Macromolecules **2005,** *38,* 1349−1356 **1349**

Electrostress Diffusion Coupling Model for Polyelectrolyte Gels

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Received October 6, 2004; Revised Manuscript Received December 6, 2004

ABSTRACT: To describe the deformation dynamics of polyelectrolyte gel, we formulate the electrostress diffusion coupling model. The model describes the interplay of the deformation of gel, permeation of water, and the transport of ions. The model gives a microscopic expression for the Onsager coefficient and allows us to discuss the effect of ionic radius. The model is then applied to the bending dynamics of a thin strip of ionic gels under stepwise application of electric field. The model qualitatively explains the relaxation behavior of an ionic gel (Nafion 117) for various kinds of ions including large counterions such as TEA$^+$ (tetraethylammonium).

I. Introduction

Polyelectrolyte gel deforms under electric field. The phenomena has attracted much attention as it could give a potential application of ionic gels as soft actuators and sensors.[1]

The deformation of ionic gels under electric field was first found for soft ionic gels such as swollen PVA gels[2] and poly(acrylamide) gels.[3] For these gels, the deformation takes place by the change of the osmotic pressure caused by the change of the ionic distribution near the gel surface.[4,5] Gels of this type, however, are not very attractive for application since their mechanical response is too slow, and they are not strong enough to be used as actuators.

Recently, another type of electroresponsive gels has been developed.[1,6−8] They are swollen polyelectrolyte gels of certain fluorocarbon networks with a counterion such as Na$^+$ plated with metal electrodes together. This gel bends under small electric fields on the order of 10 V/mm and is robust for a very large number of cycles. Asaka and Oguro considered that the deformation mechanism of this gel is different from that of the first type since the deformation of the new type gel takes place very quickly and since the deformation behavior is strongly dependent on the kind of counterions in the gel. They proposed that the bending is caused by the electro-osmosis:[9] as the ions move through the micropores of the gel under electric field, they carry a certain number of hydrated water molecules with them and change the local volume of the gel near the interface, causing the bending of the gel. On the basis of this picture, they analyzed the bending behavior theoretically for the situation that the constant electric current is applied.

Asaka and Oguro did not take into account of the permeation of water molecule caused by the pressure gradient within the bent gel. Therefore, their theory cannot explain the phenomena observed when a constant electric potential is applied to the sample. In this situation, the gel first bend quickly and then bend back slowly. The fast bending process is caused by the electro-osmosis, while the subsequent bending back process is considered to be caused by the water permeation due to the pressure gradient created in the bent gel. To describe the such relaxation, one needs a more comprehensive theory.

De Gennes, et al.[10] gave a more comprehensive theory using the phenomenological equation for the electric current and the water permeation caused by the electric field and the pressure gradient. The electric current density $\mathbf{j}_e$ and the water flux density $\mathbf{j}_s$ in the polyelectrolyte gels are coupled with the gradient of pressure p and the electric field ψ as follows

$$\mathbf{j}_e = -\sigma_e \nabla\psi - \lambda\nabla p \tag{1}$$

$$\mathbf{j}_s = -\kappa\nabla_p - \lambda\angle\psi \tag{2}$$

where σ_e is the conductance, κ is the Darcy's permeability and λ is the Onsager's coupling constant. These equations are known for porous materials to explain the electro-osmosis (water transport by electric field) and the streaming potential (electric field created by water transport). In the case of gels, the pressure field is also coupled with the deformation of the gel. The effect was qualitatively discussed by de Gennes et al., but they have not done any quantitative analysis based on their equation.

In this paper, we extend the idea of the above theory and develop the electrostress diffusion coupling model as a more formal theory for the deformation dynamics of polyelectrolyte gels under electric field. The theory is a straightforward extension of our previous work,[11−14] where we discussed the coupling of the network stress and the solvent permeation of neutral gels. In the present paper, we add a kinetic equation for the ion flux and electric potential and derive a complete set of equations for the gel deformation, water flux, and electric current The present theory expresses the Onsager coefficients by microscopic parameters (such the ionic diameter, the pore size, etc.) and allows us to

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10.1021/ma047944j CCC: $30.25

discuss the difference in the bending behavior due to ions. We apply the theory to calculate Onsager's coupling constant for various kinds of counterions of the Nafion 117 gel and compare with the experimental results of the streaming potential.[15] We also analyze the time evolution of the bending and relaxation of the gel for various kinds of counterions, and compare calculated results with experimental ones.

II. The Electrostress Diffusion Coupling Model

A. Basic Kinetic Equations. We consider an ionic gel which consists of charged polymer, water, and ions. They are denoted by the suffixes p (polymer), s (solvent) and i (ions of species i), where the suffix i runs from 1 to i_{max} if there are i_{max} ionic species. Let c_p be the number of the ionic groups attached to the polymer per unit volume and c_i be the number of free ions per unit volume, and let q_p and q_i be their charges. We impose the condition that the charge neutrality condition be satisfied in the bulk region of the gel:

$$c_p q_p + \sum_{\mathrm{i}} c_i q_i = 0 \tag{3}$$

Let w_s and w_i be the specific volume (i.e., the volume per molecule) of solvent and ion i, and w_p be the volume of polymer per unit ionic group. We impose the condition that the gel is incompressible as a whole. This condition can be written as

$$c_p w_p + c_s w_s + \sum_{\mathrm{i}} c_i w_i = 1 \tag{4}$$

To derive the kinetic equation, we write down the force balance equation for each component, the polymer, solvent and ions. Let $\mathbf{v}_p$,$\mathbf{v}_s$ and $\mathbf{v}_i$ be their average velocities.

