pH-Induced Swelling Kinetics of Polyelectrolyte Hydrogels

Y. CHU,[1,*] P. P. VARANASI,[2] M. J. McGLADE,[2] and S. VARANASI[3]

[1]Department of Environmental Science and Engineering, and Department of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599; [2]SC Johnson & Son Inc., Racine, Wisconsin 53403; and [3]Department of Chemical Engineering, The University of Toledo, Toledo, Ohio 43606

SYNOPSIS

Through swelling experiments on polyelectrolyte (HEMA/DMA) hydrogels, pH-induced swelling kinetics is found to be best described by a diffusion–mechanical relaxation incorporated model. The theory of equilibrium swelling is quantitatively combined into the model of swelling kinetics. By doing so, the advantage is taken of applying relatively more matured knowledge of gel swelling thermodynamics to predict less knowledgeable dynamic behavior of gels. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Some controlled drug release devices have been developed based on pH-sensitive swelling characters of polyelectrolyte hydrogels.[1-3] In these devices, drugs are encompassed by or dispersed into a polyelectrolyte hydrogel. A change in pH of the solution surrounding the gel will initiate a process of shifting in the equilibrium swollen state of the gel, either swelling or deswelling. In many cases, this process cannot be completed immediately. Accompanied with it starts a change in the release rate of drugs by diffusion through the gel until a new equilibrium swollen state of the gel is reached. Therefore, to study such controlled drug release devices we need a thorough understanding of both the equilibrium state and the dynamic swelling processes of polyelectrolyte gels. Most of the attention in the past has been paid to the gel equilibrium state,[4,5] which successfully explained a lot of experimental results. But the role of swelling kinetics in controlling the drug release process should not be neglected, especially when the swelling process is slow relative to a quick response of drug release kinetics.[6,7] This article is an attempt at combining both kinetics and thermodynamics together to consider the swelling process of polyelectrolyte gels. The study of the accompanied drug release process can be found elsewhere.[8]

Physical Analysis

Hydrogels are considered as polymers with a three-dimensional network. The swelling of such polymers or gels upon being immersed in a solution is classically described as a mixing of an analogous linear polymer with the solvent; the swollen gel is in fact a polymer solution although an elastic rather than viscous one.[5] The mixing tendency is a function of compatibility between polymer and solvent, which is decided by their thermodynamic properties. This mixing tendency drives solvent into the polymer network and is an expansion force for network swelling. As the swelling goes, the chains between network junctions are elongated and an elastic retractive force in the gel is then developed to oppose the swelling process. Eventually, the development of the elastic retractive force will balance the swelling expansion force and an equilibrium state of swelling will be attained.

A polyelectrolyte gel is formed by crosslinking flexible polymer chains to which ionizable groups are attached. These ionizable groups will dissociate in solution completely for strong electrolyte or partially for weak electrolyte groups and the network is left with same charged groups along its chains. These charged groups produce an electrostatic repulsion force among themselves, which will add influence to the expansion of gel network. It can be

* To whom correspondence should be addressed.

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predicted that charge density, an important factor in the electrostatic force, will play a role in changing the swelling of a gel.

For a polyelectrolyte hydrogel, the charge density ρ_e is referred to the number of charged groups per unit volume and related to the concentration of total ionizable groups in the gel C_{mo}, the apparent dissociation constant K_{app}, and pH of local solution by the following equation:

$$\rho_e = -C_{mo}\frac{K_{app}}{K_{app} + C_{H^+}} \quad (1a)$$

for an acidic gel with K_{app} on the side of low pH or

$$\rho_e = C_{mo}\frac{C_{H^+}}{K_{app} + C_{H^+}} \quad (1b)$$

for a basic gel with K_{app} on the side of high pH.

When a gel, preequilibrated at $(pH)_1$, is suddenly placed in an environment of $(pH)_2$, assuming $(pH)_2 < (pH)_1$, this increased H^+ concentration will build up a gradient in the gel surface to drive H^+ ion diffusion into the matrix where $[H^+]$ is low. When the pendant weak electrolytic group is a basic one, e.g., $-B$, the moving-in of H^+ ions will cause the following ion exchange reaction to proceed in a direction to the right side,

$$-B + H^+ = -BH^+ \quad (2)$$

producing more ionized groups $-BH^+$. As a result, the charge density is up, the increased electrostatic repulsion force then destroys the previously established force balance and the balance shifts in the direction of swelling. In the meantime, the elastic retractive force induced by the swelling becomes stronger to encounter the increased swelling force. After certain rounds of back and forth fighting, solvent is absorbed into the gel and a new equilibrium state is attained. The whole swelling process led by H^+ ions diffusion can be summarized into the following four steps:

1. H^+ ions diffuse from the outer solution into the hydrogel;
2. driven by the change of pH at local microenvironment, an ion-exchange reaction takes place to produce more charged groups;
3. the gel network relaxes under the imbalance between the expansion force and the encountered elastic retractive force;
4. solvent is imbibed into the gel as step (3) is going on.

Depending on which one is controlling, different mechanisms were proposed to describe a swelling process. Among them is the *diffusion control mechanism* suggested by Nussbaum and Grodzinsky.[9] In this mechanism, the proton transport through a charged polyelectrolyte gel was considered to be the dominating step for the swelling and is described by the continuity equations:

$$\frac{\partial \bar{C}_i}{\partial t} = -\frac{\partial \Gamma_i}{\partial x} \quad \text{for salt components} \quad (3a)$$

and

$$\frac{\partial \bar{C}_H}{\partial t} + \frac{\partial \bar{C}^s_H}{\partial t} = -\frac{\partial \Gamma_H}{\partial x} \quad \text{for proton} \quad (3b)$$

Some comments can be made for this model. The model does have a simple mathematical expression by considering no change of geometry and size of the diffusion medium. For a gel that has a considerable variation in its swelling degree accompanied to the pH range of its surrounding solution, the model is too far away from reality to be reliable. In addition, although the influence of buffer on swelling kinetics is significant and has been experimentally observed and studied by Siegel and Firestone,[10-12] no attempts have been made to include this influence while modeling a swelling kinetic process.

Another model in studying swelling kinetics is completely opposite to the diffusion control mechanism and it considers that the *mechanical relaxation* is the most important step in a swelling process. The equation of motion was used by Tanaka and Fillmore[13] to describe the relaxation process of a polyacrylmide gel.

To attain a model that can describe real swelling processes as closely as possible, this study adds to the model the long neglected important factors like buffer effect and swelling degree change effect on the swelling kinetics. The model has adopted the concepts of diffusion control and mechanical relaxation control and then tried to seek a logical connection between these two extreme cases after having studied them separately. Finally, computed data from the developed models are compared with the results obtained from pH-induced swelling experiments on HEMA/DMA polyelectrolyte hydrogels.

MODEL DEVELOPMENT

Diffusion-Limited Swelling

A symmetric flat polyelectrolyte gel with basic ionizable groups $(-B)$ is immersed in an electrolytic

solution, e.g., NaCl solution buffered with a weak acid (AH). The gel is thin and compared with other two dimensions, only the diffusion along the thickness direction is significant. Therefore, it is a one-dimensional diffusion process. The species involved in the diffusion process include ionic components like H^+, Na^+, Cl^-, and A^-, as well as the neutral species AH. The diffusion flux of ionic species is described by the Nernst-Planck equation[14]

$$\Gamma_i = -\bar{D}_i \frac{\partial \bar{C}_i}{\partial x} + \bar{\mu}_i \frac{Z_i}{|Z_i|} \bar{C}_i E + \bar{C}_i U \qquad (4)$$

When the influences from electric field and the bulk flow are neglected, the equation becomes a familiar Fick diffusion equation

$$\Gamma_i = -\bar{D}_i \frac{\partial \bar{C}_i}{\partial x} \qquad (5)$$

It should be noted that a porous membrane gel is considered to be homogeneous in macroscopic dimensions, therefore all quantities are referred to total materials rather than to pores. Considering the size change by swelling through the diffusion process, a Lagrangian coordinate system associated with the solid membrane matrix[15] is used to derive continuity equations. For salt components, the continuity equations are

$$\frac{\partial[(1+H)\bar{C}_i]}{\partial t} = -\frac{\partial(\alpha\Gamma_i)}{\partial \psi} \qquad (6)$$

where α is a ratio of total membrane area to its initial area and H is the hydration degree of the gel. The continuity equations for the rest of components are

$$\frac{\partial[(1+H)\bar{C}_{A^-}]}{\partial t} = -\frac{\partial(\alpha\Gamma_{A^-})}{\partial \psi} - (1+H) r_{AH} \qquad (7)$$

$$\frac{\partial[(1+H)\bar{C}_{AH}]}{\partial t} = -\frac{\partial(\alpha\Gamma_{AH})}{\partial \psi} + (1+H) r_{AH} \qquad (8)$$

$$\frac{\partial[(1+H)(\bar{C}_{H^+} + \bar{C}^s_{H^+})]}{\partial t} = -\frac{\partial(\alpha\Gamma_{H^+})}{\partial \psi} - (1+H) r_{AH} \qquad (9)$$

where

$$-r_{AH} = k^f_{AH} C_{AH} - k^b_{AH} C_{A^-} C_{H^+} \qquad (10)$$

is the rate of dissociation reaction of weak acid buffer AH/A^-

$$AH = A^- + H^+ \qquad (11)$$

Combining eqs. (8) and (9) gives

$$\frac{\partial[(1+H)(\bar{C}_{H^+} + \bar{C}^s_{H^+} + \bar{C}_{AH})]}{\partial t} = -\frac{\partial[\alpha(\Gamma_{H^+} + \Gamma_{AH})]}{\partial \psi} \qquad (12)$$

