (■)  $C_M = 0.5M$ ; (◆)  $C_M = 1.0M$ ; (●)  $C_M = 1.5M$ .



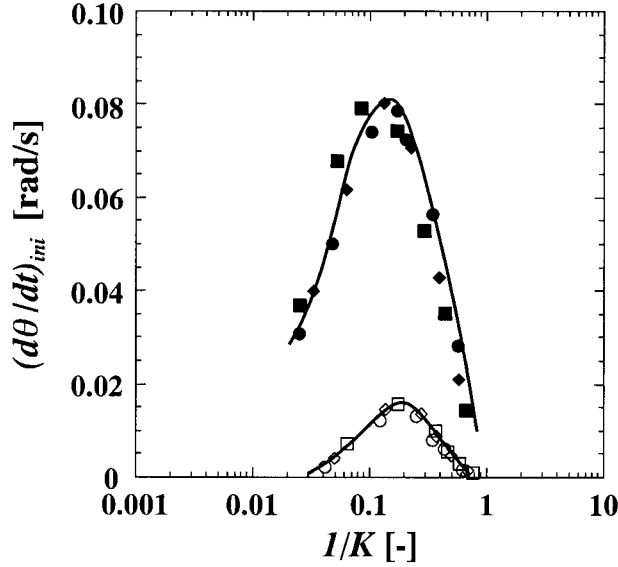
**Figure 6** Optimum condition for the quick bending.

the swelling behavior of all the membranes is also correlated by a single curve. The membranes have the maximum  $(d\theta/dt)_{\text{ini}}$  under the swelling ratio  $V/V_0$  of 0.75 that corresponds to  $1/K = 0.15$ . Therefore,  $1/K$  would be the effective simple parameter to determine an optimum combination of  $C_s$  and  $C_M$  for high-performance membranes. The existence of the optimum  $1/K (=0.15)$  for the quickest bending can be explained qualitatively in Figure 6. The bending of the membrane principally occurs through the change in osmotic pressure induced by transport of ions at the membrane–solution interface. Therefore, to understand the bending behavior of the membrane based on initial parameter of the system, we should take into account the bending potential of the system at initial condition from both equilib-

rium (osmotic pressure; whether the change in osmotic pressure accompanied with a concentration change of ions is large or not) and kinetic (transport of ions; amount of mobile ions) point of view. The following conditions should be satisfied to induce quick bending of the membranes:<sup>9</sup> (a) large difference in ionic concentrations at the membrane–solution interface, yielding large change in osmotic pressure; (b) large changeability of the swelling volume of the membrane due to the ionic transport, indicated by the derivative of the swelling curve; and (c) high conductivity of electrolyte solution to induce the quick change in the ionic concentrations at the membrane–solution interface.

In case of a small  $1/K$  (in dilute solution), although the difference in ionic concentrations be-





**Figure 7** Relationship between  $1/K$  and the corrected bending rate;  $(d\theta/dt)_{ini}$  of the membranes in the electric field of 10 V/3 cm: (■)  $C_M = 0.5M$ ; (◆)  $C_M = 1.0M$ ; (●)  $C_M = 1.5M$  in  $\text{Na}_2\text{SO}_4$  solution, respectively; (□)  $C_M = 0.5M$ ; (◇)  $C_M = 1.0M$ ; (○)  $C_M = 1.5M$  in  $\text{CuSO}_4$  solution, respectively.

tween in the membrane and in the outer solution is large [Fig. 6(a)], the changeability of the swelling volume and the conductivity of electrolyte solution are low [Fig. 6(a,b)], resulting in the slow bending. In case of a large  $1/K$  (in concentrated solution), although the conductivity of electrolyte solution is high, the difference in ionic concentrations between in the membrane and in the outer solution is small, resulting in the low changeability of the swelling volume (slow bending). In the 1–2 valent electrolyte system used in this study, the membranes show the quickest bending at around  $1/K = 0.15$ , which satisfies the initial conditions of (a) to (c) for the quickest bending. Appearance of  $1/K$  in the quickest bending was confirmed for 2-valent cation solutions. Figure 7 shows the relationship between  $1/K$  and  $(d\theta/dt)_{ini}$ . There appears the optimum  $1/K$  for the quickest bending in the 2-valent cation ( $\text{CuSO}_4$ ) solution that is similar to the case of the 1-valent cation solution. The bending rate in the 2-valent system, however, decreased over the  $C_s$  range compared to the 1-valent system. The 1-valent cation system would be effective to induce quick response of the membrane.

The fact that the bending behaviors of the membranes are correlated well by  $1/K$ , as shown

in Figures 5 and 7, proves that the osmotic pressure due to ions dominates the bending behavior. The relationship between several interrelated control factors and the bending dynamics of the gel membranes was established by using the initial system parameters alone. An anionic group concentration  $C_M$  and thickness of membrane  $\delta$  should be specified in the preparation stage according to an application. Concentration of outer electrolyte solution  $C_s$  is determined by eq. (6), using  $C_M$  and the optimum value of  $1/K$ .<sup>11</sup>

## CONCLUSION

In this paper, we clarified experimentally the bending behavior of the electro-driven hydrogel membranes and provided a method to evaluate optimum condition for designing high performance of the membrane. The following results were obtained from the experimental part.

1. The bending rate depends on initial condition of the system for a long period, which means that the initial condition of the system dominates the bending behavior. The bending rate is linearly controlled by the intensity of the applied electric field.
2. Each membrane has a maximum bending rate at a specified concentration of outer solution. The concentration of outer solution at the maximum bending rate shifts to higher concentration region of outer solution with increasing the concentration of ionic group.
3. The bending rate is correlated with the thickness of membrane, by the following equation beyond 2.5 V/cm:

$$\left(\frac{d\theta}{dt}\right)_{ini} = \frac{a}{\delta^n}$$

Based on these experimental results, following guidelines for quick response of the membrane were obtained:

1. The inverse of Donnan ratio ( $1/K$ ) is the effective simple parameter to determine the optimum condition of the concentration of the outer solution  $C_s$  and the content of ionic group  $C_M$  for the quick bending.
2. The bending rate of the electro-driven poly-

mer hydrogel membrane can be predicted by both the changeability of the swelling volume of the membrane and the conductivity in electrolyte solution at initial condition of the system.

3. The electrolyte containing univalent counter ion is effective for the quick bending of the membrane.

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