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Key Words

pH-sensitive hydrogels, swelling, 2-hydroxyethyl methacrylate, Donnan equilibria

Synopsis

Hydrogels sensitive to *pH* were prepared by copolymerizing 2-hydroxyethyl methacrylate (HEMA) with 2-dimethylaminoethyl methacrylate (DMA). The mole fraction of DMA monomer present during synthesis was fixed at 0.3, while the volume fraction of total monomer varied from 0.29 (**I**) to 1.0 (**II**). Swelling equilibria were measured in citrate or phosphate buffer for *pH* from 3.0 to 7.6. Swelling of the hydrogels depends on the volume fraction monomer present during synthesis, solution *pH* and identity of the buffer. Hydrogel **I** reached a four-fold larger swelling ratio (g swollen hydrogel/g dry hydrogel) in *pH* 3.0 citrate buffer compared to hydrogel **II**. Experimental results are interpreted on the basis of ideal Donnan equilibria.

Introduction

It is well known that hydrogels containing weakly-ionizable groups can swell extensively in aqueous media. Swelling equilibria for these hydrogels depend on the nature of the weakly-ionizable group and on the ionic composition of the solution surrounding the hydrogel. Hydrogels containing fixed carboxylic acid groups swell with increasing *pH* (Katchalsky and Michaeli, 1955; Grignon and Scallan, 1980). Conversely, hydrogels containing fixed tertiary-amine groups swell with decreasing solution *pH* (Ishihara et al., 1984).

Homogeneous 2-hydroxyethyl methacrylate (HEMA)-based hydrogels are of practical interest primarily for the manufacture of soft contact lenses (Singh and Agrawal, 1992; Tighe, 1987). The choice and concentration of solvent (diluent) during the polymerization determine whether a homogeneous or heterogeneous structure of the hydrogel is produced. If water is used as the solvent, the concentration must be below a certain critical level to

ensure the production of a clear, homogeneous hydrogel. When the water content exceeds this limit, opaque, heterogeneous hydrogels are obtained. The critical diluent concentration for water in the monomer mixture is approximately 0.50 volume fraction. The structure and physical properties of poly(HEMA) hydrogels have been reviewed by Peppas and Moynihan (1987).

In this work, we report swelling equilibria in aqueous buffer solutions for hydrogels prepared by copolymerizing HEMA with 2-dimethylaminoethyl methacrylate (DMA) to form hydrogels with basic character. Butanol, instead of water, was chosen as the diluent for the monomers so that the volume fraction of total monomer at network formation could be decreased below 0.50. Hydrogels prepared with the basic DMA monomer, instead of an acidic monomer, were selected for study so that our swelling results could be compared with those of Siegel and Firestone (1988) who studied gels formed from *n*-alkyl methacrylate esters (e.g., methyl methacrylate) and the basic DMA.

Experimental Section

Materials. 2-Hydroxyethyl methacrylate (Kodak) and 2-dimethylaminoethyl methacrylate (Polysciences) were vacuum distilled in the presence of the polymerization inhibitor Ethanox 330 [1,3,5-trimethyl-2,4,6-tris(3,5-ditertbutyl-4-hydroxybenzyl)-benzene] (Ethyl Co.) using the procedure described by Chou (1991). The crosslinking monomer ethylene glycol dimethacrylate (EGDMA) (Polysciences) was used as received. The initiator 2,2'-azobisisobutyronitrile (AIBN) (Polysciences) was recrystallized from 70/30 (v/v) water/ethanol before use. n-Butanol (Fisher Scientific, ACS grade) was used as received. Anhydrous citric acid and sodium citrate dihydrate (both ACS grade from Kodak) were used as received. Sodium chloride (NaCl), monobasic sodium phosphate and dibasic sodium phosphate heptahydrate (all certified ACS grade from Fisher Scientific) were used as received. Water used in the swelling studies was distilled, then filtered and deionized with a Barnstead Nanopure II unit.