$\bar{C}^s_{H^+}$ is the concentration of hydrogen ions bound to the polymer chains. For a basic gel

$$\bar{C}^s_{H^+} = C_m \qquad (13)$$

C_m is the magnitude of charge density. When the reversible dissociation reaction of the fixed ionizable groups is considered to proceed instantaneously, C_m for basic gel is expressed by a form of eq. (1b) as

$$C_m = \frac{C^s_{mo}}{1+H} \frac{\bar{C}_{H^+}}{K_{app} + \bar{C}_{H^+}} \qquad (14)$$

C^s_{mo} is the total molar concentration of ionizable amine groups per volume of solid polymer. Substituting eq. (14) into eq. (13) gives

$$\bar{C}^s_{H^+} = \frac{C^s_{mo}}{1+H} \frac{\bar{C}_{H^+}}{K_{app} + \bar{C}_{H^+}} \qquad (15)$$

It can be proved that eq. (15) is also correct for acidic gels.

Using the same approaches as Ruckenstein and Varanasi[16] and assuming (1) the dissociation reaction of buffer is at equilibrium everywhere all the time, i.e.

$$K_{AH} = \frac{\bar{C}_H \bar{C}_{H^+}}{\bar{C}_{AH}} \qquad (16)$$

(2) $\bar{C}_{A^-} + \bar{C}_{AH}$ is a time-independent constant through the membrane and equals to $\bar{C}_T$, we can obtain a relationship between $\bar{C}_{AH}$ and $\bar{C}_{H^+}$

$$\bar{C}_{AH} = \frac{\bar{C}_T \bar{C}_{H^+}}{K_{AH} + \bar{C}_{H^+}} \qquad (17)$$

Equation (12) can then be transformed into

$$\frac{\partial}{\partial t}\left\{\bar{C}_{H^+}\left[(1+H)\left(1 + \frac{\bar{C}_T}{K_{AH} + \bar{C}_{H^+}}\right) + \frac{C^s_{mo}}{K_{app} + \bar{C}_{H^+}}\right]\right\} = \frac{\partial}{\partial \psi}\left\{\alpha\left[\bar{D}_{H^+}\frac{\partial \bar{C}_{H^+}}{\partial x} + \bar{D}_{AH}\frac{\partial}{\partial x}\left(\frac{\bar{C}_T \bar{C}_{H^+}}{K_{AH} + \bar{C}_{H^+}}\right)\right]\right\} \qquad (18a)$$

To further simplify eq. (18a), the following dimensionless variable and constants are defined:

$$C_{mo}^{s'} = \frac{C_{mo}^{s}}{K_{app}}$$

$$\bar{C}_{T'} = \frac{\bar{C}_T}{K_{app}}$$

$$\bar{C} = \frac{\bar{C}_{H^+}}{K_{app}}$$

$$K = \frac{K_{AH}}{K_{app}}$$

$$\bar{D} = \frac{\bar{D}_{AH}}{\bar{D}_{H^+}}$$

Also, in one-dimensional swelling, $\alpha = 1$ and $dx = (1 + H)d\psi$. Equation (18a) therefore becomes

$$\frac{\partial}{\partial t}\left\{\bar{C}\left[(1+H)\left(1+\frac{\bar{C}'_T}{K+\bar{C}}\right)+\frac{C_{mo}^{s'}}{1+\bar{C}}\right]\right\} = \frac{\partial}{\partial \psi}\left\{\frac{1}{1+H}\bar{D}_{H^+}\left[\frac{\partial \bar{C}}{\partial \psi}+\bar{D}\frac{\partial}{\partial \psi}\left(\frac{\bar{C}'_T\bar{C}}{K+\bar{C}}\right)\right]\right\} \quad (18b)$$

Using dimensionless independent variables $\xi = \psi/\delta$ and $\tau = tD_{H^+}/\delta^2$, and[17]

$$\frac{\bar{D}_{H^+}}{D_{H^+}} = \left(\frac{H}{2+H}\right)^2 = \left(\frac{1-\phi}{1+\phi}\right)^2$$

eq. (18b) is further written as

$$\frac{\partial}{\partial \tau}\left\{\bar{C}\left[\frac{1}{\phi}\left(1+\frac{\bar{C}'_T}{K+\bar{C}}\right)+\frac{C_{mo}^{s'}}{1+\bar{C}}\right]\right\} = \frac{\partial}{\partial \xi}\left\{\phi\left(\frac{1-\phi}{1+\phi}\right)^2\left[1+\frac{K\bar{D}\bar{C}'_T}{(K+\bar{C})^2}\right]\frac{\partial \bar{C}}{\partial \xi}\right\} \quad (18c)$$

where ϕ is the polymer volume fraction of the swollen gel and related to the hydration degree by $\phi = 1 - H/(1 + H) = 1/(1 + H)$. The initial and boundary conditions are

$t \leq 0$

$$\bar{C} = \lambda C_0 \quad \text{for all } \xi \quad (18d)$$

$t \geq 0$

$$\frac{\partial \bar{C}}{\partial \xi} = 0 \quad \text{at } \xi = 0 \quad (18e)$$

$$\bar{C} = \lambda C_1 \quad \text{at } \xi = 1 \quad (18f)$$

Donnan ratio λ can be calculated based on the following consideration. A constraint on bulk electroneutrality is present inside the gel

$$\rho_e + \sum z_i \bar{C}_i = 0 \quad (19)$$

By the definition of Donnan ratio $\lambda^{z_i} = \bar{C}_i/C_i$ where $\bar{C}_i$ and C_i are the concentrations referred to gel and outer solution; eq. (19) can also be expressed as

$$\rho_e + \sum z_i \lambda^{z_i} C_i = 0 \quad (20)$$

Charge density ρ_e can be calculated from eq. (1b)

$$\rho_e = z_m \frac{\phi C_{mo}^{s}}{1 + \frac{1}{\lambda}10^{pH-pK_{app}}} \quad (21)$$

where pH is referred to the value in the outer solution. With eqs. (20) and (21), the Donnan ratio is numerically computed from experimental equilibrium swelling data (ϕ vs. pH).

The differential eq. (18c) has two dependent variables: hydrogen ion concentration and polymer volume ratio. To solve the equation, another relationship between these two variables should be found. As we know, the mechanical relaxation in a diffusion-controlled swelling is supposed to be instantaneous and a swelling equilibrium exists everywhere and all the time. Therefore the swelling equilibrium equation for polyelectrolytic gels[5,11] can be used as the relationship to relate the polymer volume ratio to hydrogen ion concentration:

$$\ln(1-\phi) + \phi + \chi\phi^2 + \bar{\nu}\rho_0(\phi^{1/3} - \tfrac{1}{2}\phi) = \bar{\nu}\sum(\bar{C}_i - C_i) \quad (22)$$

$\bar{\nu}$ is the solvent partial molar volume and ρ_0 is the number density (moles/liter) of polymer chains in the network at formation. χ is the Flory interaction parameter, which is determined by the compatibility of the polymer and the solvent. An increased value of χ will be associated with reduced compatibility and hence reduced swelling. The value of the interaction parameter used to be regarded as a constant but more and more experiments have proved that it is a function of polymer volume fraction. The interaction parameter for the pHEMA–water system was expressed by Peppas and Moynihan[18] as

$$\chi = 0.320 + 0.904\phi \quad (23)$$

Equation (22) can also be written as

$$\left|\frac{z_m}{z_-}\right|\phi C^s_{mo}\frac{\bar{C}}{1+\bar{C}} - \upsilon(C_s - \bar{C}_s) = \frac{1}{\bar{\nu}}[\ln(1-\phi) + \phi + \chi\phi^2] + \rho_0\left(\phi^{1/3} - \frac{1}{2}\phi\right) \quad (24)$$

