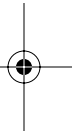




Section II

Theoretical Considerations







7 Kinetics of Smart Hydrogels

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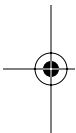
HYDROGELS

It is well known that hydrogels are three-dimensional hydrophilic polymer networks able to imbibe large amounts of water.¹⁻² The networks are composed of homopolymers or copolymers and are insoluble due to the presence of chemical or physical crosslinks. The physical crosslinks can be entanglements, crystallites,³⁻⁸ or weak associations such as van der Waals forces or hydrogen bonds.⁹⁻¹³ The crosslinks provide the network structure and physical integrity. Their thermodynamic compatibility with water allows the network to swell in aqueous media.^{1,2,14-16}

Hydrogels can be classified as neutral or ionic, based on the natures of their side groups. Based on the physical structures of their networks, they can be amorphous, semicrystalline, hydrogen-bonded, or supermolecular structures or hydrocolloid aggregates.¹⁻¹³

Another general category of hydrogels is composed of physiologically responsive hydrogels.¹⁷ Their polymer complexes can be broken or their networks can be swollen as a result of changing external environment. These systems tend to show drastic changes in their swelling ratios as a result. Some of the factors affecting the swelling of physiologically responsive hydrogels include pH, ionic strength, temperature, and electromagnetic radiation.¹⁷

Environmentally sensitive hydrogels have the ability to respond to changes in their external environment. These polymers can exhibit dramatic changes in their swelling behavior, network structure, permeability, or mechanical strength in response to changes in the pH or ionic strength of the surrounding fluid or temperature. Other



hydrogels have the ability to respond to applied magnetic fields. Additionally, some hydrogels can respond to changes in concentrations of glucose.¹⁷ Because of their natures, these materials can be used in a wide variety of applications such as separation membranes, biosensors, artificial muscles, chemical valves, superabsorbents, and drug delivery devices.¹⁷

One particular class of physiologically responsive hydrogels is dependent on pH and ionic strength. Hydrogels that exhibit pH-dependent swelling behavior are swollen from ionic networks. These ionic networks contain either acidic or basic pendant groups.^{18–29} As a result of the electrostatic repulsions, the uptake of water in the network will be increased.^{18–29}

Ionic hydrogels are swollen polymer networks containing ionic moieties that show sudden or gradual changes in their dynamic and equilibrium swelling behaviors as a result of changing the external pH. Anionic materials contain pendant groups such as carboxylic acid or sulfonic acid. In these gels, ionization occurs when the pH of the environment is above the pK_a of the ionizable group.^{18–32} As the degree of ionization increases (increased system pH), the number of fixed charges increases, resulting in increased electrostatic repulsions between the chains. This, in turn, results in an increased hydrophilicity of the network and greater swelling ratios. Conversely, cationic materials contain pendant groups such as amines.^{25–35} These groups ionize in media at pH levels below the pK_b values of the ionizable species. Thus, in a low pH environment, ionization will increase, causing increased electrostatic repulsions. The hydrogel will become increasingly hydrophilic and will swell to an increased level.

There are many advantages to using ionic materials over neutral networks. All ionic materials exhibit pH and ionic strength sensitivity. This characteristic can be exploited for applications in a wide variety of biomedical applications such as dental adhesives and restorations, controlled release devices, prodrugs and adjuvants, and biocompatible materials.²⁴ In addition, the swelling forces developed in these systems will be increased over the nonionic materials. This increase in swelling force is due to the localization of fixed charges on the pendant groups. As a result, anionic gels in media above their pK_a levels and cationic gels in media below their pK_b values reach degrees of swelling an order of magnitude higher than nonionic materials.

Here we discuss the fundamentals of the dynamic behavior of hydrogels due to changes in the surrounding environment. This is often known as the *kinetic behavior of gels* because the *kinetics* term is also used to describe dynamic transport processes.

