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Abstract

Hydrogels were synthesized by copolymerizing acrylamide with the cationic monomer [(methacrylamido)propyl]trimethylammonium chloride (MAPTAC) and the bifunctional crosslinking monomer *N,N'*-methylenebisacrylamide (BIS). A series of seven hydrogels was prepared in which the initial total monomer concentration *%T* (w/v) was varied from 10 to 40%, while the mole percents (solvent-free basis) of MAPTAC and BIS were held constant at 3.0 and 0.2, respectively. Compressive stress-strain measurements were performed on water-equilibrated hydrogel samples; the measurements are well described by the phantom theory of network elasticity. Donnan exclusion of sodium ions from the hydrogels was used to estimate the effective fixed-charge content of the hydrogels. While the nominal fixed-charge content of the hydrogels was 3.0 mole percent, the results of the sodium-exclusion experiments showed on average an effective fixed-charge content of 1.9 mole percent. The hydrolysis of pendant amide groups to anionic carboxylate functionalities may mask some of the fixed-cationic charge in the hydrogels. Swelling equilibria were measured for the *%T*-varying hydrogels in pure water and in aqueous NaCl solutions. Swelling was observed to be a strong decreasing function of *%T*. Good agreement is obtained between measured swelling equilibria in aqueous NaCl and that calculated from a Flory-type swelling model. The good agreement is facilitated by fitting an adjustable parameter in the model to swelling equilibria for the hydrogels in pure water. The experimental results presented here are all consistent with the concept of increasing chain interpenetration with rising *%T*.

Introduction

Acrylamide-based hydrogels are synthesized on a regular basis in myriad biochemistry and molecular biology laboratories for the performance of polyacrylamide gel electrophoresis (PAGE) (Allen and Maurer, 1974; Bio-Rad Laboratories, 1987). In PAGE, biomacromolecules are fractionated based on their molecular weight and net charge.

The desired effective median pore size of the polyacrylamide network is obtained by adjusting the weight ratio of total monomer to solvent and the mole fraction crosslinking monomer in the pre-gel reaction mixture. The pore sizes can be selected for optimal resolution between two macromolecular species. The wide range of applicability of PAGE is illustrated by the fractionation of oligonucleotides (MW < 1000) and high-molecular-weight RNA (MW > 10^6) (Chrambach and Rodbard, 1971).

A network prepared in a solvent may have properties very different from those of a network prepared in bulk. A network prepared in solvent has a loose network structure, whereas a network prepared in bulk has a tight network structure resulting from interpenetration of polymer chains during network formation.

Acrylamide monomer is a solid at standard temperature and pressure (as is the homopolymer); the monomer must be dissolved in solvent for polymerization at these conditions The amount of solvent (usually water) present at polymerization, or conversely the *initial total monomer concentration*, must be specified prior to the preparation of an acrylamide-based hydrogel because an acrylamide-based hydrogel may not be made in bulk. The initial total monomer concentration may be varied to alter the hydrogel structure and, in turn, alter the hydrogel properties. For this study, we define the initial total monomer concentration as the grams of monomer used for every 100 milliliters of solvent in the hydrogel feed solution; for brevity, we denote this parameter as "*%T*".

Several studies have been reported on the properties of hydrogels as a function of *%T*. These studies include swelling investigations (Geissler et al., 1988; Hasa and Janacek, 1967; Janacek and Hasa, 1966; Oppermann et al., 1985; Katayama et al., 1993; Ilavsky and Hrouz, 1983; Hooper et al., 1990), analyses of microstructure via electron microscopy (Rüchel et al., 1978) and light scattering (Geissler et al., 1988), and investigations of mechanical properties (Geissler et al., 1988; Hasa and Janacek, 1967; Janacek and Hasa, 1966; Oppermann et al., 1985; Ilavsky and Hrouz, 1983). In general, experimental observations are consistent with the concept of increasing chain interpenetration with rising %*T*.

Hooper et al. (1990) investigated the swelling properties of hydrogels prepared by copolymerizing acrylamide with the strong electrolyte [(methacrylamido)propyl]trimethylammonium chloride (MAPTAC). The authors systematically varied the hydrogel-composition parameters of mole percent charged comonomer, mole percent crosslinking monomer and initial total monomer concentration (%*T*), and studied the effects of these parameters on swelling equilibria. The Flory-Rehner framework for network swelling (Flory and Rehner, 1943; Flory, 1953) was used by Hooper et al. (1990) to describe their experimental results. The effects of crosslink density and charge density on swelling equilibria were described reasonably well by theory presented by Hooper et al., while the effect of %*T* on swelling was not reproduced correctly. Hooper et al. hypothesized that the inability of their swelling theory to describe the observed %*T* influence on swelling was related to the rise of (interchain) entanglements with increasing %*T*, and to the absence in the theory of a strong contribution to network elasticity resulting from entanglements.

One purpose of the present study is to measure swelling equilibria for a series of cationic poly(acrylamide *co*-MAPTAC) hydrogels that are identical except for the%*T* of their pre-gel reaction mixtures. A second purpose is to improve Hooper et al.'s (1990) poor description of acrylamide-based hydrogel swelling equilibria as a function of %*T*. As for Hooper et al., the Flory-Rehner theory provides the framework for our swelling description.

Experimental Section

Materials. Acrylamide and N,N'-methylenebisacrylamide (BIS) (both "electrophoresis grade") were purchased from Kodak. Ammonium persulfate (APS) and sodium chloride (NaCl) were purchased from Fisher. [(Methacrylamido)propyl]trimethylammonium chloride (MAPTAC) (50% solution in water) was purchased from Aldrich. All reagents were used as received. Water was distilled, then filtered and deionized with a Barnstead Nanopure II unit.

Synthesis. Acrylamide-based hydrogels with cationic character were prepared by the aqueous free-radical copolymerization of acrylamide, MAPTAC and BIS, the crosslinking agent. APS was used to initiate the polymerization; the initiator concentration was held at a constant value of 0.5 mg/ml for all syntheses.

The nominal hydrogel composition is determined by the relative amounts of monomers and diluent (water) present in the pre-gel reaction solution. The following variables are convenient for defining this composition:

$$\%T = \frac{\textit{mass of all monomers (g)}}{\textit{volume of water (ml)}}\,100 \tag{1}$$

$$\%C = \frac{\textit{moles of BIS in feed solution}}{\textit{total moles of monomer in feed solution}}\,100 \tag{2}$$

$$\%MAPTAC = \frac{\textit{moles of MAPTAC in feed solution}}{\textit{total moles of monomer in feed solution}}\,100 \tag{3}$$

We use *%T* interchangeably with the phrase "initial total monomer concentration."

A series of hydrogels was prepared such that *%C* and *%MAPTAC* were fixed at 0.2% and 3%, respectively, while *%T* was varied; the *%T* values used were 10, 15, 20, 25, 30, 35 and 40. Continuous networks were not formed when *%T* was below 10. *%T* values greater than 40 were not considered for this study for two reasons: (1) At 25°C, solutions with *%T* greater than 25 reach their gel points so quickly as to preclude injecting the hydrogel-feed solution into molds; the higher the *%T*, the quicker the gel point is reached. To delay the gel point, all of the hydrogel-feed solutions were cooled in an ice bath for this work. (2) The influence of rising *%T* on the swelling properties of the resulting hydrogels diminishes as *%T* approaches 40.

To illustrate the synthetic procedure, we give details for the preparation of one hydrogel (30 *%T*, 0.2 *%C*, 3 *%MAPTAC*). Added to 54.4 ml gas-free water were 16.35 g acrylamide, 0.073 g BIS and 3.15 ml MAPTAC solution. An initiator solution was also prepared: 0.150 g of APS was dissolved in 20.0 ml gas-free water. Both aqueous solutions were placed in an ice bath and stirred with magnetic spin bars until the monomers were completely dissolved (about 10 min). 4.0 ml of the APS solution was added to the monomer solution; immediately after complete mixing, the monomer solution was injected (with a syringe fitted with a large-bore needle) between silanized glass plates separated by a 1/16-inch-thick Teflon spacer. The plates were immersed in a thermostated water bath at 50°C. After 24 hr, the hydrogel sheets were freed from the plates; disks were punched from the plates using a cork borer. The hydrogel disks were soaked in water which was refreshed periodically to extract the soluble fraction and initiator residues. The soluble fraction for very similar poly(acrylamide *co*-MAPTAC) hydrogels was measured by Baker et al. (1993); it is on the order of 0.1% of the dry mass.

Swelling studies. After synthesis, the hydrogel disks were placed in pure water where they were allowed to swell to equilibrium. To monitor the swelling of the hydrogels, the masses of the hydrogels were measured periodically. Approximately one week was required to reach equilibrium swelling in water. Once equilibrium was attained, hydrogels were weighed, dried at room temperature and atmospheric pressure, and re-weighed. The swelling ratio in water is defined as the mass ratio of swollen hydrogel to dry hydrogel.

Similar procedures were performed for swelling studies in aqueous NaCl. The ionic strength of the salt solutions ranged from 10^{-5} to 1.0 M. Water-equilibrated hydrogel disks were placed in aqueous NaCl solutions and allowed to swell to equilibrium; approximately 10 days were needed to reach equilibrium. The approach to equilibrium of the hydrogels was monitored gravimetrically. The swelling ratio of the hydrogels in the salt solutions is normalized by the swelling ratio in water:

$$\textit{Swelling ratio in NaCl}_{(aq.)} = \left(\frac{\textit{mass gel in salt solution}}{\textit{mass gel in water}}\right)\left(\frac{\textit{mass gel in water}}{\textit{mass dry gel}}\right) \quad (4)$$

Each swelling ratio reported in this paper is an average of two separate swelling measurements performed in parallel.

Elemental Microanalysis. Elemental microanalyses (U. C. Berkeley College of Chemistry Microanalytical Laboratory) were performed on dried, pulverized hydrogel samples that had been extracted in water.

Compressive Stress-Strain Measurements. Compressive stress-strain experiments were performed on all hydrogels prepared except the one prepared with 10%*T*; this hydrogel was excessively compliant for the experimental treatment. Hydrogel disks, equilibrium-swollen in water, were compressed to 5% strain in steps of 0.25% strain by a Rheometrics Solids Analyzer II apparatus. Measurements were made for two samples from each hydrogel lot. The results were averaged.

Measurement of Sodium Partition Coefficients. Sodium partition coefficients were measured for all hydrogels prepared for this study for the purpose of estimating their fixed-charge densities. For these measurements, 100 ml beakers were charged with 25 ml of 10^{-3} M NaCl solution and 25 ml of water-equilibrated hydrogel. The beakers were sealed for 10 days to allow for equilibration. The masses of the hydrogels and external solutions were measured. The sodium concentrations of the external solutions were measured using a Perkin-Elmer Model 2280 atomic absorption spectrophotometer. Sodium concentrations inside the hydrogels were determined from mass balances. The sodium partition coefficient is defined as the concentration of sodium in the external solution divided by that in the hydrogel. Duplicate partition experiments were performed for each %*T*. The results were averaged.