Hydrogel Synthesis. Clear, homogeneous HEMA-based hydrogels with basic character were synthesized by the free-radical copolymerization of HEMA, DMA and the crosslinking monomer EGDMA. Butanol served as the diluent in the synthesis. AIBN was used to initiate polymerization; the initiator was held at a constant concentration of 1.7 mg/ml for all syntheses.

A series of hydrogels was prepared such that the mole percent crosslinker calculated on a diluent-free basis (*%C*) and mole percent DMA calculated on a diluent free basis (*%DMA*) were fixed at 0.5 and 30, respectively. The volume fraction total monomer in the reaction mixture was adjusted with the diluent butanol; the volume fractions used were 0.29, 0.38, 0.44, 0.77 and 1.0 (no butanol).

Appropriate volumes of HEMA, DMA, EGDMA and butanol were mixed with the appropriate mass of AIBN. The solution was degassed under a 500-mm Hg vacuum for 15 min. The solution was injected with a syringe between silanized glass plates separated by a 0.48 mm Teflon gasket. The glass plates were immersed in a water bath at 60°C. After 24 hours, the plates were removed from the bath. The hydrogel sheets were freed from the plates; disks were punched from the plates using a cork borer. The hydrogel disks were soaked in excess butanol which was refreshed periodically to extract the soluble fraction and initiator residues; the hydrogel disks were soaked in butanol for two weeks. The butanol was removed from the hydrogels via evaporation; the hydrogel disks were placed in a fume hood at standard laboratory temperature and pressure until their masses did not change (about one week).

Elemental Microanalysis. Carbon, hydrogen and nitrogen elemental microanalyses (U.C. Berkeley College of Chemistry Microanalytical Laboratory) were performed on dried, pulverized hydrogel samples that had been extracted with butanol.

Swelling Measurements. A series of buffer solutions was prepared; the buffer concentration was fixed at 0.01 M and the total ionic strength was adjusted to 0.1 M by adding NaCl. For *pH* below 5.5, citrate buffer was used; for *pH* above 5.5, phosphate

buffer was used. Dried poly(HEMA *co*-DMA) hydrogel disks were weighed, then immersed in buffer. Upon attainment of equilibrium, the hydrogels were reweighed. We report the swelling ratio, defined as the mass ratio of swollen hydrogel to dry hydrogel. Swelling experiments were performed in triplicate; Table 2 shows mean values of the swelling ratios with corresponding standard deviations.

Results and Discussion

The poly(HEMA *co*-DMA) hydrogels prepared for this work should all have the same elemental composition. Elemental microanalytical results for the five hydrogels prepared here show that they contain, on average, 55.1 wt. % carbon (standard deviation of 0.4), 8.4 wt. % hydrogen (0.1) and 2.4 wt. % nitrogen (0.1).

DMA is the only nitrogen-containing monomer in the poly(HEMA *co*-DMA) hydrogels prepared for this work. Thus, the percentage of DMA structural units in the poly(HEMA *co*-DMA) hydrogels may be estimated directly from the results of nitrogen elemental microanalysis. Table 1 lists the estimated DMA contents of the poly(HEMA *co*-DMA) hydrogels computed from nitrogen microanalytical data. On average, 11% of the DMA monomers present in the reaction mixture did not become incorporated into the network during synthesis. These lost monomers were most likely removed from the hydrogel interior during extraction.

Figure 1 shows swelling equilibria in aqueous buffer solutions for a series of basic poly(HEMA *co*-DMA) hydrogels synthesized in the presence of varying amounts of diluent. As expected, hydrogel swelling declines with rising *pH*. As *pH* falls, the tertiary-amine groups of the DMA structural units in the network become protonated, increasing the charge density of the network. The concomitant increase in mobile ion concentration inside the hydrogel raises the ion osmotic pressure which causes the observed increase in swelling.

Figure 1 also shows that at fixed *pH*, swelling decreases as a function of rising volume fraction of monomer at network formation. This result is consistent with the concept of increasing polymer interpenetration during synthesis with rising rising monomer volume fraction. As the amount of diluent in the reaction mixture of a hydrogel declines, the probability rises for intertwining of network chains during synthesis.