To calculate the value of $(C_s - \bar{C}_s)$, two special cases are considered.[5] One case is when the external electrolyte concentration C_s is very small compared with the charge density of the gel. In this case, the second term on the left side of eq. (24) may be neglected in comparison with the first one to leave an equation like

$$\left|\frac{z_m}{z_-}\right|\phi C^s_{mo}\frac{\bar{C}}{1+\bar{C}} = \frac{1}{\bar{\nu}}[\ln(1-\phi) + \phi + \chi\phi^2] + \rho_0\left(\phi^{1/3} - \frac{1}{2}\phi\right) \quad (25)$$

The second special case is opposite to the first one. In this case, the external electrolyte concentration is comparable with or larger than the charge density and eq. (24) becomes

$$|z_m|\frac{\phi^2}{4I'}\left(C^s_{mo}\frac{\bar{C}}{1+\bar{C}}\right)^2 = \frac{1}{\bar{\nu}}[\ln(1-\phi) + \phi + \chi\phi^2] + \rho_0\left(\phi^{1/3} - \frac{1}{2}\phi\right) \quad (26)$$

Simultaneously solving eqs. (18) and (22) can then give the values of polymer volume ratio ϕ, or hydration degree $H(\xi, t)$. This hydration degree is, however, only a local value. To attain an average hydration degree, $H(\xi, t)$ should be integrated through the gel. This average hydration degree will be used to compare with the experimentally measured hydration degree $H_{exp}(t)$.

$$\bar{H}_{theory}(t) = \int_0^1 H(\xi, t)\, d\xi \quad (27)$$

Mechanical Relaxation Controlled Swelling

At $t < 0$, a polyelectrolyte gel is set at an equilibrium hydration degree H_0 corresponding to its external solution. At $t = 0$, one of external medium properties, e.g., hydrogen ion concentration, is changed and this change will be transmitted to the gel to induce a swelling or deswelling process. A mechanical relaxation control swelling means a very fast proton diffusion. The diffusion is so fast that a new uniform intramembrane hydrogen ion concentration $\bar{C}_{H^+}$ can be established immediately after the external pH is varied. To this new intramembrane $\bar{C}_{H^+}$, the present hydration degree H_0 is no longer in an equilibrium state. There will be a new equilibrium hydration degree $H_{eq}(\bar{C}_{H^+})$ for the gel to attain and this process is slow. As a result, in response to the changed external pH, there is a deformed gel by the difference between the current H_0 and its prospective equilibrium hydration degree $H_{eq}(\bar{C}_{H^+})$.

From the viscoelastic point of view, this deformation can be equated as a consequence of some kind of loading no matter what paths it takes to impose this loading. Therefore, the swelling process that tries to bring the current nonequilibrium state to its equilibrium position can be viewed as a recovery response of creep initiated by deloading ($\sigma = 0$). For creep recovery response, a simple Viogt model was suggested to describe the linear viscoelastic behavior of the polymer.[19,20] The model is one of many mechanical models that describe the linear viscoelastic behavior by various combinations of springs and dashpots. The spring is purely elastic (no energy is dissipated and mass is negligible) and dashpot is purely viscous (it is rigid and mass is negligible). The Viogt model consists of one spring and one dashpot in parallel. They have the same strain and their stresses are additive. The differential equation for local longitudinal strain e in the absence of imposed forces is

$$Me + \eta\frac{de}{dt} = 0 \quad (28)$$

where M is the equilibrium bulk longitudinal modulus and η is the viscosity of the swollen gel. Both M and η are material properties. The solution for strain relaxation is

$$e = e_0\exp\left(-\frac{t}{\tau_r}\right) \quad (29)$$

$\tau_r = \eta/M$ is a characteristic time constant called the "retardation time" in the discussion of creep. At $t = \tau_r$, the strain will reach to $\exp(-1)$ of its initial value e_0. The strain of the deformed gel is related to the hydration degree by[15]

$$e = \frac{H(t) - H_{eq}(\bar{C}_i)}{1 + H_{eq}(\bar{C}_i)} \quad (30a)$$

Similarly, the initial strain is

$$e_0 = \frac{H_0 - H_{eq}(\bar{C}_i)}{1 + H_{eq}(\bar{C}_i)} \tag{30b}$$

With these expressions, eq. (29) becomes

$$H(t) = H_{eq} - (H_{eq} - H_0)\exp\left(-\frac{t}{\tau_r}\right) \tag{31}$$

for the case of mechanical relaxation controlled swelling.

Because of a limited diffusion rate of H^+, a swelling process is, in practice, unable to attain an extreme mechanical relaxation control. But when a gel is so thin that a uniform H^+ distribution can almost immediately be attained after changing the pH of its surronding medium, we may use this model without significant error.

Diffusion and Relaxation Incorporated Swelling

For a swelling process that is under a control by both diffusion and mechanical relaxation, an incorporated mechanism should be concerned. In the same model system we used before, when the external concentration of H^+ is increased, an intramembrane H^+ concentration distribution is formed due to the limited proton diffusion rate and this distribution profile changes with time. Because of the limited diffusion rate of H^+ the whole gel cannot instantaneously attain a uniform concentration of H^+ corresponding to the new external pH and the mechanical control model we have talked above is not suitable to discribe the whole gel. But considering a very thin layer between x and $x + \Delta x$ inside the gel, we can assume that the H^+ concentration in that layer is uniform at any moment even though it is changing as time. At time t, corresponding to this uniform H^+ concentration, there is a swelling degree $H(\bar{C}_{H^+})$. When time goes to $t + \Delta t$, $\bar{C}_{H^+}$ becomes $\bar{C}_{H^+} + \Delta\bar{C}_{H^+}$ for which there is a prospective equilibrium hydration degree $H_{eq}(\bar{C}_{H^+} + \Delta\bar{C}_{H^+})$ determined by swelling thermodynamics of the gel. The difference between this prospective equilibrium hydration and the current hydration degree will then make this thin layer of gel undergo a relaxation process, which was described by the mechanical relaxation control model. The same analysis can be used to other parts of the gel as long as the thickness of the concerned portion of gel is kept small enough for the H^+ concentration in it to be thought as uniform. By considering the diffusion factor through the whole gel and the mechanical relaxation factor in the local environment, we have incorporated both effects into one model. In applying eq. (31), H_{eq} is the prospective equilibrium hydration degree corresponding to the current $\bar{C}_{H^+}$, H_0 is the current hydration degree, and H is the hydration degree of the gel after a certain time t of mechanical relaxation driven by $(H_{eq} - H_0)$. Before the entire gel is equilibrated by its external medium, the local $\bar{C}_{H^+}$ is kept changing and so are H_{eq}, H_0, and H. By this means, the affectors on the diffusion of H^+ and mechanical relaxation of polymer are combined together to control the swelling kinetics of a gel.

EXPERIMENTAL

Monomers HEMA (2-hydroxyethylmethacrylate) and DMA (N,N-dimethylaminoethyl methacrylate), used as received, were degassed. After rapidly mixing with crosslinker EGDMA (ethyleneglycol dimethacrylate) and redox initiators ammonium persulfate/sodium metabisulfite, the monomer solution was poured into a gel caster and left there for 24 h at room temperature. Gels were then peeled off and washed with fresh buffer solutions. All swelling experiments were conducted at room temperature. Equilibrium swelling studies of HEMA–DMA gel were conducted in a pH range of 3.0 ~ 9.0. Buffers were used in all experiments: citric acid buffer for pH 3.0 ~ 5.0, sodium phosphate buffer for pH 6.0 ~ 7.8, and Tris buffer for pH 8.0 ~ 9.0. Sodium chloride was used to regulate the ionic strength of the buffers, and a moderately high ionic strength of $0.125M$ was chosen in all the equilibrium and kinetics experiments.

RESULTS AND DISCUSSION

Equilibrium Swelling

In the part of model development, we have seen that the pH-induced swelling process, no matter what mechanism is followed, is closely related to gel swelling thermodynamics. Therefore, the experiments on the equilibrium swelling of the concerned gels were conducted first.

Two gels were prepared and studied, gel A and gel B. The volume ratio of ionic-group-containing monomer DMA to hydrophilic monomer HEMA is 25/100 in gel A and 30/70 in gel B with a crosslinker concentration of 0.0022 (v/v). It is observed that a small change in the volume ratio of DMA/HEMA

has resulted in a remarkable change in the equilibrium swelling degree of gels (Fig. 1).

