

Kinetics and Mechanisms of Water Sorption in Hydrophobic, Ionizable Copolymer Gels

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SYNOPSIS

The aqueous kinetic swelling properties of a class of cross-linked hydrophobic polyamine copolymer gels based on *n*-alkyl esters of methacrylic acid (*n*AMA) and *N,N*-dimethylaminoethyl methacrylate (DMA) have been studied as a function of solution ionic composition (pH, ionic strength, and buffer content), gel composition, and temperature. Water uptake and swelling in these gels are driven by ionization of the DMA amine groups, which overcomes the hydrophobic tendency of these gels to exclude water in the unionized state. Sorption kinetics in initially glassy gel disks are generally biphasic, characterized by an initial phase of relatively slow water uptake followed by an accelerated phase during which significant volume expansion of the gel occurs. This sorption/swelling behavior strongly suggests a moving penetrant front mechanism. The initial rate of water sorption increases markedly as (1) solution pH decreases, (2) gel *n*AMA comonomer content decreases, (3) gel *n*AMA side-chain length decreases, and (4) temperature increases. Furthermore, the initial phase of sorption in initially glassy gels is generally non-Fickian and approaches zero-order behavior as (1) pH increases, (2) *n*AMA content increases, and (3) temperature decreases. In direct contrast, sorption in initially dry, *rubbery* gels is monophasic, but non-Fickian, and approaches zero-order behavior as temperature increases. This behavior is contrary to the Fickian sorption behavior normally observed in polymers above their glass transition temperatures. Finally, sorption kinetics critically depend upon the nature of the ions in solution: Kinetics are significantly faster in the presence of weak electrolytes than that of strong electrolytes. We discuss the importance of the rate of ion transport in determining the overall sorption kinetics and how sorption kinetics can be non-Fickian in rubbery gels. Also, we propose a mechanism for the observed enhanced kinetics in the presence of weak electrolytes.

INTRODUCTION

Dynamic penetrant sorption into initially glassy nonionic polymers generally involves a complex set of mass transport steps when the penetrant/polymer pair are of good compatibility. As the penetrant invades the polymer from the sample surface, a sharp boundary or moving front is commonly observed separating the unsolvated glassy polymer region ahead of the front from the swollen and rubbery gel phase behind it.¹ Just ahead of the front, the pres-

ence of solvent plasticizes the polymer and causes it to undergo a glass-to-rubber transition that initiates chain relaxation processes and swelling.¹⁻⁴

The time course of overall penetrant uptake often deviates from classical Fickian diffusion behavior when sorption is accompanied by a glass-to-rubber transition in the polymer.⁵⁻⁷ In Fickian sorption, the initial uptake into polymeric slabs is proportional to $t^{0.5}$ and is commonly observed in penetrant sorption into polymers well above T_g .^{7,8} In glassy polymers, however, sorption is often proportional to t^n , where the kinetic exponent n can take on values between 0.5 and 1.0. This non-Fickian or "anomalous" sorption behavior is generally associated with the concurrent processes of inward diffusion of pen-

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etrant from the solution/gel interface and the process of polymer relaxation that occurs in response to penetrant invasion and plasticization at the moving front.^{1,5,6}

Swelling processes of gels in excess electrolyte solutions become more complex when sorption of water is accompanied by ionization of the gel itself. For gels that contain weakly acidic or basic groups, the ionization state of the gel will depend upon the electrolyte composition of the bulk solution. During the process of dynamic water sorption in gels containing weakly basic groups, transport of mobile ions into the gel from the bulk solution is necessarily coupled to water sorption as the gel becomes hydrated and ionized. This coupling is required to maintain electroneutrality in the swollen gel phase. Furthermore, when the gel is initially glassy, polymer relaxation processes will also contribute to the overall dynamics of water sorption as mentioned above.

Although several reports have appeared concerning the effects of ions on the swelling equilibria and permeability of neutral and ionized gels,⁹⁻¹³ little is known about the dependence of sorption and swelling kinetics of ionic gels on diffusive transport of ions. Helfferich and others have investigated the effects of ion diffusion on the rates of certain ion-exchange reactions.¹⁴⁻¹⁹ It was shown theoretically that the rate of ion diffusion can be dramatically slowed and can even become rate-limiting for subsequent ion exchange when the resin phase contains fixed ionizable groups.¹⁵ This retardation effect arises by either the reversible binding and localization of diffusing ions to specific functional groups of the resin (diffusion-reaction)^{15,17} or the Donnan exclusion of coions from the swollen gel phase resulting in a reduced concentration gradient and, thus, diffusional driving force.¹⁷

Cross-linked copolymer gels based on *n*-alkyl esters of methacrylic acid (*n*AMA), including methyl methacrylate (MMA), ethyl methacrylate (EMA), propyl methacrylate (PMA), and butyl methacrylate (BMA) copolymerized with *N,N*-dimethylaminoethyl methacrylate (DMA) display aqueous equilibrium swelling properties that depend strongly on the pH and ion composition of the solution and on gel structure.²⁰⁻²² These gels generally undergo a sharp pH-induced swelling transition from a collapsed, hydrophobic state to a swollen ionized hydrophilic state as solution pH is reduced into the acidic range. Such swelling behavior has been attributed to alterations in the internal osmotic balance of the gel brought about by changes in the ionic composition of the external solution. The in-

herent hydrophobicity of these gels, which dominates at high pH and favors the exclusion of water, is opposed by the development of an internal ion osmotic pressure at lower pH, as a result of protonation of the gel amine groups, which induces water imbibition and gel swelling.²⁰⁻²²

Since the swelling process in initially glassy *n*AMA/DMA gels is driven by network ionization, it is expected that the processes of ion transport and polymer relaxation will be important in determining sorption kinetics in these gels. We report here the results of a series of studies on the aqueous kinetic swelling properties of *n*AMA/DMA copolymer gels. We will focus on three general aspects that are expected to affect the kinetics of water sorption: (1) the effects of gel composition (comonomer ratio and *n*AMA side-chain length), (2) the external solution composition (pH, ionic strength, and electrolyte composition), and (3) temperature. The underlying transport processes governing the observed kinetics of sorption and swelling will also be discussed.

EXPERIMENTAL

Materials

Sodium chloride, formic acid (88% solution), and glacial acetic acid (Mallinckrodt, Inc.); sodium sulfate, propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, acetamide, and methyl acetate (Aldrich Chemical Co.); citric acid (Fisher Scientific), and *n*-hexane (Fisher Scientific) were analytical reagent grade or better and were used as received. Water used in all experiments was double-distilled and deionized.

Gel Preparation

Gel samples were prepared as thin circular disks with a dry thickness of 0.28 (± 0.02) mm and diameter 9 mm according to the method described previously.²⁰⁻²²

Swelling Kinetic Experiments

Each swelling kinetic experiment was conducted in an Erlenmeyer flask containing 2 L of aqueous buffer solution at a specified pH and ionic strength. This solution volume assured that the solution composition (pH, ionic strength) would not change over the course of the sorption experiment due to ion absorption by the gel. The flask was placed in a thermostated bath that kept temperature constant

to within $\pm 0.1^\circ\text{C}$. For temperatures below room temperature, the experiment was conducted in a cold room at 4°C with heating provided by the thermostated bath to set the final experimental temperature. In general, buffered solutions contained 0.01 M citrate with NaCl added to adjust the ionic strength to the desired level. Unbuffered solutions contained 0.1 M of the respective strong electrolyte at $\text{pH } 4.0$. Solutions of the *n*-carboxylic acids (formic, acetic, butanoic, pentanoic, and hexanoic) were prepared with the same conjugate base (A^-) concentration of 1.2 mM . Stirring was provided in all experiments by a motorized stirring plate that rotated a magnetic stir bar ($5.5 \times 1\text{ cm}$) placed at the bottom of the flask.