First consider the force balance for the ion i. There are three sources for the force acting on the ions: the electric potential, the pressure field and the frictional force due to solvent (i.e., water). The force created by the electric potential field ψ is $- q_i\nabla\psi$. The force created by the pressure gradient ∇p is $- w_i\nabla p$. (This can be shown by directly calculating the total force acting on a rigid body in a pressure gradient, It can also be shown formally from the variational principle as it was done in ref 11.) The frictional force is given by $- \zeta_i(\mathbf{v}_i - \mathbf{v}_s)$, where ζ_i is the friction constant of the ion i related to solvent. Thus, the force balance equation gives

$$c_i\zeta_i(\mathbf{v}_i - \mathbf{v}_s) = -c_i q_i\nabla\psi - c_i w_i\nabla p \tag{5}$$

where the both sides of the equation are multiplied by the factor c_i to indicate explicitly that the equation stands for the force balance for the collection of ions of species i in unit volume.

The force balance equation for the polymer can also be written down in the same way. Each ionic group of the polymer feels the force $- q_p\nabla\psi - w_p\nabla p$. The polymer also feels the force transmitted through the polymer network. The force can be written as $\nabla\sigma$ for the whole polymer in unit volume, where σ is the network stress, which can be obtained by the principle of virtual work.[11] Thus, the force balance equation is written as

$$c_p\zeta_p(\mathbf{v}_p - \mathbf{v}_s) = -c_p q_p\nabla\psi - c_p w_p\nabla p + \nabla\cdot\sigma \tag{6}$$

where ζ_p is the friction constant of the polymer related to solvent.

Finally, the force balance equation for the solvent is written as

$$\zeta_p c_p(\mathbf{v}_s - \mathbf{v}_p) + \sum_i \zeta_i c_i(\mathbf{v}_s - \mathbf{v}_i) = -c_s w_s\nabla p \tag{7}$$

The left-hand sides represents the reaction of the frictional force acting on the solvent due to the relative motion of polymer and ions, and the right-hand side represents the force due to the pressure gradient.

The electric current density is given by

$$\mathbf{j}_e = c_p q_p\mathbf{v}_p + \sum_i c_i q_i\mathbf{v}_i = \sum_i c_i q_i(\mathbf{v}_i - \mathbf{v}_p) \tag{8}$$

and the charge neutrality condition (3) imposes that

$$\nabla\mathbf{j}_e = 0 \tag{9}$$

Similarly, the incompressible condition (4) imposes the following equation:

$$\nabla(c_p w_p\mathbf{v}_p + c_s w_s\mathbf{v}_s + \sum_i c_i w_i\mathbf{v}_i) = 0 \tag{10}$$

Equations 5, 6, 7, 9, and 10 make a closed set of equations for $\mathbf{v}_p$, $\mathbf{v}_s$, $\mathbf{v}_i$, ψ, and p, and they can be solved under proper boundary conditions, which will be discussed later. The set of equations can also be derived from the variational principle[16] as was done in ref 11.

B. Electrostress Diffusion Coupling Model. The set of equations given in the previous section can be rewritten to a simpler form. First eqs 5−7 give the following equation

$$\nabla(\sigma - p\mathbf{I}) = 0 \tag{11}$$

where $\mathbf{I}$ is the unit tensor, and eqs 3 and 4 have been used. Equation 11 stands for the overall force balance equation for the bulk of the material.

Second, if we define the volume flux $\mathbf{j}_s$ by

$$\mathbf{j}_s = c_s w_s(\mathbf{v}_s - \mathbf{v}_p) + \sum_{\mathrm{i}} c_i w_i(\mathbf{v}_i - \mathbf{v}_p) \tag{12}$$

we get the following set of equations, which only involves the polymer velocity $\mathbf{v}_p$, the volume flux $\mathbf{j}_s$, and the electric current $\mathbf{j}_e$.

$$\mathbf{j}_e = -\sigma_e\nabla\psi - \lambda\nabla p \tag{13}$$

$$\mathbf{j}_s = -\kappa\nabla p - \lambda\nabla\psi \tag{14}$$

Here, the conductivity σ_e, the Darcy constant κ, and the electro-osmotic constant λ are given by

$$\sigma_e = \frac{c_p {q_p}^2}{\zeta_p} + \sum_i \frac{c_i {q_i}^2}{\zeta_i} \tag{15}$$

$$\lambda = -\frac{q_p}{\zeta_p}(1 - \phi_p) + \sum_i \frac{c_i q_i w_i}{\zeta_i} \tag{16}$$

$$\kappa = \frac{(1 - \phi_p)^2}{c_p\zeta_p} + \sum_i \frac{c_i {w_i}^2}{\zeta_i} \tag{17}$$

where $\phi_p = c_p w_p$ is the volume fraction of the polymer.

Several comments are needed for eqs 15−17.

First, notice that the expressions given above (eqs 13−17) satisfy the reciprocal relation, and the positive definiteness of the Onsager coefficient. ($\sigma_e > 0$, $\kappa > 0$, and $\sigma_e\kappa - \lambda^2 > 0$. The last equation can be proved easily by the Schwartz inequality.)

Second, $\mathbf{j}_s$ defined in eq 12 involves the effect of ions. This is because $\mathbf{j}_s$ stands for the volume transported by free molecules(namely solvent and ions) other than those belonging to polymer network. However, as we shall see later, in most cases, $\mathbf{j}_s$ is dominated by the term due to solvent molecules. So we shall call $\mathbf{j}_s$ solvent flux in this paper. The wording can be made rigorous if one considers the limit of $w_i \to 0$. In this limit, $\mathbf{j}_s$ totally comes from the solvent flux and one can call $\mathbf{j}_s$ solvent flux.