Two buffers were used to control solution *pH* in the swelling experiments: for *pH* less than 5.5, citrate buffer; for *pH* greater than 5.5, phosphate buffer. Hydrogel ionization and, in turn, hydrogel swelling, is expected to decrease with rising solution *pH*. However, as shown in Figure 1, equilibrium swelling for the hydrogels was higher in *pH* 5.6 phosphate buffer than in *pH* 5.1 citrate buffer. It appears that the specific nature of the buffer salts used to maintain solution *pH* have a significant effect on hydrogel swelling properties. Siegel and Firestone (1988) observed similar behavior for hydrophobic poly(methyl methacrylate *co*-DMA) hydrogels swollen to equilibrium in citrate and in phosphate buffers.

The buffer effect on swelling shown in Figure 1 can be explained by considering the distribution of polyvalent anions in the citrate and phosphate buffer systems (Siegel and Firestone, 1988; Firestone, 1989). Since the hydrogels contain fixed-cationic charges, Donnan equilibria favor partitioning of multivalent anions into a hydrogel over monovalent anions. Further, fewer multivalent anions are required to neutralize an equivalent number of fixed charges on the network. As the concentration of multivalent anions in the solution increases at constant ionic strength, the concentration of counterions inside the hydrogel declines, reducing the counterion osmotic pressure and swelling of the hydrogel. The *pKa*'s for citrate are 3.15, 4.78 and 6.40, while those for phosphate are 2.14, 7.10 and 12.12. At the same *pH*, there are more multivalent anions in citrate buffer than in phosphate buffer. Therefore, consistent with the results shown in Figure 1, the hydrogels should reach a higher degree of swelling in phosphate buffer than in citrate buffer.

Following Siegel and Firestone (1988), Donnan-equilibrium theory can be used to describe qualitatively the buffer effect on hydrogel swelling as a function of solution *pH*. Assuming that ion concentrations equal ion activities, we write the following equation for all mobile ions, including hydrogen ions:

$$C_i = \lambda^{Z_i} C_i^* \tag{1}$$

where C_i and C_i^* are the ith mobile ion concentrations inside and outside the hydrogel, respectively, Z_i is the valence of the ith mobile ion and λ is the Donnan ratio (Siegel, 1990). (The Donnan ratio is derived in the Appendix.) ΔC_{tot}, the difference between the total ion concentration inside and outside the hydrogel, is given by:

$$\Delta C_{tot} = \sum_i \left(\lambda^{Z_i} - 1\right) C_i^* \tag{2}$$

To solve for λ, we use the constraint of bulk electroneutrality inside the hydrogel:

$$\sum_i Z_i C_i^* \lambda^{Z_i} + \frac{\rho \lambda 10^{-pH}}{K_a + \lambda 10^{-pH}} = 0 \tag{3}$$

where *pH* is the solution *pH* of the external solution, ρ is the concentration of ionizable amine groups in the hydrogel and K_a is the dissociation constant of the protonated, fixed amine groups.

Parameter ρ may be estimated from the following hydrogel properties: the dry density, the fraction of DMA structural units in the network, the swelling ratio under the conditions of interest and the volume fraction monomer at network formation. The dry density of HEMA-based hydrogels is approximately 1.2 g/cm^3. For the hydrogels prepared with total monomer volume fractions 0.29 and 0.44, ρ is approximately 0.20 and 0.46 M,

respectively. Dissociation constant K_a was set to $10^{-7.7}$, an appropriate value for a protonated tertiary-amine group. Values of C_i^* were computed from solution pH and the added buffer and salt concentrations, taking into account the multiple buffer pK_a values.

The swelling equilibria of ionized hydrogels are determined by a balance of three main forces: (1) the free energy of mixing of the network chains with solvent, (2) the net osmotic pressure within the network resulting from the mobile counterions surrounding the fixed-charge groups (ion swelling pressure) and (3) the elastic retractile response of the network (elastic swelling pressure) (Flory, 1953; Tanaka, 1981). Forces (1) and (2) favor hydrogel swelling, while force (3) opposes it.