SWELLING OF NEUTRAL HYDROGELS

It is well known that Flory and Rehner¹⁴ developed the initial depiction of the swelling of crosslinked polymer gels using a Gaussian distribution of polymer chains. They developed a model to describe the equilibrium degree of crosslinked polymers postulating that the degree to which a polymer network swelled was governed by the elastic retractive forces of the polymer chains and the thermodynamic compatibility of the polymer and the water molecules. In terms of the free energy of the system, the total free energy change upon swelling can be described as:

$$\Delta G = \Delta G_{elastic} + \Delta G_{mix} \quad (7.1)$$

where $\Delta G_{elastic}$ is the contribution due to the elastic retractive forces and ΔG_{mix} represents the thermodynamic compatibility of the polymer and the swelling agent.

Upon differentiation of Equation (7.1) with respect to the number of water molecules in the system at constant temperature (T) and pressure (P), an expression can be derived for the chemical potential change in the water in terms of the contributions due to swelling.

$$\mu_1 - \mu_{1,0} = \Delta\mu_{elastic} + \Delta\mu_{mix} \quad (7.2)$$

where μ_1 is the chemical potential of the swelling agent within the gel and $\mu_{1,0}$ is the chemical potential of the pure fluid. At equilibrium, the chemical potential of the swelling agent inside and outside the gel must be equal; therefore, the elastic and mixing contributions to the chemical potential will balance one another at equilibrium.

The chemical potential change upon mixing can be determined from the heat of mixing and the entropy of mixing.¹⁴⁻¹⁶ Using appropriate thermodynamic relationships, the chemical potential of mixing can be expressed as:

$$\Delta\mu_{mix} = RT \left(\ln(1 - v_{2,s}) + v_{2,s} + \chi_1 v_{2,s} \right) \quad (7.3)$$

where $v_{2,s}$ is the volume fraction of the polymer in the gel and χ_1 is the polymer water interaction parameter.¹⁴⁻¹⁶

The elastic contribution to the chemical potential is determined from the statistical theory of rubber elasticity.³⁶ The elastic free energy depends on the number of polymer chains in the network and the linear expansion factor. For gels that are crosslinked in the absence of water, the elastic contribution to the chemical potential^{14-16,36} is written as:

$$\Delta\mu_{elastic} = RT \left(\frac{V_1}{v\bar{M}_c} \right) \left(1 - \frac{2\bar{M}_c}{\bar{M}_n} \right) \left(v_{2,s}^{1/3} - \frac{v_{2,s}}{2} \right) \quad (7.4)$$

where v is the specific volume of the polymer, V_1 is the molar volume of the swelling agent, \bar{M}_c is the molecular weight of the polymer chains between junction points, and \bar{M}_n is the molecular weight of the polymer chains if no crosslinks had been introduced.

Equation (7.4) was developed for the case where the polymer chains had been crosslinked in the presence of the water. If they were, the elastic contributions must account for the volume fraction density of the chains during crosslinking.³ For polymer gels crosslinked in the presence of water, the elastic contribution to the chemical potential is:

$$\Delta\mu_{elastic} = RT \left(\frac{V_1}{\nu \bar{M}_c} \right) \left(1 - \frac{2\bar{M}_c}{\bar{M}_n} \right) \nu_{2,r} \left(\left(\frac{\nu_{2,s}}{\nu_{2,r}} \right)^{1/3} - \frac{\nu_{2,s}}{2\nu_{2,r}} \right) \quad (7.5)$$

where $\nu_{2,s}$ is the volume fraction of the polymer in the relaxed state. The relaxed state of the polymer is defined as occurring immediately after crosslinking of the polymer but prior to swelling or deswelling.

By combining Equations (7.3) and (7.4), the swelling behavior of neutral hydrogels crosslinked in the absence of water can be described by the following equation:

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{(\nu/V_1) [\ln(1-\nu_{2,s}) + \nu_{2,s} + \chi_1 \nu_{2,s}]}{\left(\nu_{2,s}^{1/3} - \frac{\nu_{2,s}}{2} \right)} \quad (7.6)$$

For the case of gels prepared by crosslinking in the presence of water, the equation for the swelling of the polymer gel can be obtained by combining Equations (7.3) and (7.5) since the mixing contributions for both cases are the same. The swelling of networks crosslinked in the presence of water can then be written as:

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{(\nu/V_1) [\ln(1-\nu_{2,s}) + \nu_{2,s} + \chi_1 \nu_{2,s}]}{\nu_{2,r} \left(\left(\nu_{2,s}/\nu_{2,r} \right)^{1/3} - (\nu_{2,s}/2\nu_{2,r}) \right)} \quad (7.7)$$

SWELLING OF IONIC HYDROGELS

Several factors affect the swelling of ionic hydrogels. Some of the major factors are the degree of ionization in the network, the ionization equilibrium, and the nature of the counterions. As the ionic content of a hydrogel is increased in response to environmental stimulus, increased repulsive forces develop and the network becomes more hydrophilic. The result is a more highly swollen network. Because of Donnan equilibrium, the chemical potential of the ions inside the gel must be equal to the chemical potential of the ions in the water outside the gel.