Swelling Theory for Hydrogels

The framework which defines swelling equilibria in gel/solvent systems has existed for many years (Frenkel, 1940; Flory and Rehner, 1943); it is a direct extension of the basis for defining phase equilibria in linear-chain polymer solutions. For equilibrium between two coexisting phases α and β) the chemical potential μ of every component i is the same in both phases, i.e.,

$$\mu_i^{\alpha} = \mu_i^{\beta} \tag{5}$$

For swelling of a hydrogel in a solvent, α represents the gel phase and β represents the external phase, or bath surrounding the gel. Equation 5 applies for all components which can exist in both phases, i.e., for all diffusible species. When i represents the solvent (component 1), Equation 5 is commonly recast in the form:

$$\Delta\Pi_{swelling} = -\frac{\mu_1^{gel} - \mu_1^{bath}}{V_1} = 0 \tag{6}$$

where $\Delta\Pi_{swelling}$ is the osmotic swelling pressure and V_1 is the solvent molar volume. When non-zero, $\Delta\Pi_{swelling}$ provides a driving force for hydrogel volume change.

$\Delta\Pi_{swelling}$ shows a complex dependence on hydrogel and solution properties. The commonly-used Flory-Rehner theory (Flory, 1953) consists of three contributions:

$$\Delta\Pi_{swelling} = \Delta\Pi_{mixing} + \Delta\Pi_{elastic} + \Delta\Pi_{ion} = 0 \tag{7}$$

where $\Delta\Pi_{mixing}$ is the contribution from polymer/solvent mixing, $\Delta\Pi_{elastic}$ is the elastic contribution from deforming the network chains from their reference state, and $\Delta\Pi_{ion}$ represents the contribution from ion/solvent mixing and electrostatic effects. Equation 7 is analogous to a mechanical equilibrium balance—solvent moves into or out of the hydrogel until $\Delta\Pi_{swelling}$ is zero, i.e., until the three forces working to expand or contract the hydrogel are balanced. Equation 7 coupled with Equation 5 define the degree of swelling (equilibrium gel composition) for specified conditions.

The Flory-Rehner theory contains several assumptions that have been the subject of much discussion. The first assumption is the principle of separability of the elastic and polymer/solvent mixing contributions to the total swelling pressure (Gee et al., 1965; Yen and Eichinger, 1978; Brotzman and Eichinger, 1981; Brotzman and Eichinger, 1982; Brotzman and Eichinger, 1983; Neuburger and Eichinger, 1988; Deloche and Samulski, 1988; Zhao and Eichinger, 1992a,b). The second assumption is that $\Delta\Pi_{mixing}$ is given by the theoretical description of polymer/solvent mixing for the uncrosslinked, infinite-molecular-weight polymer solution at the same concentration and in the same solvent as those of the the network (McKenna et al., 1988; Geissler et al., 1988; Horkay et al., 1989a; Horkay et al., 1989b; Horkay et al., 1993; Geissler et al., 1991).

An examination of the validity of the assumptions inherent in the Flory-Rehner theory is beyond the scope of the present study. We accept the first assumption that the elastic, mixing and ion terms are linearly additive. However, we recognize that assuming that the $\Delta\Pi_{ion}$ term is separable is questionable because placing hydrophilic fixed-charge groups onto a polymer should have an influence on polymer/solvent mixing. For our purposes here, we assume that the fraction of charged structural units in the networks prepared for this study is sufficiently low to have a negligible effect on the $\Delta\Pi_{mixing}$ term. This assumption appears to be valid for highly-swollen, lightly-charged hydrogel networks (Ricka and Tanaka, 1984; Hooper et al., 1990). We are not concerned here with the second assumption, because for $\Delta\Pi_{mixing}$ we use the Flory-Huggins theory with a Flory χ parameter fitted to network swelling data.

To use Equation 7, we must specify the dependence of the three swelling-pressure contributions on hydrogel and solution properties. As stated above, we use Flory-Huggins theory for $\Delta\Pi_{mixing}$:

$$\Delta\Pi_{mixing} = -\frac{R\,T}{V_1}\left(ln\left(1 - \phi_2\right) + \phi_2 + \chi\phi_2^2\right) \tag{8}$$

Here, R is the gas constant, T is temperature, ϕ_2 is the volume fraction of polymer in the hydrogel, V_1 is the molar volume of the solvent and χ is the Flory parameter that characterizes the polymer-solvent interaction energy.

Because of complex polymer/solvent mixing effects, the applicability of Equation 8 to hydrogel systems is questionable. More realistic models for polymer/solvent mixing in aqueous systems have been developed to describe specific interactions (i.e., hydrogen bonding) between solution components (Prange et al., 1989; Marchetti and Cussler, 1990). However, these models are more complex mathematically than the Flory-Huggins theory. For highly-swollen polyelectrolyte hydrogels, it has been noted that $\Delta\Pi_{mixing}$ is usually small compared to $\Delta\Pi_{ion}$ and $\Delta\Pi_{elastic}$ (Oppermann, 1992; Harsh and Gehrke, 1990). An order-of-magnitude analysis of the terms in Equation 7 shows that the influence of χ becomes minor for charged hydrogels at high degrees of swelling. Therefore, we take a simple approach and use the Flory-Huggins equation for $\Delta\Pi_{mixing}$.

To obtain a reasonable value for χ, we regressed the Flory χ parameter from swelling data reported by Hooper et al. (1990) for uncharged acrylamide-based hydrogels equilibrium swollen in pure water. For the regression (within the Flory-Rehner approximation), Equation 8 was used for $\Delta\Pi_{mixing}$ and Equation 9 was used for $\Delta\Pi_{elastic}$ (N set equal to unity); $\Delta\Pi_{ion}$ was set equal to zero. A best-fit value for χ of 0.48 was obtained; χ was held constant at this value in the calculations described here.

The two most common network-elasticity theories consider the idealized cases of the affine network (Flory, 1953) and the phantom network (James and Guth, 1947). These two theories can be considered to be the two limits of a continuum of how neighboring chains (constraints) effect crosslink fluctuations (Brownian motion). In the affine network, crosslink fluctuations are totally suppressed and components of each chain vector transform linearly with deformation. In the phantom network, crosslinks fluctuate freely, unaffected by the presence of neighboring chains or by the state of deformation. The affine network model is frequently used to describe the elastic contribution to gel swelling. However, this model gives a poor description of elastic properties when applied over a large range of strain, and is particularly unsuitable for swollen networks whose properties are presumably closer to those of a phantom network (Mark and Erman, 1988). For isotropic swelling of a perfect tetrafunctional network, elasticity theory gives:

$$\Delta\Pi_{elastic} = - C_c R T N \left(\frac{\phi_2}{\phi_{2c}}\right)^{1/3} \tag{9}$$

where C_c is the concentration of crosslinks in the reference state, i.e. at hydrogel preparation, ϕ_{2c} is the volume fraction of hydrogel in the reference state and N is a semi-empirical parameter. $N = 1$ for the phantom model and $N = 2$ for affine model, i.e. the limiting theories differ by a factor of two. N can be regressed from swelling data to give an estimate of the effective crosslink density for a hydrogel. Equation 9 is derived elsewhere (Mark and Erman, 1988; Treloar, 1975).

Fixed charges on the network are confined to the hydrogel phase, along with an equal number of counterions. Because of the fixed charges, there is an unequal distribution of mobile ions between the hydrogel and the external solution, producing an osmotic-pressure difference between the two phases. This osmotic-pressure difference introduces an additional contribution to the swelling pressure. Ideal Donnan equilibria have been successfully used to characterize this contribution to the swelling pressure for acrylamide-based hydrogels (Ricka and Tanaka, 1984; Hooper et al., 1990). A complete description of the effect of fixed and mobile ions on hydrogel swelling would require expressions for ion-ion, ion-solvent and ion-polymer interactions; these interactions are neglected in the ideal Donnan equilibria, giving the expression

$$\Delta\Pi_{ion} = R\,T \sum_{i} \left(C_i^{gel} - C_i^{bath}\right) \tag{10}$$

where C_i^{gel} and C_i^{bath} represent, respectively, mobile ion concentrations within the hydrogel and within the bath surrounding the hydrogel. Equation 10 assumes that the ion concentrations are small and the osmotic coefficient is unity (Katchalsky, 1971).

The concentration of ions in the external solution is fixed by experimental conditions. The concentration of mobile ions within the hydrogel is calculated (for use in Equation 10) according to ideal Donnan equilibria: the chemical potential of an ionic species in the hydrogel phase must be equal to its chemical potential in the external solution, and the constraint of electroneutrality is placed on all charged species, fixed and mobile, in the hydrogel phase. For a hydrogel in solution containing a single 1:1 salt we have

$$\left(C_+^{gel}\right)\left(C_-^{gel}\right) = \left(C_s^{bath}\right)^2 \tag{11}$$

where C_s^{bath} refers to the concentration of 1:1 electrolyte in the external solution. Equation 11 assumes that the mean ionic activity coefficient of the diffusible salt in the hydrogel phase is equal to that in the bath. To maintain electroneutrality, the number of positive ions must equal the number of negative ions in the hydrogel phase. We write for univalent electrolytes:

$$C_+^{gel} + I\,C_{mc}\,\frac{\phi_2}{\phi_{2c}} = C_-^{gel} \tag{12}$$

where I represents the fraction of structural units in the hydrogel that contain bound positive charges and C_{mc} denotes the molar concentration of monomer at network formation. The second term on the left-hand side of Equation 12 gives the concentration of fixed positive charges in the hydrogel phase.

Equilibrium swelling for a given hydrogel and solution conditions is determined by substituting Equations 8, 9 and 10 into Equation 7, and substituting for C_+^{gel} in Equation 11 by using Equation 12. These steps leave two equations with two unknowns, ϕ_2 and C_-^{gel}. An iterative procedure using a generalized Newton-Raphson routine was used to solve the equations.

