Multiple Phases in Ionic Copolymer Gels

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This study presents a theoretical description of multiple phases in ionic copolymer gels. The equations for the dissociation equilibrium of the fixed charges in the gel are solved together with a Flory-type swelling model which incorporates both polyelectrolyte and polyampholyte effects. This model correctly predicts the qualitative shape of the gel swelling vs pH curve. Although several phases could appear when hydrogen bonding effects are significant, the possibility of having very long relaxation times due to the slow ion exchange kinetics in the gel should be carefully examined. [S0031-9007(97)04290-7]

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Multiple phases have been reported in gels consisting of randomly distributed positively and negatively charged groups [1,2] where monomers interact through repulsive polyelectrolyte or attractive polyampholyte electrostatic interactions [3]. When acrylic acid monomers are used in the gel preparation, hydrogen bonding can also occur. We show that the shape of the swelling ratio vs bath pH curve is dictated by the internal pH and can be predicted when the dissociation equilibria are considered in a Flory-type swelling theory that incorporates the polyelectrolyte and polyampholyte interactions characteristic of these ionic gels. In addition, this theory predicts that several phases can appear when hydrogen bonding occurs.

The experimental system considered is the copolymer gel of methacryl-amido-propyl-trimethyl-ammonium chloride (MAPTAC) and acrylic acid (AAc) prepared with a total monomer concentration of 700 mM [1,2]. The swelling behavior of this copolymer has been experimentally studied with many different molar ratios. In this study we consider the 460 mM AAc/240 mM MAPTAC unbalanced hydrogel which shows a typical multiple phases behavior [1,2]. The gels were prepared in water with 8.6 mM of metylenebisacrylamide (BIS) crosslinker. The bath pH was varied from 2 to 12 by adding hydrochloric acid below pH 7 and sodium hydroxide above pH 7. The bath was saturated with nitrogen gas to avoid the effect of bicarbonate ions.

Swelling and dissociation equilibria; hydrogen bonding.—The free energy of mixing between monomer and solvent molecules is expressed according to the Flory-Huggins lattice theory [4] and the elastic contribution to the free energy is obtained from the affine network model [4,5]. The translational free energy of the mobile ions is evaluated as a McMillan-Mayer ideal solution. For the Coulombic contribution, we assume that the charges bound to the polymer are distributed over a thermally smoothed quasilattice and interact according to a screened Coulombic potential [3] such that

$$\Delta F_{\text{lattice}} = -\frac{AN_{\text{fe}}e^2}{8\pi\varepsilon}\,\frac{\exp(-\kappa r)}{r}, \qquad r = 2\left(\frac{3V}{4\pi(N_{f+} + N_{f-})}\right)^{1/3}, \qquad \kappa = \left(\frac{e^2 N_A c_{\text{mobile}}}{\varepsilon k_B T}\right)^{1/2}, \quad \text{and}$$

$$c_{\text{mobile}} = 2\left[\left(\frac{N_{f+} - N_{f-}}{2N_A V}\right)^2 + c_s^2\right]^{1/2}, \tag{1}$$

where A is a geometrical constant of the order of unity, e the electron charge, ε the dielectric permittivity of the solvent, and r the distance between nearest neighbors in the quasilattice. The gel volume is given by V, κ is the reciprocal Debye length in the gel, N_A is Avogadro's number, k_B is Boltzmann's constant, T is the absolute temperature, and c_{mobile} is the concentration of mobile ions inside the gel. The term c_s represents the concentration of HCl or NaOH in the bath, N_{f+} and N_{f-} are the number of positive and negative fixed charges, and $N_{\text{fe}} \equiv N_{f+} + N_{f-} - |N_{f+} - N_{f-}|$ is the effective number of fixed charges giving rise to attractive electrostatic interactions. The expression for N_{fe} differs slightly from that used in Ref. [3] to account for the fact that Eq. (1) is not valid for highly unbalanced gels. Note that the expression for N_{fe} used here vanishes when only one type of charge is present and gives the correct value when the polyampholyte effect is important [3].