Third, eq 15 may look strange as it says that the immobile charges fixed to the polymers contribute to the electrical conductivity. However, this term represents the effect of electro osmosis and must be included. To see this, consider the experiment of the measurement of electrical conductivity, where electric field is applied to a fixed sample of conductive gel with no pressure gradient ($\nabla p = 0$). In this situation, the solvent flows with the velocity $\mathbf{v}_s = (q_p/\zeta_p)\nabla\psi$ according to eq 6. This solvent flow is actually observed as the effect of electro-osmosis in the experiment. The mobile ions then move with the velocity $\mathbf{v}_s - (q_i/\zeta_i)\nabla\psi$. Therefore, the net electrical current is given by

$$\mathbf{j}_\mathrm{e} = \sum_\mathrm{i} c_i q_i \left(\mathbf{v}_\mathrm{s} - \frac{q_i}{\zeta_i}\nabla\psi\right) = (\sum_\mathrm{i} c_i q_i)\frac{q_p}{\zeta_p}\nabla\psi - \sum_\mathrm{i}\frac{c_i q_i^{\,2}}{\zeta_i}\nabla\psi = -\left(\frac{c_p q_p^{\,2}}{\zeta_p} + \sum_\mathrm{i}\frac{c_i q_i^{\,2}}{\zeta_i}\right)\nabla\psi \quad (18)$$

where the charge neutrality condition (3) has been used. Therefore, there must be a term representing the polymer contribution. In practice, however, the polymer contribution to the electrical conductivity is not very large for the materials discussed here as we shall see later.

Fourth, the Onsager coupling constants consists of two terms

$$\lambda_i = \frac{1}{6\pi\eta}\sum_\mathrm{i}\frac{c_i q_i w_i}{a_i} \quad (19)$$

$$\lambda_p = -\frac{1}{6\pi\eta}(1-\phi_p)c_p q_p \xi_b^{\,2} \quad (20)$$

The first term λ_i represents the effect of water molecules hydrated to counterion, while the second term λ_p stands for the usual effect of electro-osmosis (namely the motion of water by electric field). As we shall show later, both terms seems to be important in interpreting the experimental data.

Equations 11, 13, and 14, together with the charge neutrality condition (3) and the incompressible condition (4) form the closed set of equations.

C. Boundary Condition. To solve the set of equations, we need boundary conditions. The boundary conditions are very important in the present problem. In the above derivation, we have implicitly assumed that the ion concentration is homogeneous. In fact, (5) is valid only for this case.

If the ion concentration is not homogeneous, additional term $-k_\mathrm{B}T\nabla c_\mathrm{i}$ must be added on the right-hand side of eq 5. With such a term, the kinetic equations cannot be written in a simple form such as eqs 13 and 14, and one needs to solve the full set of equations for the spatial distribution of ions as was done in ref 4. Therefore, the assumption of constant ion concentration simplifies the set of equations significantly.

The assumption of constant ion concentration is valid in the bulk region of the gel, but it is not valid near the boundaries (the boundary between gel and outer solution or the boundary between gel and electrode) where the ions are subject to double layer potential. In the present treatment, the complex phenomena taking place near the boundaries are all dealt with by the boundary conditions. Therefore, the boundary conditions are not expected to be given by standard forms such as Dirichlet or Neumann type. In the following, we give a few example of the boundary conditions, but they are by no means complete.

To solve the set of equations, three kinds of boundary conditions are needed, each describing the mechanical condition, the solvent permeation condition and the electric current condition. The first two are already discussed in ref 12.

(i) Mechanical Balance. If the mechanical force $\mathbf{f}_{bc}$ acting on the boundary is known, the mechanical balance equation has to be imposed:

$$(\sigma - p\mathbf{I})\mathbf{n} = \mathbf{f}_\mathrm{bc} \quad \text{for a deformable boundary} \quad (21)$$

where $\mathbf{n}$ is the unit vector normal to the boundary. On the other hand, if the velocity of the gel network at the boundary $\mathbf{v}_{bc}$ is known, the equation to be imposed is

$$\mathbf{v}_p = \mathbf{v}_{bc} \quad \text{for gels fixed to aboundary} \quad (22)$$

Equation 21 is for neutral gels. For ionic gels, the equation has to be modified. Near the boundary, the ion concentration is not homogeneous. If the term $k_\mathrm{B}T\nabla c_\mathrm{i}$ is added on the right-hand side of eq 5, the force balance equation becomes $\nabla(\sigma - (k_\mathrm{B}T\sum_i c_i + p)\mathbf{I}) = 0$. Accordingly, for the ionic gels, the boundary condition must become

$$(\sigma - (k_\mathrm{B}T\sum_i c_\mathrm{i} + p)\mathbf{I})\mathbf{n} = \mathbf{f}_{bc} \quad (23)$$

If the gel is free (i.e., if there is no external force acting on the gel surface), $\mathbf{f}_{bc}$ is given by $-(k_\mathrm{B}T\sum_i c_\mathrm{i} + p)\mathbf{n}$ in the solution, and eq 23 becomes

$$(\sigma - (k_\mathrm{B}T\sum_i [[c_\mathrm{i}]] + [[p]])\mathbf{I})\mathbf{n} = 0 \quad (24)$$

where $[[c_\mathrm{i}]]$ (and $[[p]]$) are the jump of the ion concentration (and the pressure) across the boundary. The term $k_\mathrm{B}T\sum_i[[c_\mathrm{i}]]$ stands for the ionic contribution of the osmotic pressure. It is an extra unknown and must be determined by some sort of constitutive equation. Alternatively as we are ignoring the time variation of ion concentration, we may assume that $k_\mathrm{B}T\sum_i[[c_\mathrm{i}]]$ is constant independent of time. In such a case, the ionic osmotic pressure term can be eliminated from the set of equations by redefining $\sigma - k_\mathrm{B}T\sum_i[[c_\mathrm{i}]]\mathbf{I}$ as σ.