Theory for Networks in Uniaxial Compression (or Extension)

We assume that the sample volume and composition remain constant with deformation. For both the phantom and affine network theories, the axial force f acting along the x axis for a network in compression is (Mark and Erman, 1988):

$$f = 2\left(\frac{F\,k\,T}{L_{i1}}\right)\left(\frac{V}{V_c}\right)^{2/3}\left(\alpha - \alpha^{-2}\right) \tag{13}$$

where k is the Boltzmann constant, V is the volume of the undistorted, swollen network, V_c is the volume of the network at preparation, L_{i1} is the initial, undistorted, axial length of the network at volume V, α is the deformation ratio relative to the initial sample dimensions and F is the elastic "front factor." For a perfect, tetrafunctional network F equals $\nu/2$ for the affine model and $\nu/4$ for the phantom model where ν is the number of chains in the network. Equation 13 is derived from first principles elsewhere (Treloar, 1975; Flory, 1953; Mark and Erman, 1988)

For comparison with theory, experimental data are generally represented in terms of the reduced stress $[f^*]$:

$$[f^*] = \frac{f\,\phi_2^{1/3}}{A_d\left(\alpha - \alpha^{-2}\right)} \tag{14}$$

where A_d is the cross-sectional area of the undeformed, dry sample (subscript d denotes the dry sample). We note the following relations before proceeding:

$$\phi_2^{1/3} = L_d / L_{i1} \tag{15}$$

$$V_d = A_d L_d \tag{16}$$

$$\phi_{2c} = V_d / V_c \tag{17}$$

Inserting Equation 14 into Equation 13 leads to

$$[f^*] = 2\left(\frac{F\,k\,T}{V_d}\right)\phi_{2c}^{2/3} \tag{18}$$

Noting that, for a perfect tetrafunctional network, the number of crosslinks C equals $v / 2$ and using Equation 17, we obtain

$$[f^*]_{phantom} = C_c R\,T\,\phi_{2c}^{-1/3} \tag{19}$$

$$[f^*]_{affine} = 2\,C_c R\,T\,\phi_{2c}^{-1/3} \tag{20}$$

Equations 19 and 20 show that for a phantom network or an affine network, the reduced stress is predicted to be independent of deformation and swelling. However, ample experimental data show that $[f^*]$ does depend on deformation and swelling (Pak and Flory, 1979; Erman and Flory, 1978; Mark, 1979a,b).

Charge Density Estimation Via Donnan Exclusion.

When a hydrogel with a net positive-charge density is in equilibrium with a 1:1 electrolyte (aqueous) solution, the mobile cations are partially excluded from the hydrogel via Donnan exclusion (Overbeek, 1956; Richards, 1980). Information of ion partitioning between hydrogel and external solution may be used to estimate the charge density of an ionized hydrogel (Harsh and Gehrke, 1990). The equations for Donnan equilibria presented above may be used to estimate hydrogel charge densities. Equation 12 may be substituted into Equation 11 to eliminate C_-^{gel}, resulting in the following equation (for 1:1 electrolytes):

$$\left(C_+^{gel}\right)\left(C_+^{gel} + I\, C_{mc}\, \frac{\phi_2}{\phi_{2c}}\right) = \left(C_+^{bath}\right)^2 \qquad (21)$$

I, the fraction of hydrogel structural units containing fixed-positive charges, may be calculated using Equation 21 provided the following quantities are known: C_{mc}, the molar concentration of monomer at network formation; ϕ_{2c}, the volume fraction of polymer in the hydrogel at preparation; and C_+^{bath} / C_+^{gel}, the partition coefficient of the diffusible cation between the external solution (bath) and hydrogel.

Results and Discussion

Since only the initial total monomer concentration *%T* differed between all hydrogels synthesized, all hydrogels should have the same elemental composition. Table 1 shows the results from elemental microanalysis. Excellent agreement between samples was observed. The favorable microanalysis allows us to use *%T* as a basis for comparing the hydrogels in this study.

Interpretation of the elemental-microanalysis data is complicated by the chemical similarity of the monomers. We could not invert the microanalysis data to give monomer mole fractions. Interpretation of the data is further complicated by the presence of residual solvent (water) in the dried hydrogel samples submitted for analysis. Since hydrogels are composed of hydrophilic polymer, some water is adsorbed to the polymer backbone. Water is inevitably trapped in the interior as a pre-swollen hydrogel particle dries.

The theoretical weight percents of atomic elements for a copolymer hydrogel may be computed from the known composition of the original monomer solution, assuming complete monomer conversion. Also shown in Table 1 are theoretical estimates of the elemental composition based on the reaction stoichiometry. When making the calculations we assumed the samples submitted for analysis contained 5% adsorbed/trapped water. The calculated values agree qualitatively with the observed values.

Figure 1 shows measured swelling equilibria in deionized water for poly(acrylamide *co*-MAPTAC) hydrogels as a function of the initial total monomer concentration *%T*. The crosslink density was fixed at 0.2 *%C* and the charge density was fixed at 3.0 *%MAPTAC* for these hydrogels. As expected, swelling in water declines with rising*%T* because of rising chain interpenetration. Also shown in Figure 1 are predicted swelling curves calculated using the swelling model presented above; the predicted curves for the phantom model and the affine model were generated by setting the parameter N equal to 1.0 and 2.0, respectively. The nominal hydrogel composition parameters (*%T*, *%C* and *%MAPTAC*) were used in the calculations. The observed dependence of swelling on *%T* is stronger than those predicted by the affine and phantom models; this result is similar to that reported by Hooper et al. (1990).

Use of the nominal values of the crosslink density and charge density of the hydrogels in the swelling calculations leads to poor agreement between theory and experiment (see Figure 1). We therefore obtained, from independent experiments, effective values for these parameters. The crosslink densities of the hydrogels were estimated by conducting mechanical stress-strain analyses, while the charge contents of the hydrogels were estimated from the Donnan exclusion of sodium ions.

%T-varying hydrogel disks, equilibrium swollen in pure water, were subjected to compressive stress-strain analysis. Figure 2 shows representative compressive stress-strain data for the two runs performed on the 25*%T* hydrogel samples; as predicted by theory, reasonably straight lines are obtained when the stress (force per unit sample area) is plotted against the quantity ($\alpha - \alpha^{-2}$). For the 15, 20, 30, 35 and 40*%T* hydrogels, stress-strain data were of similar quality.

Compression moduli for the 25*%T* samples were obtained from the slopes of best-fit lines drawn through the data in Figure 2. Table 2 lists and Figure 3 shows compression moduli for all hydrogels analyzed. An interesting aspect of Figure 3 is that a best-fit line through the moduli does not intersect with the origin, but intersects with the positive abscissa at roughly 11 *%T*. This occurs because at high diluent concentrations (low *%T* values), crosslinks tend to be wasted in elastically ineffective loops (Oppermann et al., 1985; Tobita and Hamielec, 1990). The growing chains are so dilute that a significant fraction of crosslinks are wasted as chains crosslink upon themselves, forming loops. Therefore for acrylamide-based systems at low *%T* values, the effective crosslink density is less than the nominal crosslink density. As *%T* rises, it is likely that loop formation declines (Tobita and Hamielec, 1990). At *%T* values below 10 (with a *%C* of 0.2 and a *%MAPTAC* of 3), loop formation is so dominant that no continuous network is formed. We were able to produce a hydrogel using 10 *%T* but, as the intercept of the plot predicts, this hydrogel was too fragile to be subjected to mechanical testing. Results similar to those shown in Figure 3 were obtained by Oppermann et al. (1985) for unionized polyacrylamide hydrogels tested in the unswollen state.

In Figure 4, we compare predictions of the phantom model limit and affine model limit (Equations 19 and 20, respectively) to experimental compressive stress-strain data for poly(acrylamide *co*-MAPTAC) hydrogel networks prepared with different *%T*. The observed [*f**], calculated using Equation 14, are in fair agreement with those predicted by the phantom model. This agreement is reasonable because at high degrees of swelling, the effect of constraints on crosslink fluctuations diminish; the phantom theory assumes that constraints have no effect on network elasticity. Stress-strain behavior coinciding with the phantom limit has been observed in compression and in tension for swollen networks ($\phi_2 \geq 0.2$) (Mark, 1979a). (We are considering *highly* swollen networks in the present work; ϕ_2 was about 0.03 for the 40 *%T* hydrogel equilibrium swollen in water and about 0.005 for the 15 *%T* hydrogel.) A negative deviation from the phantom theory is observed for the 15 *%T* hydrogel, consistent with the idea of a significant fraction of wasted crosslinks for this hydrogel. A positive deviation from phantom theory is seen with the 40 *%T* hydrogel, consistent with the concept of rising entanglement density with increasing *%T* (Janacek and Hasa, 1966; Hasa and Janacek, 1967). Interchain trapped entanglements add to the mechanical strength of a network material by acting as effective crosslinks (Ball et al., 1981; Edwards and Vilgis, 1986).

The results shown in Figure 4 indicate that the phantom theory of elasticity adequately describes the compressive stress-strain behavior in water for highly-swollen poly(acrylamide *co*-MAPTAC) hydrogels. It appears that network defects (loops, entanglements) play a minor role in the stress-strain behavior of the hydrogels studied here.

The theory upon which the phantom model is based assumes that the network chains obey Gaussian statistics (Mark and Erman, 1988; Treloar, 1975). Gaussian statistics allows for network chains to be extended to infinity; however, real chains have finite extendibility (Hill, 1960; Treloar, 1975). Although the results shown in Figure 4 are for highly-swollen hydrogels (consisting of at least 98% water), non-Gaussian corrections to the phantom elasticity theory (to correct for the finite extendibility of the network chains) appear not to be needed.

Donnan-exclusion measurements of sodium ions from the positively-ionized, *%T*-varying hydrogels were conducted for the purpose of estimating hydrogel charge densities. Table 3 lists and Figure 5 shows sodium partition coefficients (external sodium concentration/hydrogel sodium concentration) obtained from the procedure described earlier. As expected, sodium exclusion is an increasing function of *%T*. The concentration of fixed charges in the hydrogels based on polymer (*%MAPTAC*) is nominally constant for the hydrogels in this study; however, the concentration of fixed charges based on *hydrogel volume* rises with increasing *%T*. The higher the fixed-charge concentration based on hydrogel volume, the more efficient is the hydrogel in excluding sodium.

Effective values of *I*, the fraction of cationic structural units in the hydrogels, were calculated from Equation 21 using the results of the partition experiments. Table 3 lists and Figure 6 shows *I* (expressed as a percentage) as a function of *%T*. The nominal value of *I* is 3.0%, while the measured value is 1.9% (averaged across all %*T*). Apparently 37% of the fixed cationic charges are "missing". Two mechanisms, possibly working in concert, may explain the missing charge density. It is possible that a fraction of cationic functionalities are missing from the hydrogel networks: some positively-ionized MAPTAC monomers may not have been incorporated into the network during synthesis; some fixed-cationic functionalities may have been removed after synthesis via amide hydrolysis. More likely, given the majority of acrylamide-derived structural units in the hydrogels, hydrolysis of pendant amide functional groups to anionic carboxylate groups is responsible for masking some of the cationic charges.