In each experiment, two preweighed, initially dry gel disks were placed in a porous basket that was suspended in the buffer solution. The basket was readily removed to facilitate sampling of the disks. Periodically, the samples were removed from the solution and weighed after the excess surface water was removed by blotting with a laboratory tissue. The disks were then returned to the buffer solution. Solution pH was measured before and after every experiment and was found to be constant to within 0.03 pH unit in every case.

The extent of swelling for each sample disk at time t is expressed as the swelling ratio $SR(t)$, where $SR(t) = (\text{g water sorbed at time } t) / (\text{g dry gel})$, and is calculated as $(W_t - W_0) / W_0$, where W_t and W_0 are the sample weights at time t and in the dry (initial) state, respectively. The swelling ratio expressed in this manner is the amount of water sorbed at any time normalized to the dry weight of the sample. This normalization is useful when all samples have the same initial thickness. All data plots for each kinetic experiment show the mean swelling ratio for the duplicate samples with the corresponding standard error bars inserted for each time point. The error bars are usually smaller than the size of the symbols used.

RESULTS

Effect of Stirring Rate

To eliminate resistances associated with stagnant film layers on the disk surfaces, sorption kinetics were determined as a function of solution stirring rate. The stirring rate was set to a predetermined value as measured by a stroboscope tachometer, which was used to measure the rotation speed (rpm) of the main shaft of the motorized stirring unit. Figure 1 shows the initial water-sorption kinetics of the

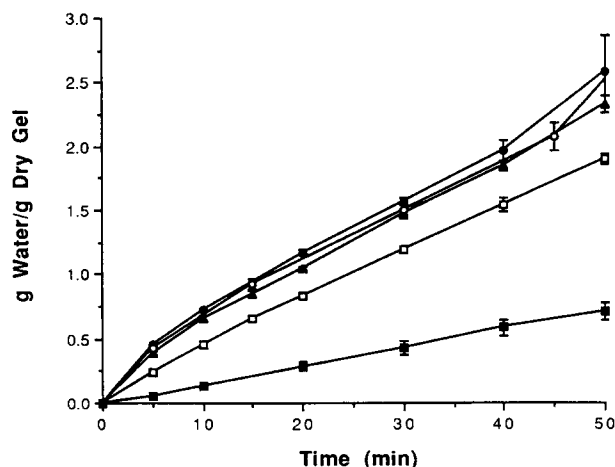


Figure 1 Effect of stirring rate on initial water-sorption kinetics of the MMA/DMA 70/30 mol % gel at $\text{pH } 4.0$ and 25°C : (■) no stirring; (□) 170 rpm; (▲) 220 rpm; (○) 390 rpm; (△) 525 rpm.

MMA/DMA 70/30 mol % gel in 0.01 M citrate/ NaCl buffer at $\text{pH } 4.0$. These curves indicate that sorption under static conditions (no stirring) was significantly slower than under conditions of stirring. Furthermore, as the stirring rate was increased to speeds in excess of approximately 220 rpm, the sorption curves converged into a single curve. All subsequent sorption experiments were conducted with stirring speeds of 450 rpm or more to maintain well-stirred conditions.

Effect of Gel Composition

The effects of varying gel comonomer ratio and *n*-alkyl ester side-chain length on the aqueous sorption kinetics of *n*AMA/DMA gels are shown in Figures 2 and 3, respectively, in which the swelling ratio is plotted as a function of time. Several features of these sorption curves are apparent and are characteristic of water sorption in glassy *n*AMA/DMA gels. The transient portion of each curve is generally biphasic, or sigmoidal, characterized by an initial phase of relatively slow water uptake followed by an accelerated phase observed just prior to the establishment of swelling equilibrium. Sorption kinetics for MMA/DMA gels of various comonomer ratios at a constant pH of 3.0 are presented in Figure 2. Gels containing 70/30, 78/22, 82/18, and 86/14 mol % MMA/DMA were prepared and showed initial sorption rates that decrease sharply as the content of the hydrophobic comonomer (MMA) increases. The 70/30 mol % gel has an initial sorption phase duration of about 1 h; the 78/22 gel, 2 h; and the 82/18 gel, of about 3.5 h. The 86/14 gel has a

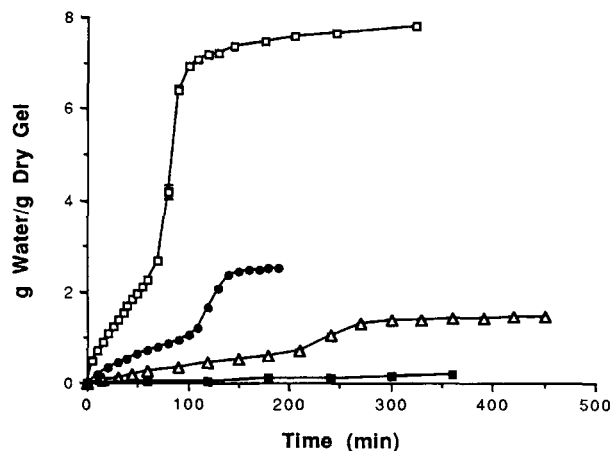


Figure 2 Effect of comonomer ratio on the swelling kinetics of MMA/DMA gels in 0.01M citrate buffer at pH 3.0, $I' = 0.1M$ and 25°C: (□) 70/30 mol %; (●) 78/22 mol %; (△) 82/18 mol %; (■) 86/14 mol %.

very slow sorption rate, with sorption still in progress after 6 h. The final swelling equilibrium greatly decreases as MMA content increases, as was reported previously.^{21,22}

The effect of the *n*-alkyl ester side-chain length of the *n*AMA comonomer on sorption kinetics at a constant pH of 3.0 is shown in Figure 3. The gels used in this experiment all had *n*AMA/DMA comonomer ratios of 70/30 mol % and differed only in the side-chain length of the *n*AMA comonomer. Shown are the sorption curves for gels with *n*AMA side-chain lengths of C₁ (MMA/DMA), C₂ (EMA/DMA), and C₃ (PMA/DMA) (sorption properties of the C₄ gel will be discussed later). The initial

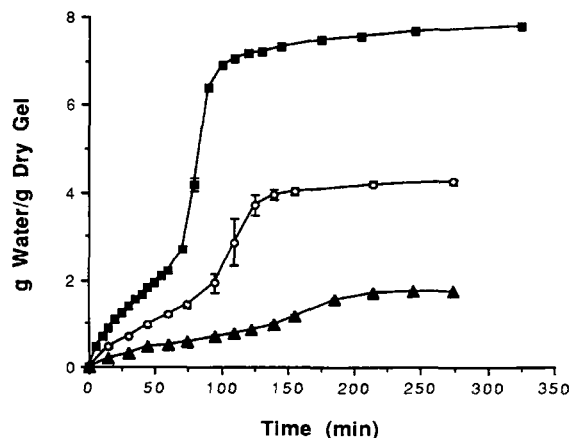


Figure 3 Effect of *n*-alkyl ester side-chain length on the swelling kinetics of 70/30 mol % *n*AMA/DMA gels in 0.01M citrate buffer at pH 3.0, $I' = 0.1M$ and 25°C: (■) MMA/DMA; (○) EMA/DMA; (▲) PMA/DMA.

