Deformation of Ionic Polymer Gels by Electric Fields

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ABSTRACT: When an electric field is applied to an ionic gel in a buffer solution, the anode side of the gel shrinks if the gel is contacting with the electrode, while it swells if the gel is placed with sufficient separation from the electrode. We calculate the changes of ion concentration profiles under an electric field, taking account of ion transports and electrochemical reactions. Combining these results with Flory's theory for the swelling of ionic gels, we explain the above phenomena. We predict that the swelling behavior is governed by the concentration of the dominant ions and that the swelling speed is proportional to the square of the electric current.

1. Introduction

Gels consisting of ionic polymers deform when an electric field is applied through the solution immersing the gel. The first observation of the electric-field-induced deformation was made by Tanaka et al.,[1] who found that when a rodlike specimen of a copolymer of acryl acid–acrylamide gel is placed between electrodes, the anode side of the gel shrinks as shown in Figure 1a. A similar phenomenon was also observed by other workers.[2-4] Tanaka and his co-workers first interpreted the phenomenon as the electric field pushes the negatively charged gel toward the anode and squeezes the anode side of the gel. Later, however, this interpretation was questioned when Shiga and Kurauchi[5] found that, if the same specimen is placed at a fixed position separated from the electrodes, the anode side of the gel swells as in Figure 1b. Shiga et al.[5,6] pointed out that these phenomena are induced by the change in the ionic distribution under the electric field. Hirose[7] has shown that the change of pH or ionic concentration can indeed induce the volume change of the gel. However, the dynamics of ions in ionic gels has not been discussed, although the pH change in neutral gels has been studied by Hirose et al.[8] Up to the present, there have been no quantitative or even qualitative theories for the field-induced deformation of the ionic gels. Theories are apparently needed, since the swelling behavior is rather complex, depending on pH, salt concentrations, and the strength of the electric field. For example, Shiga et al.[5] found that, in some gels, the swollen part starts to shrink as the electric field is kept applied, and there has been no explanation for the phenomenon.

In this paper, we propose a semiquantitative theory which describes such swelling and deswelling behavior under an electric field. We shall calculate the ionic distribution inside and outside the gel and show that the above phenomena can indeed be explained.

Although the theory developed here is general, we focus our attention on a specific system, i.e., the acryl acid–acrylamide copolymer gel, the acidic group (carboxyl) of which dissociates as

$$-COOH \rightleftharpoons -COO^- + H^+ \qquad (1)$$
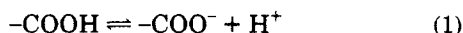
The ions in the solutions are H^+, OH^-, and monovalent cations A^+ and anions B^-, which we associate with Na^+ and Cl^-, respectively. For this system, we study under

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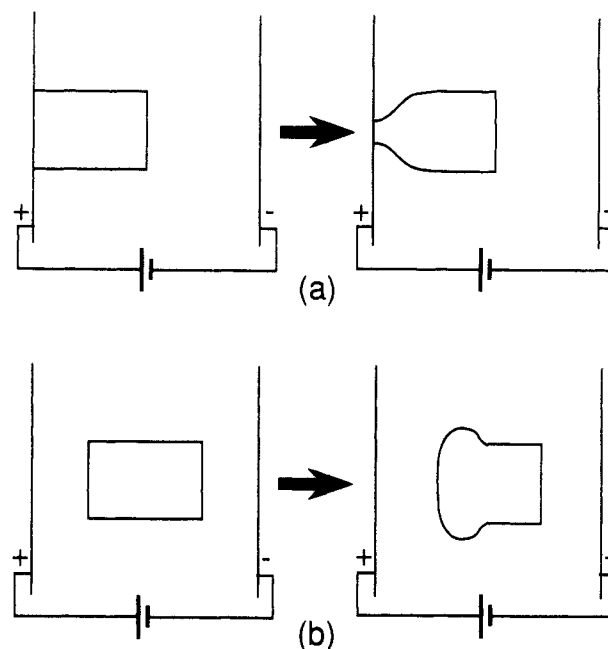‡ Toyota Central Research and Development Laboratories, Inc.

Figure 1. Illustration of the deformation of a cationic gel under an electric field. If the gel is contacting with the anode, the anode side shrinks (a), while, if the gel is placed between the electrodes, the anode side swells (b).

what conditions the gel swells or shrinks when an electric field is switched on.

We approach this question by the following two steps. First, we use an earlier theory for the equilibrium volume of an ionic gel and construct a diagram which tells us whether the gel swells or not when the ionic concentrations of A^+ and B^- are varied. Next, we consider the dynamics of ion distributions in the presence of an electric field. Finally, by combining these results, we give a physical explanation for the swelling behavior.

In this paper, we do not take account of the deformation of gels explicitly. This is to demonstrate the essential physics in the simplest way. A complete theory has to include the motion of water and gel in such a way as is developed in ref 9. Such a theory will be published in the future. With these effects neglected, the present theory has to be regarded as a semiquantitative one.

2. Equilibrium Volume of an Ionic Gel

2.1. Flory's Theory. First, we consider the equilibrium volume of an ionic gel. This problem has been studied by many authors,[10,11] and elaborate theories have been

developed. Here, following Rička and Tanaka,[12] we shall use the simplest theory which neglects the spatial correlation in ionic distributions.

According to Flory,[11] the equilibrium volume V of a gel is determined by the following condition:

$$\Pi_{\text{network}}(V) + RT\sum_i (c_{ig} - c_{is}) = 0 \tag{2}$$

where $\Pi_{\text{network}}(V)$ is the osmotic pressure of a hypothetical neutral gel in which ionic groups of the gel are not dissociated at all, R is the gas constant, T is the absolute temperature, and c_{is} and c_{ig} denote the ionic concentration of species i in the outer solution and in the gel, respectively. The subscript i stands for A, B, H, or OH and denotes the ions A^+, B^-, H^+, or OH^-; for notational simplicity, the signs indicating the ion charge are omitted in this paper.

The physics underlying eq 2 is the following. If the gel has no charge, its volume is determined by two opposing effects. One is the attractive interaction between polymer and solvent, which tends to swell the gel. The other is the network elasticity, which resists the expansion. These two effects are both included in $\Pi_{\text{network}}(V)$, and the condition $\Pi_{\text{network}}(V) = 0$ determines the equilibrium volume of the neutral gel. On the other hand, if the gel has electric charges, the concentration of free ions inside the gel is not equal to that outside the gel. This unbalance in the concentration creates an additional contribution to the osmotic pressure and swells the gel. This effect is included in the second term of eq 2.