The base-catalyzed hydrolysis of polyacrylamide to give carboxylate functionalities in the polymer chain is a well known reaction (Kheradmand et al., 1988; Truong et al., 1986; Higuchi and Senju, 1972; Aksberg and Wagberg, 1989). Conditions favorable for amide hydrolysis existed for the hydrogels in this study during synthesis (Kheradmand et al., 1988). Although slow under mild conditions, rates of polyacrylamide hydrolysis are known to increase with rising temperature: the hydrogels were synthesized at 50°C for 24 hours. Also, the cationic character of the poly(acrylamide *co*-MAPTAC) network chains provide for the local enhancement of the concentration of OH^- ions via electrostatic attraction.

The elemental microanalysis results provide independent evidence for hydrolysis of pendant amide groups to carboxylate functionalities. Ammonia is the product of base-catalyzed amide hydrolysis (Streitwieser and Heathcock, 1981). A comparison of calculated and observed results shows that the hydrogel nitrogen and hydrogen contents are lower than expected from the reaction stoichiometry. From the microanalytical results, we estimate amide hydrolysis to be on the order of a few percent for the hydrogels in this study. Significant loss of elemental nitrogen from the hydrogels via hydrolysis of cationic MAPTAC structural units to anionic methacrylate structural units would involve a concomitant loss of elemental carbon from the hydrogels. Loss of elemental carbon via hydrolysis of MAPTAC units is not supported by the microanalytical results. Put another way, the elemental carbon to nitrogen ratio increases upon acrylamide-unit hydrolysis and decreases upon MAPTAC-unit hydrolysis; the observed carbon to nitrogen ratio supports acrylamide-unit hydrolysis.

For positively ionized hydrogels equilibrium swollen in low-ionic-strength media, the *pH* in the hydrogel interior is likely much higher than neutral because of Donnan exclusion of protons. Therefore, since the nominal *pKa* of acrylic acid is 4.3, any hydrolysis products on the network chains will be fully ionized to the carboxylate form.

The fixed-charge density of a hydrogel is measured indirectly from a Donnan-exclusion experiment. The actual number of fixed charges is not determined—only the net charge is determined. For example, a exclusion experiment based on ideal Donnan equilibria will necessarily give the same answer if the hydrogel contains a cationic fixed-charge density of 2 mole percent and an anionic fixed-charge density of zero or a cationic fixed-charge density of 3 mole percent and an anionic fixed charge density of 1 mole percent. For highly-swollen lightly-charged hydrogels, it is known that swelling is governed by the net charge of the hydrogel (Katayama et al.; Baker et al., 1992). The net charge is important because it is the osmotically-active counterions that principally drive the swelling of highly-swollen lightly-charged hydrogels. In pure water, hydrogels containing both cationic fixed charges and anionic fixed charges (ampholytic hydrogels) may become self-neutralized to a degree; excess free ions not needed to satisfy electroneutrality are dialyzed from the hydrogel interior. If some hydrolysis has occurred, then the hydrogels in this study are partially self-neutralized and the concentration of osmotically-active counterions inside the hydrogels less than it would be with no hydrolysis.

Unfortunately, the lowered values of *I* for the hydrogels determined by the Donnan-exclusion experiments (Figure 6) only partially accounts for why the measured swelling equilibria in water shown in Figure 1 is over predicted by the swelling theory. When the independently-obtained values for the charge density *I* (calculated from the Donnan exclusion experiments using Equation 21) and crosslink concentration C_c (calculated from the compressive stress-strain data using Equation 19) are inserted into the swelling theory (Equation 7), quantitative agreement is not obtained between the observed swelling ratios and those predicted by theory. Other authors have reported similar results for hydrophilic networks (Peppas and Merrill, 1977; Harsh and Gehrke, 1990; Vasheghani-Farahani et al., 1990).

To correct for deficiencies in our swelling description, we add the parameter N to the elastic term $\Delta\Pi_{elastic}$ (Equation 9). We have used the swelling data shown in Figure 1 to fit values for N from Equation 7; as expected, N is of order unity. Table 2 shows the fitted values of N for each corresponding $\%T$ value. N values range from 1.02 at 10 $\%T$ to 3.30 at 40 $\%T$. We used the nominal hydrogel composition parameters ($\%T$, 0.2 $\%C$, 3.0 $\%MAPTAC$) in the fits.

The fitted values of N, determined from swelling equilibria for the $\%T$-varying hydrogels in water, are used to predict hydrogel-swelling equilibria in aqueous NaCl. Figure 7 shows measured and calculated swelling equilibria in aqueous NaCl solutions for hydrogels prepared with 10 or 15 $\%T$; Figure 8 shows measured and calculated results for hydrogels with 20 - 40 $\%T$. Calculated curves were generated by using Equation 7 with fitted values for N. Agreement is good between measured and calculated results probably because the deficiencies of the theory are compensated by the parameter N, which is a function of $\%T$.

Fitting the parameter N in the swelling model to swelling data in pure water as a function $\%T$ is equivalent to fitting the Y-intercepts in Figures 7 and 8. We have fit the Y-intercepts in Figures 7 and 8 and then allowed the volume (ϕ_2) dependence of the swelling model to predict the shape of the swelling curve as a function of NaCl concentration. It appears that the volume dependence of the swelling model is correct; however, to obtain quantitative performance, the model must be scaled to experimental data. The parameter N provides such scaling.

Kinetic models of network formation have been developed by Miller and Macosko (Miller and Macosko, 1976; Macosko and Miller, 1976; Miller and Macosko, 1987) and by Tobita and Hamielec (1989, 1990). These models may be used to calculate average network properties such as the crosslink density and molecular weight between crosslinks, provided that the reactivity ratios for the monomers are known. Tobita and Hamielec (1990) have developed a kinetic model for the free-radical copolymerization of acrylamide and N,N'-methylenebisacrylamide (BIS). Confirming the results of various studies (Weiss et al., 1979; Hecht et al., 1985; Rüchel et al., 1978; Cohen et al., 1992), the model of Tobita and Hamielec predicts that inhomogeneous, imperfect networks are formed by copolymerizing acrylamide with BIS. We did not attempt to use the kinetic models mentioned above to predict network properties because reactivity ratios for the acrylamide-BIS-MAPTAC terpolymerization are not currently available.

Conclusions

Cationic acrylamide-based hydrogels were prepared with the same overall composition and with different initial total monomer concentrations *%T*. Hydrogel swelling equilibria in pure water were observed to decline dramatically with rising *%T*. Raising the *%T* in the pre-gel reaction mixture allows for increased chain interpenetration and improved efficiency of the crosslinking reaction in the resulting hydrogel.

Mechanical compressive stress-strain measurements were performed on *%T*-varying hydrogels equilibrated in pure water. The results are consistent with those expected for highly swollen networks; fair agreement is obtained with the phantom theory of elasticity.

The Donnan exclusion of sodium ions from the cationic hydrogels were measured in order to estimate the fixed-charge densities of the hydrogels. The results show one-third of the cationic charges apparently missing. It is postulated that some of the cationic charges were masked in the Donnan-exclusion experiments by anionic carboxylate functionalities placed on the network chains by the hydrolysis of pendant amide groups.

Good agreement between theory and experiment is obtained for %T-varying hydrogels equilibrated in aqueous NaCl. The good agreement is facilitated by fitting a parameter N in the swelling model to swelling equilibria for the hydrogels in deionized water. N is a weak function of %T, is of order unity, and serves to correct for deficiencies in the theoretical description of hydrogel swelling.

Appendix

The Elasticity Expression for Networks in Compression (or Tension)

Assuming Gaussian chain statistics, the following elastic free energy expression has been derived (Treloar, 1975; Flory, 1953; Mark and Erman, 1988)

$$\Delta A_{el} = F\,k\,T\left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right) \tag{A1}$$

where the front factor F equates to $\nu/2$ for the affine network model and to $\xi/2$ for the phantom network model, k is the Boltzmann constant, T is temperature and λ_t is the ratio of the final length to the reference length along the t th direction. The quantity ν is the number of network chains and ξ is the cycle rank; for a perfect tetrafunctional network, $\xi = \nu/2$.

The elastic equation of state specifies the relationship between the applied forces, the resulting deformations, and the molecular structure of the network. Thermodynamics gives the following expression

$$\tau_t = V^{-1}\,\lambda_t\left(\frac{\partial \Delta A_{el}}{\partial \lambda_t}\right)_{T,V}, \quad t = 1, 2, 3 \tag{A2}$$

where τ_t is the stress along the t th coordinate direction, and is defined as the force per unit deformed area. V is the volume of the network just prior to application of deformation.

To interpret Equation A2, consider a rectangular block of network with sides L_{o1}, L_{o2} and L_{o3} and volume V_o in the reference state [Figure A1(b)]. Our networks are formed in solution; therefore V_o represents the total volume of polymer and solvent. Figure A1(c) shows the dimensions L_{i1}, L_{i2} and L_{i3} at the start of the experiment; volume V is larger than V_o because the hydrogels were equilibrium-swollen in water after synthesis. Incompressibility is assumed in that the sample volume does not change upon application of the stress.

The deformation ratio λ_t along the t th direction is defined as

$$\lambda_t = L_t/L_{ot} \ , \quad t = 1, 2, 3 \tag{A3}$$

Thus the three deformation ratios are related to the final volume and the reference volume by

$$\lambda_1\lambda_2\lambda_3 = V/V_o \tag{A4}$$

The deformation ratio α_t relative to the initial dimensions is defined by

$$\alpha_t = L_t/L_{it} = (V/V_o)^{-1/3}\lambda_t \ , \quad t = 1, 2, 3 \tag{A5}$$

The volume fractions of polymer present during network formation, ϕ_{2c}, and during the stress-strain experiment, ϕ_2, are needed to proceed. These are

$$\phi_{2c} = V_d/V_o \tag{A6}$$

$$\phi_2 = V_d/V \tag{A7}$$

where V_d is the volume of the dry network. Notice that V/V_o equals ϕ_{2c}/ϕ_2.

The deformation ratios λ_1, λ_2 and λ_3 are not independent of each other because of the requirement indicated by Equation A4. It is therefore necessary to re-write Equation A2 in the form

$$\tau_t = V^{-1}\,\lambda_t \sum_{i=1}^{3} \left(\frac{\partial \Delta A_{el}}{\partial \lambda_i^2}\right) \frac{\partial \lambda_i^2}{\partial \lambda_t} \tag{A8}$$

Using Equation A1, Equation A8 becomes

$$\tau_t = \left(\frac{F\,k\,T}{V}\right) \lambda_t \sum_{i=1}^{3} \frac{\partial \lambda_i^2}{\partial \lambda_t} \tag{A9}$$

The state of deformation for extension or compression along the axial dimension is

$$\lambda_1 = \alpha\,(V/V_o)^{1/3} \tag{A10}$$

while along the normal dimension it is

$$\lambda_2 = \lambda_3 = \alpha^{-1/2}\,(V/V_o)^{1/3} \tag{A11}$$

where α is the ratio of the final length along the direction of deformation to the initial undistorted length at volume V. For compression, $\alpha < 1$.