The molar concentration of fixed ionizable groups in a copolymerized gel can be calculated from

$$C^s_{mo} = \frac{\rho_{\text{ionizable monomer,gel}}}{(MW)_{\text{ionizable monomer}}} \quad (32)$$

where $\rho_{\text{ionizable monomer,gel}}$ is referred to the density of the monomer-containing ionizable groups in the polymer gel. With the assumption of addition of volume, the density of DMA in the p(HEMA/DMA) polymer can be calculated from

$$\rho_{DMA,gel} = \rho_p \frac{(\rho V)_{DMA,monomer}}{(\rho V)_{DMA,monomer} + (\rho V)_{HEMA,monomer}} \quad (33)$$

where ρ_p is an experimentally measurable density for the p(HEMA/DMA) copolymer. The concentration of ionizable groups in the copolymer gels can be adjusted by varying the volume ratio of DMA to HEMA, which, along with the ionization degree—a function of pH, decides the charge density of the gel, then the electrostatic swelling force, and ultimately the equilibrium swelling degree. At a fixed pH value, higher C^s_{mo} will lead to a larger swelling degree in a certain range. This is consistent with our experimental results. In Figure 1, at each value of pH the swelling degree of gel B is higher than the value of gel A.

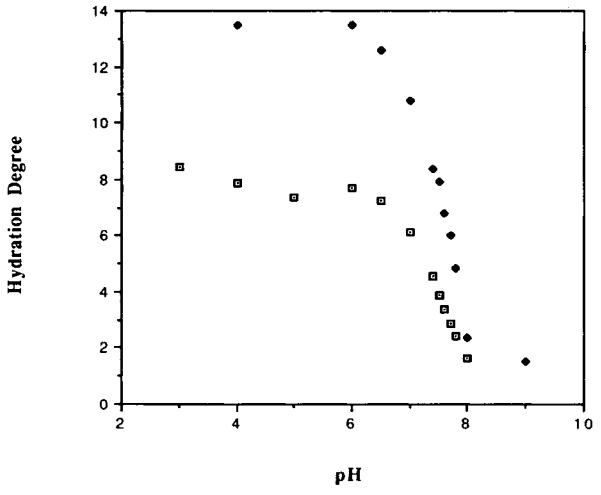


Figure 1 Experimental results showing the degrees of equilibrium swelling of hydrogels at different pH values of external solution. The square symbol is for gel A and diamond for gel B.

The change of pH alters the ionization degree of ionizable groups, and therefore the swelling degree. For a gel with a basic ionizable group (here, an amine group), the concentration increase of H^+ protonates the amine groups on the chain by an acid–base equilibrium process. As more groups are ionized, the charge density and the corresponding swelling degree are increased. In Figure 1 the equilibrium swelling degree changes very abruptly in a rather narrow range of pH 6.5 ~ 8.0. When the pH continues decreasing until below 6.5, the swelling degree change is very small. This is because the ionization process of the groups has approached its saturation stage and further increase of H^+ concentration will not much increase the number of the charged groups. The theoretical results calculated from eq. (22) are plotted in Figure 2(a)–(d), showing the effect on the equilibrium swelling degree of crosslinking density, concentration of ionizable groups, ionic strength of solution, and hydrogen ion concentration. Qualitatively, the model has predicted the pH effect well by comparing Figure 2(d) and Figure 1. For a quantitative prediction, the values of crosslinking density ρ_0, concentration of total ionizable groups C^s_{mo}, and Donnan ratio λ have to be known. In the present study, the crosslinking density (0.476 mol/L) is measured with an equilibrium swelling method and Donnan ratios (0.5 ~ 0.6) are calculated from experimental data by using eqs. (20) and (21). A comparison of equilibrium swelling behavior between theory and experiment is shown in Figure 3(a) where the values of C^s_{mo} are calculated from gel compositions.

We can see from Figure 3(a) that the quantitative match is not very good. This inconsistency is understandable considering that the real structure of a gel is much more complicated than that described in the model here. The charge density calculated from polymer monomer compositions can only be thought as an approximate value, which is helpful in getting a rough idea about the magnitude of gel charge density. A point should be made that the objective of our study here is to analyze the dynamic swelling process and to develop proper kinetics models. Therefore any failure from the side of gel thermodynamics should not confuse our judgment on swelling kinetics. For that reason, it is acceptable to make some adjustments of the parameters involved in the equilibrium swelling equation before the equation is introduced into the calculation of swelling dynamic models. The adjusted C^s_{mo} are the values from which the experimental equilibrium swelling data can be fitted by eq. (22) [Fig. 3(b) and (c)] and are listed in Table I, together with the cal-

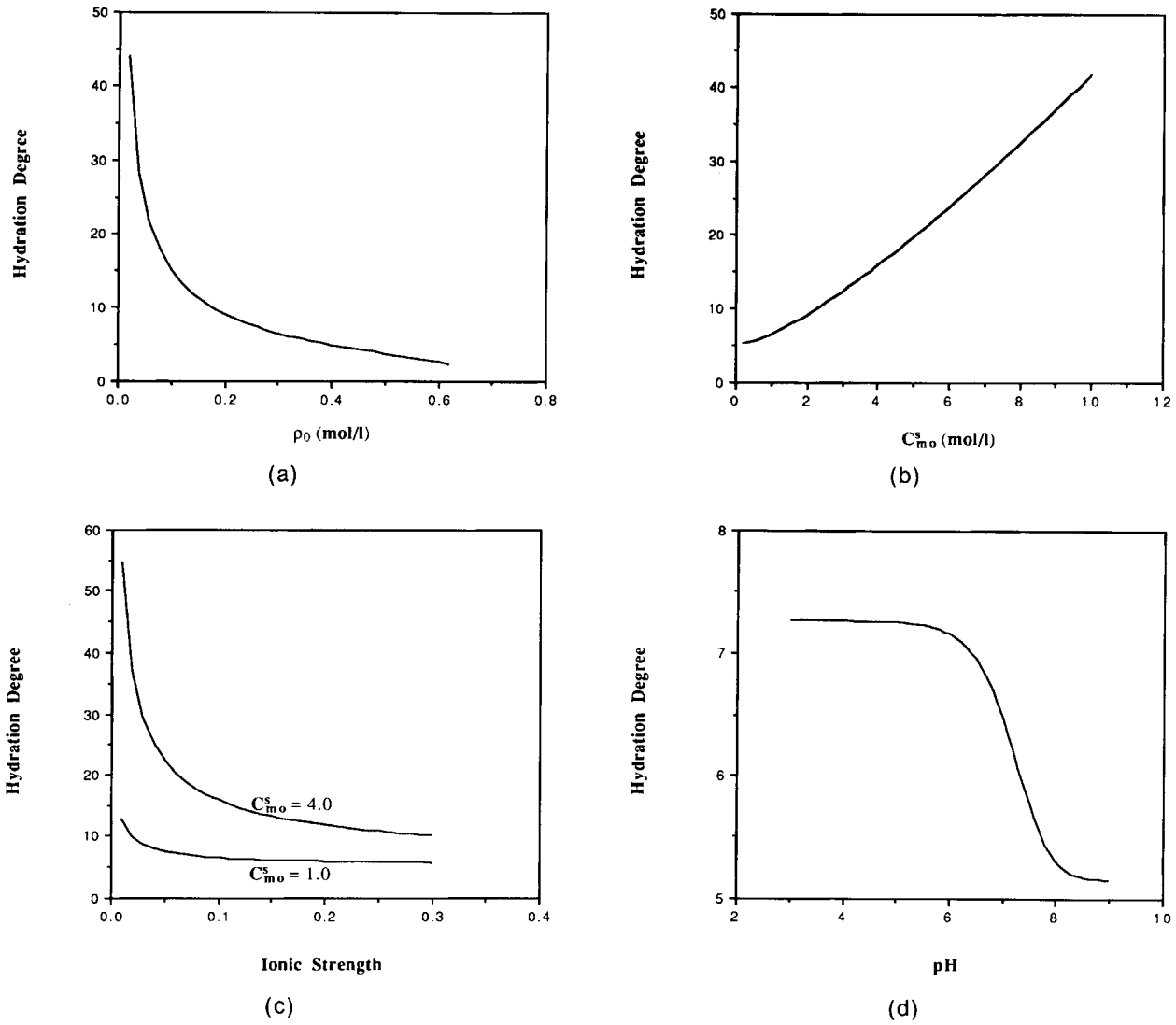


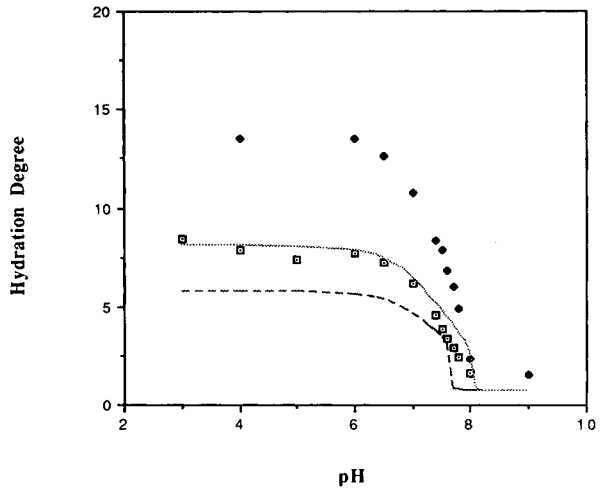
Figure 2 (a) The relationship between degree of equilibrium swelling and crosslinking density of polymer. (b) The relationship between the degree of equilibrium swelling of polymer and the concentration of ionizable groups in the solid polymer. (c) The relationship between degree of equilibrium swelling of polymer and ionic strength of external solution at different polymer charge densities. (d) The change of the degree of equilibrium swelling of polymer with the value of pH of external solution.