Given the functional form of $\Pi_{\text{network}}(V)$, we can calculate the equilibrium volume V from eq 2. However, since our purpose here is to determine whether the gel swells or shrinks, we shall focus our attention on the following term:

$$\Delta\Pi \equiv RT\sum_i (c_{ig} - c_{is}) \tag{3}$$

Since $\Pi_{\text{network}}(V)$ is always a decreasing function of V, which follows from a thermodynamic stability condition, eq 2 indicates that, if $\Delta\Pi$ increases upon the imposition of an electric field, the gel swells, while it shrinks if $\Delta\Pi$ decreases.

Now the ionic distribution in the equilibrium state is given by the Donnan theory.[11] At boundaries of a gel, an electric double layer creates a jump in the electric potential (Donnan potential) $\Delta\tilde{\psi} = \tilde{\psi}_g - \tilde{\psi}_s$. Hence, the ratio of the ion concentration is given by

$$c_{ig}/c_{is} = \exp(-z_i\Delta\psi) \quad \text{for } i = \text{A, B, H, and OH} \tag{4}$$

where $z_i e$ denotes the charge of the ion i ($z_A = 1$, $z_B = -1$, $z_H = 1$, and $z_{OH} = -1$), and $\Delta\psi \equiv e\Delta\tilde{\psi}/k_B T$ is the jump of the nondimensional electric potential. In both regions of gel and solution, the charge neutrality condition must be satisfied:

$$c_{As} + c_{Hs} = c_{Bs} + c_{OHs} \quad \text{in solution} \tag{5}$$

$$c_{Ag} + c_{Hg} = c_{Bg} + c_{OHg} + c_{Cg} \quad \text{in gel} \tag{6}$$

where c_{Cg} is the concentration of the dissociated $-COO^-$ ions in the gel. Finally, the dissociation equilibria for water and the carboxyl group are written as

$$c_{Hs} \cdot c_{OHs} = c_{Hg} \cdot c_{OHg} =$$
$$K_w \ (\simeq 10^{-14} \ \text{mol}^2/\text{L}^2 \text{ at room temperature}) \tag{7}$$

and

$$\frac{c_{Hg} \cdot c_{Cg}}{c_M - c_{Cg}} = K_g \tag{8}$$

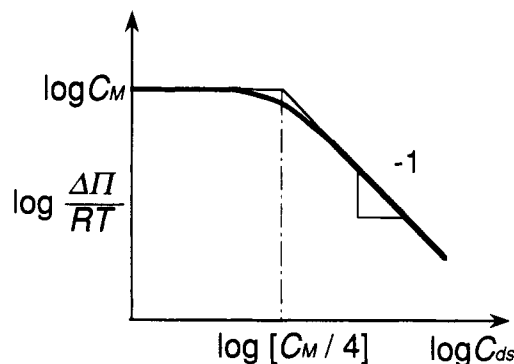where c_M is the concentration of the carboxyl groups in

Figure 2. Ionic contribution to the osmotic pressure, $\Delta\Pi$, of a completely dissociating gel schematically plotted against the concentration of the dominant ion $c_{ds} = \max (c_{As}, c_{Bs})$ in a logarithmic scale.

the gel, and K_g is their dissociation constant.

Equations 4–8 are 8 independent equations for 10 unknowns, c_{As}, c_{Ag}, c_{Bs}, c_{Bg}, c_{Hs}, c_{Hg}, c_{OHs}, c_{OHg}, c_{Cg}, and $\Delta\psi$; note that the relation

$$c_{Hs} \cdot c_{OHs} = c_{Hg} \cdot c_{OHg}$$

is automatically satisfied due to eq 4. Thus, if two of them are given, the rest can be determined.

2.2. Osmotic Pressure Map. We shall now study $\Delta\Pi$ as a function of c_{As} and c_{Bs}. This choice of independent variables is only for convenience for later discussion; the dynamics of the ions A^+ and B^- are governed by diffusion only, while the dynamics of H^+ and OH^- involves dissociation and association reactions of water and gel and is much more complicated. Therefore, we focus our attention on c_A and c_B. The concentration of H^+, or pH, of the outer solution is calculated from eqs 5 and 7 as

$$c_{Hs} = \frac{1}{2}[c_{Bs} - c_{As} + ((c_{As} - c_{Bs})^2 + K_w)^{1/2}] \tag{9}$$

The solution is alkaline if $c_{As} > c_{Bs}$ and acid if $c_{As} < c_{Bs}$.

The set of equations 4–8 is written in a compact form. Defining $P \equiv \exp(-\Delta\psi)$, we can show that

$$\left(P - \frac{1}{P}\right)(c_{As} + c_{Hs}) = \frac{c_M K_g}{P c_{Hs} + K_g} \tag{10}$$

When c_{As} and c_{Bs} are given, c_{Hs} is determined by eq 9, and P can be obtained from eq 10 numerically. The osmotic pressure $\Delta\Pi$, defined in eq 3, is calculated by

$$\Delta\Pi/RT = \left(P + \frac{1}{P} - 2\right)(c_{As} + c_{Hs}) \tag{11}$$

In the case of $K_g \to \infty$ (completely dissociating gel), eq 10 can be solved easily. Introducing c_{ds} as

$$c_{ds} = c_{As} + c_{Hs} = c_{Bs} + c_{OHs} \tag{12}$$

we obtain

$$P = \frac{1}{2}\left[\frac{c_M}{c_{ds}} + \left[\left(\frac{c_M}{c_{ds}}\right)^2 + 4\right]^{1/2}\right] \tag{13}$$

and

$$\Delta\Pi/RT = [(c_M)^2 + 4(c_{ds})^2]^{1/2} - 2c_{ds} \tag{14}$$

This is schematically plotted in Figure 2. Notice that c_{ds} can be written as

$$c_{ds} = \frac{1}{2}[c_{As} + c_{Bs} + ((c_{As} - c_{Bs})^2 + K_w)^{1/2}] \tag{15}$$