The equilibrium swelling is obtained from the condition that the osmotic pressure in the gel is equal to the osmotic pressure in the bathing electrolyte solution $\Pi_{\text{gel}} = \Pi_{\text{bath}}$, that is

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$$-\frac{1}{\overline{v}_{\mathrm{site}}}[\ln(1-\phi)+\phi+\chi\phi^2]+\frac{\phi_0}{N_x\overline{v}_{\mathrm{site}}}\left[\frac{1}{2}\frac{\phi}{\phi_0}-\left(\frac{\phi}{\phi_0}\right)^{1/3}\right]+c_{\mathrm{mobile}}-2c_s$$
$$-\frac{A}{2}\frac{N_{\mathrm{fe}}}{N_AV}\frac{e^2}{12\pi\varepsilon k_BT}\frac{\exp(-\kappa r)}{r}\left\{1+\kappa r-\frac{3\kappa r}{2}\left[1+\left(\frac{2N_AVc_s}{N_{f+}-N_{f-}}\right)^2\right]^{-1}\right\}=0\,, \tag{2}$$

where the osmotic pressure of the gel, $\Pi_{\mathrm{gel}} \equiv -\partial F/\partial V$, has four terms [3] coming from the respective contributions to the free energy, while that of the bath is evaluated by considering only the free energy of the ideal solution of mobile ions. In Eq. (2) $\overline{v}$ site represents the molar volume of the lattice sites, ϕ is the polymer volume fraction in the gel, χ is the Flory interaction parameter, ϕ_0 is the polymer volume fraction in the reference state, and N_x is the average number of monomer molecules between crosslinks. Gel volumes and polymer volume fractions in the swollen and reference state are related through $V/V_0 = \phi_0/\phi$, where V_0 is the gel volume in the reference state.

The net charge bound to the polyampholyte gel causes the pH inside the gel to be different from that of the external bath. If the internal pH becomes close to the pK's of the MAPTA and AAc functional groups, their ionization degree must be calculated from the equations

$$K_{a,\mathrm{eff}}=\frac{[A^-][\mathrm{H}^+]}{[A^0]} \quad \text{and} \quad \frac{[B^0][\mathrm{H}^+]}{[B^+]}\,, \tag{3}$$

where $[A^-]$, $[B^+]$, $[A^0]$, and $[B^0]$ denote the molar concentration of ionized and unionized acid and base groups, respectively, and $K_{a,\mathrm{eff}}$ and K_b are the equilibrium constants. The effective value for the dissociation constant of acrylic acid is related to that in absence of hydrogen bonding K_a by

$$K_{a,\mathrm{eff}}=\frac{K_a}{1+\beta}\,,\quad \beta=\frac{[A^0]\ldots}{[A^0]\,./.}\,, \tag{4}$$

where $[A^0]\ldots$ and $[A^0]\,./.$ denote the concentration of unionized acid groups in the hydrogen bonded and free states, respectively. Thus, Eq. (4) represents the equilibrium between the free unionized acid groups and those forming hydrogen bonds and β takes the meaning of an equilibrium constant. The molar concentration of hydrogen ions $[\mathrm{H}^+]$ inside the gel can be obtained from the multiionic Donnan equilibrium [3,4] of hydroben, hydroxide, sodium, and chloride ions, which gives us

$$[\mathrm{H}^+]^4+\left(K_{a,\mathrm{eff}}+K_b+\frac{[B][\mathrm{H}^+]_{\mathrm{bath}}}{c_s}\right)[\mathrm{H}^+]^3+\left(K_{a,\mathrm{eff}}K_b-[\mathrm{H}^+]^2_{\mathrm{bath}}+\frac{K_{a,\mathrm{eff}}([B]-[A])[\mathrm{H}^+]_{\mathrm{bath}}}{c_s}\right)[\mathrm{H}^+]^2$$
$$-\left[(K_{a,\mathrm{eff}}+K_b)[\mathrm{H}^+]^2_{\mathrm{bath}}+\frac{K_{a,\mathrm{eff}}K_b[A][\mathrm{H}^+]_{\mathrm{bath}}}{c_s}\right][\mathrm{H}^+]-K_{a,\mathrm{eff}}K_b[\mathrm{H}^+]^2_{\mathrm{bath}}=0\,, \tag{5}$$

where $[A]$ and $[B]$ denote the total concentration of ionized and unionized acid and base groups, respectively. These concentrations correspond to the actual swelling state of the gel and not to those in the reference state. Thus, the values of N_{f+} and N_{f-} appearing in Eq. (2) must be evaluated as $N_AV[B^+]$ and $N_AV[A^-]$, respectively, with $[B^+]$ and $[A^-]$ given by Eqs. (3) and (4) and $[\mathrm{H}^+]$ given by Eq. (5). Since the gel volume used to evaluate $[A]$ and $[B]$ in Eq. (5) must also be the equilibrium volume determined from Eq. (2), Eqs. (2) and (5) are to be solved simultaneously.