Ionization equilibrium is established in the form of a double layer of fixed charges on the pendant groups and counterions in the gel. Finally, the nature of counterions in the water will affect the swelling of the gel. As the valences of the counterions increase, they are more strongly attracted to the gel and will reduce the concentrations of ions needed in the gel to satisfy Donnan equilibrium conditions.

The swelling behavior of polyelectrolyte gels was initially described as a result of a balance between the elastic energy of the network and the osmotic pressure developed as a result of the ions. In electrolytic solutions, the osmotic pressure is associated with the development of a Donnan equilibrium. This pressure term is also affected by the fixed charges developed on the pendant chains.¹⁸⁻²⁹ The elastic term is described by the Flory expression derived from assumptions of Gaussian chain distributions.

Equations for the equilibrium swelling of ionic hydrogels were developed by equating three contributions to the free energy of the swollen gel. These contributions are due to mixing of the polymer and water, network elasticity, and ionic contributions. The general equation is given as:

$$\Delta G = \Delta G_{mix} + \Delta G_{el} + \Delta G_{ion} \quad (7.8)$$

In terms of the chemical potential, the difference between the chemical potential of the swelling agent inside the gel and outside the gel is:

$$\mu_1 - \mu_{1,0} = \Delta\mu_{elastic} + \Delta\mu_{mix} + \Delta\mu_{ion} \quad (7.9)$$

For weakly charged polyelectrolytes, the elastic contribution and mixing contributions will not differ from the case of nonionic gels. However, for highly ionizable materials there are ionization effects on the elastic and mixing terms.^{26–29} As defined by this equation, at equilibrium the elastic, mixing, and ionic contributions to the chemical potential change must add up to zero.

The ionic term in Equation (7.9) is strongly dependent on the ionic strength and nature of the ions. Ricka and Tanaka³⁰ and Brannon-Peppas and Peppas^{22,23} developed expressions to describe the ionic contributions to the swelling of polyelectrolytes. Assuming that the polymer networks under conditions of swelling behave similarly to dilute polymer solutions, the activity coefficient can be approximated as one and activities can be replaced with concentrations. The ionic term in Equation (7.9) becomes:

$$\Delta\mu_{ion} = RTV_1\Delta c_{tot} \quad (7.10)$$

where Δc_{tot} is the difference in the total concentration of mobile ions within the gel.

The difference in the concentration of mobile ions is due to the fact that the charged polymer requires the same number of counterions to remain in the gel to achieve electroneutrality. The difference in the total ion concentration can then be calculated from the equilibrium condition for the salt.

Brannon-Peppas and Peppas^{22,23} developed expressions for the ionic contributions to the swelling of polyelectrolytes for anionic and cationic materials. The ionic contribution for anionic networks is:

$$\Delta\mu_{ion} = \frac{RTV_1}{4I} \left(\frac{v_{2,s}^2}{v} \right) \left(\frac{K_a}{10^{-pH} + K_a} \right)^2 \quad (7.11)$$

For cationic networks, the ionic contribution is:

$$\Delta\mu_{ion} = \frac{RTV_1}{4I} \left(\frac{v_{2,s}^2}{v} \right) \left(\frac{K_b}{10^{pH-14} + K_b} \right)^2 \quad (7.12)$$

In these expressions, I is the ionic strength, K_a and K_b are the dissociation constants for the acid and base, respectively. It is significant to note that this expression has related the ionic contribution to the chemical potential to characteristics about the polymer/swelling agent that are readily determinable.