In the usual situation, $K_w^{1/2}$ ($\simeq 10^{-7}$ mol/L) is much smaller
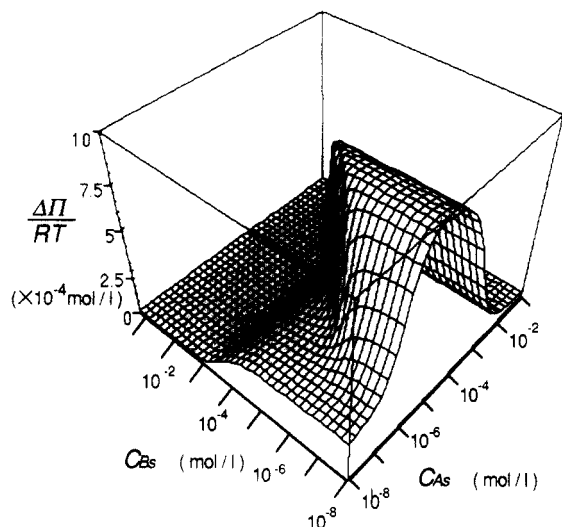
Figure 3. Bird's eye view of (c_{As}, c_{Bs}) dependence of $\Delta\Pi$ for the system of $K_g = 6 \times 10^{-5}$ mol/L and $c_M = 10^{-3}$ mol/L.
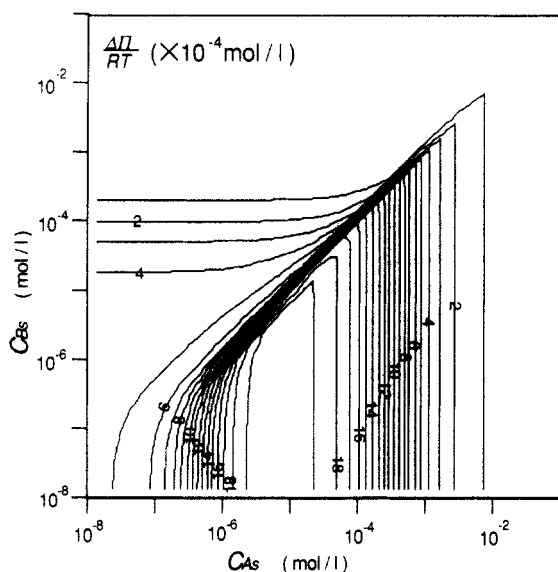

Figure 4. Contour map of $\Delta\Pi$ (c_{As},c_{Bs}) for the same system as shown in Figure 3.

than c_{As} or c_{Bs}, so that

$$c_{ds} = \frac{1}{2}[c_{As} + c_{Bs} + ((c_{As} - c_{Bs})^2)^{1/2}] = \max(c_{As}, c_{Bs}) \quad (16)$$

Hence, $\Delta\Pi$ is determined by the concentration of the dominant ion. Equation 14 is simplified as

$$\Delta\Pi/RT = \begin{cases} c_M & \text{for } c_{ds} \ll c_M \\ c_M^2/4c_{ds} & \text{for } c_{ds} \gg c_M \end{cases} \quad (17)$$

As a more realistic system, we use $K_g = 6 \times 10^{-5}$ mol/L (poly(acryl acid) gel) and solve eq 10 numerically for a gel concentration of $c_M = 10^{-3}$ mol/L; the results are plotted in Figures 3 and 4. It is seen that, in this case also, $\Delta\Pi$ is insensitive to the concentration of the minor ions and is mainly determined by the dominant ion. The dependence is shown in Figure 5. We now discuss the characteristic aspects of the curves in Figure 5. To simplify the mathematics, we shall assume

$$K_w^{1/2} \ll K_g \ll c_M \quad (18)$$

which is satisfied in the above example.

(A) **Alkaline Region, $c_{As} > c_{Bs}$.** In the alkaline region, the COOH groups in the gel are completely dissociated, so that the function $\Delta\Pi(c_{As})$ is similar to that in Figure
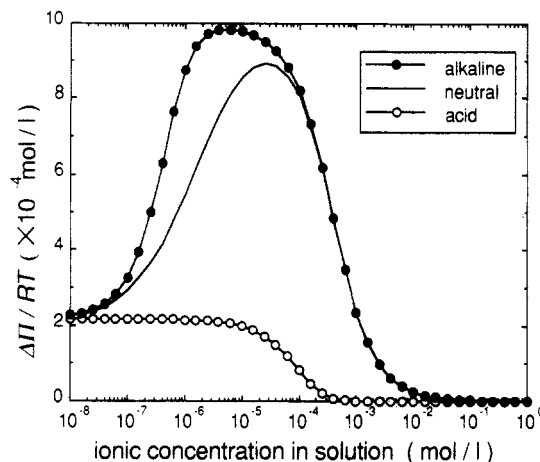

Figure 5. $\Delta\Pi/RT$ plotted against c_{As} (for the alkaline and neutral lines) or c_{Bs} (for the acid line).

2. If c_{As} is much larger than c_M, $\Delta\Pi/RT$ is equal to $c_M^2/4c_{As}$. When c_{As} becomes less than c_M, $\Delta\Pi/RT$ becomes equal to c_M. A difference, however, arises when c_{As} becomes very small, where $\Delta\Pi$ decreases and approaches a constant value. This is because the COOH is partially associated at very low ionic concentrations of A^+. In the limit of $c_{As} = c_{Bs} = 0$, the ionic concentration in the gel is given by

$$c_{Cg} = c_{Hg} = (c_M K_g)^{1/2} \quad (19)$$

Hence

$$\Delta\Pi/RT = c_{Hg} = (c_M K_g)^{1/2} \quad (20)$$

The transition from the complete dissociation to the partial dissociation takes place at

$$c_{As} \simeq K_w^{1/2}$$

(B) **Acid Region, $c_{As} < c_{Bs}$.** In the acid region, $\Delta\Pi/RT$ is equal to $(c_M K_g)^{1/2}$ for very small values of c_{Bs} for the same reason mentioned above. When c_{Bs} becomes comparable to $(c_M K_g)^{1/2}$, $\Delta\Pi/RT$ starts to decrease. The decrease is much steeper than that in the alkaline region. This is because the dissociation of the gel is suppressed as c_{Bs} increases. Indeed, the dissociation equation (8) is written as

$$c_{Cg} = \frac{c_M K_g}{c_{Hg} + K_g} \simeq \frac{c_M K_g}{c_{Hs} + K_g} \simeq \frac{c_M K_g}{c_{Bs}} \quad (21)$$

where we have used the fact that $P \simeq 1$ and $c_{Hs} = c_{Bs}$ in the region of $c_{Bs} \gg (c_M K_g)^{1/2}$. Thus, from eqs 17 and 21, it follows that

$$\Delta\Pi/RT = \frac{(c_{Cg})^2}{4c_{Bs}} = \frac{K_g^2 c_M^2}{4(c_{Bs})^3} \propto c_{Bs}^{-3} \quad (22)$$

which should be compared with

$$\Delta\Pi/RT \propto c_{As}^{-1}$$

in the alkaline region.