(ii) Solvent Permeation at the Boundary. If the solvent can permeate freely across the boundary, the pressure p must be continuous across the boundary.

$$[[p]] = 0 \quad \text{for a permeable wall} \quad (25)$$

On the other hand, if the solvent cannot permeate through the boundary, the boundary condition becomes

$$\mathbf{j}_s\mathbf{n} = 0 \quad \text{for an impermeable wall} \tag{26}$$

The above boundary conditions represent two extreme cases. In reality, we expect that solvent permeation is neither completely free nor completely blocked. A natural assumption is

$$\mathbf{j}_s\mathbf{n} = \kappa b[[p]] \tag{27}$$

where κ_b is a constant characterizing the boundary. The permeation may also depend on the discontinuity of the electric potential $[[\psi]]$, but not much is known for these phenomena as far as we know.

(iii) Electric Potential and Electric Current. At the electrode, the electric potential changes dramatically across the electric double layer. As we have assumed that the charge neutrality is satisfied everywhere in the bulk, the electric double layer has to be treated as a discontinuity in the electric potential. Thus, the electric potential ψ in the bulk next to the electrode is related to the electric potential in the electrode $\psi_{electrode}$ by

$$\psi = \psi_{electrode} - \Phi \tag{28}$$

The discontinuity Φ stands for the double layer potential. The relation between Φ and electric current is complex in general. A simple model is to assume that no chemical reaction takes place at the electrode, and that the electric double layer is described by a linear capacitor $\Phi = CQ$ where Q is the charge density of the electric double layer and C is the capacitance per unit area of the double layer. In such a case, the boundary condition is given by

$$\mathbf{j}_e\mathbf{n} = \dot{\Phi}/C \tag{29}$$

This model is valid provided that Φ is less than a critical value F_c. If Φ becomes larger than F_c, electro chemical reaction takes place at the electrode, and the current $\mathbf{j}_e\mathbf{n}$ becomes a complex nonlinear function of Φ and the ion concentration at the electrode.

III. The Onsager Coefficients in Gels

A. Ion Size Dependence. We now estimate the Onsager coefficient using a simple model for the friction constants ζ_i and ζ_p. We assume that the friction constant of free ions ζ_i is given by the Stokes–Einstein law

$$\zeta_i = 6\pi\eta a_i \tag{30}$$

where η is the viscosity of solvent and a_i is the ion radius. To estimate ζ_p, we assume that the gel consists of microchannels of characteristic length ξ_b. Then the friction constant of polymer gel per unit volume is given by $6\pi\eta/\xi_b^2$. This gives

$$\zeta_p = \frac{6\pi\eta}{\xi b^2 c_p} \tag{31}$$

By eqs 30 and 31, the Onsager coefficients are written as

$$\sigma_e = \frac{1}{6\pi\eta}\left\{\sum_i \frac{c_i q_i^2}{a_i} + c_p^2 q_p^2 \xi_b^2\right\} \tag{32}$$

$$\lambda = \frac{1}{6\pi\eta}\left\{-(1-\phi_p)c_p q_p \xi_b^2 + \sum_i \frac{c_i q_i w_i}{a_i}\right\} \tag{33}$$

$$\kappa = \frac{1}{6\pi\eta}\left\{(1-\phi_p)^2 \xi_b^2 + \sum_i \frac{c_i w_i^2}{a_i}\right\} \tag{34}$$

For a gel which involves the counterion only, we may assume that $c_i = c_p$ and $q_i = -q_p$. In such a situation, eqs 32–34, are further simplified as

$$\sigma_e = \frac{c_p q^2_p}{6\pi\eta\xi_b}\left\{c_p \xi_b^3 + \frac{\xi_b}{a_i}\right\} \tag{35}$$

$$\lambda = \frac{c_p q_p \xi_b^2}{6\pi\eta}\left\{-(1-\phi_p) + \frac{3}{4\pi}\left(\frac{a_i}{\xi_b}\right)^2\right\} \tag{36}$$

$$\kappa = \frac{(1-\phi_p)^2 \xi_b^2}{6\pi\eta}\left\{1 + \left(\frac{4\pi}{3(1-\phi p)}\right)^2 c_p \xi_b^3 \left(\frac{a_i}{\xi_b}\right)^5\right\} \tag{37}$$

where we have assumed that the specific volume of an ion wi is given by $(4\pi/3)a_i^3$.

For typical swollen polyelectrolyte gel of fluorocarbon, we can take $\phi_p \sim 0.5$, $\xi_b \sim 1.0$[nm] and $c_i \sim 1.0/z$ mol/L,[15] where z denotes the valence of the counterion. Using these values, eqs 35–37 are calculated as a function of the Stokes radius of the counterions, and they are shown in Figure 1.

Figure 1a shows the electric conductivity σ_e. It is seen that the electric conductivity is mainly determined by ions. This is because $\xi_b \gg a_i$ in most cases.

Figure 1b shows the coupling constant λ. The term λ_p is independent of ion radius, while λ_i becomes more and more important as the ion size becomes larger (or as the pore size becomes smaller).

Figure 1c shows the Darcy's permeation coefficient κ. It is seen that κ is usually determined by the pore size of the gel. Again this is because $\xi_b \gg a_i$ in the usual situation.

B. Comparison with Experiments for Streaming Potential. We now compare our theory with the experiment of Xie and Okada[15] who measured the streaming potential for Nafion 117 gel for various kinds of counterions. Figure 2 shows the streaming potential coefficient $|\Delta\psi/\Delta p| = \lambda/\sigma_e$ plotted against the Stokes radius of ions. Filled triangles are the experimental results and open circles are the calculated value. In the theoretical calculation, a_i is determined by the experimental value for the electrical conductivity in an infinite dilute solution.[17] (Notice that a_i determined in this way represents the radius of the hydrated ion, not the isolated ion). The pore size ξ_b are reported in ref 15. These results are tabulated in Table 1. For ϕ_p and c_i, we use the value $\phi_p \sim 0.7$ and $c_i \sim 1.0/z$ mol/L, which are reported in ref 15.