sorption rate and final degree of swelling are observed to decrease as the *n*AMA side-chain length increases.

pH-Dependence

The influence of solution pH on the water-sorption kinetics of the MMA/DMA 70/30 mol % gel in 0.01M citrate/NaCl buffer and unbuffered HCl/NaCl solutions at ionic strength 0.1M and 25°C are shown in Figure 4A and B, respectively. The rate of water uptake is highly pH-dependent in both types of electrolyte solutions with the rate significantly increasing as pH is decreased. However, sorption kinetics are markedly faster in the buffered citrate/NaCl solutions [Fig. 4(A)] than in the unbuffered HCl/NaCl solutions [Fig. 4(B)] at any specified pH (note the difference in scaling of the ordinates),

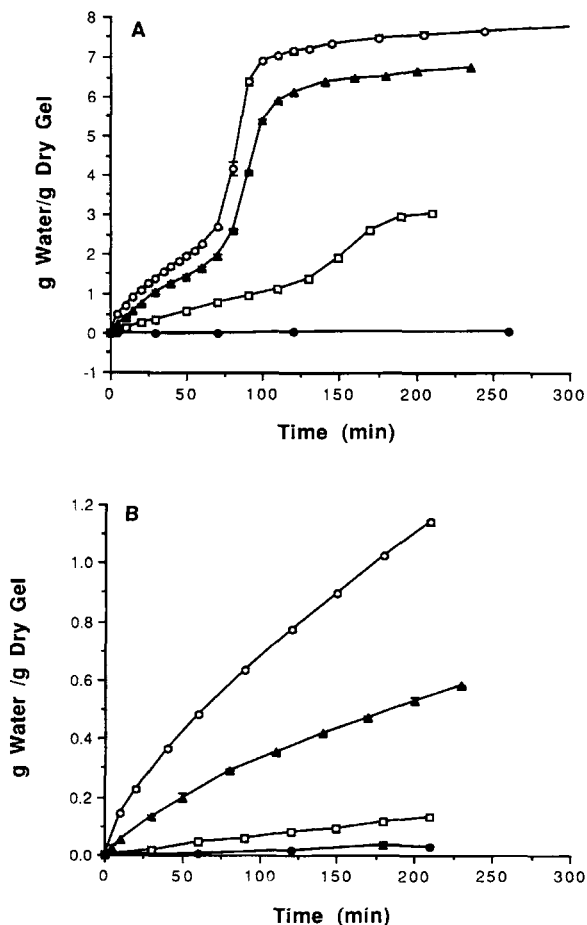


Figure 4 Effect of solution pH on the swelling kinetics of the MMA/DMA 70/30 mol % gel: (A) in 0.01M citrate buffer; (B) in unbuffered HCl/NaCl solution all at $I' = 0.1M$ and 25°C: (○) pH 3.0; (▲) pH 4.0; (□) pH 5.0; (●) pH 7.0.

except at pH 7.0, where sorption kinetics in both types of solutions occurs to a very limited extent.

Temperature Dependence

The sorption kinetics of the 70/30 mol % MMA/DMA and BMA/DMA gels at pH 4.0 measured as a function of temperature in 0.01 M citrate/NaCl solutions are presented in Figures 5 and 6, respectively. Whereas both copolymers have initial water-sorption rates that increase significantly with temperature, it is evident that the general sorption profiles for the BMA/DMA gel (Fig. 6) differ markedly from those of Figures 2–5. The characteristic bi-phasic sorption behavior exhibited by the glassy gels with shorter side chains (MMA/DMA, EMA/DMA, and PMA/DMA at all comonomer ratios) is conspicuously absent from the BMA/DMA sorption profiles. These curves have initial sorption phases that extend out to 70–80% of the equilibrium value and show no rate acceleration. It is noteworthy that the BMA/DMA 70/30 gel has the lowest glass temperature (31.1°C [Ref. 21]) of all the gels studied here, which is near or less than all except one of the experimental temperatures investigated. In spite of these differences, the initial sorption rate increases significantly with temperature. The trends for the temperature dependence of the kinetic sorption curves of the BMA/DMA gel are qualitatively similar to those of MMA/DMA in both sorption rate and extent. However, the swelling curves for BMA/DMA are monophasic and the swelling ratios are significantly lower than those for the MMA/DMA gels.

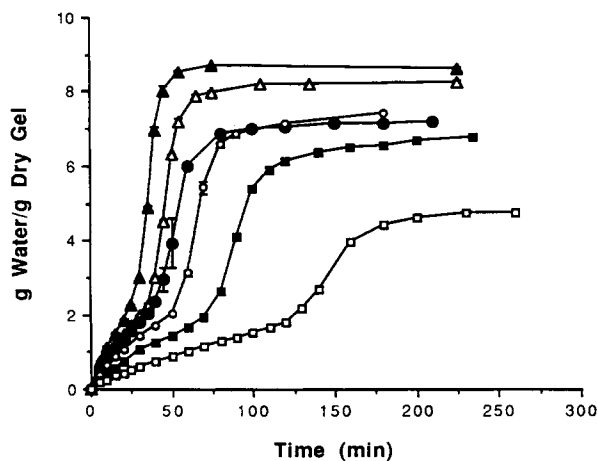


Figure 5 Temperature dependence of the swelling kinetics of the MMA/DMA 70/30 mol % gel in 0.01 M citrate buffer at pH 4.0 and $I' = 0.1 M$: (\square) 10°C; (\blacksquare) 25°C; (\circ) 35°C; (\bullet) 42°C; (\triangle) 50°C; (\blacktriangle) 60°C.

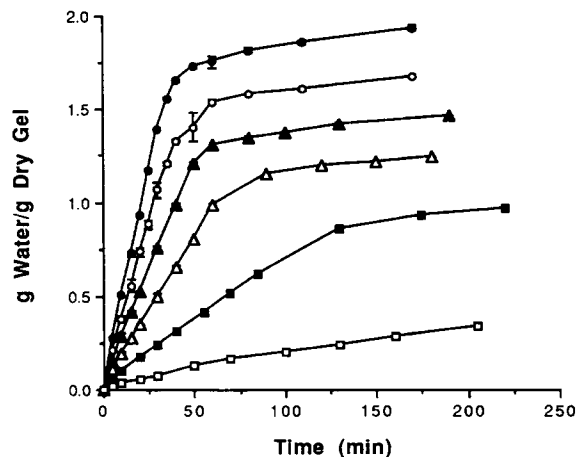


Figure 6 Temperature dependence of the swelling kinetics of the BMA/DMA 70/30 mol % gel in 0.01 M citrate buffer at pH 4.0 and $I' = 0.1 M$: (\square) 10°C; (\blacksquare) 25°C; (\triangle) 35°C; (\blacktriangle) 42°C; (\circ) 50°C; (\bullet) 60°C.