Writing Equation A9 as

$$\tau_1 = \left(\frac{F\,k\,T}{V}\right) \lambda_1 \sum_{i=1}^{3} \frac{\partial \lambda_i^2}{\partial \alpha} \frac{\partial \alpha}{\partial \lambda_1} \tag{A12}$$

and using Equations A10 and A11 leads to

$$\tau_1 = 2\left(\frac{F\,k\,T}{V}\right)\left(\frac{V}{V_o}\right)^{2/3}\left(\alpha^2 - \alpha^{-1}\right) \tag{A13}$$

The deformed area may be represented as

$$A_{def} = V/L_1 = V/\!\left(L_{i1}\alpha\right) = L_2 L_3 \tag{A14}$$

The axial force f is obtained by multiplying both sides of Equation A13 by the deformed area:

$$f = 2\left(\frac{F\,k\,T}{L_{i1}}\right)\left(\frac{V}{V_o}\right)^{2/3}\left(\alpha - \alpha^{-2}\right) \tag{A15}$$

which gives Equation 13.

Derivation of the Elastic Contribution to the Swelling Pressure $\Delta\Pi_{swelling}$

(Following Queslel and Mark (1985) and Flory (1953).)

In an isotropic dilation of a hydrogel, the three extension ratios are equal:

$$\lambda_1 = \lambda_2 = \lambda_3 = \left(\frac{\phi_{2c}}{\phi_2}\right)^{1/3} \tag{A16}$$

An expression for the network-elastic contribution to the swelling pressure is obtained by differentiating $\Delta A_{elastic}$ (Equation A1) with respect to n_1, the number of water molecules in the hydrogel:

$$\Delta\Pi_{elastic} = -\frac{1}{V_1}\left(\frac{\partial \Delta A_{elastic}}{\partial n_1}\right)_{T,\,P} \tag{A17}$$

The square of the extension ratio is related to n_1 in the following manner:

$$\lambda^2 = \left(\frac{n_1\,V_1 + V_o}{V_o}\right)^{2/3} \tag{A18}$$

The differentiation is thus:

$$\left(\frac{\partial \Delta A_{elastic}}{\partial n_1}\right)_{T,\,P} = \left(\frac{\partial \Delta A_{elastic}}{\partial \lambda^2}\right)_{T,\,P}\left(\frac{\partial \lambda^2}{\partial n_1}\right)_{T,\,P} \tag{A19}$$

with

$$\left(\frac{\partial \lambda^2}{\partial n_1}\right)_{T,P} = \frac{2}{3}\left(\frac{\phi_{2c}}{\phi_2}\right)^{-1/3} \frac{V_1}{V_o} \tag{A20}$$

and, for the phantom network case:

$$\left(\frac{\partial \Delta A_{elastic}}{\partial \lambda^2}\right)_{T,P} = \frac{3}{2}\,\xi\, k\, T \tag{A21}$$

The final result of the differentiation is

$$\left(\frac{\partial \Delta A_{elastic}}{\partial n_1}\right)_{T,P} = \xi\, k\, T\left(\frac{\phi_{2c}}{\phi_2}\right)^{1/3} \frac{V_1}{V_o} \tag{A22}$$

Substituting Equation A22 in Equation A17 and noting that ξ equals the number of crosslinks for a perfect, tetrafunctional phantom network, we arrive at the result:

$$\Delta\Pi_{elastic} = -\, C_c\, R\, T \left(\frac{\phi_2}{\phi_{2c}}\right)^{1/3} \tag{A23}$$

which is Equation 9 above (excluding the parameter *N* that we have added). Note that we have employed molar quantities in Equation A23.

The Relationship Between Polymer Volume Fractions and Measurable Quantities

The polymer volume fraction ϕ_2 is related to the swelling ratio *SR* by the following equation:

$$\phi_2 = \frac{1/\rho_p}{1/\rho_p + (SR - 1)/\rho_w} \tag{A24}$$

where ρ_p is the density of the dry polymer (taken to be 1.12 g/cm^3) and ρ_w is the density of water (1.0 g/cm^3).

The volume fraction of polymer at network preparation ϕ_{2c} is related to the total monomer concentration $\%T$ through the following equation:

$$\phi_{2c} = \frac{(\%T)/100/\rho_p}{1/\rho_w + (\%T)/100/\rho_p} \tag{A25}$$

The Assumptions Inherent in the Flory-Rehner Theory of Network Swelling

The Flory-Rehner theory of network swelling assumes that there are three separable contributions to network swelling: the contribution from polymer/solvent mixing; the contribution from deforming the network chains from their reference state; and the contribution for ion/solvent mixing and electrostatic effects.

Differences in solvent activity have been observed between solutions of crosslinked and uncrosslinked polymers. These differences have called into question the validity of the principle of separability (Gee et al., 1965; Yen and Eichinger, 1978; Brotzman and Eichinger, 1981; Brotzman and Eichinger, 1982; Brotzman and Eichinger, 1983; Neuburger and Eichinger, 1988; Zhao and Eichinger, 1992a,b). Eichinger and coworkers have attributed the differences to a solvent-dependent network elastic free energy of swelling. Toward this end, elasticity models that depend on solvent thermodynamic parameters have been proposed (Deloche and Samulski, 1988; Zhao and Eichinger, 1992b).

In addition, the Flory-Rehner theory assumes that the theoretical description for polymer/solvent mixing in the network is given by the theoretical description of polymer/solvent mixing for the uncrosslinked, infinite-molecular-weight polymer solution at the same concentration and in the same solvent as those of the network. However, McKenna et al. (1988) have found a crosslink dependence for the effective Flory interaction parameter χ for swollen networks. Freed and Pesci (1989) have computed a crosslink dependence for the effective χ parameter for polymer networks.

Examining the assumption concerning polymer/solvent mixing, Geissler and colleagues (Geissler et al., 1988; Horkay et al., 1989a; Horkay et al., 1989b; Horkay et al., 1993; Geissler et al., 1991) found that the mixing term for the network polymer is generally smaller than that of the equivalent uncrosslinked polymer solution of infinite molecular weight. The decrease in the mixing contribution due to the crosslinks was attributed to structural differences between polymers in a network and polymers in solution. In networks, the mobility of the polymer segments is hindered by crosslinks, and consequently the degree of freedom of the network chains is lower. Geissler and colleagues concluded that the thermodynamic behavior of swollen networks is described satisfactorily by a swelling theory containing separable elastic and mixing contributions, provided that the mixing contribution is for a polymer network, not for a polymer solution.

Hydrophobic and Model Networks Prepared in Solvent

Experimental and theoretical studies have been reported concerning the elastic properties of hydrophobic networks prepared in solvent; materials studied include natural rubber (Price et al., 1970), *cis*-polybutadiene (de Candia et al., 1972) and silicone networks (Johnson and Mark, 1972). In general, improved agreement between experimental stress-strain data and theoretical predictions of simple elasticity theories were obtained for networks prepared in solvent, compared to results obtained for networks prepared in the dry state. The improved agreement between theory and experiment was attributed to the relative absence of permanent physical entanglements in networks prepared in solvent (Price et al., 1970; de Candia et al., 1972).

Model networks may be prepared by end-linking bifunctional silicone chains of known lengths; in this way, networks are obtained with a negligible number of defects such as loops and pendant chains (dangling ends). Studies of the elastic (Patel et al., 1992) and swelling behavior (Brotzman and Eichinger, 1983; Patel et al., 1992; Besbes et al., 1993) in organic solvents have been reported for model networks prepared from well-characterized silicone polymers. Patel et al. (1992) found that the Flory-Rehner approximation, coupled with the phantom network model, gave good agreement with swelling results for model silicone networks when the experimentally-measured elastic modulus was used in the swelling calculations.

Hydrophilic Networks Prepared in Solvent

Ilavsky and Hrouz (1983) studied the effect of *%T* on the discontinuous volume collapse of ionized acrylamide-based hydrogels in acetone/water solutions; a similar study was conducted by Katayama et al. (1993). Both Ilavsky and Hrouz and Katayama et al. showed that the extent of discontinuous collapse decreased with rising *%T*. This result is consistent with the concept of increasing chain interpenetration with rising *%T*. These authors also observed that the acetone concentration at which the discontinuous collapse occurred did not change with the *%T* of the networks. This result was attributed to the fact that the monomer mole fractions were fixed as changes were made in *%T*. Katayama et al. (1993) concluded that the point at which the discontinuous volume collapse occurs should be determined primarily by specific interactions between the network polymer and the acetone/water mixture, and that the specific chemical properties of the network chains remain similar (at constant composition) as the *%T* changes.

Rüchel et al. (1978) examined structures of acrylamide-based hydrogels by transmission-electron microscopy of freeze-etched specimens. Influences were investigated of *%T*, mole fraction crosslinking monomer, use of different crosslinkers and the catalyst concentration. The hydrogels were examined immediately after synthesis and were not equilibrium-swollen in the solvent. All acrylamide-based hydrogels visualized by electron microscopy revealed a cellular structure in the submicron range. This structure is in contrast to the generally held assumption of a random meshwork of crosslinked individual polyacrylamide strands. A series of hydrogels produced with varying *%T* indicated that cell size decreases with rising %T; this observation is consistent with the known sieving properties of acrylamide-based hydrogels (Chrambach and Rodbard, 1971).

Geissler et al. (1988) prepared a series of acrylamide-based hydrogels varying in %T. An experimental comparison was made between the values of M_{os}, the longitudinal osmotic modulus observed by quasi-elastic light scattering, the osmotic modulus K_{os}, observed by swelling-pressure measurements, and the shear modulus G, measured by mechanical deformation. The osmotic and shear modulus measurements showed good-solvent scaling behavior (de Gennes, 1979). Geissler et al. showed that significant differences may exist between values of M_{os} measured by dynamic light scattering and the nominally equivalent parameter obtained by macroscopic measurements of the swelling pressure and the shear modulus, $M_{os} = K_{os} + 4G/3$. These differences were attributed to the different ways in which averages over the polymer concentration in the network contribute to the results of the various experiments. According to Geissler et al. (1988), discrepancies between such averages arise in samples that display concentration heterogeneities.

Oppermann et al. (1985) investigated the mechanical properties and swelling behavior of unionized and ionized acrylamide-based hydrogels prepared with varying %T. The ionized networks were prepared by hydrolysis of the unionized networks, thus preserving the network topology. The mechanical measurements showed that the networks prepared in a solvent contain a large portion of crosslinks that are wasted in elastically ineffective loops.