Figure 2 shows calculations for ΔC_{tot}, the difference in total ion concentration inside and outside the hydrogel. ΔC_{tot} is related to the ion swelling pressure; consistent with the observed swelling behavior, ΔC_{tot} is a decreasing function of rising pH for each buffer. Also consistent with experimental results, the calculations indicate that at a fixed pH, a higher value of ΔC_{tot} is obtained for phosphate buffer than for citrate buffer.

As shown in Figure 2, larger values of ΔC_{tot} were calculated for a fixed-charge concentration of 0.46 M (volume fraction total monomer at preparation of 0.44) than for 0.20 M (0.29). This result is as expected because the Donnan effect dictates that the ability of a hydrogel to exclude coions increases with rising hydrogel charge density. However, the larger value for ΔC_{tot} calculated for the "0.44" hydrogel, which translates to a larger ion swelling pressure, does not lead to larger swelling for this hydrogel compared to that observed for the "0.29" hydrogel (Figure 1). Repeating the Donnan-equilibria calculations for all hydrogels prepared for this study shows that the ion-swelling pressure increases with the fixed-charge density of the hydrogels, which depends on the volume fraction of total monomer at network formation.

However, the results of the Donnan calculations are apparently inconsistent with the observed swelling equilibria that show hydrogel swelling to decline with increasing volume fraction total monomer. An explanation for this inconsistency is clear if the effect of total

monomer volume fraction at network formation on hydrogel swelling is considered along with the concept that hydrogel swelling follows from a balance of forces. For the poly(HEMA *co*-DMA) hydrogels prepared for this work, increasing the total monomer volume fraction at network formation increases the ion swelling pressure by raising the fixed-charge density of the hydrogels at fixed *pH*, but also serves to increase the elastic-swelling pressure by raising the degree of interpenetration of network chains. It appears that the increase in elastic-swelling pressure dominates over the increase in ion swelling pressure, leading to a net decrease in hydrogel swelling (at fixed *pH*) with rising total monomer volume fraction at network formation.

Donnan equilibria have been used previously to describe quantitatively the effects of *pH* and ionic strength of monovalent ions for highly-swollen, lightly-charged acrylamide-based hydrogels (Ricka and Tanaka, 1984; Gehrke et al., 1986). Attempts to develop a more quantitative description of the swelling behavior of relatively hydrophobic poly(HEMA *co*-DMA) hydrogels in this study were not successful. Here we briefly discuss some of the deficiencies in the theory of Donnan equilibria that relegate it to providing only a qualitative description of the swelling of the hydrogels prepared for this work (Firestone, 1989; Siegel, 1990). The calculations presented here assume that the dielectric constant of the hydrogel interior is equal to that of the external solution. A hydrogel achieving a swelling ratio of 6 in aqueous solution contains 17% polymer by weight. Under such circumstances, the dielectric constant inside the hydrogel is likely to be lower than that of the external solution. Therefore, the osmotic activity of the ions inside the hydrogel is less than that calculated here.

The calculations presented above used free-solution values for the buffer pK_a's and the pK_a of the fixed tertiary-amine groups. However, it is likely that the dielectric environment inside the hydrogels interferes with the chemical equilibria associated with charging the weakly-ionizable species, including the fixed tertiary-amine groups and the buffer ions. Ionization of weakly-ionizable species is suppressed in a poor dielectric environment,

effectively lowering the pK_a of the fixed tertiary-amine groups and raising the pK_a's of the citrate and phosphate ions. Because the dielectric constant of the hydrogel interior is likely to increase with rising hydrogel swelling, it is reasonable to expect that the pK_a of the fixed-charge groups varies with the hydrogel-swelling ratio.

As pointed out by Siegel (1990), several other phenomena may influence the swelling of hydrogels; these include electrostatic interactions between fixed and mobile charged species (Katchalsky, 1954; Katchalsky and Michaeli, 1955), counterion condensation (Gehrke et al., 1986; Nagasawa, 1974) and ionic crosslinking of the ionized network accomplished by multivalent counterions (Ricka and Tanaka, 1984). None of these phenomena can be readily included in the theory of ideal Donnan equilibria.