Equations (7.11) and (7.12) can be combined with the previous equations developed for nonionic networks. For the case of anionic polymer gels that were crosslinked in the presence of water, the equilibrium degree of swelling can be described by:

$$\frac{V_1}{4I} \left(\frac{v_{2,s}^2}{v} \right) \left(\frac{K_a}{10^{-pH} + K_a} \right)^2 = \left(\ln(1 - v_{2,s}) + v_{2,s} + \chi_1 v_{2,s} \right) + \left(\frac{V_1}{vM_c} \right) \left(1 - \frac{2\bar{M}_c}{M_n} \right) v_{2,r} \left(\left(\frac{v_{2,s}}{v_{2,r}} \right)^{1/3} - \frac{v_{2,s}}{2v_{2,r}} \right) \quad (7.13)$$

For the cationic hydrogels prepared in the presence of water, the equilibrium degree of swelling is:

$$\frac{V_1}{4I} \left(\frac{v_{2,s}^2}{v} \right) \left(\frac{K_b}{10^{pH-14} + K_b} \right)^2 = \left(\ln(1 - v_{2,s}) + v_{2,s} + \chi_1 v_{2,s} \right) + \left(\frac{V_1}{vM_c} \right) \left(1 - \frac{2\bar{M}_c}{M_n} \right) v_{2,r} \left(\left(\frac{v_{2,s}}{v_{2,r}} \right)^{1/3} - \frac{v_{2,s}}{2v_{2,r}} \right) \quad (7.14)$$

The abrupt change in swelling characteristics can be observed with hydrogels of various compositions. For example, Figure 7.1 indicates the swelling behavior of a gel made of poly(acrylic acid) grafted with chains of 200-mol weight poly(ethylene glycol) and swollen in water at 37°C. The figure shows the calculated values of M_c according to Equation (7.14). Such studies can be used to calculate the equivalent mesh sizes of the same networks by simple application of the Flory theory as indicated in Figure 7.2.

KINETICS OF SMART HYDROGELS

For many applications, the equilibrium swelling of the polyelectrolyte gels may not be the most important characteristic. For some applications, it is vital that the gel be able to exhibit fully reversible swelling and deswelling in response to pH changes or ionic strength. The rates at which a gel swells or collapses in response to changes in the environmental pH are vital in determining whether the gel is suitable for a given application.

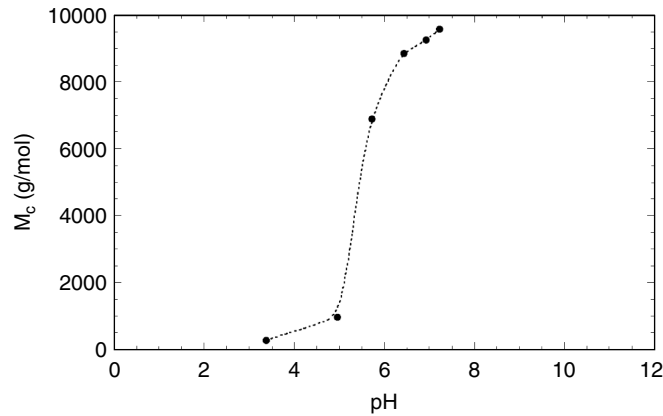


FIGURE 7.1 The effect of environmental pH on the molecular weight between crosslinks, M_c , calculated using Equation 7.14 for a polymer network of PAA-g-PEG2000.

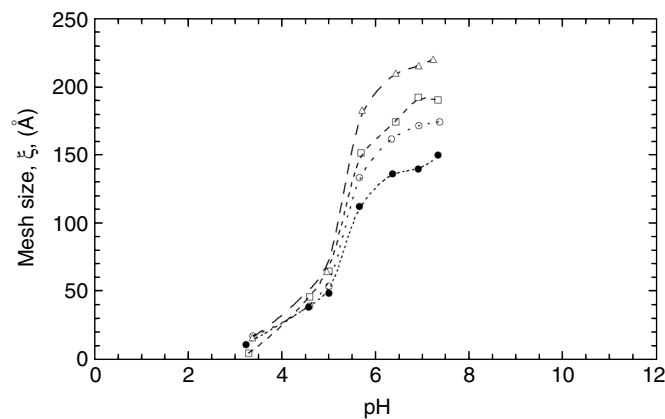


FIGURE 7.2 The effect of environmental pH on the mesh size, ξ_c , based on the values of M_c calculated using Equation 7.14 for PAA-g-PEG polymer networks with PEG grafts of molecular weights of 200, 400, 1000, and 2000.