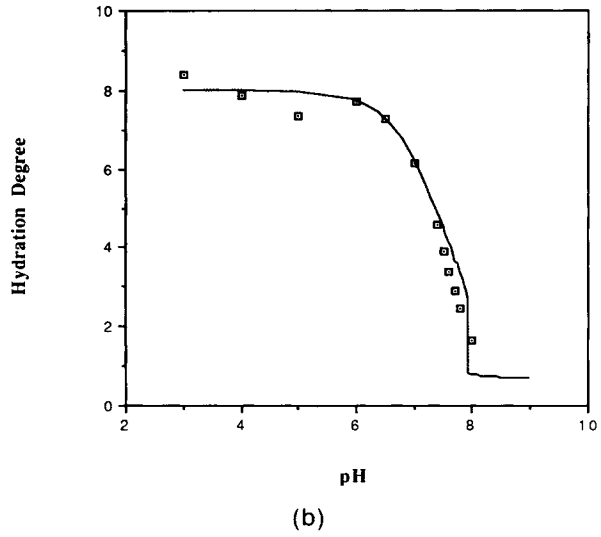
culated results. It can be seen that their values are not too far from each other. These experimentally determined $C^s_{mo,exp}$ will be used in the future to predict gel swelling kinetic behavior.

Kinetics Studies

A gel immersed in a solution is attached by a liquid stagnant film and the components from the solution must diffuse through this film before they reach the gel surface. The diffusion resistance provided by the film is apparent and even able to be dominant in some cases. To decrease the influence from this stagnant film, all kinetics experiment were conducted in a stirred solution medium.

Based on the information of phase transition from equilibrium swelling studies, the initial observation on the swelling process of a gel is made by following the time course of swelling degree after gel samples preequilibrated at pH 8.0 were transferred into





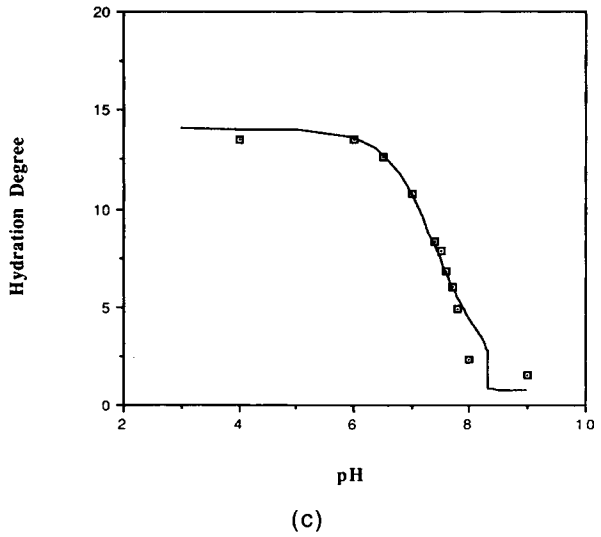


Table I The Values of C^s_{mo} for Gel A and Gel B

Polymer Materials	Gel A	Gel B
$\rho_{DMA,gel}$[a] (g/cm^3)	0.2315	0.3512
C^s_{mo} (mol/L) (cal.)[b]	1.473	2.234
C^s_{mo} (mol/L) (exp.)	2.200	4.000

[a] The values of C^s_{mo} (cal.) are calculated from the compositions of the gels and those of C^s_{mo} (exp.) are the values from which the experimental equilibrium swelling data can be fitted by eq. (22).

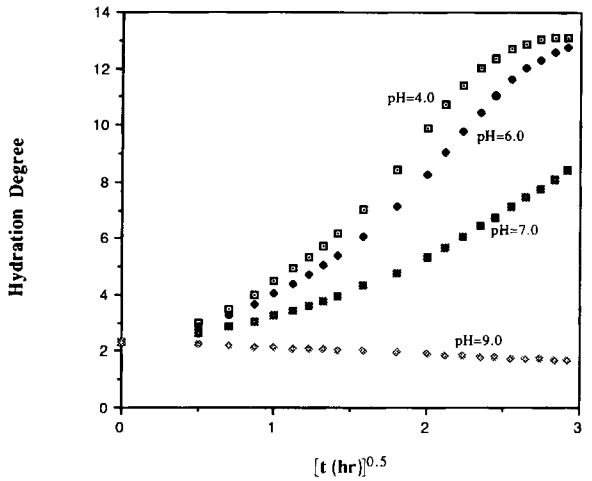
[b] The specific gravities of monomers HEMA and DMA are 1.034 and 0.933 (g/cm^3), respectively. The molecular weight of DMA is 157.21.

buffer solutions at pH 4.0, 6.0, 7.0, and 9.0, respectively [Fig. 4(a) and (b)].

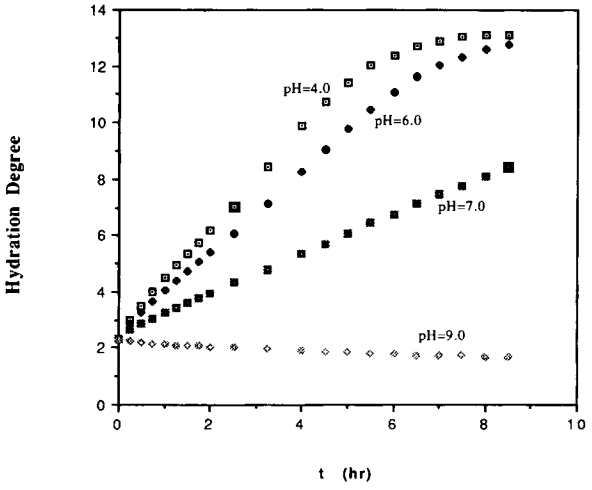
The swelling characters of uncharged polymers fall into one of the three cases:[21,22] Fickian or normal swelling, non-Fickian or anomalous swelling, and Case 2 swelling. In Fickian swelling, when a steady surface equilibrium is established immediately and the diffusion coefficient is a constant or is a function of the concentration of solvent only, the initial swelling rate is proportional to the square root of the time. In non-Fickian swelling, the curve of swelling against the square root of the time is sigmoid in shape. In Case 2 swelling, a sharp advancing front separating the inner glassy core from the outer swollen, rubbery shell exists and moves forward at a constant velocity. Therefore the initial swelling rate is directly proportional to time. For a gel with a slab geometry, if we write the rate expression of initial solvent increase as

$$M_s = k_s t^n \tag{34}$$

Figure 3 (a) Comparison of equilibrium swelling of gels between the experimental results and the computed data, which were based on the values of calculated C^s_{mo}. Square and diamond symbols are experimental results for gel A and gel B, respectively. Dashed and solid lines are the computed results for gel A and gel B, respectively. (b) Comparison of equilibrium swelling of gel A between the experimental results and the computed data, which were based on the experimental values of C^s_{mo}. Square symbols are experimental results and the solid line is the computed results. (c) Comparison of equilibrium swelling of gel B between the experimental results and the computed data, which were based on the experimental values of C^s_{mo}. Square symbols are experimental results and the solid line is the computed results.



(a)



(b)

Figure 4 (a) Time course of swelling of gel B in buffer solutions. The gel had been preequilibrated in a phosphate buffer solution of pH 8.0 and of ionic strength 0.125*M* before being put into buffer solutions that have same ionic strength but different values of pH: 4.0, 6.0, 7.0, and 9.0, respectively. (b) Time course of swelling of gel B in buffer solutions. (The data are the same as that in (a) but plotted in the coordinate of t instead of $\sqrt{t}$.)

where k_s is constant, then $n = 0.5$ is Fickian swelling, $n = 1.0$ is Case 2 swelling, and the region $0.5 < n < 1.0$ is non-Fickian swelling. It is suggested that non-Fickian diffusion is observed only when investigations are carried out below the second-order transition temperature T_g of the polymer.[23] It means that if a non-Fickian diffusion is observed experimentally the polymer must be in glassy state.