Conclusions

Clear, homogeneous, *pH*-sensitive poly(HEMA *co*-DMA) hydrogels were prepared in a solvent. The mole fraction of DMA monomer present during synthesis was fixed at 0.3, while the volume fraction of total monomer was varied from 1.0 to 0.29 by adding butanol to the reaction mixture.

Swelling equilibria for the hydrogels were measured in aqueous citrate buffer (below *pH* 5.5) and in phosphate buffer (above *pH* 5.5). Swelling of the hydrogels depends on the volume fraction of total monomer present at network formation and on solution *pH*. Also, swelling is a function of the identity of the buffer salts used to maintain solution *pH*.

Ideal Donnan theory is used to describe qualitatively poly(HEMA *co*-DMA) hydrogel swelling as a function of solution *pH* and buffer identity. While Donnan equilibria have been used to describe qualitatively the swelling behavior of strongly hydrophilic, lightly-charged hydrogels, the theory fails to be quantitative for relatively hydrophobic poly(HEMA *co*-DMA) hydrogels. The poor dielectric environment inside a lightly-swollen hydrogel may explain the lack of quantitative performance of the Donnan theory.

Appendix: Derivation of the Donnan Constant, λ

(Following Siegel, 1990)

For ionized hydrogels, Donnan equilibria permit us to determine inside ion concentrations from the corresponding concentrations in the outer solution. It is assumed that an electrostatic potential exists between the hydrogel phase and the outer solution due to the excess of mobile ions inside the hydrogel. This potential, considered to be uniform throughout the hydrogel phase, is just sufficient to prevent the exodus of mobile ions from the hydrogel by diffusion. In the presence of the potential, the equilibrium requirement for each ion is that its electrochemical potential be the same inside and outside the hydrogel:

$$\mu_i^0 + R\,T\,ln\,a_i + Z_i\,F\,\psi = \mu_i^0 + R\,T\,ln\,a_i^* \qquad \text{(A1)}$$

where μ_i^0 is the standard chemical potential of the ion, ψ is the electrostatic potential difference between the phases, F is the Faraday constant and a_i and a_i^* are the ionic activities in the hydrogel and in the outer solution, respectively. Equation A1 rearranges to

$$a_i = a_i^*\, e^{-Z_i F\,\psi / R\,T} \qquad \text{(A2)}$$

Since ψ must be the same for all ions, it is notationally convenient to define the Donnan ratio, λ

$$\lambda = e^{-F\,\psi / R\,T} \qquad \text{(A3)}$$

Assuming that in each phase, activity is equal to concentration, Equation A2 becomes

$$C_i = \lambda^{Z_i} C_i^* \qquad \text{(A4)}$$

which is Equation 1 in the text.