(C) **Neutral Region, $c_{As} = c_{Bs}$.** The unmarked line in Figure 5 denotes the plot of the neutral line, $\Delta\Pi(c_{As},c_{As})$, against c_{As}. The behavior is similar to that in the alkaline region. It can be shown that $\Delta\Pi(c_{As},c_{As})$ takes a maximum at

$$c_{As} = \frac{1}{\sqrt{2}} c_M \left(\frac{K_w^{1/2}}{K_g}\right)^{1/2}$$

and the maximum value of $\Delta\Pi/RT$ is approximately equal to c_M.

3. Ion Dynamics

3.1. Kinetic Equations. Having seen the equilibrium behavior, we now consider how the ionic distributions change when an electric field is imposed. As was mentioned in section 1, we do not consider the deformation of the gel; we shall calculate the ionic distributions assuming that the shape of the gel is fixed by some external constraints. Also, we shall discuss the one-dimensional problem only; generalization to the three-dimensional case is easy.

Writing down the kinetic equations for the ion distributions is straightforward. There are five unknowns, the concentrations of mobile ions, c_A, c_B, c_H, and c_{OH}, and the concentration of dissociation carboxylic ions c_C, all of which depend on the position x and time t. The mobile ions diffuse in the electric field. At the same time, the ions H^+, OH^-, and $-COO^-$ are created (or annihilated) by the dissociation–association reaction:

$$H^+ + OH^- \rightleftharpoons H_2O \tag{23}$$

$$H^+ + -COO^- \rightleftharpoons -COOH \tag{24}$$
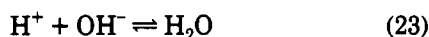
The dynamics of c_A and c_B is described by the diffusion equations

$$\frac{\partial c_A}{\partial t} = D_A \frac{\partial}{\partial x}\left(\frac{\partial c_A}{\partial x} + c_A \frac{\partial \psi}{\partial x}\right) \tag{25}$$

$$\frac{\partial c_B}{\partial t} = D_B \frac{\partial}{\partial x}\left(\frac{\partial c_B}{\partial x} - c_B \frac{\partial \psi}{\partial x}\right) \tag{26}$$

where D_A and D_B are the diffusion constants of A^+ and B^-, respectively, and ψ is the nondimensional electric potential. The kinetic equations for c_H, c_{OH}, and c_C involve the effects of the dissociation reactions, eqs 23 and 24:

$$\frac{\partial c_H}{\partial t} = D_H \frac{\partial}{\partial x}\left(\frac{\partial c_H}{\partial x} + c_H \frac{\partial \psi}{\partial x}\right) + r_1 + r_2$$

$$\frac{\partial c_{OH}}{\partial t} = D_{OH} \frac{\partial}{\partial x}\left(\frac{\partial c_{OH}}{\partial x} - c_{OH} \frac{\partial \psi}{\partial x}\right) + r_1$$

$$\frac{\partial c_C}{\partial t} = r_2 \tag{27}$$

where r_1 and r_2 represent the amount of ions produced (or absorbed) in a unit time by the reactions of eqs 23 and 24, respectively.

In the above equations, the electric potential ψ is an unknown. In principle, ψ should be determined by the Poisson equation. However, this introduces a very small length, i.e., the Debye's screening length ξ_D, into the problem and causes a problem in numerical simulations. This difficulty is avoided if we impose the local charge neutrality condition everywhere

$$c_A + c_H = c_B + c_{OH} \quad \text{in solution} \tag{28}$$

$$c_A + c_H = c_B + c_{OH} + c_C \quad \text{in gel} \tag{29}$$

With this restriction, the characteristic length in this system is $(\partial \psi/\partial x)^{-1}$, which is in general much larger than ξ_D. In most cases, the results obtained with this restriction agree with those obtained with the Poisson equation except in the small length scale of ξ_D.

Taking the time derivative of eqs 28 and 29 and substituting eqs 25–27, we have

$$\sum_i z_i D_i \frac{\partial}{\partial x}\left(\frac{\partial c_i}{\partial x} + z_i c_i \frac{\partial \psi}{\partial x}\right) = 0 \tag{30}$$

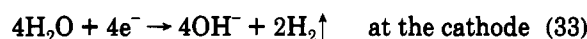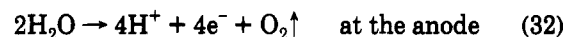Notice that the left-hand side of eq 30 is the divergence of the electric current

$$J = e \sum_i z_i D_i \left(\frac{\partial c_i}{\partial x} + z_i c_i \frac{\partial \psi}{\partial x}\right) \tag{31}$$

Thus eq 30 guarantees that the electric current J is constant.

Equation 27 involves further unknowns r_1 and r_2 which depend on the detail of the reaction kinetics. However, their precise specifications are not necessary since the dissociation reactions are much faster than the diffusion processes. Therefore, c_H, c_{OH}, and c_C are determined by the dissociation equilibria and the charge neutrality conditions, eqs 7, 8, 28, and 29, for given values of c_A and c_B which are determined by the diffusion equations.

To summarize, in order to determine the ionic distributions, we have to solve the set of three partial differential equations (25), (26), and (31). Next we shall consider the boundary conditions for these equations.