Ionic Strength Dependence

The effects of solution ionic strength (I') on water-sorption kinetics in the MMA/DMA 70/30 gel in both buffered citrate and dilute HCl solutions at a constant pH of 4.0 are shown in Figures 7 and 8, respectively. The solutions contained added NaCl to adjust the ionic strength to the desired level. Figure 7 indicates that, in buffered citrate solutions, sorption rate increases with ionic strength up to $I' = 0.056 M$, but then decreases as I' is increased fur-

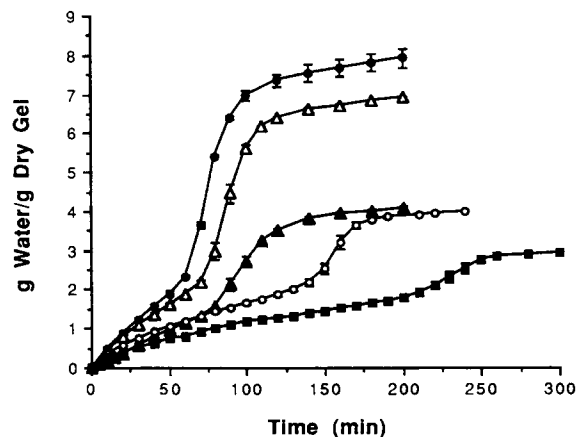


Figure 7 Effect of solution ionic strength (I') on the swelling kinetics of the MMA/DMA 70/30 mol % gel in 0.01 M citrate buffer at pH 4.0 and 25°C. NaCl was added to adjust the ionic strength of each solution to the final level. (\blacktriangle) $I' = 0.013 M$ (no added NaCl); (\bullet) $I' = 0.056 M$; (\triangle) $I' = 0.106 M$; (\circ) $I' = 0.306 M$; (\blacksquare) $I' = 0.506 M$. Dashed lines indicate final swelling equilibria.

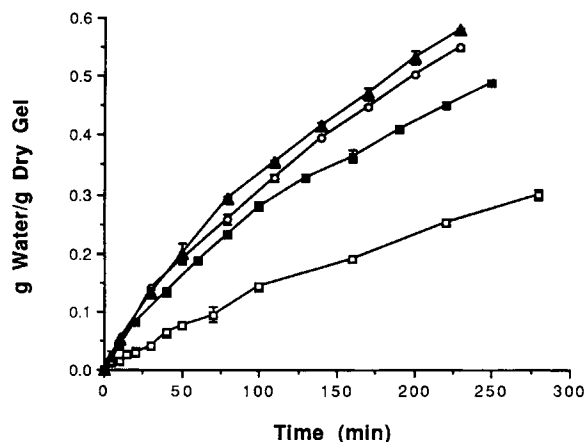


Figure 8 Effect of solution ionic strength (I') on the swelling kinetics of the MMA/DMA 70/30 mol % gel in dilute HCl solution at pH 4.0 and 25°C. NaCl was added to adjust the ionic strength of each solution to the final level. (\square) $I' = 0.0064M$; (\circ) $I' = 0.05M$; (\blacktriangle) $I' = 0.10M$; (\blacksquare) $I' = 0.50M$.

ther. It is interesting to observe that although the initial sorption rates and final equilibria are similar in $I' = 0.013M$ and $0.306M$ solutions, the acceleration point is reached considerably earlier at the lower ionic strength.

Similar sorption behavior is observed in unbuffered HCl/NaCl solutions as a function of I' as shown in Figure 8. Two additional observations are made: (1) as with the pH-dependent data of Figure 4(A) and (B), sorption kinetics are significantly slower in HCl/NaCl solutions than in citrate/NaCl solutions at the same pH and ionic strength. This suggests that the rate and mechanism of sorption depend strongly on the identity of mobile ions and buffer species, and (2) the nonmonotonicity in sorption rate in HCl/NaCl solutions does not correlate with the final swelling ratio, which monotonically decreases over this range in I' , as indicated in Table I.

Table I Equilibrium Swelling Ratio and Ordinal Swelling Rates of the MMA/DMA 70/30 Gel in NaCl Solution as a Function of Solution Ionic Strength at pH 4.0 (25°C)

$I' (M)$	Equilibrium Swelling Ratio (g water/g dry gel)	Rank Order of Initial Sorption Rate
0.0064	27.6	4 (slowest)
0.05	13.8	2
0.10	8.1	1 (fastest)
0.50	3.3	3

Analysis of Kinetic Exponents

To obtain a more quantitative understanding of the nature of the sorption kinetics in n AMA/DMA gels, the initial phase sorption data of each experiment were fit to a rate equation of the form:

$$SR(t) = kt^n \quad (1)$$

where $SR(t)$ is the measured sample swelling ratio at time t (as defined earlier), k is the swelling rate front factor, and n is the kinetic exponent. Equation (1) is a phenomenological rate law where the kinetic exponent n provides insight into the type of sorption mechanism that is operative. For example, for Fickian kinetics in which the rate of penetrant diffusion is rate-limiting, $n = 0.5$, whereas values of n between 0.5 and 1.0 indicate the contribution of non-Fickian processes such as polymer relaxation. Values of n were obtained from the slope of a log-log plot of swelling ratio versus time for data points up to the acceleration point. The 95% confidence limits for n were also computed.

The resulting values of the kinetic exponent n in 0.01M citrate buffer at 25°C are tabulated in Tables II–IV as functions of n AMA/DMA comonomer ratio, n -alkyl ester side-chain length, and pH, respectively. The data of Tables II–IV indicate that the initial-phase water-sorption kinetics are generally non-Fickian. Furthermore, sorption appears to approach Case II behavior (n increases toward unity) as the solution pH is increased or the hydrophobic (MMA) comonomer content increases. In each case, n increases as final swelling decreases. The length of the n -alkyl ester side chain appears not to have a systematic effect on the kinetic exponent (Table IV), although final swelling sharply decreases as side-chain length increases.²¹

Table II Effect of Comonomer Ratio on the Kinetic Exponent n in 0.01M Citrate Buffer (25°C)

Gel	Composition (mol %)	pH	$n (\pm 95\% \text{ CI})$
MMA/DMA	70/30	3.0	0.616 (± 0.014)
MMA/DMA	78/22	3.0	0.708 (± 0.012)
MMA/DMA	82/18	3.0	0.865 (± 0.021)
MMA/DMA	86/14	3.0	1.220 (± 0.133)
MMA/DMA	70/30	4.0	0.814 (± 0.037)
MMA/DMA	78/22	4.0	0.881 (± 0.025)
MMA/DMA	82/18	4.0	0.994 (± 0.051)

Table III Effect of *n*-Alkyl Side-chain Length on the Kinetic Exponent *n* in 0.01M Citrate Buffer (25°C)

Gel	Composition (mol %)	pH	Chain Length	<i>n</i> ($\pm 95\%$ CI)
MMA/DMA	70/30	3.0	1	0.616 (± 0.014)
EMA/DMA	70/30	3.0	2	0.716 (± 0.036)
PMA/DMA	70/30	3.0	3	0.661 (± 0.060)
MMA/DMA	70/30	4.0	1	0.814 (± 0.037)
EMA/DMA	70/30	4.0	2	0.816 (± 0.030)
PMA/DMA	70/30	4.0	3	0.864 (± 0.099)
BMA/DMA	70/30	4.0	4	0.801 (± 0.037)