Many researchers have studied the dynamic swelling of polyelectrolyte networks. The early work of Katchalsky¹⁸⁻²⁰ in the area of polyelectrolytes established the fact that the collapse and expansion of poly(methacrylic acid) gels occurred reversibly by simply adjusting the pH of the fluid. The group of Tanaka²¹ performed significant work in this area as well and confirmed the reversible behavior of polyelectrolyte networks. Ohmine and Tanaka³¹ also observed the sudden collapse of ionic networks in response to sudden changes in the ionic strength of the swelling media. Studies by Khare and Peppas³² examined the swelling kinetics of poly(methacrylic acid) or poly(acrylic acid) with poly(hydroxyethyl methacrylate). They observed pH- and ionic strength-dependent swelling kinetics in these gels.

A model was developed by Brannon-Peppas and Peppas to describe the dynamic swelling of ionic hydrogels in response to ionic strength changes.³⁷ When an ionic gel swells in response to pH changes, there is a corresponding change in the volume or the length for one-dimensional transport. Based on the swelling, the strain in the gel, ϵ , can be calculated at any time during the swelling as:

$$\epsilon = \frac{l - l_o}{l_o} \quad (7.15)$$

where l is the length at any time and l_o is the initial length.

In this analysis, it was assumed that the responses of the material (strain) to the inputs were additive and time-independent of the applied inputs. Therefore, the Boltzmann superposition principle can be invoked and the time-dependent strain in response to changes in environmental pH or ionic strength can be represented³⁷ by:

$$\epsilon(t) = \int_0^t L(t - \tau) \frac{\partial I(\tau)}{\partial \tau} d\tau \quad (7.16)$$

where $\frac{\partial I(\tau)}{\partial \tau}$ is the change in pH or ionic strength and $L(t - \tau)$ is termed the ionic mechanochemical compliance and is a function of the polymer.

Assuming isotropic swelling in the hydrogel, the volume swelling ratio of the gel can be written as:

$$Q(t) = \frac{V_s(t)}{V_d} = \frac{l(t)^3}{l_o^3} = (1 + \epsilon(t))^3 \quad (7.17)$$

where $V_s(t)$ is the volume of the swollen gel at any time and V_d is the volume of the initially dry polymer. By combining Equations (7.16) and (7.17), the swelling of an ionic gel in response to ionic strength changes can be described by:

$$Q(t) = \left[1 + \int_0^t L(t - \tau) \frac{\partial I(\tau)}{\partial \tau} d\tau \right]^3 \quad (7.18)$$

Figure 7.3 shows an analysis of this behavior; data are presented for the equilibrium and dynamic responses of hydrogels swollen successively from one pH to another in order to determine the kernel of the previous equation.

ALTERNATIVE DYNAMIC ANALYSIS OF SWELLING

Water transport into polymeric hydrogels has been investigated over the past several decades, with several notable contributions made to the understanding of deviations from classical Fickian diffusion.³⁸⁻⁴⁰ Due to the viscoelastic properties of polymers,

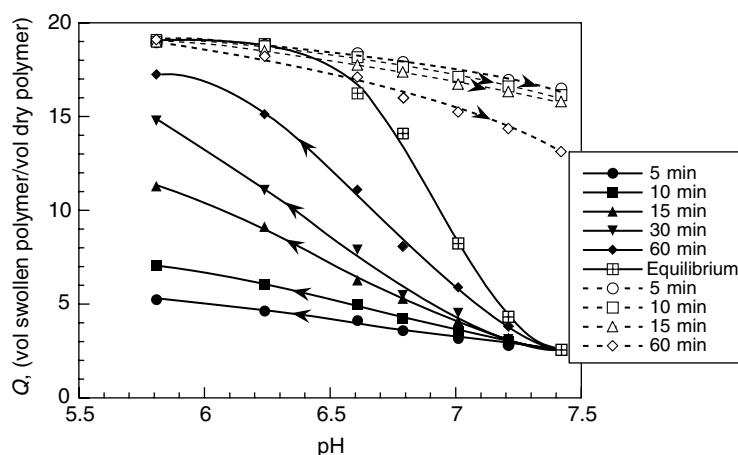


FIGURE 7.3 Results of experiments designed to derive the linear kernel function $L(t - \tau)$ of a hydrogel system. Hydrogel discs of polydiethylaminoethyl methacrylate-g-ethylene glycol PDEAEM-g-EG were preequilibrated and transferred from one pH to another and allowed to swell/deswell. The legend denotes the time between transfers.