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Figures

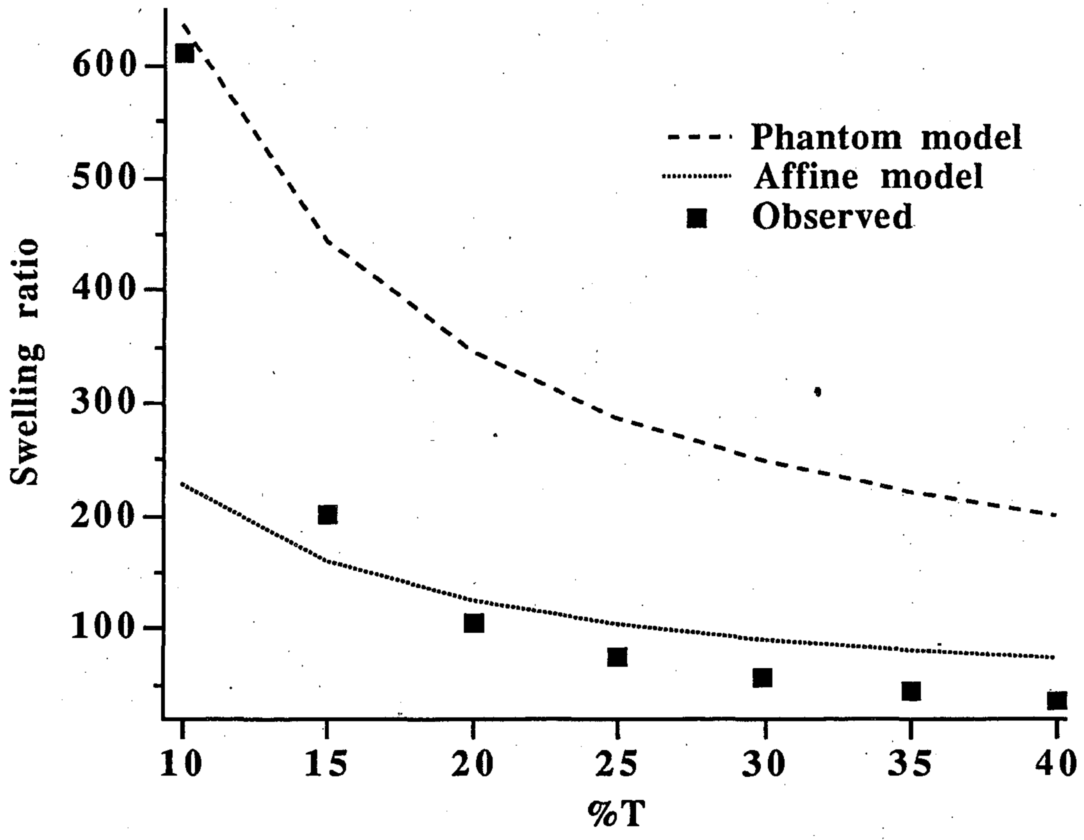

Figure 1. Swelling ratios (g swollen gel/g dry gel) in water for poly(acrylamide *co*-MAPTAC) hydrogels prepared with varying initial total monomer concentrations *%T*. The observed swelling ratios are compared with model predictions. Predicted swelling curves were generated using the nominal values of the hydrogel structural parameters (*%T*, 0.2 *%C*, 3.0 *%MAPTAC*).

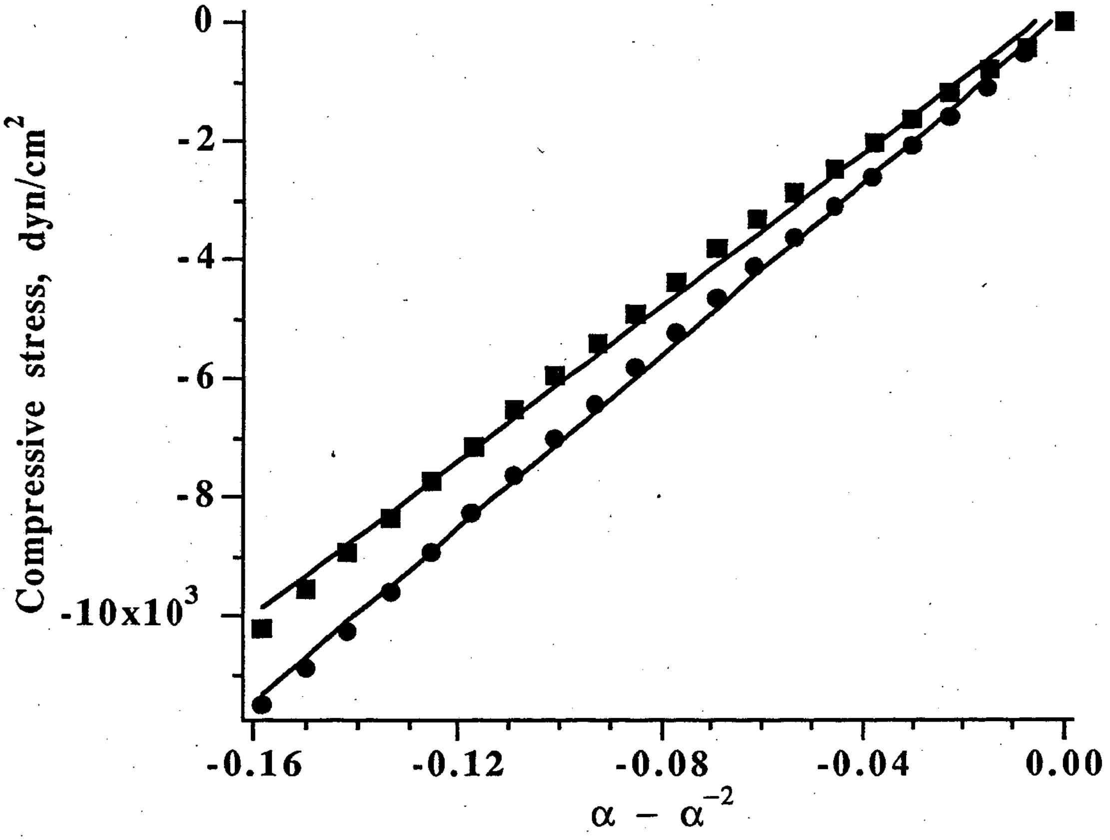

Figure 2. Compressive stress-strain data for the 25 %*T* hydrogel samples. The hydrogel was equilibrium-swollen in pure water before the compressive tests were performed.

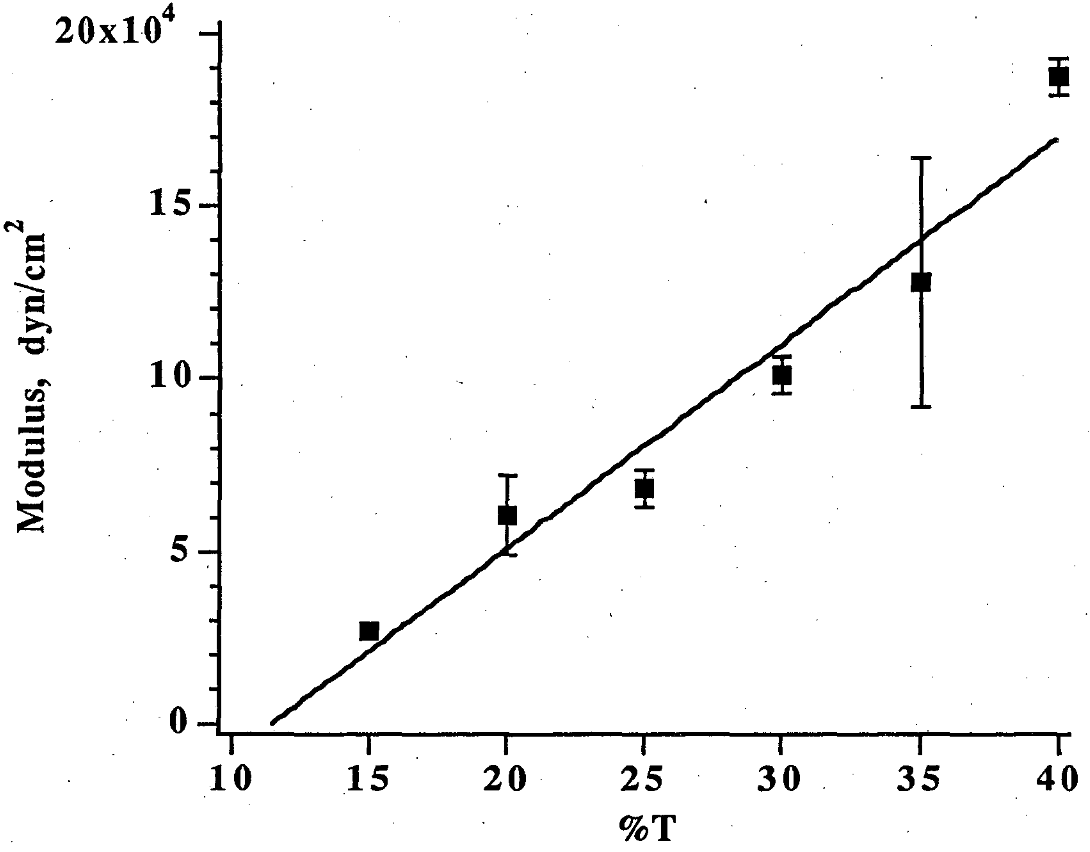

Figure 3. Compression moduli determined from compressive stress-strain measurements for hydrogels prepared with different *%T*.

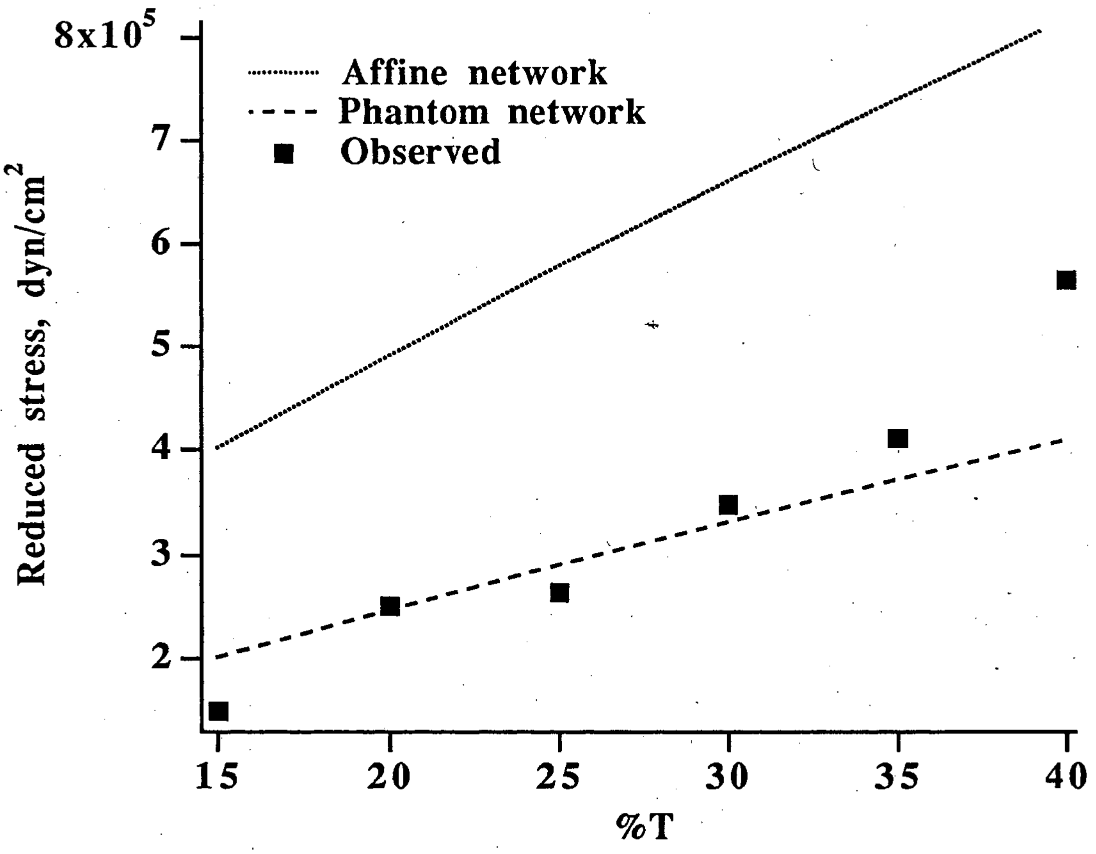

Figure 4. Reduced stress [*f**] plotted as a function of *%T*. Here experiment is compared with predictions from the phantom and affine theories of elasticity.