In Figure 2, we plotted λ in two ways, one includes both λ_p and λ_i and the other includes λ_i only. Figure 2 clearly indicates that we need to include both λ_p and λ_i: the water flux term λ_p is necessary to explain the experimental results for both cases of $z = 1$ and $z = 2$.

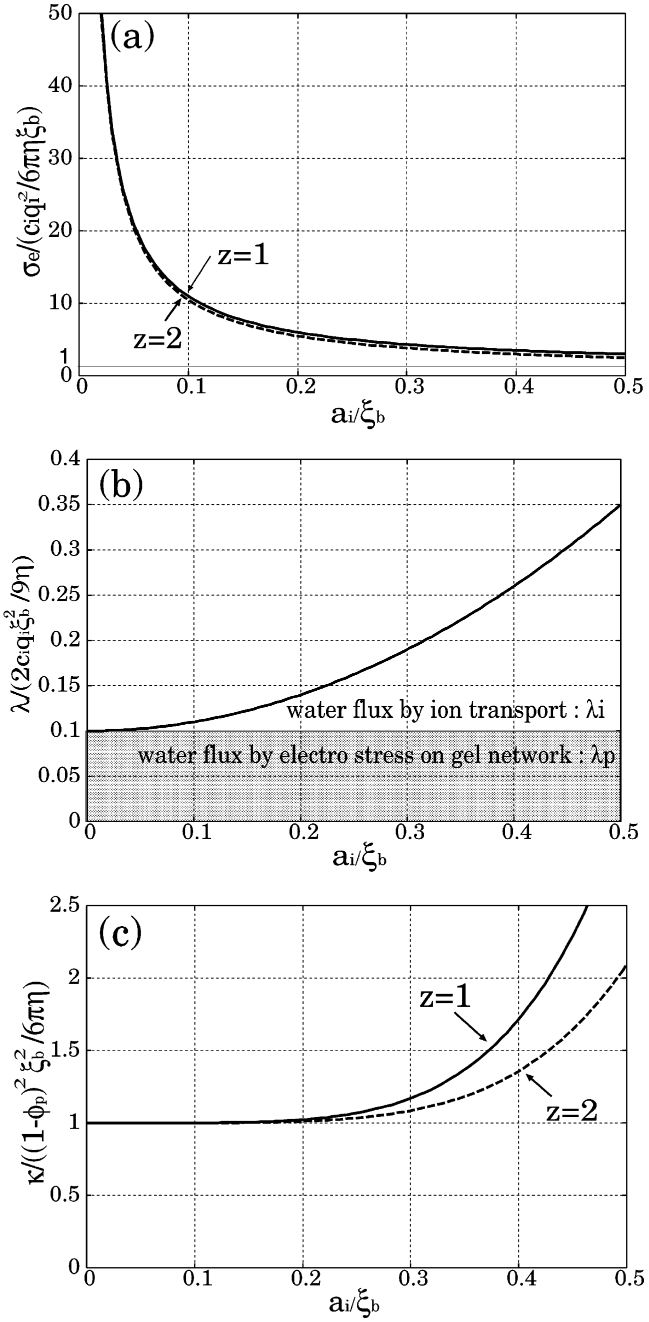

Figure 1. (a) Electric conductivity σ_e related to the ratio of the Stokes radius of a counterion a_i to the pore size of the gel ξ_b. (b) Cross-coefficient λ related to the ratio a_i/ξ_b. (c) Darcy's permeation coefficient κ related to the ratio a_i/ξ_b. Here, $\phi_p \sim 0.5$ and $c_i\xi_b{}^3 \sim 1.0/z$ are used.

IV. Bending and Relaxation Dynamics of a Gel

A. Basic Equations. We now discuss the bending dynamics of the polyelectrolyte gel when a constant electric field is applied stepwisely. We consider the situation that the applied electric field is low enough so that there is no electro chemical reaction taking place at the electrode.

The gel we consider is a strip of film of thickness h. We take a coordinate as it is shown in Figure 3, the origin is at the center of the film, and the x axis is normal to the film. Let $R(t)$ be the radius of the curvature of the film at time t.

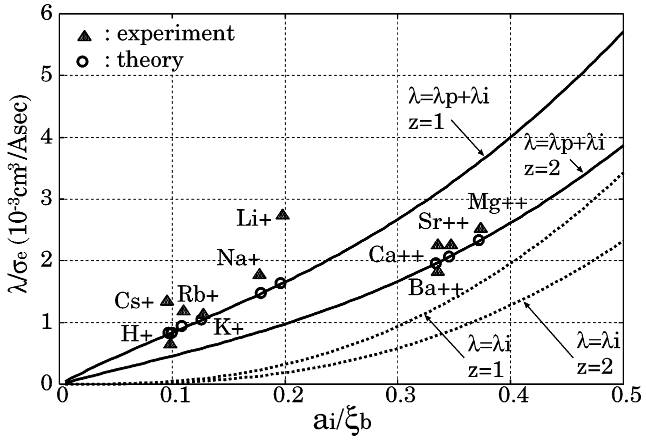

Figure 2. Calculated water transference coefficient λ/σ_e related to a_i/ξ_b with the experimental results of the streaming potential $|\Delta\psi/\Delta p| = \lambda/\sigma_e$ for various kinds of counterions in the Nafion 117 observed by Xie and Okada.[15] Here, $\phi_p \sim 0.7$ and $c_i\xi_b{}^3 \sim 2.2/z$ are used. The coupling constant λ is calculated in two cases, $\lambda = \lambda_p + \lambda_i$ and $\lambda = \lambda_i$.