The equilibrium constant β in Eq. (4) may be evaluated from an appropriate theoretical model of the energetic and entropic contributions to the free energy associated with hydrogen bonding and depends critically on the distance between acrylic acid groups. No hydrogen bonds appear if the interacting groups are too far apart. There is a minimum distance or, equivalently, a critical concentration of unionized acid groups $[A^0]_{\mathrm{cr}}$ necessary to give rise to hydrogen bonds in the gel. This behavior can be approximated with the step function

$$\beta([A^0])=\begin{cases}0 & \text{if } [A^0]<[A^0]_{\mathrm{cr}}\\ \beta & \text{if } [A^0]>[A^0]_{\mathrm{cr}}\end{cases}, \tag{6}$$

Finally, the hydrogen bonding must also be taken into account in the swelling equilibrium of the gel. This interaction can be understood as a modification of the interaction between monomers and can be easily incorporated into the theory through the value of the Flory parameter χ which accounts for the difference in the free energies of interaction between solvent and monomers. We use the linear relation

$$\chi=\chi_0+\Delta\chi\frac{[A^0]\ldots}{[A]}\,, \tag{7}$$

where χ_0 is the value of Flory parameter in the absence of hydrogen bonding and $\Delta\chi > 0$ the increase in χ associated with the formation of hydrogen bonds. Equation (7) shows that the polymer network becomes less hydrophilic because of hydrogen bonding between monomers. Although Eqs. (4), (6), and (7) constitute a simplification of the hydrogen bonding problem, correct qualitative results can be obtained.

Ion-exchange kinetics.—We now consider the exchange of sodium ions in the gel with hydrogen ions in the bath that occurs when a gel sample initially equilibrated in a high pH bath is changed to a lower pH bath. In this case hydrogen ions bind to AAc monomers to give unionized AAc groups. We ignore hydrogen bonding here for reasons that become clear later and assume that the ion exchange process can be modeled as a diffusion-limited chemical reaction. We approximate the cylindrical diffusion in the gel as a one-dimensional diffusion problem since it does not change the order of magnitude of the relaxation time. In addition, we use the fact that the concentration of hydrogen ions is much smaller than that of the sodium ions over a significant time interval of the ion exchange process. In this case the minority carrier limit of ambipolar diffusion [6] gives us

$$\frac{\partial[\mathrm{H}^+]}{\partial t} = D_{\mathrm{H}^+}\frac{\partial^2[\mathrm{H}^+]}{\partial x^2} - \frac{\partial[A^0]}{\partial t}, \tag{8}$$

where D_{H^+} is the diffusion coefficient of the hydrogen ion. Substitution of the local equilibrium condition for the ion binding $[A^0] = [A][\mathrm{H}^+]/([\mathrm{H}^+] + K_a)$ into Eq. (8) yields

$$\frac{\partial[\mathrm{H}^+]}{\partial t} = D_{\mathrm{H}^+,\mathrm{eff}}\frac{\partial^2[\mathrm{H}^+]}{\partial x^2},$$

$$\frac{D_{\mathrm{H}^+}}{D_{\mathrm{H}^+,\mathrm{eff}}} = 1 + \frac{[A]K_a}{([\mathrm{H}^+] + K_a)^2}. \tag{9}$$

Since $[\mathrm{H}^+] \ll K_a = 10^{-4.5}$ M we can use the approximation $D_{\mathrm{H}^+,\mathrm{eff}} \approx D_{\mathrm{H}^+}/(1 + [A]/K_a) \ll D_{\mathrm{H}^+}$. Initially there is an excess of binding sites available in the gel so that almost all the incoming hydrogen ions are immediately bound to these sites and cannot thus diffuse freely through the gel. From Eq. (9), a typical time for the gel to attain the steady state is $\tau_{d-r} \approx l^2/D_{\mathrm{H}^+,\mathrm{eff}} \approx \tau_d(1 + [A]/K_a)$, where $\tau_d \equiv l^2/D_{\mathrm{H}^+}$ is the typical relaxation time for pure diffusion and l is the gel radius in the swollen state. This equation is only approximately valid, since the actual cylindrical diffusion proceeds slightly faster than the one-dimensional diffusion considered here, diffusion boundary layer effects [6] have been omitted, and the minority carrier assumption for the hydrogen ions fails at the end of the ion exchange process. However, we are concerned only with the order of magnitude of τ_{d-r}, and we expect the above equation to be accurate enough for our purposes.