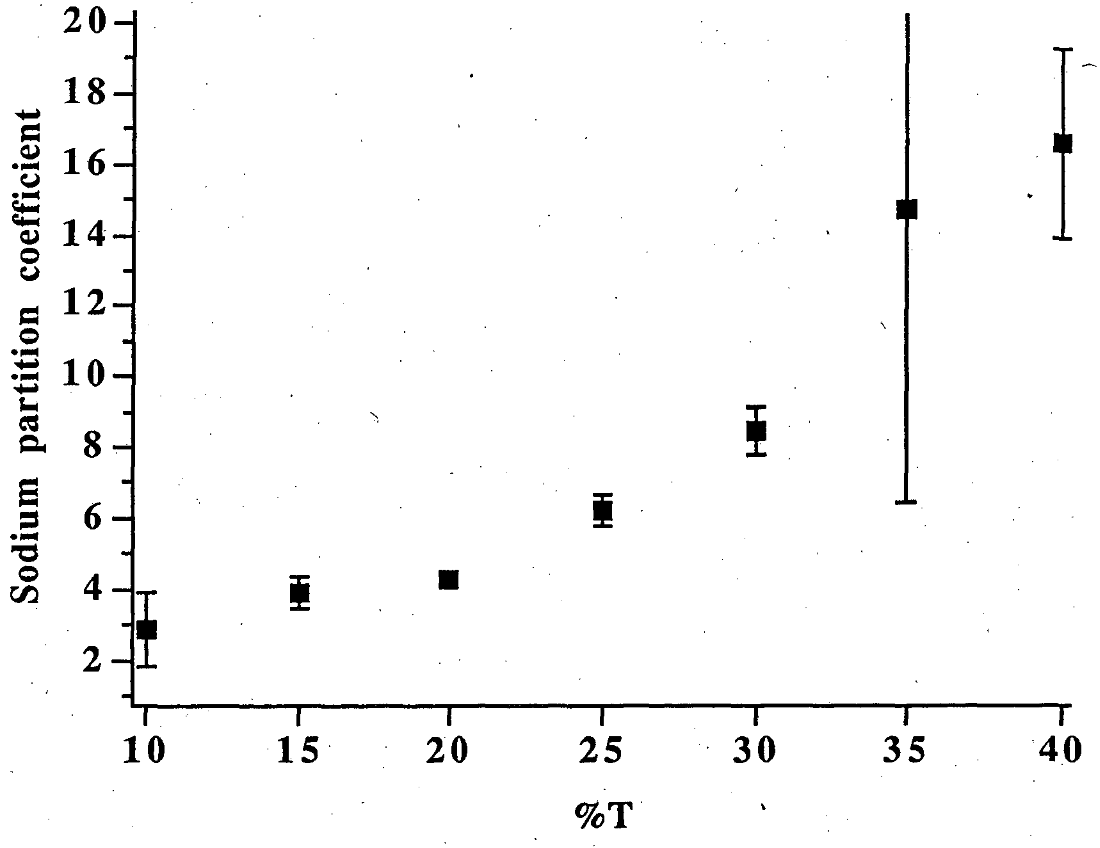

Figure 5. Sodium partition coefficients determined for %*T*-varying hydrogels. The partition experiment is described in the text.

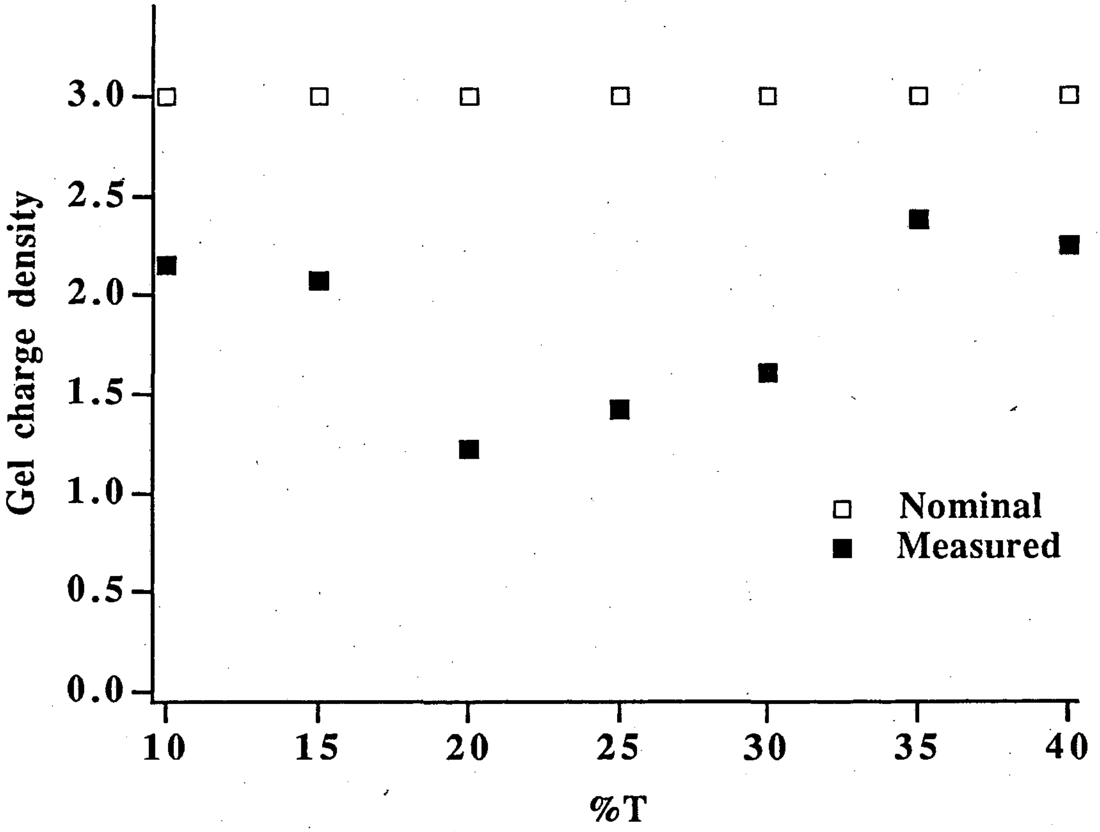

Figure 6. Effective hydrogel charge densities determined for %*T*-varying hydrogels. The effective charge densities were estimated from the ideal Donnan partitioning of sodium ions into the hydrogels. The hydrogels were nominally prepared with 3% cationic monomer.

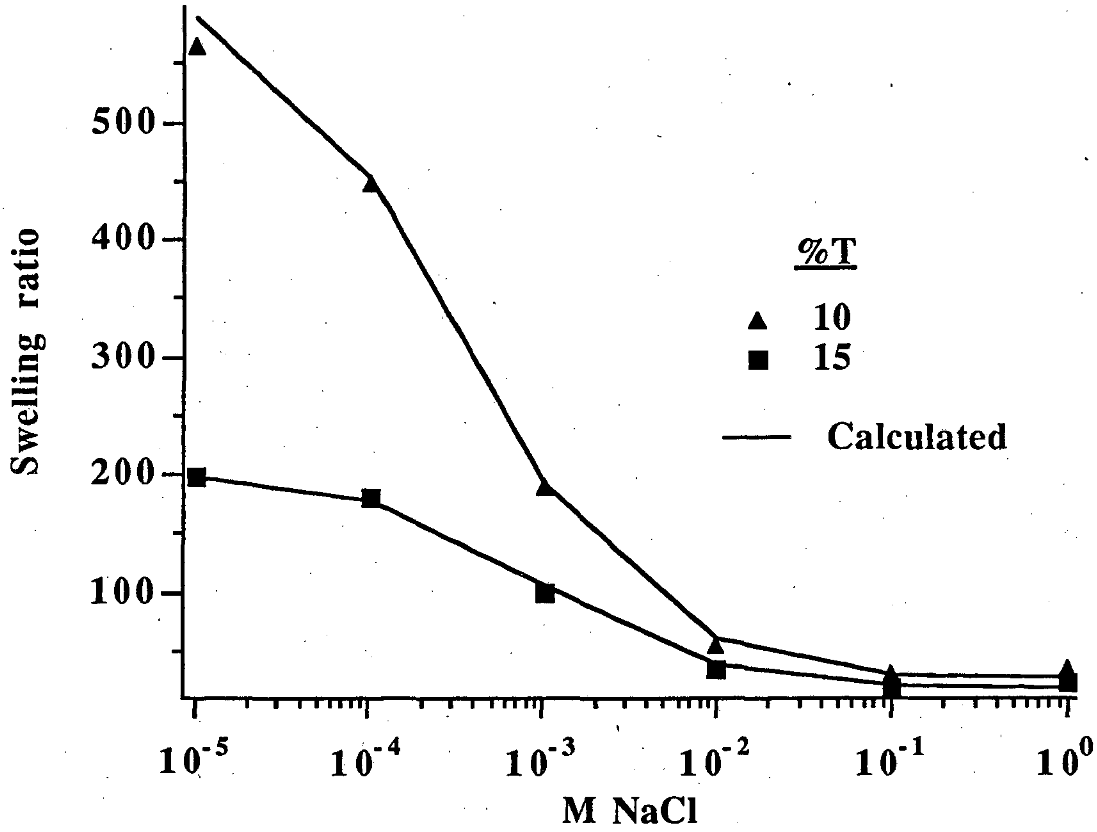

Figure 7. Swelling equilibria in aqueous NaCl for poly(acrylamide *co*-MAPTAC) hydrogels prepared with *%T* of 10 or 15: comparison of experiment with theory.