3.2. Boundary Conditions. (A) At Electrodes. We assume that there are no electrode reactions for A^+ nor B^- and that the only electrochemical reaction taking place at the electrodes is the electrolysis of water:

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2\uparrow \quad \text{at the anode} \tag{32}$$

$$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2\uparrow \quad \text{at the cathode} \tag{33}$$

These reactions are assumed not to perturb the diffusions of A^+ and B^-. Hence, the boundary conditions at the electrode are that the ionic currents of A^+ and B^- are zero:

$$j_A = -D_A\left(\frac{\partial c_A}{\partial x} + c_A \frac{\partial \psi}{\partial x}\right) = 0 \tag{34}$$

$$j_B = -D_B\left(\frac{\partial c_B}{\partial x} - c_B \frac{\partial \psi}{\partial x}\right) = 0 \tag{35}$$

The condition at the electrodes also determines the electric current J. If the experiment is done under constant current, J is given explicitly. If the voltage between the electrodes is fixed, J is determined implicitly by the condition that the difference in the electric potential between the electrodes is equal to the imposed value.

(B) Gel–Solution Boundaries. In the equilibrium state, the discontinuity in the ionic concentrations and the electric potential at the gel–solution boundary is determined by the Donnan theory. If an electric field is applied, the system is not in equilibrium, and in general the Donnan theory is not valid. However, for the usual electric field, the perturbation from the equilibrium state is very small. Indeed the magnitude of the perturbation can be estimated by

$$\frac{\text{drift velocity of ions by electric field}}{\text{diffusion velocity over the length of } \xi_D} \simeq \frac{DeE/k_BT}{D/\xi_D} =$$

$$\frac{eE\xi_D}{k_BT} \tag{36}$$

where E is the applied electric field, and D is the characteristic diffusion constant of mobile ions. In a typical condition of $E = 10$ V/cm and $\xi_D = 200$ Å, the ratio

is about 10^{-3}. Thus, for the usual strength of the electric field, we may assume that the Donnan condition is always satisfied. Using the subscript g and s to denote the values at the gel side and the solution side of the interface, respectively, we can write the Donnan condition as

$$\frac{c_{ig}}{c_{is}} = \exp[-z_i(\psi_s - \psi_g)] \quad \text{for } i = A, B \quad (37)$$

The other condition to be satisfied is the continuity in the ionic currents

$$D_i\left(\frac{\partial c_{is}}{\partial x} + z_i c_{is}\frac{\partial \psi_s}{\partial x}\right) = D_i\left(\frac{\partial c_{ig}}{\partial x} + z_i c_{ig}\frac{\partial \psi_g}{\partial x}\right) \quad \text{for } i = A, B \quad (38)$$

4. Numerical Simulation

4.1. Parameters. We solve the above set of equations numerically. As the initial state, we choose the equilibrium state with no current:

$$c_A = c_{A0} \text{ and } c_B = c_{B0} \quad \text{in the solution at } t = 0$$

The time evolution of the ionic concentrations is obtained by the following procedure:

1. For given values of c_A and c_B at time t, we calculate c_H, c_{OH}, and c_C using the conditions of the local charge neutrality and dissociation equilibria.

2. Using the values of c_i at time t, we obtain $\partial\psi/\partial x$ by eq 31.

3. From the diffusion equations (25) and (26) and the boundary conditions (34)–(38), we obtain c_A and c_B at the next time step $t + \Delta t$ and go to the step 1.

Calculation is done for the following set of parameters.

(a) Initial concentrations in the solution:

$$c_{A0} = c_{B0} = 10^{-3} \text{ mol/L (neutral condition)} \quad (39)$$

(b) Concentration of COOH group in the gel:

$$c_M = 10^{-3} \text{ mol/L} \quad (40)$$

(c) Dissociation constant of –COOH:[13]

$$K_g = 6 \times 10^{-5} \text{ mol/L} \quad (41)$$

(d) Diffusion constants of ions:

$$D_A = D_B = D_H = D_{OH} = 10^{-5} \text{ cm}^2/\text{s} \quad (42)$$

(e) Current density:

$$J = 10^{-4} \text{ A cm}^{-2} \quad (43)$$

(f) Gel size:

$$0.5 \text{ cm} \quad (44)$$

Although the actual diffusion constants of ions depend on the species and salt concentration,[14] they are chosen to be equal to each other since it simplifies the subsequent analysis greatly.

For the values given above, the initial concentrations of ions inside and outside the gel are calculated to be $c_{As} = c_{Bs} = 10^{-3}$ mol/L, $c_{Ag} = 1.6 \times 10^{-3}$ mol/L, $c_{Bg} = 0.6 \times 10^{-3}$ mol/L, $c_{Hs} = c_{OHs} = 10^{-7}$ mol/L, $c_{Hg} = 1.6 \times 10^{-7}$ mol/L, $c_{OHg} = 0.6 \times 10^{-7}$ mol/L, and $c_{Cg} = 1.0 \times 10^{-3}$ mol/L (almost completely dissociated). Notice that c_H and c_{OH} are much smaller than c_A and c_B. For the current of eq 43, the (initial) velocity of ions in the solution is

$$V_s = \frac{J}{(c_{As0} + c_{Bs0})e} = 5 \times 10^{-4} \text{ cm/s} \quad (45)$$
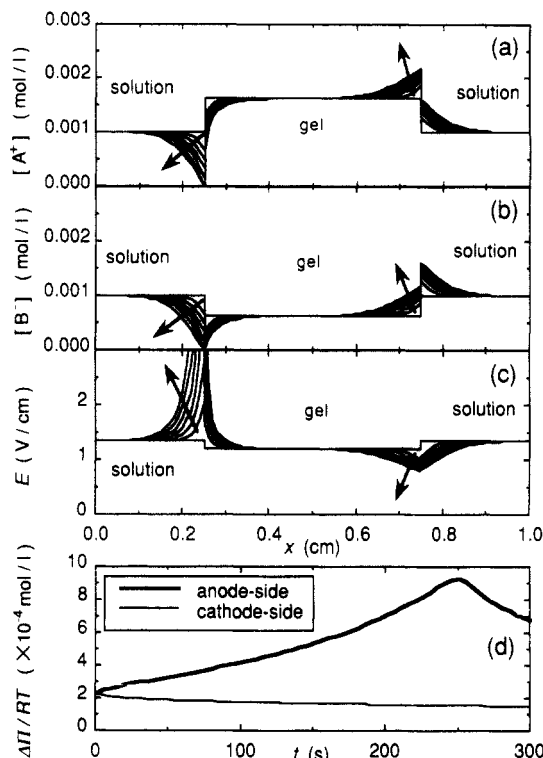
Three cases are considered here:

Figure 6. Results of the numerical simulation for the gel placed between electrodes. Time evolutions of (a) $c_A(x,t)$, (b) $c_B(x,t)$, and (c) $E \equiv \partial\psi(x,t)/\partial x$ are plotted against the spatial coordinate, and (d) osmotic pressure differences $\Delta\Pi/RT$ on the cathode side and the anode side are plotted against time. The curves in a–c represent the results for $t = 0, 50, 100, 150, 200, 250,$ and 300 s. The time evolution of the profile is indicated by the arrows.
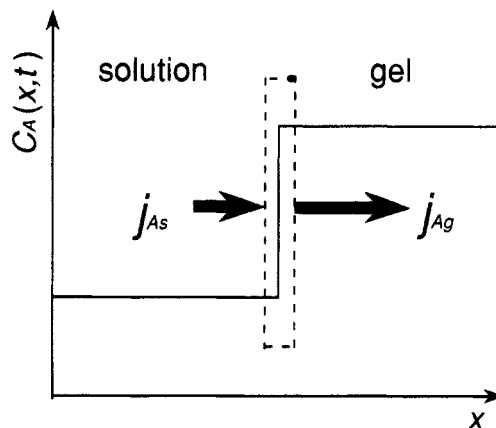

Figure 7. Schematic figure of ion flux to explain the decrease of $c_A(x,t)$ at the anode-side gel–solution boundary shown in Figure 6. The ion flux flowing into the boundary region (left arrow) is smaller than that flowing out of the region (right arrow).

(A) The gel is placed between the electrodes, sufficiently separated from them.

(B) The gel is contacting with the cathode.

(C) The gel is contacting with the anode. The results are discussed in the next section.

4.2. Results. We shall first describe the results qualitatively and explain why the anode side of the gel swells in cases A and B, while it shrinks in case C.

(A) Figure 6 shows the results for case A. Near the anode side of the gel boundary, c_A and c_B decrease, while they increase near the cathode side. The reason for this is clear (see Figure 7). Consider the flux of A^+ flowing in and out of the small region at the anode side boundary. In the range of ionic concentrations studied here, the velocity of
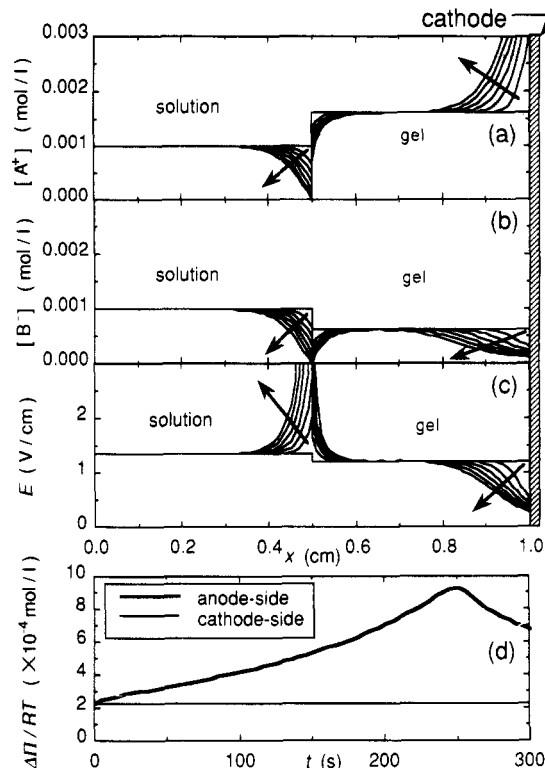
Figure 8. Similar to Figure 6 for the gel placed contacting with the cathode.

Figure 9. Similar to Figure 6 for the gel placed contacting with the anode.

A^+ in the gel is given by

$$V_g = J/(c_{Ag} + c_{Bg})e \simeq 0.9V_s \qquad (46)$$

which is almost the same as the velocity in the solution V_s. However, since c_{Ag} is larger than c_{As}, the outgoing flux is larger than the incoming flux. Hence, c_A decreases at the anode-side gel boundary. Since $\Delta\Pi$ is a decreasing function of c_{As} in the region studied here (see Figure 5), $\Delta\Pi$ increases with time. This is the reason why the gel swells on the anode side.

Similar consideration leads us to the conclusion that, on the cathode side, $\Delta\Pi$ decreases with time, and therefore the gel should shrink. Experimentally, there has been no report on the shrink on the cathode side. However, at this stage, this disagreement may not be considered serious because (i) the change in the osmotic pressure on the cathode side is small (see Figure 6d) and (ii) careful measurement of the volume change on the cathode side has not been executed. It will be interesting to check this point experimentally.

Figure 6d shows the time dependence of $\Delta\Pi$. As explained above, $\Delta\Pi$ increases with time near the anode, while it decreases near the cathode. It is also seen that $\Delta\Pi$ on the anode side has a maximum. This maximum corresponds to the maximum in the $\Delta\Pi$–c_A curve shown in Figure 5. It takes place when the concentration c_A outside the gel becomes comparable to $c_M(K_w^{1/2}/K_g)^{1/2}$. Experimentally, Shiga and Kurauchi[5] found that when a dc field is kept applied for an extended period of time, the deformation of the gel stops and then the anode side starts to shrink. It is conceivable that this phenomenon corresponds to the maximum in Figure 6d. Further analyses are needed to confirm this point since the present calculation takes no account of the deformation of the gel.