which are enhanced by the presence of crosslinked networks, anomalous water diffusion can be observed. This behavior is bound by pure Fickian diffusion and Case II transport. Case II or constant rate transport has been observed for several polymer/water systems.⁴⁰

Transport in all these physical situations can generally be reduced to three types of driving forces: a water concentration gradient, a polymer stress gradient, and osmotic forces. Osmotic behavior is observed as a result of the hydrophilicity of the polymer network; its magnitude is amplified when a hydrophilic solute is imbedded in the matrix such as in the case of swelling-controlled release devices.

As an important application, swelling-controlled release systems for drug delivery are based on the above principles by which an appropriate polymer can counterbalance normal Fickian diffusion by hindering the release of an embedded drug, leading to an extended period of drug delivery and possibly zero-order release.⁴¹ The presence of a polymer network surrounding a drug or protein molecule has also been shown⁴² to act as a stabilizer, maintaining biological activity until the solute is released.

Despite significant work to accurately model water transport in hydrogels,^{43–46} simpler molecular models are needed. This can be done with the use of a diffusional Deborah (De) number, a measure of water motion relative to polymer relaxation; Sw relates water motion to solute release.

In nonswelling systems or where the relative relaxation time of a polymer is much shorter than the characteristic diffusion time for water transport, Fickian diffusion is observed, with water transport controlled by a concentration gradient. Once solvated, these polymers assume an equilibrium state almost immediately. In cases where polymer relaxation is the rate limiting step to water transport, Case II transport or time-independent diffusion is observed. However, in many systems, the

water uptake mechanisms lead to transport behavior intermediate to Fickian and Case II transport, termed *anomalous transport*. Specific polymeric systems exhibiting the limiting cases of Fickian and Case II transport have been identified by Frisch et al.⁴⁵ and Thomas and Windle.⁴⁷

Many experimental parameters can affect the kinetic swelling behavior of polymers. The effects of sample geometry on water uptake as described by the power law model have been investigated.^{48,49} The effects of crosslinking density,⁵⁰ drug loading,⁵¹ and copolymer composition⁴² on swelling kinetics have also been determined experimentally. Recently, Colombo et al.⁵² found a strong correlation between front motion and drug release kinetics. Case II drug release resulted when water and degradation fronts were synchronized.

There have been many investigations of diffusion in polymers, with results showing a range of transport behavior. In swelling polymer systems, stresses arising during the polymer swelling process have significant effects on water uptake behavior. Crazing phenomena have been noted in extreme systems; in other systems, these stresses can cause anomalous or Case II transport.⁴⁴

Alfrey et al.⁴⁴ identified Case II transport with the existence of a sharp water front advancing at a constant velocity. Their results indicated that a polymer placed into a thermodynamically compatible water will swell and rearrange to accommodate the water, leading to anomalous and possibly Case II transport, while poor waters will be restricted to diffusion in the pore space inside the polymer, leading to Fickian transport. The rate of water uptake and compatibility of the polymer with a particular water leads to stresses occurring between the rubbery and glassy areas of the swelling polymer that were found to crack or craze in the presence of especially good waters.

Similarly, Hopfenberg and Frisch³⁹ showed how the type of transport observed for the same polymer/water pair can range from pure Fickian to Case II with variations in the temperature and water activity. The same group⁴⁵ also noted that two different waters had sharply different uptake characteristics in a glassy epoxy polymer. Benzene diffusion was observed to obey Case II transport, while methylene chloride diffusion into the same polymer was Fickian. By mixing the two waters, anomalous water uptake was observed, with the motion of the water front described by a linear combination of the two effects:

$$v = N_a k_a t^{1/2} + N_b k_b t \quad (7.19)$$

where v is the front velocity, N_a and N_b represent the mole fraction of each water, and k_a and k_b are the uptake rate constants for pure liquid a or b .