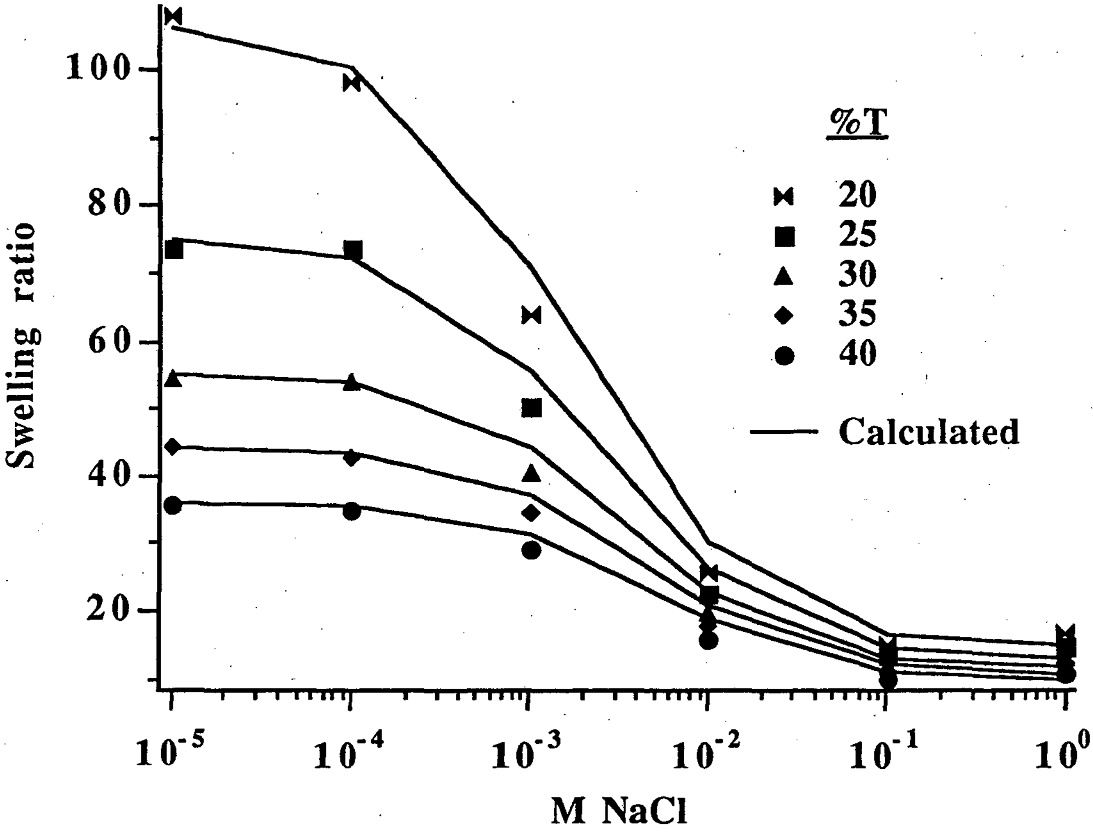

Figure 8. Swelling equilibria in aqueous NaCl for poly(acrylamide *co*-MAPTAC) hydrogels prepared with 20 - 40 *%T*: comparison of experiment with theory.

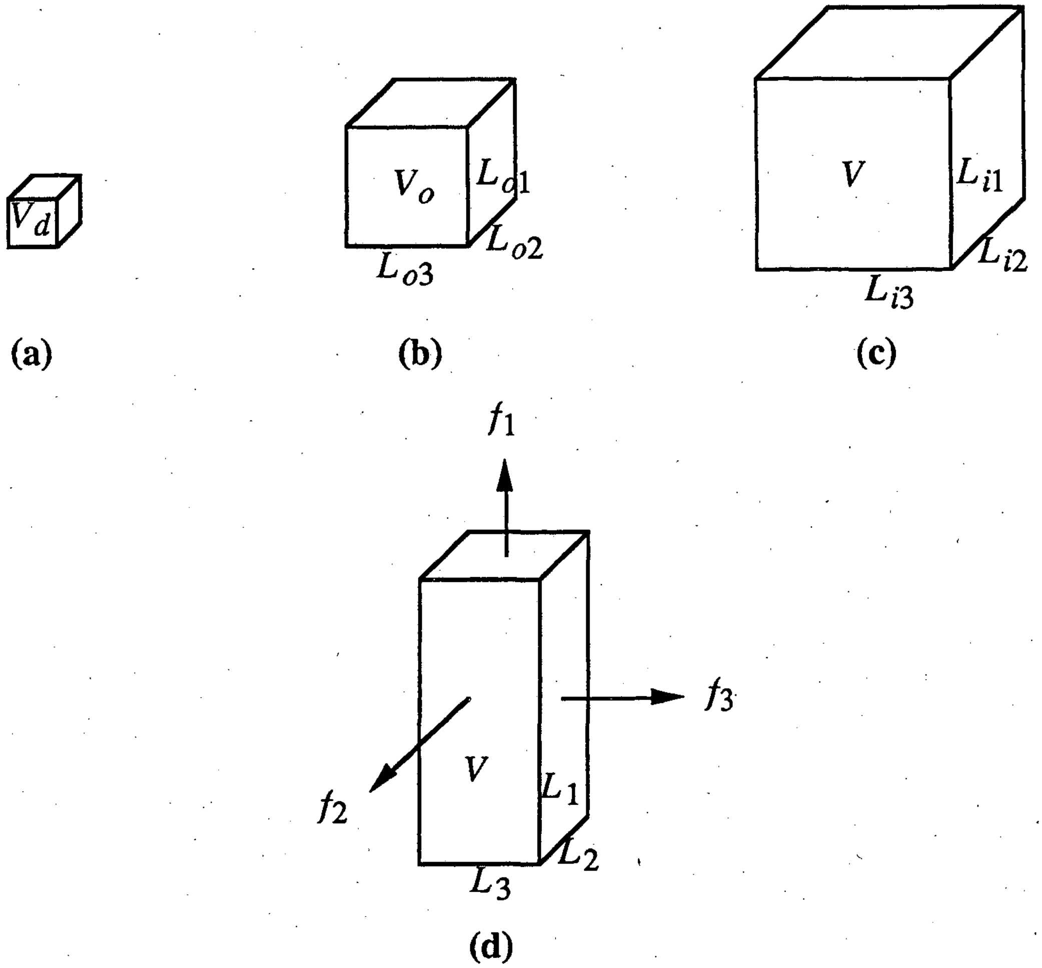

Figure A1. (a) A block of dry network at volume V_d. (b) The same block at the reference volume V_o. The reference state is the state at which the network is formed and is characterized by the %T parameter, or initial total monomer concentration. (c) The same block at the initial state before the application of the deformation. The volume V is the state of equilibrium swelling in water. (d) The final dimensions of the block after the stresses are applied.

Tables

Table 1. Elemental microanalytical results for %T-varying poly(acrylamide *co*-MAPTAC) hydrogels. The observed results are presented as an average over all seven gels prepared; values in parentheses are standard deviations. Theoretical values are calculated assuming 5 wt. % water was trapped inside the collapsed, dry networks submitted for analysis.

Element	Observed	Theoretical
C	42.0 (0.1)	42.0
N	15.3 (0.1)	16.0
H	7.81 (0.05)	8.0

Table 2. Swelling ratios and compressive stress-strain moduli for %*T*-varying poly(acrylamide *co*-MAPTAC) hydrogels in fresh water. The hydrogels were prepared with 0.2%*C* and 3%*MAPTAC*. Values in parentheses are standard deviations. Also listed are values for the empirical parameter *N*; see the text for an explanation of *N*.

%*T*	Swelling ratio, g swollen gel/g dry gel	Modulus x 10^4, dyn/ cm^2	*N*
10	613.0 (5.0)	-	1.02
15	200.9 (2.0)	2.7 (0.2)	1.70
20	106.9 (1.7)	6.1 (1.1)	2.22
25	75.5 (1.4)	6.8 (0.5)	2.49
30	55.4 (0.1)	10.1 (0.5)	2.81
35	44.5 (0.1)	12.8 (3.6)	3.04
40	36.2 (1.4)	18.7 (0.6)	3.30

Table 3. Sodium partition coefficients obtained from the Donnan-exclusion experiment described in the text. Also listed are values for the hydrogel fixed-charge density *I* calculated using Equation 21. The nominal value for *I* is 3 %.

%T	Partition coefficient[a]	*I*[b]
10	2.8 (1.1)	2.2
15	3.9 (0.4)	2.1
20	4.2 (0.2)	1.2
25	6.2 (0.4)	1.4
30	8.4 (0.6)	1.6
35	14.7 (8.3)	2.4
40	16.6 (2.7)	2.2

[a] (Concentration sodium in external solution)/(concentration of sodium in the hydrogel)

[b] Expressed as the percent positively-ionized structural units in the hydrogels

Table 4. Swelling ratios (g swollen gel/g dry gel) for %*T*-varying poly(acrylamide *co*-MAPTAC) hydrogels in aqueous NaCl solutions. Values in parentheses are standard deviations.

M NaCl	10 %*T*	15 %*T*	20 %*T*	25 %*T*	30 %*T*	35 %*T*	40 %*T*
1.0x10^{-5}	565.2 (21.2)	198.2 (1.6)	107.9 (3.7)	73.4 (2.8)	54.5 (0.1)	44.1 (0.2)	35.5 (1.1)
1.0x10^{-4}	446.3 (20.7)	179.0 (1.9)	98.1 (5.5)	73.7 (2.5)	53.9 (0.3)	42.8 0.1)	35.0 (1.3)
1.0x10^{-3}	187.9 (9.7)	98.1 (0.6)	63.8 (1.2)	50.1 (1.6)	40.4 (0.3)	34.3 (0.1)	29.2 (0.8)
0.010	55.2 (0.5)	34.4 (0.4)	25.4 (0.4)	22.3 (0.1)	19.6 (0.6)	17.5 (0.2)	15.7 (0.8)
0.10	29.6 (0.3)	19.3 (0.3)	15.0 (0.7)	13.2 (0.2)	11.9 (0.4)	10.9 (0.1)	9.9 (0.1)
1.0	34.3 (2.3)	22.6 (0.1)	16.6 (0.2)	14.6 (0.1)	13.1 (0.4)	12.2 (0.1)	10.6 (0.5)
5.0	43.9 (1.4)	29.1 (0.3)	21.6 (0.7)	19.5 (0.7)	17.1 (0.6)	15.4 (0.2)	13.8 (0.4)