(B) Figure 8 shows the results of case B, where the gel is contacting with the cathode. Near the cathode, c_A increases, while c_B decreases. The reason is obvious: since fluxes of ions A^+ and B^- are zero at the electrodes, A^+ is
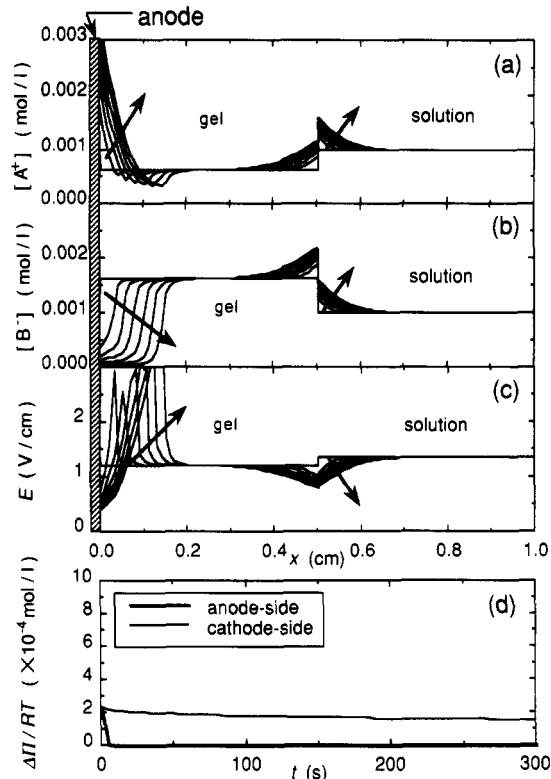
accumulated near the cathode and B^- is taken away from the cathode. The difference $c_A - c_B$ is compensated by the OH^- ions generated at the cathode due to the electrolysis of water, eq 33. The time dependence of the osmotic pressure is shown in Figure 8d. Note that $\Delta\Pi$ is a well-defined quantity even when the gel is contacting with the electrode because there are 2 degrees of freedom in this system and $\Delta\Pi$ can be calculated from c_{Ag} and c_{Bg} (instead of c_{As} and c_{Bs}) at gel–electrode boundaries. From the figure, we notice that, though c_{As} increases considerably at the cathode, the change in $\Delta\Pi$ is small. This is because $\Delta\Pi$ depends weakly on c_A when c_A increases.

(C) Figure 9 shows the results of case C, where the gel is contacting with the anode. In this case, the behavior near the anode is quite different from that of the solution–gel boundary. At the anode, H^+ ions are produced by the electrolysis of water. This suppresses the dissociation of carboxyl groups near the anode. As a result, $\Delta\Pi$ decreases very quickly. Thus the gel shrinks when it is kept in contact with the anode. This phenomenon has been observed by many authors.[4]

5. Theoretical Analysis

5.1. Equation in Alkaline Region. Having seen the qualitative aspects, we shall now study quantitative aspects, especially how the concentrations at the boundary change with time and how they are affected when the electric current is varied. For that purpose, we shall restrict ourselves to the phenomena taking place near boundaries, assuming that the gel and the solution have infinite size. Four boundaries are considered: the cathode and anode side boundaries between solution and gel and those between gel and electrodes.

To simplify the analysis, we shall assume that the outer solution is alkaline and that the gel is completely dissociated. We also assume, as in the numerical simulation, that the diffusion constants of the ions are the same. Under

these assumptions, the time evolution equations for the ionic concentrations become very simple.

In the alkaline region, we may set $c_H = 0$. Thus the charge neutrality condition is written as

$$c_A = c_B + c_{OH} \quad \text{in solution}$$

$$c_A = c_B + c_{OH} + c_M \quad \text{in gel} \quad (47)$$

where c_M is used instead of c_C because the gel is completely dissociated in the alkaline region. Equation 31 now becomes

$$D\frac{\partial}{\partial x}\left(\sum z_i c_i\right) + D\frac{\partial \psi}{\partial x}\sum c_i = \frac{J}{e} \quad (48)$$

The first term on the left-hand side is zero because of the charge neutrality condition. When we define the characteristic velocity as

$$V = J/ec_M$$

eq 48 gives

$$\frac{\partial \psi}{\partial x} = \frac{J}{De(c_A + c_B + c_{OH})} = \begin{cases} \dfrac{c_M}{2Dc_A}V & \text{in solution} \\[2mm] \dfrac{c_M}{D(2c_A - c_M)}V & \text{in gel} \end{cases} \quad (49)$$

Equation 25 then becomes

$$\frac{\partial c_A}{\partial t} = D\frac{\partial^2 c_A}{\partial x^2} \quad \text{in solution} \quad (50)$$

$$\frac{\partial c_A}{\partial t} = D\frac{\partial^2 c_A}{\partial x^2} - \frac{\partial}{\partial x}\left(V\frac{c_M c_A}{2c_A - c_M}\right) \quad \text{in gel} \quad (51)$$

The conditions at the boundary between solution and gel are (see eq 13)

$$c_A|_{gel} = \frac{1}{2}\left[\frac{c_M}{c_A} + \left(\left(\frac{c_M}{c_A}\right)^2 + 4\right)^{1/2}\right]c_A\Big|_{solution}$$

(Donnan equilibrium) (52)

$$-D\frac{\partial c_A}{\partial x} + \frac{Vc_A c_M}{2c_A - c_M}\Big|_{gel} = -D\frac{\partial c_A}{\partial x} + \frac{V}{2}c_M\Big|_{solution}$$

(continuity of ion flux) (53)

From eqs 50 and 51 and the boundary conditions (52) and (53), one can calculate $c_A(x,t)$. Notice that these equations do not include c_B. Since $\Delta\Pi$ is determined only by c_A in the alkaline region, the time evolution of $\Delta\Pi$ in the alkaline region is independent of c_B; thus, for example, adding HCl does not affect the swelling or deswelling behavior as far as the system is alkaline.

5.2. Solution–Gel Boundary. An analytic solution of the above equations can be obtained for a short time after the imposition of the electric field. On the right-hand side of eq 51, the magnitudes of the first and second terms are estimated as Dc_A/ξ_t^2 and Vc_A/ξ_t, respectively, where $\xi_t = (Dt)^{1/2}$ is the characteristic diffusion length in time t. (It will be confirmed later that the characteristic length scale in time t is $(Dt)^{1/2}$ rather than Vt.) Thus the ratio between the two terms is

$$\frac{\text{convective term}}{\text{diffusion term}} = \frac{V\xi_t}{D} \simeq (V^2 t/D)^{1/2} \quad (54)$$

Therefore, if $t < D/V^2$, the second term in eq 51 can be neglected, so that

$$\frac{\partial c_A}{\partial t} = D\frac{\partial^2 c_A}{\partial x^2} \quad \text{in both solution and gel} \quad (55)$$