Figure 1 shows the swelling behavior predicted by our theory for the 460 mM AAc/240 mM MAPTA unbalanced polyampholyte. The volume fraction of the polymer has been estimated as $\phi_0 = 0.46\ \mathrm{M} \times 0.07\ \mathrm{M}^{-1} + 0.24\ \mathrm{M} \times 0.2\ \mathrm{M}^{-1} = 0.08$ since the monomer concentration in the pregel solution is $[A]_0 + [B]_0 = 700$ mM and the molar volume of the monomers are ca. $0.07\ \mathrm{M}^{-1}$ and $0.2\ \mathrm{M}^{-1}$. The terms N_x, χ, and $p\mathrm{K}_b$ were estimated in a previous study as $N_x = 300$, $\chi = 0.3$, and $p\mathrm{K}_b = 11.5$. The other values used are $p\mathrm{K}_a = 4.5$, $\Delta\chi = 0.5$, $\overline{v}_{\mathrm{site}} = 0.02\ \mathrm{M}^{-1}$, $A = 0.6$, $\beta = 5$, and $[A^0]_{\mathrm{cr}} = 0.096$ M. The experimental results shown in Figs. 2 and 4 of Ref. [2] can be explained with this theory: In particular, our theory can explain the swelling behavior at high and low pH, the intermediate plateau corresponding to the more collapsed state, the existence of other phases in the approximately neutral pH range, and the discontinuous transitions between phases. However, more phases seem to have been observed in the experiments reported in Refs. [1] and [2].

The wide plateau observed in Fig. 1 around neutral pH can be easily understood with the aid of Fig. 2. At low ionic strengths the only available counter ion to maintain charge electroneutrality is the hydrogen ion. As a result, the internal pH drops and the concentration of ionized AAc groups decreases. Therefore, the gel is only allowed to keep a very small net charge concentration on the order of the ionic strength. For this to be possible, about half of the acrylic acid groups must be unionized since the gel is 460 mM AAc and 240 mM MAPTAC in the reference state. This occurs when the pH inside the gel is close to the $p\mathrm{K}_a = 4.5$. The open circles in Fig. 2 show that this is the case. This explains also why the gel is so collapsed in this pH range, since the translational contribution to the osmotic pressure of the gel practically vanishes due

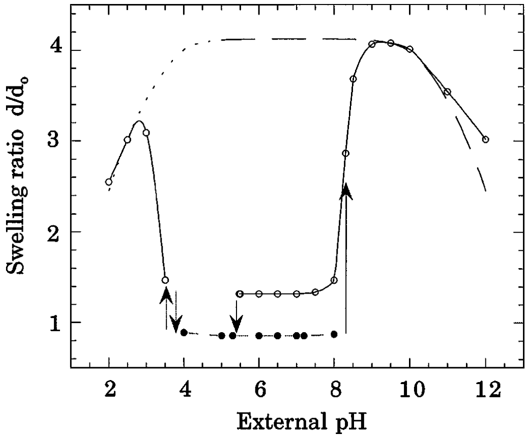

FIG. 1. Equilibrium swelling ratio d/d_0 vs external pH. The points correspond to calculated values and the arrows indicate discontinuous transitions to and from the hydrogen bonded states represented with solid circles. The upper curve represents nonequilibrium states that can be reached when transferring the gel from a high pH to low pH bath. This upper curve has been changed from long dashed (high pH) to dotted lines (low pH) to indicate that the nonequilibrium states are more unstable in low pH media.

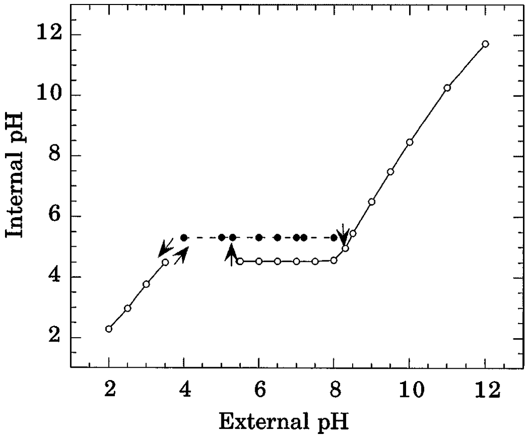

FIG. 2. Internal pH vs external pH curves calculated from Eqs. (3)–(5). Note that the internal pH is constant over the external pH range $4 < p\mathrm{H} < 8$, and this plateau is in correspondence with that observed in Fig. 1.