Table 1. Ratios of the Stokes Radius of a Counterion Calculated from the Molar Conductivity in the Infinite Dilute Solution[17] to the Pore Size of the Swollen Nafion 117 Observed by Xie and Okada[15]

counterion	Stokes radius a_i (Å)	pore size[a] ξ_b (Å)	ratio a_i/ξ_b
H^+	1.3	13.0	0.10
Li^+	2.12	11.0	0.19
Na^+	1.64	9.6	0.17
K^+	1.12	9.0	0.12
TEA^+	2.60	(8.8)	0.30
Ca^{2+}	2.76	8.2	0.34

[a] For TEA^+ (tetraethylammonium ion ($[C_2H_5]_4N^+$)), the pore size is not observed experimentally, and we set the typical value at 0.30 for a large counterion.

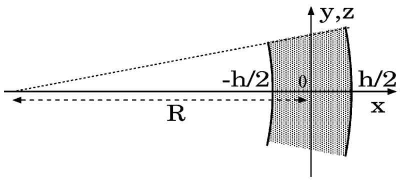

Figure 3. Model of the one-dimensional bending of a polyelectrolyte gel.

When the film bends with curvature $1/R(t)$, the displacement $\mathbf{u}(\mathbf{r}, t)$ at a material point $\mathbf{r}$ of the film is given by.

$$u_x = u_x(x, t) \tag{38}$$

$$u_y = \frac{x_y}{R(t)} \tag{39}$$

$$u_z = \frac{x_z}{R(t)} \tag{40}$$

Thus, the swelling ratio $f(x, t) \equiv \nabla \mathbf{u}(\mathbf{r}, t)$ is given by

$$f(x, t) = \frac{\partial u_x}{\partial_x} + \frac{2x}{R(t)} \tag{41}$$

The stress σ is given by the constitutive equation for the gel network. Here we use the linearized form for the stress tensor:

$$\sigma_{ij} = K\sum_k \frac{\partial u_k}{\partial x_k}\delta_{ij} + G\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3}\sum_k \frac{\partial u_k}{\partial x_k}\delta_{ij}\right) \quad (42)$$

where K is the bulk modulus and G is the shear modulus of gels. For the deformation given by eqs 38−40, this can be written as

$$\sigma_{xx}(x, t) = \left(K + \frac{4}{3}G\right)f(x, t) - \frac{4G}{R(t)}x \quad (43)$$

$$\sigma_{yy}(x, t) = \left(K - \frac{2}{3}G\right)f(x, t) + \frac{2G}{R(t)}x \quad (44)$$

The force balance equation $\partial(\sigma_{xx} - p)/\partial x = 0$ and the boundary condition ($\sigma_{xx} - p = 0$ at $x = \pm h/2$) gives

$$p(x, t) = \sigma_{xx}(x, t) + p_i \quad (45)$$

The torque balance is described by

$$\int_{-h/2}^{h/2} \mathrm{d}x\, (\sigma_{yy}(x, t) - p(x, t))x = 0 \quad (46)$$

From eqs 43 and 45, the pressure $p(x, t)$ is calculated by

$$p(x, t) = \left(K + \frac{4}{3}G\right)f(x, t) - \frac{4G}{R(t)}x \quad (47)$$

Equations 44, 46, and 47 lead the relation between the curvature $R(t)$ and the swelling ratio $f(x, t)$ as follows.

$$\frac{1}{R(t)} = \frac{4}{h^3}\int_{-h/2}^{h/2} \mathrm{d}x\, f(x, t)x \quad (48)$$

From eqs 13 and 14, it follows that

$$j_s(x, t) = -\left(\kappa - \frac{\lambda^2}{\sigma_e}\right)\frac{\partial p}{\partial x} + \frac{\lambda}{\sigma_e}j_e(x, t) \quad (49)$$

Equations 47 and 49 give

$$j_s(x, t) = -\left(\kappa - \frac{\lambda^2}{\sigma_e}\right)\left(K + \frac{4}{3}G\right)\frac{\partial f}{\partial x} + \left(\kappa - \frac{\lambda^2}{\sigma_e}\right)\frac{4G}{R(t)} + \frac{\lambda}{\sigma_e}j_e(x, t) \quad (50)$$

By the continuity equation $\partial f/\partial t = -\partial j_s/\partial x$, the time evolution for the swelling ratio is given by

$$\frac{\partial f}{\partial t} = D'\frac{\partial^2 f}{\partial x^2} \quad (51)$$

where the charge conservation law $\partial j_e/\partial x = 0$ has been used, and D' is defined by

$$D' = \left(\kappa - \frac{\lambda^2}{\sigma e\text{-}}\right)\left(K + \frac{4}{3}G\right) \quad (52)$$

which stands for the effective diffusion coefficient of ionic gels.

We assume that the electrode is impermeable ($j_s(x = \pm(h/2)) = 0$). This gives the following boundary condition:

$$\frac{\partial f}{\partial x} = \frac{\lambda}{D'\sigma_e}j_e(x, t) \pm \frac{4G}{K + \frac{4}{3}G}\frac{1}{R(t)} \text{ at } x = \pm h/2 \quad (53)$$

The set of equations can be solved analytically. Here we discuss the qualitative feature of the solution, and compare them with experiments.

B. Initial Curvature. When the electric field is switched on, there will be a current in a very short time which form a double layer at the electrode. The time τ_e needed for the formation of the electric double layer is essentially determined by the bulk conductivity σ_e and the capacitance C of the electric double layer.

$$\tau_e \simeq \frac{hC}{\sigma_e} \simeq \frac{\epsilon\kappa_D h}{\sigma_e} \quad (54)$$

where we have used the a simple double layer model for the capacitance of the double layer ($C \simeq \epsilon\kappa_D$ (ϵ being the dielectric constant of water and κ_D is the Debye parameter given by $\kappa_D = (\sum_i c_i q_i^2/\epsilon k_B T)^{1/2}$. τ_e is very short; about 0.1∼0.5[msec] at room temperature for typical Nafion 117 gel.