The temperature dependence of the kinetic exponent *n* for the 70/30 MMA/DMA gels in 0.01M citrate buffer at pH 4.0 is indicated in Figure 9. In the case of the MMA/DMA sorption, *n* decreases monotonically with increasing temperature, indicating that water sorption becomes increasingly Fickian at elevated temperatures. The values of *n* for the BMA/DMA gel shows the opposite temperature dependence with *n* increasing toward unity and sorption approaching Case II behavior as temperature increases. This non-Fickian behavior for the BMA/DMA gel is noteworthy since the T_g of the dry gel is 31°C, below most of the experimental temperatures. A contrast can be drawn with non-ionized gels that, at temperatures above T_g , display Fickian sorption kinetics.^{6,8}

Sorption kinetics of the BMA/DMA gel were also

Table IV Effect of Solution pH on the Kinetic Exponent *n* in 0.01M Citrate Buffer (25°C)

Gel	Composition (mol %)	pH	<i>n</i> ($\pm 95\%$ CI)
MMA/DMA	70/30	3.0	0.616 (± 0.014)
MMA/DMA	70/30	4.0	0.814 (± 0.037)
MMA/DMA	70/30	5.0	0.883 (± 0.023)
MMA/DMA	78/22	3.0	0.708 (± 0.012)
MMA/DMA	78/22	4.0	0.881 (± 0.025)
MMA/DMA	82/18	3.0	0.865 (± 0.021)
MMA/DMA	82/18	4.0	0.994 (± 0.051)
EMA/DMA	70/30	3.0	0.716 (± 0.036)
EMA/DMA	70/30	4.0	0.816 (± 0.030)
EMA/DMA	70/30	4.5	0.837 (± 0.055)
EMA/DMA	70/30	5.0	1.020 (± 0.059)
PMA/DMA	70/30	3.0	0.661 (± 0.060)
PMA/DMA	70/30	4.0	0.864 (± 0.099)
PMA/DMA	70/30	4.5	0.939 (± 0.064)

measured in *n*-hexane at various temperatures in order to determine whether Fickian behavior would be observed when penetrant sorption proceeds in the absence of gel ionization. Figure 10 shows the resulting sorption profiles in *n*-hexane at 25, 35, and 45°C, whereas the corresponding values of *n* are indicated in Figure 9. The values of *n* for *n*-hexane sorption in the BMA/DMA gel appear to be fairly invariant over this temperature range and are reasonably close to 0.5, indicating a predominantly Fickian sorption mechanism. It should be noted that the exponents appear to be consistently above 0.5, but the deviation is small.

Effect of Solution Electrolyte Composition

In comparing the data presented in Figure 4 (A) and (B) and Figures 7 and 8, it is apparent that the kinetics of water sorption in *n*AMA/DMA gels are

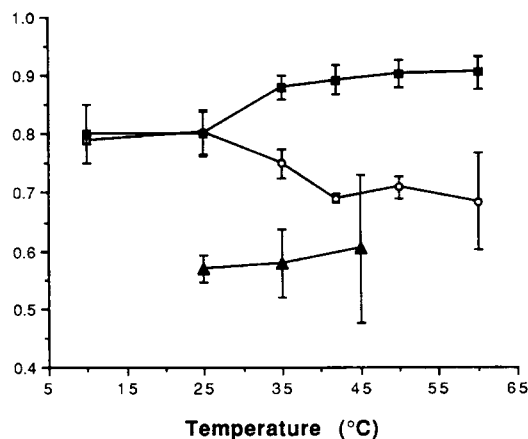


Figure 9 Temperature dependence of the kinetic exponent *n* for the (○) MMA/DMA 70/30 mol % gel in 0.01M citrate buffer at pH 4.0; (■) BMA/DMA 70/30 mol % gel in 0.01M citrate buffer at pH 4.0; (▲) BMA/DMA 70/30 mol % gel in *n*-hexane.

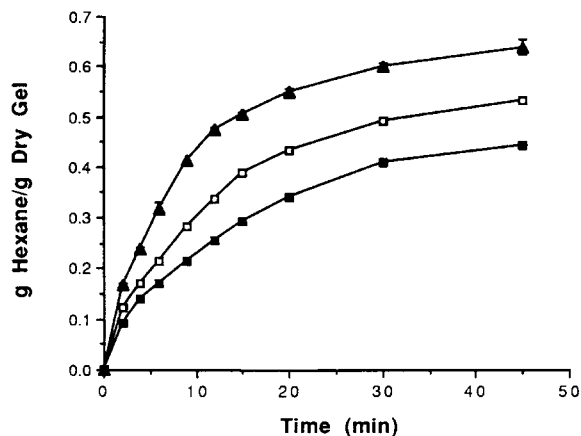


Figure 10 Swelling kinetics of the BMA/DMA 70/30 mol % gel in *n*-hexane at (■) 25°C; (□) 35°C; (▲) 45°C.

strongly influenced by the specific ions and buffer species in solution and are not simply determined by solution pH and total ionic strength alone. As noted earlier, and most striking, is the fact that sorption is much faster in the presence of citrate buffer compared with unbuffered HCl/NaCl solutions. In an effort to elucidate the basis for these ionic effects, additional sorption data were obtained in solutions of various chemical compositions including nonionic compounds structurally related to buffer ions employed, a homologous series of *n*-alkyl carboxylic acids, and a series of strong electrolyte sodium salts.

A mechanism considered for the rate enhancement observed in buffered solutions was the organic structure of buffer species employed. Organic anions, in addition to serving as gel counterions, may be capable of specific (hydrophobic) interactions with the network chains that could result in a plasticization effect. This mechanism was tested by two experimental approaches. The first involved measuring sorption kinetics in an acetate buffer and then in unbuffered aqueous solutions containing equimolar neutral compounds structurally related to acetic acid. The neutral compounds tested were methyl acetate and acetamide. If a plasticization mechanism is involved, then neutral, structurally related compounds could produce the same effect. The second experiment involved the effect of aqueous solutions containing a series of *n*-alkyl carboxylic acids of increasing chain lengths. If the counterion interacts with the gel via its organic backbone, then the sorption rate should increase with carboxylate chain length since more hydrophobic contacts can be made per molecule of acid.

Figure 11 shows sorption kinetics in the presence of 0.01 *M* acetate buffer, unbuffered methyl acetate (0.01 *M*), and unbuffered acetamide (0.01 *M*) solutions at pH 4.0 and $I' = 0.05 M$ (NaCl). As a comparison, the sorption curve in HCl/NaCl (pH 4.0, $I' = 0.05 M$) from Figure 8 is also included. The nonionic compounds have no effect on the sorption rate, which is similar in both cases to that in HCl/NaCl solution alone. Sorption in acetate buffer, however, is clearly faster and comparable to that in 0.01 *M* citrate buffer at pH 4.0 (Fig. 7).