For a charged polymer like the gels we studied here, the criteria set by the swelling exponents in eq. (34) are not so definitive.[12] Actually, even if we observed sigmoidadlly shaped curves in the swelling behavior of gel B at pH 4.0, 6.0, and 7.0 [Fig. 4(a)], it is very unlikely that the gel preequilibrated at pH 8.0 containing about 65% (w/w) water would still be a glassy polymer. In fact, it was shown by Allen et al.[24] that pHEMA crosslinked with glycol dimethacrylate had a T_g of 0°C at 40% water content even though the dry polymer has a T_g of about 100°C.[25] In addition, a moving front was clearly observed during our experiments. Both the non-Fickian swelling phenomenon and the experimentally observed moving front deviate from classical Fickian diffusion behavior in rubbery gel in which swelling kinetics are Fickian. Firestone and Siegel[7] also observed non-Fickian swelling behavior with their rubbery BMA/DMA gels. Their explanation is due to interactions of the ions with the ionizable amines on the gel since the non-Fickian behavior observed in aqueous solution would disappear with *n*-hexane sorption in BMA/DMA gels even though they conjecture that a moving front that often appears in glassy polymers exists in their BMA/DMA gels during swelling. The moving front or swelling front in glassy polymers often can be explained through the concept of glass-to-rubber relaxation. For a rubbery polymer, the glass transition does not exist any more. However, the expansion of polymer chains that are crosslinked and/or entangled together is hardly visualized to occur instantaneously when a considerable change in volume is involved, i.e., a phase transition. Therefore, we think that even for rubbery polymers, mechanical relaxation of polymer chains still can play a role in swelling, depending on the degree of change in volume. The moving front in rubbery polymers is then due to the mechanical relaxation.

Comparison between experimental results and model predicted data also shows that mechanical relaxation of polymer materials is not a trivial factor that can be neglected under our experimental conditions (Fig. 5). The two models used in the comparison are based on the diffusion control mechanism and diffusion–relaxation incorporating control mechanism, respectively. At the initial stage of swelling, the diffusion distance of H^+ ion is small and mechanical relaxation is a controlling factor in swelling. Therefore, the model based on the pure H^+ ion diffusion control mechanism fits poorly with the experimental results. With the same parameter values, however, the diffusion–mechanical relaxation incorporated model fits the experimental data well with a sigmoidal shape in the initial swelling stage. As the time goes on, diffusion distance becomes

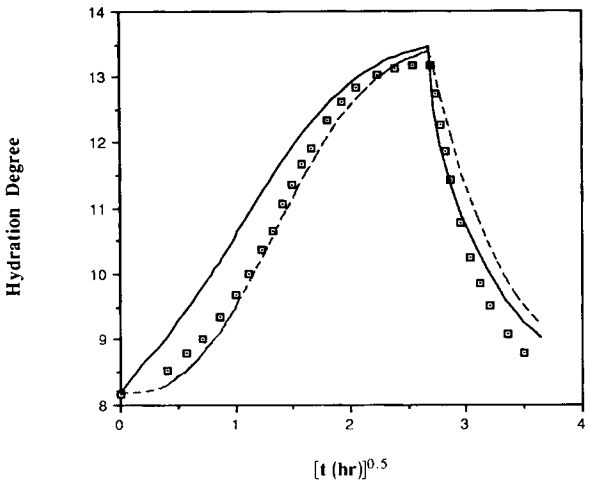


Figure 5 Comparison between models and experiment. The points are from one of the experiments. The solid and dashed lines are from the diffusion controlled swelling model and diffusion–mechanical relaxation incoporated controlled swelling model, respectively. In the experiment, the time course of swelling of gel B was initiated by transferring the gel from a buffer solution of concentration 0.01*M*, ionic strength 0.125*M*, and pH 7.4 into another buffer that has the same concentration and ionic strength but pH 6.0. The deswelling process of the gel was initiated by putting the swollen gel back into the previous buffer.

longer and diffusion influence becomes more important. Both diffusion control and diffusion–relaxation incorporated control models can provide same good prediction on swelling. This comparison strongly suggests that the model considering the structure relaxation factor is closer to reality, especially in the initial stage of a swelling.

Another comparison is made in the diffusion–relaxation incorporated model itself when the parameters required by equilibrium swelling equation have been given different values (Fig. 6). The purpose of this comparison is to see how strong the correctness of equilibrium swelling equation can affect the prediction of swelling kinetics behavior of a gel. The comparison shows that although accuracy of the parameters in the equilibrium swelling equation will not induce mistakes in discerning the mechanisms of swelling kinetics, it is indeed a necessary condition for a quantitative prediction of kinetics. The advantage of combining the knowledge of swelling thermodynamics into kinetic modeling is that the study of swelling kinetics can be conducted completely based on the gel structure and its physical properties.

A good equilibrium swelling prediction is a necessary condition for a swelling kinetics study, but it is not sufficient. Other factors special for kinetic processes should also be addressed. These factors include buffer concentration C_T, relative diffusivity $\bar{D}$, and retardation time τ_r when a mechanical relaxation of polymer chains is involved.

The Effect of $\bar{C}_T$

The interesting observations about buffers made by Siegel and Firestone consist of three experiments. The first one is a comparison between the equilibrium swelling study of MMA/DMA in HCl/NaCl solution and one in citric acid/NaCl solution at pH 4.0, at several ionic strengths. At low ionic strength, swelling is considerably greater for the unbuffered HCl/NaCl system. At high ionic strengths swelling is independent of the buffer system. The second experiment compares swelling kinetics for MMA/DMA gels in citrate/NaCl, acetate/NaCl, and unbuffered HCl/NaCl solutions. All solutions are at pH 4.0 and ionic strength I of 0.1*M*. The gels in buffered solutions have much more rapid swelling rates than in the unbuffered solution, although the first experiment has shown that one of the buffered solutions, citric acid/NaCl, had a smaller equilibrium swelling ability than the unbuffered solution. Siegel and Firestone explained this "anomalous" phenomenon by the plasticization of the organic anions composed in the weak acid buffer molecules. For this reason they did the third experiment in

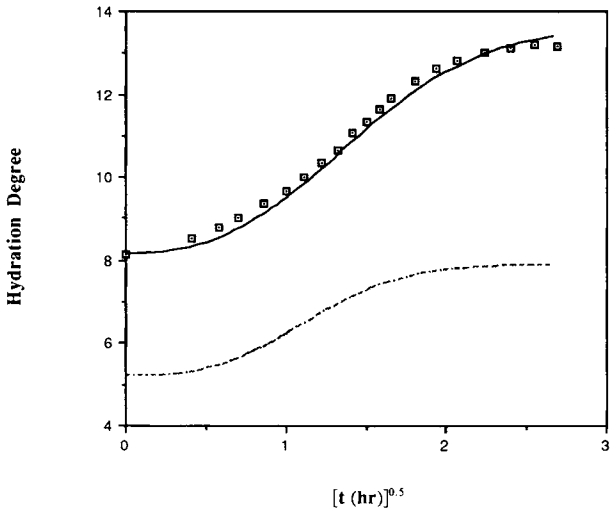


Figure 6 Example of showing the significant influence of information for equilibration swelling of a gel on the model prediction of swelling kinetics of the gel. Points are experiment results; solid and dashed lines are calculated results at C^s_{mo} = 4.0 mol/L and C^s_{mo} = 2.234 mol/L, respectively.

which the chemicals with same organic anions but without buffer function are added to HCl/NaCl system. Apparently, the hypothesis of plasticization by organic anions is not a good answer because the swelling kinetics are virtually same as those for HCl/NaCl solutions without these additives. In their later paper, Firestone and Siegel[7] proposed that the presence of buffer may increase the amount of available protons by simply obtaining them from the source bound to the weak electrolyte and by overcoming the so-called Donnan exclusion barrier. More recently, a mechanism for buffer-enhanced swelling rates has been postulated.[12] Here, we are trying to explain the buffer effect through the concept of carrier originally brought up by Engasser and Horvath.[26]

Before the work of Engasser and Horvath, the role of buffer in increasing the transport rate of H^+ was limited to the static point of view. This view was doubted by Engasser and Horvath because, they argued, the concentration of buffer is very low and the static theory is not good enough to explain how such a small amount of buffer could induce such a big increase in the transport of proton. They thought that in addition to the static role, buffer possibly played a dynamic role in proton transfer and facilitated the diffusion of H^+ through a porous medium. The facilitation concept considers that the conjugate base of the acid–base pair forming the buffer acts as a "carrier" that binds H^+ ions reversibly and augments their transport rate by setting up an alternative path. The work of Ruckenstein and Varanasi[16] shows that under certain conditions, the facilitation factor can increase the apparent diffusivity of H^+ ions by several orders of magnitude of the diffusion coefficient of H^+ ions. This will significantly vary the behavior of a system that is under H^+ diffusion control.