During the time τ_e, water is transferred from one electrode to the other, creating a large pressure gradient near the electrodes. For $t < \tau_e$ there will be no pressure gradient in the bulk region since this motion is essentially caused by the electro-osmosis. Therefore, for $t < \tau_e$, j_s is given by

$$j_s = -\lambda\psi = \frac{\lambda}{\sigma_e}j_e \quad (55)$$

Therefore, the total volume W transferred from one electrode to the other during time τ_e;

$$W = \int_0^{\tau_e} \mathrm{d}t'\, j_s(h/2, t) \quad (56)$$

is proportional to the total amount of the electric charge Q transferred during the time τ_e, i.e.,

$$W = \frac{\lambda Q}{\sigma_e} \quad (57)$$

Thus, the initial swelling ratio $f(x, 0)$ is given by

$$f(x, 0) = -W\delta\left(x + \frac{h}{2} + 0\right) + W\delta\left(x - \frac{h}{2} - 0\right) \quad (58)$$

The initial curvature $1/R(0)$ is calculated from eq 48 as follows.

$$\frac{1}{R(t)} = \frac{4W}{h^2} = \frac{4}{h^2}\frac{\lambda}{\sigma_e}Q \quad (59)$$

This equation indicates that the magnitude of the initial bending is proportional to the total charge transferred from one electrode to the other. This is indeed in agreement with experimental observation.

C. Relaxation Time. As a result of the initial charging of the electric double layer, a large pressure gradient is created near the electrodes: the initial pressure distribution is given by eqs 47 and 58. Accordingly, the water starts to flow from the high-pressure region to the low-pressure region. As a result, the gel starts to bend back. The relaxation of the bending can

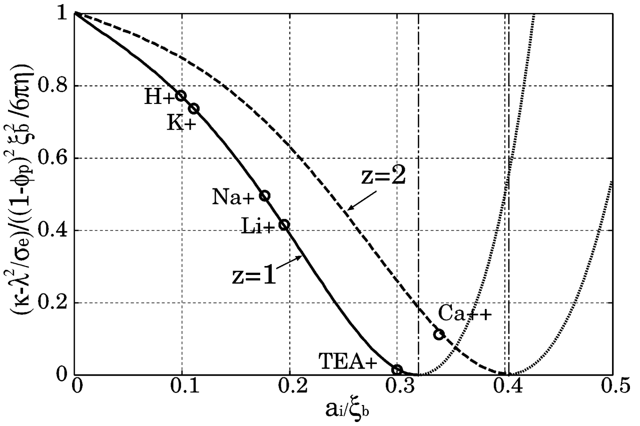

Figure 4. Effective solvent permeation ratio ($\kappa - \lambda^2/\sigma_e$) related to a_i/ξ_b in the relaxation process. We take $\phi_p \sim 0.7$ and $c_i\xi_b{}^3 \sim 2.2/z$. The permeation ratio becomes smaller as the size of a counterion larger.

be calculated by eq 48, where $f(x, t)$ is obtained by solving eq 51 under the boundary condition eq 53.

The characteristic relaxation time τ_{relax} of of this process is given by

$$\tau_{relax} \simeq \frac{h^2}{D'} = \frac{h^2}{\left(\kappa - \frac{\lambda^2}{\sigma_e}\right)\left(K + \frac{4}{3}G\right)} \qquad (60)$$

For a gel which involves counterion only, it follows from eqs 35−37 that $\sigma_e\kappa - \lambda^2$ can be rewritten as

$$\sigma_e\kappa - \lambda^2 = \frac{c_i q_i^{\,2} \xi_b^{\,2}}{(6\pi\eta)^2 a_i}\{c_i w_i - (1 - \phi_p)\}^2 \qquad (61)$$

Therefore, D' becomes very small when the volume of the counterion w_i becomes about $(1 - \phi_p)/c_i$.

Figure 4 shows an example of the calculated value of the effective permeation coefficient $\kappa - \lambda^2/\sigma_e$ for various ions for a typical swollen polyelectrolyte gel of fluorocarbon networks.[15] It is seen that D' vanishes at $a_i/\xi_b = 0.32$.

D. Comparison with Experiments. 1. Experiments. To compare the previous theory with experiments, we measured the bending and relaxation behavior of ionic gel for stepwise application of electric field. The Nafion 117 gel was plated with gold by the chemical plating method in the same way as it is described in refs 7 and 18. The composite was cut into a ribbon with a width of 1 mm and a length of 15 mm. The ribbon was vertically pressed by the gold electrode contact, immersed in the distilled water, and the displacement of the free end (10 mm from the fixed point) of the ribbon was measured by a laser displacement meter LC2100/2220 (Keyence, Japan) when a step voltage is applied across the film.

The electrochemical measurements were carried out simultaneously. The sinusoidal voltages were applied to the specimens by a waveform generator FC 200 (Yokogawa Electric Co.) via, a potentiostat HA-501G (Hokoto Denko Co. Ltd.).

Figure 5 shows the displacement of the gel swollen with various kinds of counterions. The displacement Δx is related to the curvature radius R by $\Delta x = R(1 - \cos(L/R))$, where L is the length of the gel, which is 10[mm].