Aqueous solutions of *n*-alkyl carboxylic acids were prepared with equimolar conjugate base carboxylate concentrations of 1.2 *mM*. This was done to normalize the counterion concentration across acids of different pKa values. The results, shown in Figure 12, indicate that sorption rate systematically increases with increasing chain length of the carboxylate anion. These data suggest that gel counterions with appreciable hydrophobic character are able to interact with the gel and accelerate the rate of water sorption. In addition, as shown in Table V, the final swelling at equilibrium in the presence of these acids *decreases* with increasing acid chain length and is significantly greater than in citrate buffer solution at the same pH and ionic strength. Thus, the buffer effects in these gels are complex and may have opposite influences on swelling kinetics and equilibria.

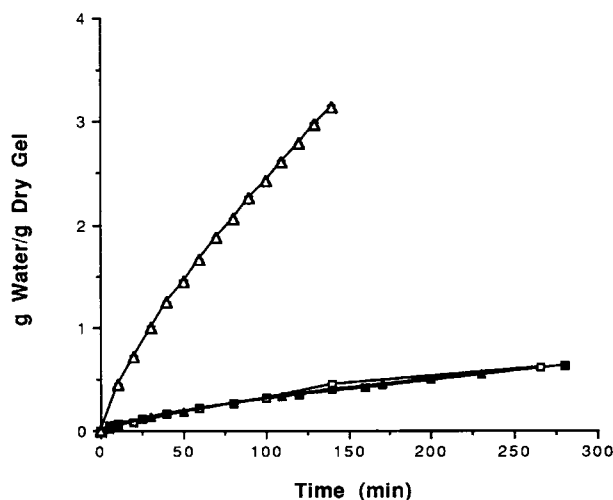


Figure 11 Water-sorption kinetics of the MMA/DMA 70/30 mol % gel in the presence of the nonionic additives acetamide and methyl acetate and in buffered and unbuffered solutions all at pH 4.0, $I' = 0.1 M$ and 25°C: (Δ) 0.01 *M* acetate buffer; (■) 0.01 *M* acetamide; (□) 0.01 *M* methyl acetate; (▲) dilute HCl.

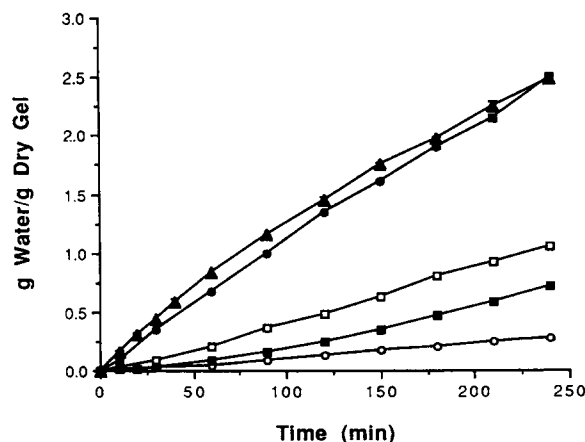


Figure 12 Water-sorption kinetics of the MMA/DMA 70/30 mol % gel in the presence of *n*-alkyl carboxylic acids of various chain lengths at pH 4.0 and an equivalent conjugate base concentration of 0.0012M and 25°C: (○) formate-C1; (■) acetate-C2; (□) butanoate-C4; (●) pentanoate-C5; (▲) hexanoate-C6.

DISCUSSION

Morphology of Swelling Curves

The swelling curves of all gels studied in this work, except those consisting of BMA/DMA, are biphasic or sigmoidal in nature and are characterized by a slow initial phase followed by an accelerated phase just prior to the approach to equilibrium. This morphology has been observed for organic penetrant sorption into glassy, nonionic polymers^{2,23-25} and was noted previously for water sorption in an *n*AMA/DMA gel,²⁰ where it was argued that the sigmoidicity of the curves could be traced to a "moving front" mechanism of water sorption.

All gels studied here, with the exception of BMA/DMA gels, are glassy in the dry, unhydrated state at the temperatures of study.²¹ Thus, during the initial phase of water sorption, a gel disk will consist of a relatively unpenetrated glassy core surrounded by a swollen, rubbery gel periphery. The interface between these two phases constitutes a swelling front that moves inward with time. For a thin, flat disk, two such swelling fronts will form corresponding to water penetration into each face of the disk. The presence of the glassy core places a kinetic constraint on the swelling of the rubbery periphery, permitting expansion to occur only in the direction normal to the swelling fronts. When the two fronts meet in the vicinity of the sample midplane, the glassy core disappears, and subsequent swelling now occurs in three dimensions and is unconstrained.

Thus, the sudden acceleration seen in the swelling curves is attributed to the disappearance of the glassy core and the shift from constrained to unconstrained swelling.

This proposed mechanism was tested previously by measuring aqueous swelling kinetics in a series of MMA/DMA disks of varying thickness.²⁰ It was found that swelling curves were identical during the initial sorption phase, but the onset of the acceleration was progressively delayed as disk thickness increased. A second confirmation of the moving front hypothesis comes from studies in which release of a water-soluble solute incorporated into the dry, glassy gels was shown to be rate-controlled by gel swelling, up to the point of the swelling acceleration.²⁶

For this swelling mechanism, the time point at which acceleration occurs serves as a rough indicator of the moving front velocity. It is evident from Figures 2, 3, 4(A), 5, (7)–(9), 11, and 12 that the front velocity is strongly affected by copolymer composition, pH, ionic strength, buffer composition, and temperature.

The shape of the swelling curve during the initial sorption phase is also of interest. The exponent *n*, defined by eq. (1) and listed for various conditions in Tables II and III, can be used to characterize the process that limits the swelling kinetics. For example, if the moving front moves extremely slowly, then the swollen rubbery phase behind the front would be expected to be nearly at equilibrium with the outer solution, which should lead to zero-order swelling kinetics (*n* = 1). Alternatively, if the front moves quickly compared with water/gel interdiffusion in the rubbery gel phase, then anomalous sorption kinetics will be observed (*n* < 1). The latter behavior is observed in most cases. For example, as

Table V Equilibrium Swelling of the MMA/DMA 70/30 Gel in *n*-Alkyl Carboxylic Acid Solutions at pH 4.0 (25°C)

<i>n</i> -Alkyl Carboxylic Acid	pKa	Equilibrium Swelling Ratio (g water/g dry gel ± SD)
Formate (C1)	3.75	Not determined ^a
Acetate (C2)	4.76	30.5 (±0.2)
Butanoate (C4)	4.82	29.5 (±0.3)
Pentanoate (C5)	4.86	27.5 (±0.2)
Hexanoate (C6)	4.80	20.5 (±0.3)

^a Equilibrium swelling was not determined due to an unstable solution pH.

the DMA content is reduced in MMA/DMA gels, the time to acceleration increases (front velocity decreases), and the kinetic exponent n increases toward unity (compare Fig. 2 with Table II). A similar correlation is seen as a function of pH (Fig. 4 and Table IV) and temperature (Fig. 5 and circles in Fig. 9). These experiments indicate that the sorption mechanism indeed becomes increasingly dominated by the moving front as the overall sorption rate decreases. Studies in which side-chain length and ionic strength are varied, however, do not lead to conclusive results in this regard.