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Figures

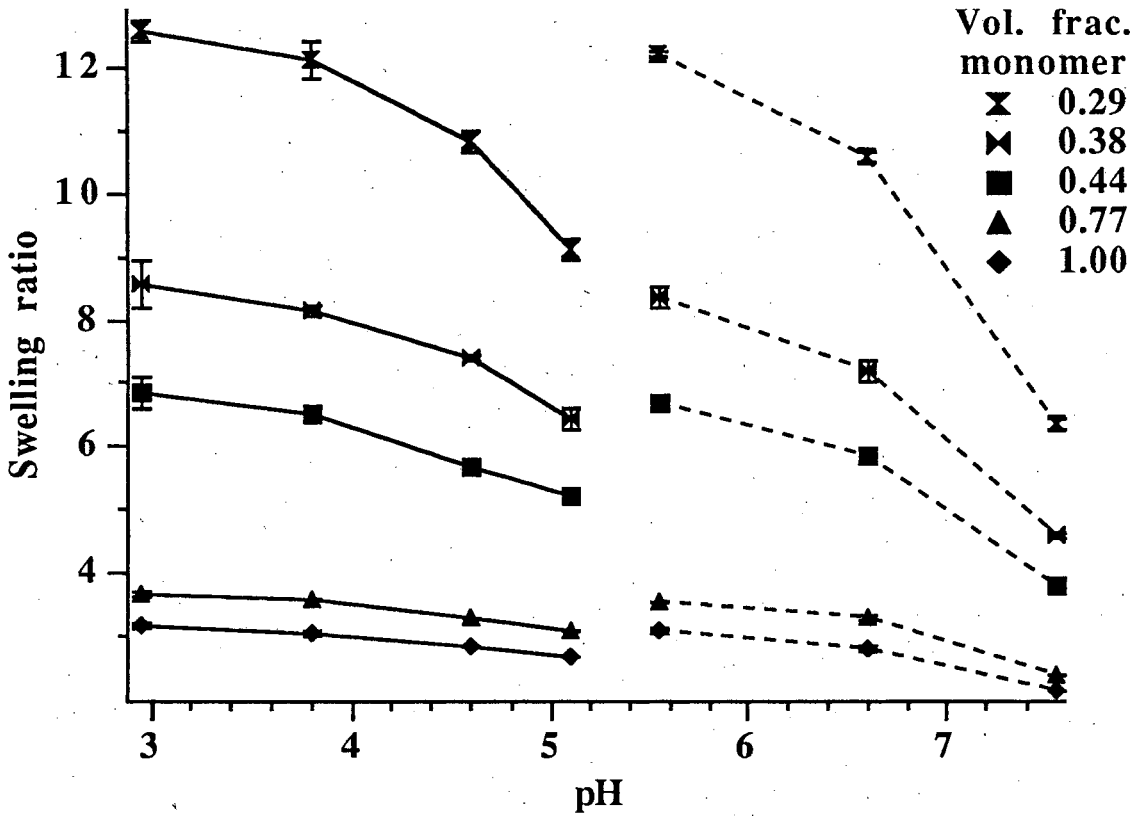

Figure 1. Swelling ratios (g swollen gel/g dry gel) in 0.01 M buffer solutions for poly(HEMA *co*-DMA) hydrogels. The overall ionic strength of each buffer solution was adjusted to 0.1 M with NaCl. Citrate buffer was used below *pH* 5.5 (solid lines); phosphate buffer was used above *pH* 5.5 (dashed lines). The hydrogels were prepared with different volume fraction total monomer in the reaction mixture (plotting parameter). Data points are connected by lines to guide the eye.