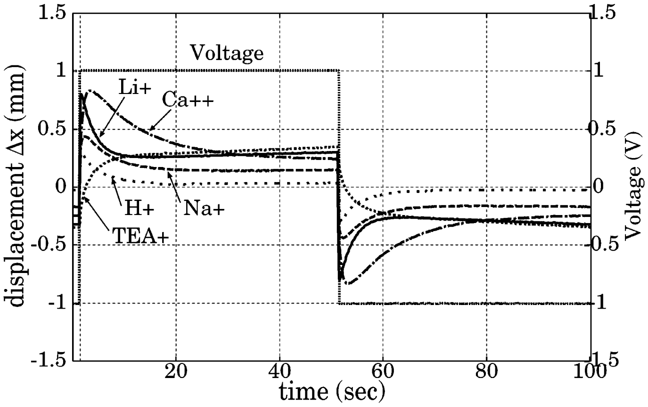

Figure 5. Experimental results of bending and relaxation process of the Nafion 117 for various counterions under the constant voltage. The preparation of the Nafion gel with gold and the displacement measurements were carried out as reported in the previous papers.[7,18]

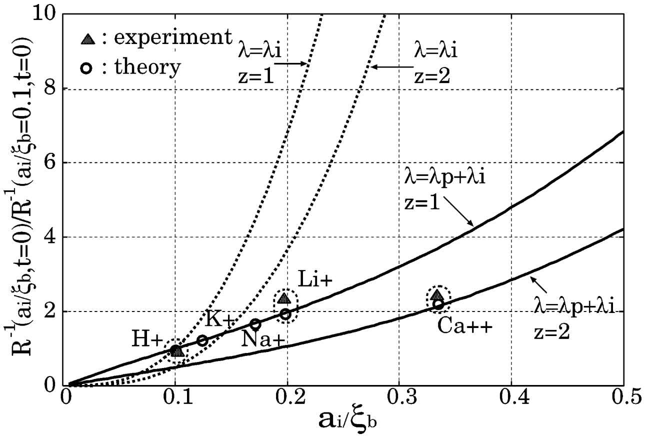

Figure 6. Calculated ratio of the initial curvature of various counterions to that of proton (H$^+$): $R_{H^+}(0)/R(0)$. The ratio is calculated for two cases of $\lambda = \lambda_p + \lambda_i$ and $\lambda = \lambda_i$ with experimental results.

It is seen that the bending behavior of the gel varies significantly depending on the kind of counterions. We now analyze the behavior using our theory.

2. Initial Bending. Figure 6 shows the initial curvature of the gel for various counterions taking the initial curvature for proton (H$^+$) as the reference.

The initial curvature is calculated for two cases, the case of $\lambda = \lambda_p + \lambda_i$ and that of $\lambda = \lambda_i$, and is compared with experiments. It is seen that to get good agreement it is necessary to use $\lambda = \lambda_p + \lambda_i$.

3. Relaxation Time. From the experimental results, the relaxation times are obtained as 8.0 s for H$^+$, 20 s for Na$^+$, 12 s for Li$^+$, and 45 s for Ca^{2+}. To compare these with theory, we plotted the ratio of the relaxation time to that for H$^+$ in Figure 7. The theoretical value is calculated using the parameter shown in Table 1. It is seen that the agreement between the theory and experiments are good.

As it was discussed previously, the relaxation time increases with the increase of the Stokes radius of the counterion. If the ratio between the Stokes radius of ions a_i and the pore size ξ_b becomes large enough, all water molecules in the pore are hydrated to counterion and the relaxation times goes to infinity. This prediction qualitatively explains the relaxation behavior for the bulky counterion such as TEA$^+$(Tetraethylammonium).

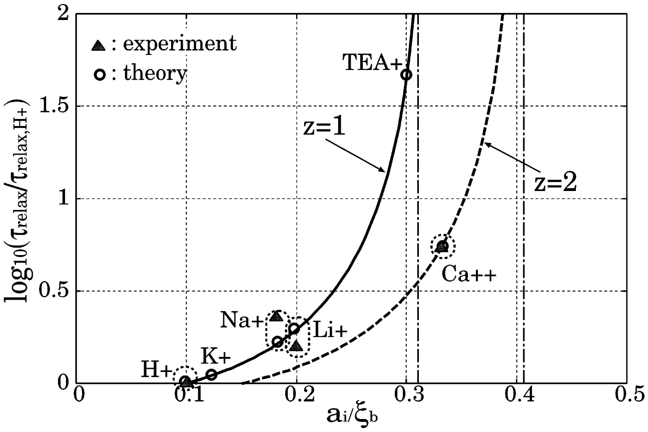

Figure 7. Calculated ratio of the relaxation time for various counterions to that of proton (H^+): $\tau_{relax}/\tau_{relax}$, H^+, is shown with the experimental results. The relaxation time becomes larger as the size of a counterion larger. When a_i/ξ_b goes to 0.32, the relaxation time becomes infinity and the relaxation disappears.

V. Summary

We have constructed the electrostress diffusion coupling model for the polyelectrolyte gels. The theory gives a microscopic expression for the Onsager coefficients in terms of the Stokes radius of the ion and size of the micropore of the gel. The theory describes the water flux induced by the electric stress of charged networks in the electro-osmotic constant, which previous theories cannot describe. This effect is confirmed by two experimental results of the streaming potential and the initial curvature of the bending.

The present theory aims at describing the dynamics of ionic gels in the bulk region. We have ignored the spatial variations of ion concentration, and described the dynamics by three elements, the deformation of the polymer network, the permeation of fluid components, and the electric current. Such treatment is justified if we know the boundary conditions. The boundary conditions proposed here are simple examples, and many features are ignored such as the change of the ion distribution, the change of double layer potential, electrochemical reaction and the effect of surface stress, etc. Part of these problems can be answered by conducting the boundary layer analysis for the full set of equations. We shall address these problems in the future.

We have calculated the relaxation time of the relaxation process of the gel for various counterions and showed that the relaxation time becomes larger as the Stokes radius of the counterion becomes larger. These results explains the bending behavior of a gel of such as TEA^+ (tetraethylammonium).

Acknowledgment. This work is partially supported by the Japan Science and Technology Agency (CREST-JST).

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MA047944J