The transport of H^+ through the gel matrix is mainly a molecular diffusion process and the driving force for this process is an H^+ concentration gradient. For the most part of the pH range, this concentration gradient is small and so is the diffusion rate. When a weak acid buffer, for example, AH/A^-, is added into the solution, by the reversible dissociation reaction eq. (11), the conjugated base A^- will pick up H^+ in the place where H^+ concentration is high, diffuse through the matrix, and then release H^+ in the place where H^+ concentration is low. The recovered A^- will diffuse back and repeat the same process until H^+ becomes even in all positions. Through the whole process, the buffer acts as a carrier of H^+ whose diffusion path is parallel to the diffusion of H^+ itself and whose diffusion driving force is the concentration gradient of buffer conjugate acid. Because the buffer concentration can be made much higher than the H^+ ion concentration, the amount of H^+ transported via buffer may greatly exceed the amount by the diffusion of H^+ itself and then the buffer is facilitating the transport of H^+.

When a polyelectrolyte basic gel that has been preequilibrated at a buffer solution of high pH is transferred into a buffer solution of low pH, a H^+ concentration gradient will be set up between the external solution and the gel matrix and drive H^+ diffusing from the external solution into the matrix. At the same time, the buffer conjugate acid concentration gradient resulting from the uneven H^+ concentration distribution will augment the diffusion process of H^+. When the buffer concentration is high, the concentration of the conjugate acid is high and more H^+ ion can be facilitated into the matrix. For a swelling process in which the diffusion of H^+ ions is in control or plays an important role, the facilitation function of the buffer will mean a lot to the swelling kinetics. Therefore, a more rapid swelling rate is expected when the buffer concentration is increased. This expectation has been confirmed by our experiment. In the experiment, several parallel swelling processes of gels were conducted simultaneously in the buffer solutions that have the same components, pH, and ionic strength but different concentrations. The gel specimens used in these parallel swelling processes were cut from the same piece of gel and had been preequilibrated in the buffer, which is the same as the swelling buffer except for the values of pH. The changes of swelling degrees of these gels are displayed in Figures 7 and

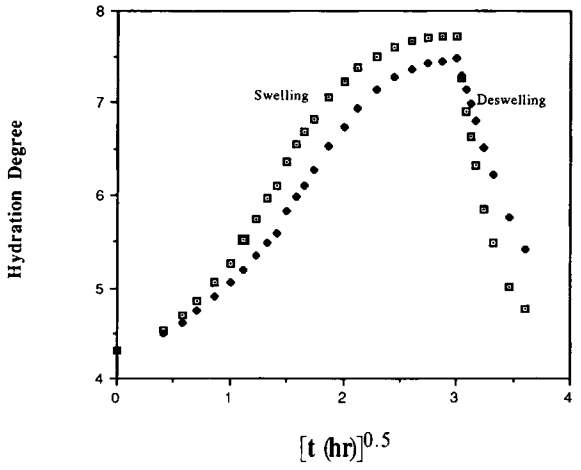


Figure 7 Experiment results showing the effect of buffer concentration on the swelling and deswelling rates of gel A. Squares, $C_T = 0.03M$; diamonds, $C_T = 0.01M$.

8. For both gel A and gel B, the swelling rate is increased with the buffer concentration. This fact indicates that the diffusion of H^+ is indeed one of the controlling factors in a swelling process of a polyelectrolyte gel in an electrolyte solution. We can also see an almost indifferent initial swelling rate at different buffer concentrations. This is because at the very beginning of the swelling process, the diffusion distance is short and the effect of diffusion limitation is not very obvious. During these experiments, we did not observe a systematic relationship between equilibrium swelling degree and buffer concentration, therefore it is assumed that the equilibrium swelling degree of a gel is independent of buffer concentration and small variations of equilibrium swelling degree of a gel at the same pH but different buffer concentrations are considered experimental errors. An average equilibrium swelling degree of a gel has been used in all buffers to make the comparison more clear. The curve of swelling degree vs. time at each buffer concentration is correspondingly moving up or down to keep the slope of the curve, i.e., the swelling rate, unchanged during this adjustment.

Figure 9 shows the effect of total buffer concentration on the kinetics of swelling as predicted by our kinetic model, which takes into account the resistances offered by both the diffusion of hydrogen ions into the gel and the relaxation of polymer chains. By comparing Figure 9 with Figures 7 and 8, it appears that the trends predicted by the model agree fairly well with the trends observed in our experiments.

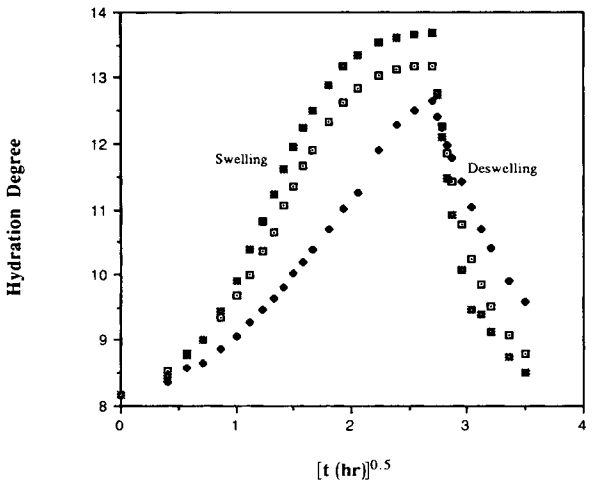


Figure 8 Experiment results showing the effect of buffer concentration on the swelling and deswelling rates of gel B. Solid square, C_T = 0.03M; open square, C_T = 0.01M; diamond, C_T = 0.005M.

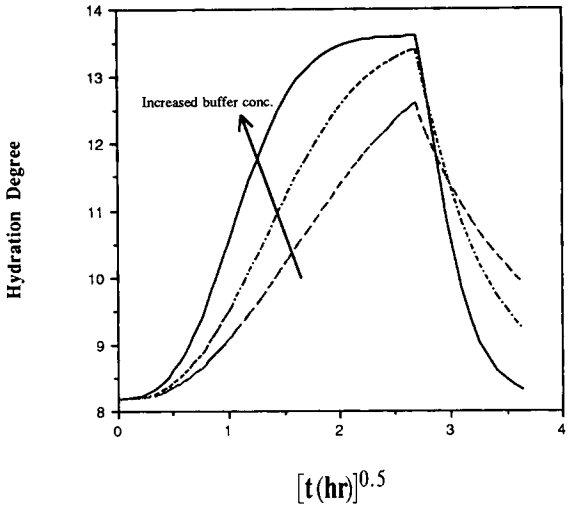


Figure 9 The effect of buffer concentration on the swelling kinetics of gel, plotted from the data calculated based on the diffusion-mechanical relaxation controlled swelling model.

The swelling process is reversible when the swollen polyelectrolyte basic gel is moved into a buffer solution of higher pH. In this case, the intramembrane H^+ ion concentration is higher than that in external solution and H^+ ions will diffuse out of the gel matrix. As we discussed before, the decrease of intramembrane hydrogen ion concentration will lower the effective charge density of a basic gel and therefore the electrostatic expansion force, which will consequently induce a deswelling process in the gel. With the same facilitation mechanism, buffer is helping H^+ ions out the gel matrix. The higher the buffer concentration, the faster H^+ ions are moving out and the more rapid the deswelling rate. This conclusion has been verified both experimentally and theoretically (Figs. 7, 8, and 9).

From the discussion of buffer effect, a specific factor for the proton diffusion, we suggested that the diffusion of H^+ may be a controlling step in the pH-sensitive swelling process of a polyelectrolyte hydrogel.

The Effect of $\bar{D}$

Another kinetic parameter that might affect the swelling process is the relative diffusivity $\bar{D}$. $\bar{D}$ is defined as the ratio of the diffusivity of buffer conjugate acid AH to that of H^+ in the gel matrix. For the diffusion of small molecules or ions through a polymer matrix, if the electrostatic interactions between the diffusing particles and the charged polymer chains are not concerned, the reduction of dif-

fusivity of the diffusing particles results only from the mean increase in path length of diffusion due to the obstruction of impenetrable polymer chains. Therefore, its effect on the diffusivities of neutral species AH and ionic species H^+ should be the same and the relative diffusivity $\bar{D}$ may equal one. Traveling through a positively charged network, H^+ ions, however, as one of the co-ions in a cationic gel, can avoid the electrostatic interaction with the fixed charges, but will interact with the counterions, which are highly concentrated in the intramembrane fluid. As a result of this electrostatic interaction, H^+ ions diffuse more slowly than neutral AH within the gel and their relative diffusivity $\bar{D}$ will be greater than 1; even their diffusivities in solvent may be the same.