Osmotic pressure is also an important factor in water uptake kinetics for polymer systems restrained by crosslinks.^{48,53} These investigators utilized an osmotic pressure driving force to account for water uptake; however, they did not consider the increase in osmotic pressure for solute-loaded samples, which can be significant in a number of systems, leading to entirely different water uptake kinetics in the same polymeric material.

Gehrke et al.⁵⁴ investigated water uptake in poly(2-hydroxyethyl methacrylate), an important biomedical polymer used frequently in controlled drug delivery systems. They found that water uptake and front velocities were dependent on the square

root of time, indicating Fickian transport. It was theorized that this was a result of the small sizes of water molecules relative to the pore space in the network thereby having no convective flux term. In cases where transport was facilitated by a concentration gradient and polymer relaxation occurred quickly, Fickian diffusion was expected.

Although less common, Super Case II transport has been reported to occur in certain polymer/water systems. Jacques et al.⁵⁵ observed an increase over the initial rate of n-hexane sorption into polystyrene and poly(phenylene oxide) as the polymer swelled. The sorption kinetics were seen to be strong functions of polymer composition, partial pressure (and therefore activity) of hexane, and temperature. The diameters of polystyrene spheres were also seen as major factors in swelling kinetics, with Case II diffusion occurring in larger diameter samples.⁵⁶

There have been many experimental investigations to elucidate the state of a water (particularly water in polymer networks).⁵⁷⁻⁵⁹ In hydrogels of certain compositions, water can bind with the polymer chains, creating a rigid area around the mesh that is not accessible to solute or water diffusion. This can greatly influence the type of transport observed, since the effective porosity of the material is decreased by bound water. Koda⁵⁷ determined that the velocity of ultrasonic waves was decreased markedly in polyelectrolyte hydrogels, indicating the presence of bound water.

The diffusional De number is expressed as a ratio between the characteristic polymer relaxation time and a characteristic diffusion time:

$$De = \frac{\lambda}{\theta} = \frac{\lambda D_{1,2}}{(\delta(t))^2} = \frac{\text{Relaxation time}}{\text{Diffusion of solvent}} \quad (7.20)$$

where λ is the characteristic relaxation time for the polymer when subjected to swelling stresses and δ is the characteristic water diffusion time into a swelling sample.^{60,61} The δ is defined as the square of the half thickness of a thin disc sample divided by the diffusion coefficient of water in the polymer ($\delta^2/D_{1,2}$). If either the relaxation time ($De \gg 1$) or water diffusion ($De \ll 1$) dominates the swelling process, the time dependence is Fickian; however, if De is on the order of 1, the two processes will occur on the same time scale, leading to anomalous transport behavior.

Wang et al.⁴⁶ developed an equation separating concentration gradient-dependent flux from stress relaxation:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[D(c, x, t) \frac{\partial c}{\partial x} - B(c, x, t) S c \right] \quad (7.21)$$

where D and B represent the diffusion coefficient and water mobility, respectively. S is a dimensionless variable similar to a De number, comparing the partial stress of the water to the total water uptake. Case II diffusion is observed when stress relaxation dominates.

Berens and Hopfenberg⁶² also approached the problem by separating stress relaxation terms from diffusive flux:

$$M_t = M_{\infty,F} \left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 k_F t) \right] + \sum_i M_{\infty,i} [1 - \exp(-k_i t)] \quad (7.22)$$

where $M_{\infty,F}$ is the equilibrium amount of sorption in the polymer before relaxation, k_F is a diffusional rate constant, $M_{\infty,i}$ represents the amount of water uptake during the i th relaxation process, and k_i is the corresponding relaxation rate constant. This model explicitly separated the diffusional and relaxation characteristics of water uptake. It was shown to fit experimental data, but many fitting parameters were necessary and it required information about a spectrum of relaxation processes.

CONCLUSIONS

In conclusion, several frameworks exist for the analysis of the kinetics of fast swelling of gels. Several recent theories from our laboratory^{63–70} have indicated that it is possible to predict the exact swelling behavior of both neutral and ionic gels under various conditions. Such results can be used to analyze the behaviors of gels under various conditions. However, it must be noted that the exact analyses of such systems are significantly more complicated because of the presence of other thermodynamic components such as ions and small molecular weight compounds.

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