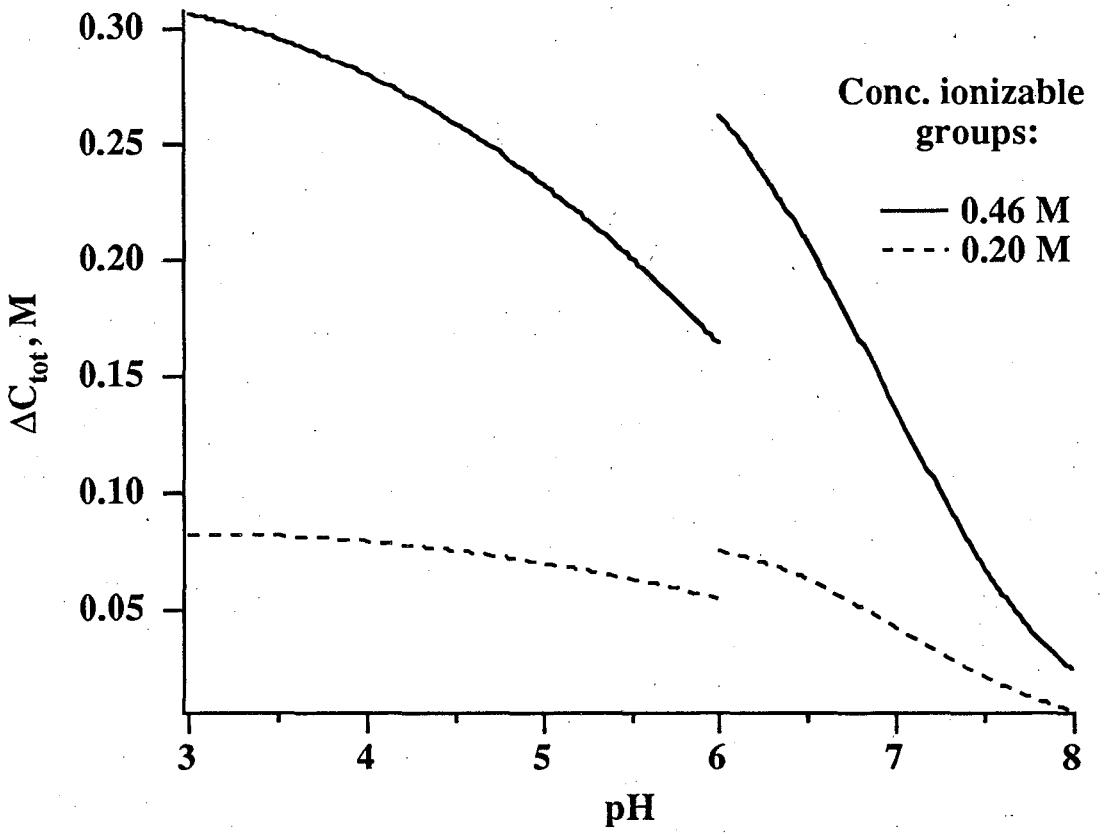

Figure 2. Predictions based on the ideal Donnan equilibria for the difference in total free ion concentration inside and outside the hydrogel, ΔC_{tot}. $pH \leq 6$: 0.01 M citrate buffer with NaCl added to achieve an ionic strength of 0.1 M. $pH \geq 6$: 0.01 M phosphate buffer with NaCl added to achieve an ionic strength of 0.1 M. The predictions were made for two concentrations of ionizable amine groups in the hydrogels, 0.20 (broken lines) and 0.46 M (solid lines).

Tables

Table 1. Percent DMA units in poly(HEMA *co*-DMA) hydrogels estimated from nitrogen elemental microanalysis. The hydrogels were synthesized in varying amounts of solvent (butanol); the volume fraction total monomer present during synthesis is listed here. The hydrogels were, nominally, 30 *%DMA* and 0.5 *%C*.

Monomer vol. frac.	%DMA units
0.29	26.9
0.38	26.3
0.44	25.5
0.77	29.2
1.0	26.3

Table 2. Swelling ratios in 0.01 M citrate or phosphate buffer for poly(HEMA *co*-DMA) hydrogels prepared with varying amounts of diluent. NaCl was added to each buffer solution to achieve a total ionic strength of 0.1 M. Citrate buffer was used below *pH* 5.5; phosphate buffer was used above *pH* 5.5. The hydrogels were, nominally, 30 *%DMA* and 0.5 *%C*.

	Volume fraction total monomer at preparation[a]				
pH	0.29	0.38	0.44	0.77	1.0
3.0	12.6 (0.2)	8.6 (0.4)	6.8 (0.2)	3.7 (0.1)	3.1 (0.1)
3.8	12.1 (0.3)	8.1 (0.1)	6.5 (0.1)	3.6 (0.1)	3.0 (0.1)
4.6	10.8 (0.2)	7.4 (0.1)	5.7 (0.1)	3.3 (0.1)	2.8 (0.1)
5.1	9.1 (0.2)	6.4 (0.2)	5.2 (0.1)	3.1 (0.1)	2.7 (0.1)
5.6	12.2 (0.1)	8.4 (0.2)	6.7 (0.1)	3.5 (0.1)	3.1 (0.1)
6.6	10.6 (0.1)	7.2 (0.2)	5.8 (0.1)	3.3 (0.1)	2.8 (0.1)
7.6	6.4 (0.1)	4.6 (0.1)	3.8 (0.1)	2.4 (0.1)	2.1 (0.1)

[a]Swelling ratios (g swollen gel/g dry gel) are reported with corresponding standard deviations

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