This expectation has been indirectly verified by matching the experimental and computational results. Under low buffer concentrations, at a short time during which diffusion control effect is not so obvious, with $\bar{D}$ of value 1, the computed swelling degree of the gel can match the experiment very well. After a certain period of time, the swelling degree calculated from $\bar{D} = 1$ will start leveling off and can never attain its expected equilibrium swelling degree in a reasonable lab time scale (Fig. 10). If we believe that in a real situation after a certain period of time, a highly charged shell is formed that retards the diffusion of H^+ but not that of neutral species AH, then the influence of the buffer to the diffusion is more obvious and the value of relative diffusivity $\bar{D}$ may be larger than 1. Actually, a value of 3.5 of $\bar{D}$ can result in a good consistency between calculated values and experimental results during the later stage of swelling.

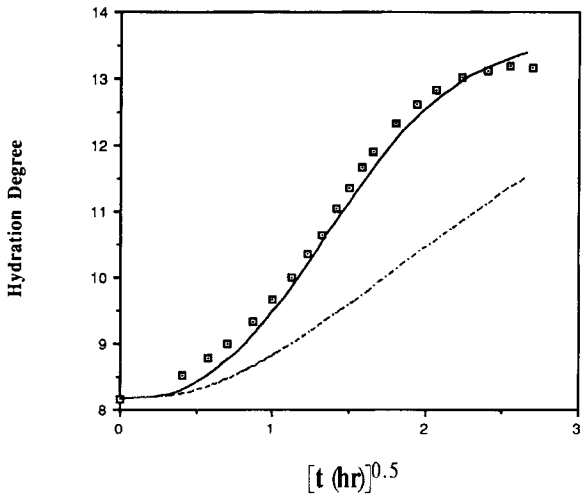


Figure 10 Influence of the value of relative apparent diffusivity $\bar{D}$ on adequate model prediction of swelling kinetics. The points are experimental data, and solid and dashed lines are computed results when the value of $\bar{D}$ is 3.5 and 1.0, respectively.

The Effect of τ_r

Retardation time τ is a mechanical parameter characterizing the viscoelastic property of a gel. When a load is put on a gel specimen, a deformation occurs to the gel. The value of τ_r represents how well the gel resists this deformation. A larger value of τ_r means a slower relative movement between gel structure unit. If the deformation is to expand the chain length of a crosslinked network for swelling, τ_r will have same physical meaning as swelling time, a concept proposed by Tanaka and Fillmore[13] in their swelling kinetics study.

From experimentally measured longitudinal modulus and viscosity of the gel that is used in our swelling experiment, the retardation time τ_r is calculated to have a value of 2.578×10^4 s. The magnitude of swelling time has been observed to spread in a wide range from 1.7×10^3 s by Grimshaw et al.[15] for a PMAA gel membrane to $3.0 \times 10^4 \sim 2.5 \times 10^5$ s by Tanaka and Fillmore[13] for 2.5% polyacrylamide gel particles. This broad variation in swelling time of course results from the different compositions and physical properties of the gels that were used in their measurements. In addition, according to the definition of swelling time, it is also dependent on some scaling argument, like the radius of a gel particle or the thickness of a gel slab.

We feel that the swelling time defined from the characteristic time of the mechanical motion equation does not reflect the true meaning of a mechanical relaxation process in a gel. Take a non-Fickian or Case 2 swelling process as an example. In either case, the mechanical relaxation is important for their initial swelling stage. During this initial stage, typically for a Case 2 swelling, only the outer layer of gel is intruded by solvent and undergoes a mechanical relaxation according to the advancing front mechanism; the area beyond the front is still intact. At this stage of swelling, the mechanical relaxation going on in the outer shell of the gel has nothing to do with the thickness of the gel membrane. The relaxation should be completely decided by the structure of the gel, the properties of the invading solvent, and the interactions between them. But the thickness does have something to do with the questions that are raised in estimating the whole performance of swelling of a gel, as when the advancing fronts will meet to cause an abrupt increase of solvent intake and how hard the diffusing species can permeate

through the membrane. In a non-Fickian swelling where diffusion and relaxation share responsibility for the swelling, it is hard to imagine how the thickness can affect the local relaxation process.

Based on the argument described above, we feel more comfortable to take the retardation time τ_r as a characteristic time in the description of mechanical relaxation of the gel network. The decrease of τ_r means an increased rate of readjustment in the gel structure in response to the change in conditions. When the value of τ_r is small enough, the readjustment can proceed instantaneously and swelling becomes diffusion control. Inversely, the increase of τ_r makes this readjustment difficult and its extreme case will be the mechanical controlled swelling. Between these two extremes is the diffusion and relaxation incorporated control. Figure 11 is a comparison between experimental results and theoretical prediction with a retardation time of 2×10^4 s, which is not far from the experimental value of 2.6×10^4 s.

CONCLUSION

The diffusion of H^+ ions through polyelectrolyte matrices is concluded as an important factor in gel swelling processes by comparing theoretical analysis with experimental results from the buffer effect on the swelling kinetics of gels induced by the change of pH of external solution medium. An unusual non-Fickian swelling behavior observed in a rubbery polymer was explained through mechanical relaxation of polymer chains. The swelling kinetics model that accommodates the influence of buffer, mechanical relaxation, and the change of gel hydration degree shows good predictability.

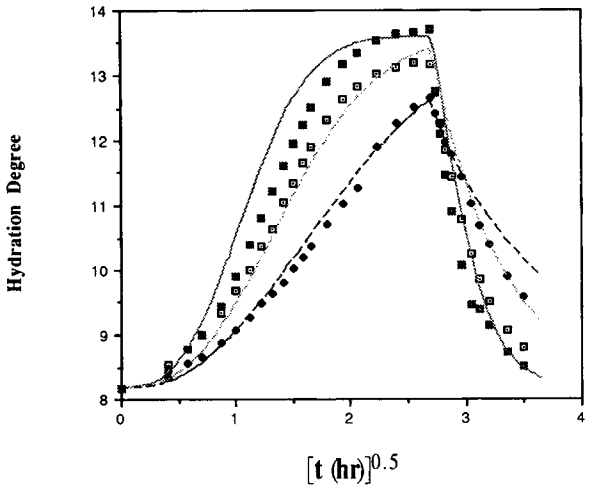


Figure 11 Comparison between experiment and model (diffusion–mechanical relaxation incorporated swelling) data of swelling and deswelling processes at different buffer concentrations. The points are from experiment and the lines are from model. Solid square and solid line, $C_T = 0.03M$; open square and dot-dash line, $C_T = 0.01M$; diamond and dashed line, $C_T = 0.005M$.

NOMENCLATURE

C_0, C_1	concentration of hydrogen ions in external solution
C_i	concentration of species i in external solution
C_m	concentration of fixed ionized groups in gel
C_{mo}	concentration of fixed ionizable groups in gel
C_e	concentration of electrolytes in external solution
$\bar{C}_e$	concentration of electrolytes inside gel
$\bar{C}_i$	concentration of species i inside gel
$\bar{C}_T$	total buffer concentration in gel
$C^s_{H^+}$	concentration of hydrogen ion reversibly bound to the membrane
C^s_{mo}	concentration of fixed ionizable groups in solid polymer
D_i	diffusivity of species i
$\bar{D}_i$	diffusivity of species i inside membrane
e	strain of a gel
H	hydration degree of gel, defined as the volume fraction of solvent to solid volume
I'	ionic strength of external solution
k	rate constant of enzymatic reaction
k_i^b, k_i^f	backward and forward rate constants of reversible dissociation reaction of species i
K_1, K_2	equilibrium constants for protonation and deprotonation of active form of enzyme, respectively
K_{app}	apparent dissociation constant of ionizable groups in membrane
K_i	equilibrium constant of reversible dissociation reaction of species i
M	equilibrium bulk longitudinal modulus of a gel
r_i	molar rate of consumption of species i
t	time
x	material distance coordinate
z_m	valency of ionizable groups in membrane

Greek Letters

α	ratio of membrane area to corresponding dry membrane area

γ	radius of pore
γ_s	radius of diffusion species
Γ_i	diffusion flux of species i
δ	thickness of solid gel membrane
λ	Donnan ratio
ξ	dimensionless distance
ρ_e	charge density
ρ_0	crosslinking density
ρ_p	specific gravity of polymer
τ	dimensionless time
τ_r	relaxation time
ϕ	volume ratio of polymer in gel
ψ	fixed distance coordinate
χ	Flory interaction parameter
$\bar{\nu}$	solvent partial molar volume
η	viscosity of gel

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