Notice that the time region for this equation to be valid is rather large; D/V^2 is equal to 40 s for the case studied here. Furthermore, since the change in c_A is small, the boundary conditions (52) and (53) can be approximated as

$$c_A|_{gel} = P_0 c_A|_{solution} \quad (56)$$

$$\frac{\partial c_A}{\partial x}\Big|_{gel} - \frac{\partial c_A}{\partial x}\Big|_{solution} = \frac{V\bar{c}_A}{D} \quad (57)$$

where

$$P_0 = \frac{1}{2}\left[\frac{c_M}{c_{As0}} + \left(\left(\frac{c_M}{c_{As0}}\right)^2 + 4\right)^{1/2}\right]$$

and

$$\bar{c}_A = \left(\frac{c_{Ag0}}{2c_{Ag0} - c_M} - \frac{1}{2}\right)c_M$$

The set of linear equations (55)–(57) can be easily solved as

$$c_A(x,t) = c_{Ag0} - P_0\int_0^t G(x,t-t')\,\alpha\,dt' \quad \text{in gel} \quad (58)$$

$$c_A(x,t) = c_{As0} - \int_0^t G(x,t-t')\,\alpha\,dt' \quad \text{in solution} \quad (59)$$

where the position of the boundary is set to zero and $G(x,t)$ and α are defined by

$$G(x,t) = (4\pi Dt)^{-1/2}\exp\left(-\frac{x^2}{4Dt}\right)$$

and

$$\alpha = \frac{2V\bar{c}_A}{1 + P_0}$$

In particular, the concentration on the solution side of the boundary is

$$c_A(x=-0,t) = c_{As0} - \frac{2}{\sqrt{\pi}}\frac{\bar{c}_A}{1 + P_0}\left(\frac{V^2 t}{D}\right)^{1/2} \quad (60)$$

Thus the concentration decreases in proportion to $\sqrt{t}$.

5.3. Cathode–Gel Boundary. At the cathode, c_A increases with time and becomes much larger than c_M. Hence, the flux of A^+ in the gel near the cathode is approximated as

$$j_A = -D\frac{\partial c_A}{\partial x} + \frac{c_M c_A}{2c_A - c_M}V \simeq -D\frac{\partial c_A}{\partial x} + \frac{c_M}{2}V \quad (61)$$

Thus the diffusion equation and the boundary condition become

$$\frac{\partial c_A}{\partial t} = D\frac{\partial^2 c_A}{\partial x^2}$$

$$D\frac{\partial c_A}{\partial x} = \frac{c_M}{2}V \quad \text{at } x = 0$$

The solution is then given by

$$c_A(x,t) = c_{Ag0} + \frac{c_M}{2}V\int_0^t G(x,t-t')\,dt'$$

Thus, at the boundary

$$c_{Ag}(x{=}0,t) = c_{Ag0} + \frac{c_M}{2\sqrt{\pi}}(V^2 t/D)^{1/2} \tag{62}$$

This equation holds not only for short time but also for long time.

5.4. Anode–Gel Boundary. At the anode, H^+ is produced by the electrochemical reaction. Therefore, the gel becomes acidic even if the initial solution is alkaline. As a result, one cannot write down a simple equation for c_A or c_B. However, it is clear that the concentration c_B at the anode increases in proportion to $\sqrt{t}$ and that consequently the osmotic pressure decreases in proportion to $t^{-3/2}$ (see eq 22).

The time evolution of the concentration profile is slightly complicated. Figure 9 suggests that two dynamic processes are involved. One is the motion of the frontier of the depletion layer of B^-, which moves with a certain velocity; thus, the thickness of the depletion layer is increased in proportion to t. The other is the growth of the accumulated region of A^+, whose length scale increases in proportion to $\sqrt{t}$. Thus, in a long time, the depletion layer grows faster than the diffusion layer and causes the minimum in $c_A(x,t)$.

5.5. Scaling Analysis. In the long-time region, the above linear approximation becomes invalid. However, important conclusions can be derived by dimensional analysis. For the problem defined by eqs 50–53, the parameters involved in the problem are V (ms^{-1}), D (m^2 s^{-1}), c_{A0}, c_{B0}, and c_M (mol/L). Hence, by dimensional analysis, $c_A(x,t)$ can be written as the following functional form:

$$c_A(x,t) = c_{A0} f\!\left(\frac{Vx}{D}, \frac{V^2 t}{D}, \frac{c_{A0}}{c_M}, \frac{c_{B0}}{c_M}\right) \tag{63}$$

This equation is valid at any time, provided the interference between the boundary effects is not important.

Equation 63 indicates that the solution of the nonlinear equation for various currents J, which is proportional to V, can be superimposed if the length x and time t are properly scaled. In particular, the concentration of A^+ at the gel–solution boundary is written as

$$c_{As}(t) = c_{A0} f\!\left(\frac{V^2 t}{D}, \frac{c_{A0}}{c_M}, \frac{c_{B0}}{c_M}\right) \tag{64}$$

Consequently, the osmotic pressure is written as

$$\Delta\Pi = \Delta\Pi_0 f\!\left(\frac{V^2 t}{D}, \frac{c_{A0}}{c_M}, \frac{c_{B0}}{c_M}\right) \tag{65}$$

Thus, if the current is increased by a factor λ, the time necessary to reach the same value of the osmotic pressure decreases by factor λ^{-2}. In particular, the characteristic time t^* giving the maximum in the anode-side value of $\Delta\Pi(t)$ shown in Figure 6d is proportional to J^{-2}.

Notice that the above conclusion holds also for the general set of equations and the boundary conditions (eqs 25–30 and 34–38). The general equations involve many additional parameters, D_A, D_B, K_g, etc. However, the only dimensionless parameter which involves the time t is $V^2 t/D$. Thus the osmotic pressure is also written in the form of eq 65, and the same scaling law holds for time and length scale when the current J is varied.

6. Conclusion

In this paper, we have developed a semiquantitative theory for the deformation of ionic gels under an electric field. The theory predicts the following results for a cationic gel:

(i) The anode side shrinks if the gel is contacting with the anode, while the anode side swells and then shrinks if the gel is sufficiently separated from the anode.

(ii) The cathode side shrinks slightly in both contacting and noncontacting cases. These features are in agreement with experiments. The present theory also predicts the following:

(i) The characteristic time of deformation is proportional to the inverse square of the applied current (section 5.5).

(ii) If the diffusion constants of ions are the same, the deformation dynamics is governed by the concentration of the dominant ions, i.e., $[A^+]$ in the alkaline region and $[B^-]$ in the acidic region (section 5.1).

(iii) The characteristic length scale for the change of the ionic distribution increases in proportion to $\sqrt{t}$. It will be interesting to check these points experimentally.

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