The swelling curves for the BMA/DMA gel, shown as a function of temperature in Figure 6, are not sigmoidal in shape. This can be explained by noting that the glass temperature for this gel in the dry state is 31°C,²¹ which is below most of the experimental temperatures. This indicates that the dry gel is rubbery. (Note: The swelling data at 10°C was not recorded for a sufficiently long period to determine whether an acceleration might occur at a later time.) Thus, there will be no glassy core in this gel and, hence, no kinetic constraint on the swollen polymer phase. If an unswollen core exists, it will be able to deform rapidly as the swelling process proceeds.

Although no acceleration point exists for the rubbery BMA/DMA gels, the swelling kinetics in aqueous solutions are still highly non-Fickian, as indicated by the values of the swelling kinetic exponents (Fig. 9). This behavior is unusual for sorption in rubbery polymers, in which swelling kinetics are generally Fickian.^{7,8} However, the kinetics of n -hexane sorption in BMA/DMA gels, which occurs without gel ionization, is essentially Fickian in nature (Figs. 9 and 10). Apparently, the non-Fickian behavior observed in aqueous solution is due to interactions of the ions with the ionizable amines on the gel. This will be discussed further in the following section. It should also be noted that the "swelling velocity" can be determined roughly for the BMA/DMA gels by observing the times at which the swelling curves flatten out.

Swelling Mechanisms

It is well known that penetrant sorption into glassy, *nonionic* polymers often exhibits non-Fickian or anomalous kinetics.^{1,5-7} Deviation from Fickian behavior is attributed to the contribution of network chain relaxation processes that are induced by the plasticizing effect of the penetrant.^{1,5,6} The swelling kinetic exponent can be related to the "Deborah

number," which is the ratio of the characteristic polymer relaxation time to the characteristic interdiffusion time for the penetrant in the rubbery polymer phase,²⁷ and a "swelling interface number,"^{28,29} which compares the characteristic diffusion time to the time required for the two moving fronts to meet and vanish.

The process by which hydrophobic, ionizable n AMA/DMA gels swell in aqueous electrolyte solutions is more complex than is the swelling process for neutral, hydrophobic glassy gels. For ionizable gels, the transport of mobile ions and the interactions of these ions with the ionizable groups attached to the gel play a central role in determining the rate and non-Fickian nature of water sorption. Four lines of evidence support this assertion: (1) the boundary layer influences on water-sorption kinetics (Fig. 1), (2) the strong dependence of sorption rate on mobile ion structure (strong vs. weak electrolyte, hydrophobicity: Figs. 11 and 12), (3) the correlation of sorption rate with swelling *endpoint* in the presence of the weak electrolyte citrate and the absence of this correlation in strong electrolyte solutions (Table I), and (4) the non-Fickian nature of water sorption in *rubbery* BMA/DMA gels, contrasted with the nearly Fickian n -hexane-sorption kinetics in the same gel (Fig. 9).

Apparently, the non-Fickian water sorption behavior of n AMA/DMA gels is caused, in part, by ion transport and cannot simply be attributed to the polymer relaxation processes as with nonionic glassy gels. Nevertheless, when the gel is glassy, the relaxation processes that occur at the glass/rubber interface cannot be ignored. Figure 4(A) shows that the velocity of the swelling front (derived from the time of acceleration of the swelling curve; see above) decreases about twofold between pH 5 and pH 4, but it remains approximately constant when pH is further lowered to 3. Apparently, the ion transport and reaction do not limit progress of the swelling front below pH 4. However, the velocity of the swelling front can increase by increasing temperature, as demonstrated in Figure 5. Polymer relaxation processes thus appear to be important when ion transport is not a rate-controlling factor. As temperature increases, polymer relaxation becomes faster, leading to faster swelling. In addition, the swelling kinetic exponent decreases with increasing temperature for glassy gels (Fig. 9), indicating that interdiffusion of water with the gel is becoming more rate-limiting.

Based on these considerations, a mechanism for swelling of hydrophobic, ionizable gels in ionic so-

lutions can be proposed. A moving front is postulated to exist that separates the swollen and ionized gel periphery from the unswollen, unionized core. The movement of the swelling front into the dry core involves four mass transfer events: (1) transport of protons and counterions to the front, (2) ionization of the uncharged gel amine groups at the front, (3) expansion (relaxation) of the polymer in the vicinity of the ionized interface, and (4) equilibration of the swollen polymer with ions in the external solution, with concomitant readjustment of degree of swelling. Under different circumstances, any one of these steps may be rate-limiting. In the following, we will discuss each step with respect to experimental results.

Step 1: Proton and Counterion Transport

The sorption data of Figure 4 (A) and (B), and Figures 7, 8, 11, and 12 indicate that solution composition profoundly affects the water-sorption kinetics under conditions of identical pH and ionic strength. The initial sorption rate is significantly increased in the presence of weak organic electrolytes such as citrate or *n*-alkyl carboxylates compared with that in simple strong electrolyte solutions. However, addition of nonionizable organic compounds such as methyl acetate or acetamide has no effect on sorption rate (Fig. 11). In addition, the enhancement effected by organic electrolytes increases with increasing carbon chain length (Fig. 12).

Two explanations for the effect of solution composition on sorption kinetics can be proposed. First, the development of an ionized gel periphery during the course of sorption and swelling will reduce the partitioning of mobile ions into the gel layer from the external solution by Donnan exclusion. Exclusion of coions (of which hydrogen ion is the most important in the present case) necessarily retards the entry of counterions through electrical coupling.^{14,15} Thus, the presence of the charged gel periphery will serve to decrease the proton flux and the supply of protons to the swelling front. Similarly, Gehrke and Cussler¹⁶ found that the swelling of a weak acid polyacrylamide hydrogel in alkaline solution was rate-limited by H^+/Na^+ ion exchange due to the Donnan exclusion of hydroxide ions.

The Donnan barrier to hydrogen ions can, however, be circumvented if the solution contains weakly acidic buffer species. The protonated unionized form of the weak acid buffer can "carry" or "deliver" hydrogen ions across the swollen gel phase without being Donnan excluded. Once at the swelling front,

the hydrogen ion can be transferred from the unionized acid moiety to an unionized gel amine group that serves as a hydrogen ion acceptor (pKa of the amine group is well above that of the weak acid, making the hydrogen ion transfer favorable). After delivering the proton, the ionized carrier (conjugate base of the weak acid) simply serves as a counterion within the ionized gel phase.

An alternative explanation is that the presence of unionized weak electrolyte in the external solution simply augments the number of available protons (in the form of bound protons) that can be delivered to the swelling front. For example, the effective concentration of available protons (both bound and unbound) in 0.01 M citrate buffer at pH 4.0 is equivalent to a solution of dilute HCl at approximately pH 3.0, nearly a 10-fold increase in the hydrogen ion "concentration" over solutions containing only strong acid at the same pH. However, when a direct comparison of initial sorption rates is made between 0.01 M citrate buffer at pH 4.0 [Fig. 4(A)] and dilute HCl solution at pH 3.0 [Fig. 4(B)], it is readily seen that kinetics remain significantly faster in the presence of weak electrolyte even when "bound" hydrogen ions are accounted for. Therefore, this second proposed mechanism cannot account completely for the observed effect of buffer species.