to the absence of net fixed charge and compensating counterions, and the Coulombic attractive interactions become very important because of the polyampholyte effect [3]. However, if the concentration of unionized groups increases above the critical value, some of them form hydrogen bonds, an effect which rapidly propagates through a cooperative zipper mechanism leading to the gel collapse. We have shown above that the hydrogen bonding effectively changes the dissociated constant to a lower value [see Eq. (4)], so that less ionized groups will be present for a given pH. In our case, the value $\beta = 5$ leads to $p\mathrm{K}_{a,\mathrm{eff}} \approx 5.3$. Again, it is clear from the solid circles shown in Fig. 2 that the pH inside the gel takes a value very close to $p\mathrm{K}_{a,\mathrm{eff}}$ for all the hydrogen bonded states. Different values of β and $[A^0]_{\mathrm{cr}}$ could have been used in the computations, but reasonable choices reproduced the same qualitative behavior with the only noticeable difference being that the discontinuous transition from the swollen to the collapsed hydrogen bonded states shown in Fig. 1 for $p\mathrm{H} \approx 5.3$ was not always observed. That is, both the swollen and collapsed states are observed from pH 3.5 to pH 8. Given the uncertainties involved in the gel parameters employed [3], no quantitative fitting of the theory to the experimental points was attempted. Also, in order to check that the discontinuous transitions are not an artifact resulting from the step function in Eq. (6), continuous functions such as the exponential function $a\exp[-b(\phi_0/\phi)^3]$, where a and b are two constants, were also used instead of Eq. (6), and the same qualitative results were obtained.

Although special care was taken in all the experimental work of Refs. [1] and [2] to avoid kinetic effects it has recently been shown [3] that the kinetics of ion exchange processes in polyampholitic hydrogels can sometimes be much longer than expected due to the dissociation equilibria of the functional groups and other phenomena not yet fully understood. Let us examine this question now. If we accept that the ion exchange process within the gel is essentially a diffusion limited chemical reaction in which a minority carrier hydrogen ion substitutes for the sodium cation initially present in the gel, then a typical time for the gel concentration equilibrium would be

$$\tau_{d-r} \approx \left(\frac{V}{V_0}\right)^{2/3} \frac{l_0^2}{D_{\mathrm{H}^+}}\left(1 + \frac{[A]}{K_a}\right) \approx 4\ \mathrm{h}\,, \qquad (10)$$

where we have introduced the values $l_0 = 170\ \mu\mathrm{m}$, $D_{\mathrm{H}^+} = 8 \times 10^{-5}\ \mathrm{cm}^2/\mathrm{s}$, $V/V_0 \approx 4^3$, $[A] = [A]_0 V_0/V = 0.46\ \mathrm{M}/4^3 \approx 7\ \mathrm{mM}$, and $K_a = 10^{-4.5}\ \mathrm{M}$. Equation (10) shows that the effective diffusion-reaction time can be several orders of magnitude greater [7] than that characteristic of pure diffusion ($\tau_d \approx 1$ min). Note that even higher values of τ_{d-r} might be possible, since we have assumed that the diffusion coefficient of hydrogen ions in the gel is the same as in a dilute aqueous solution. The presence of charged groups is known to decrease the counterion diffusion coefficient in ion exchangers by over an order of magnitude [8] even in the absence of the ion binding effects present here. For example, decreasing D_{H^+} by a factor of 5, would give relaxation times of the order of 1 day. The upper discontinuous curve in Fig. 1 has been calculated by assuming that the hydrogen ions in the bath have not had enough time to equilibrate with the gel and that the functional acid and base groups are all dissociated. This can occur around neutral pH where the ionic strength of the bath is very low. Thus, if a gel equilibrated in a high pH bath is moved to a lower pH bath around neutral pH, it will remain in the same swollen state until the sodium ions have had enough time to exchange with the hydrogen ions that must also equilibrate with their functional groups. This time, however, can be much shorter if the gel is moved to a much lower pH bath where the swollen state is more unstable and the gel should undergo the continuous transition to the more collapsed equilibrium state relatively faster. In this context, it might be significant that the multiple phases not reproduced by this simplified theory are located around neutral pH, and become unstable in slightly acidic baths (see, e.g., Fig. 4 of Ref. [2]). Therefore, although multiple phases can appear when the hydrogen bonding effects are significant, the possibility of having very long experimental relaxation times due to the slow ion exchange kinetics in the gel should be carefully examined in future experiments.

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