These putative mechanisms are consistent with the finding that water-sorption kinetics are significantly faster in weak acid buffers (citrate or acetate) than in simple strong electrolyte solutions such as NaCl at the same pH and ionic strength. Furthermore, the inability of nonionizable organic compounds (methyl acetate and acetamide) to enhance the rate is consistent with these notions since they cannot "carry" or otherwise supply protons. The increase in water-sorption rate observed as pH decreases in citrate solutions [Fig. 4(A)] is also consistent with the hydrogen ion carrier theory. As solution pH decreases, the ionization equilibrium of citrate will shift to produce more total undissociated carboxylic acid groups (hydrogen ion carriers), which will increase the diffusional flux of carrier species into the gel. It should be noted that decreasing pH also serves to increase the activity and thus the diffusional flux of free hydrogen ions into the gel, thereby increasing sorption rates [Fig. 4(B)]. However, the magnitude of this effect is much less when only strong electrolytes are present due to the expected Donnan exclusion of hydrogen ions from the gel phase.

In addition, the data of Table I indicates that the initial sorption rate of the MMA/DMA 70/30 gel

in unbuffered NaCl solutions at pH 4.0 is not driven by the swelling stress that exists between the constrained swollen gel phase and the glassy core in the vicinity of the swelling front, as was proposed in some models of penetrant sorption into nonionic polymers.^{7,30,31} The initial sorption rate does not correlate with the final swelling equilibrium (Table I) that would be expected if a stress mechanism were operative.

Step 2: Ionization of Gel Amine Groups at the Swelling Front

If proton transport into the gel was rate-limiting (no polymer relaxation limitations), Fickian sorption kinetics would be expected, since with time protons must diffuse further into the gel in order to effect further ionization and swelling. However, we observe distinctly non-Fickian kinetics even in the rubbery BMA/DMA gels, where relaxation processes are assumed to be absent. This behavior can be explained if it is assumed that the ionization process at the front is partially rate-limiting.

We propose that the ionization of the amines at the front should be regarded as an activated process. The initial state of such a process consists of protons, either free or bound to a weak acid buffer, which are in the vicinity of the front, but have not yet ionized the amines at the front. The final state occurs when those surface amines (located at the front before ionization occurs) are ionized by the protons and become part of the swollen phase. Between these two states is the transition state, where the surface amines are ionized by the protons but are still located at the front. To approach the transition state, protons must climb the "energy hill," which is due to the low dielectric constant of the core. When the amines become ionized, they can then move away from the core into the swollen gel region, which is of higher dielectric constant. This leads to a reduction in energy.

When the activated process described above is slow compared to proton and counterion diffusion to the front, one can expect that ionization at the front is rate-limiting, and this could conceivably lead to Case II (constant rate) swelling. If we assume that the thickness of the interfacial zone in which ionization occurs at the front is approximately constant, then we can conceive that the swelling process can be controlled initially by that zone, but as swelling increases, the diffusion process becomes slower and eventually rate-limiting. Thus, the anomalous swelling exponents might be seen as a gradual switch

from Case II to Fickian kinetics with increasing time. If the preceding analysis is valid, then one might conceive of a dimensionless group, analogous to the swelling interface number, that would be the ratio of the proton diffusion time (again for either free or buffer-bound protons) to the time associated with the surface ionization process. With the aid of this dimensionless number, one might predict the swelling exponent, assuming that proton diffusion and surface ionization are the limiting processes.

It is noteworthy that as temperature increases the swelling exponent also increases for BMA/DMA gels (Fig. 9). Although one would expect the surface ionization rate to increase with increasing temperature, it also should be noted that the proton diffusion rate may also increase due to the higher degree of swelling seen at higher temperatures. The degree by which temperature affects diffusion and interfacial ionization kinetics will determine the temperature effect on n . It is noteworthy that the temperature effect on the kinetic exponent n is opposite for glassy MMA/DMA gels. This will be discussed in the next paragraph.

Step 3: Expansion of the Polymer in the Vicinity of the Ionized Interface

For rubbery polymers, there are no major barriers between the transition state and the final state, and the ionized polymer at the front rapidly relaxes toward the final state. However, when the dry core is in the glassy state, a significant kinetic barrier exists. For glassy polymers, this barrier is probably more significant than that due to the interfacial ionization process. Insofar as increasing temperature facilitates the traversal of this barrier, it is not surprising that, for the glassy polymers, the swelling exponent decreases with temperature, indicating more Fickian control of the swelling process.

The data from experiments using n -alkyl carboxylates of Figure 12 and Table V provide evidence that gel/organic counterion interactions also modulate swelling rates. Increasing the hydrophobicity of the carboxylate simultaneously *increases* the water-sorption rate (Fig. 12) and *decreases* gel equilibrium swelling (Table V). Carboxylates with longer hydrocarbon chains probably can concentrate at the hydrophobic swelling front and increase the sorption rate by plasticizing the chains, although a definitive mechanism is not known. The decrease in the final swelling equilibrium likely results from specific interactions such as carboxylate adsorption to network chains through hydrophobic contacts or by ion-

pairing with the ionized gel amine groups. Adsorption of *n*-alkyl carboxylic acids³² and sodium alkyl sulfonates³³ to anion-exchange resins has been shown to increase sharply with an increase in length of the alkyl group.

Step 4: Equilibration of the Swollen Polymer with the External Solution

The last step in the swelling process involves the final mechanical relaxation of the swollen gel and the redistribution of mobile ions between the gel interior and the external solution. As indicated in most of the swelling curves, gel expansion still occurs, to a limited extent, subsequent to the accelerated phase. At this stage, the dry core has disappeared and the entire bulk of the gel is hydrated, although not homogeneously. Further expansion takes place as a result of final mechanical relaxation throughout the bulk of the gel.

In addition, ion-exchange processes can lead to alterations in degree of swelling. When proton transport is facilitated by the presence of a buffer, the gel interior will be enriched with buffer counterions. To the extent that other strong electrolytes are present in the external solution (such as NaCl), the buffer counterions within the gel will be exchanged for the predominating anion in solution (e.g., Cl⁻) and neutral salts (here NaCl) will also enter the gel. This process can significantly affect the final degree of swelling, depending on solution conditions. For example, in the citrate/NaCl buffer system used predominantly in this work, multivalent citrate anions will exist in the gel interior above about pH 3.5 (citrate pK's: 3.2, 4.8, 6.4). These multivalent anions will be exchanged for monovalent chloride ions from the solution that will increase the osmolality, and thus osmotic pressure, of the gel interior. This will cause further expansion of the gel. Diffusion of neutral salt will also alter the osmotic balance of the gel and thus the final degree of swelling.

CONCLUSIONS

The aqueous kinetic swelling behavior of hydrophobic, ionizable gels is more complex than for nonionic gels. Based on experimental data in which both gel structure and solution conditions were varied, we have attempted to identify processes that are important during swelling in *n*AMA/DMA gels. These include proton diffusion, interfacial ionization at the

swelling front, the glass/rubber transition at that front, and final relaxation and equilibration with external ions.

Of significance is that the precise nature of the solution ions can affect swelling results profoundly. Although the use of carboxylate buffers in the swelling medium increases the complexity of the system, their ability to accelerate the swelling kinetics in these ionizable gels by serving as proton carriers appears to be a quite interesting and useful mechanism. In addition, we have shown that the deviation from Fickian kinetics observed in these gels is not simply a result of polymer relaxation processes associated with the glass-to-rubber transition, but is a more general property of these hydrophobic ionizable gels.

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