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Swelling Equilibria for Positively Ionized Polyacrylamide Hydrogels

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ABSTRACT: Swelling equilibria are reported for polyacrylamide gels in water and for copolymer gels containing acrylamide and [(methacrylamido)propyl]trimethylammonium chloride (MAPTAC) in aqueous NaCl solutions. Gel swelling was investigated as a function of gel structure (cross-link density and monomer concentration), degree of gel ionization (relative amount of charged comonomer) and solution ionic strength. A gel-swelling model is presented which describes polymer/solvent mixing effects using a recently proposed lattice model developed for aqueous/polymer systems; this model accounts for hydrogen bonding in aqueous solutions by distinguishing between different types of contact sites on a solvent molecule or polymer segment. The elastic contribution to swelling is represented using a network theory which accounts for nonaffine displacement of network junctions under strain; polyelectrolyte effects on swelling are described using ideal Donnan theory. Swelling equilibria for uncharged polyacrylamide networks in water are correlated using the gel-swelling model. The model describes reasonably well the effect of cross-link density on swelling but fails to reproduce accurately the dependence of swelling on monomer concentration at preparation. Exchange-energy parameters obtained from polyacrylamide gel-swelling measurements are used to predict swelling in salt solutions for acrylamide/MAPTAC copolymer gels. The model predicts well the effect of gel charge density and solution ionic strength on swelling; however, the effect of monomer concentration is not accurately predicted. Further work is needed to quantify the effect of monomer concentration on the swelling and elastic properties of polyacrylamide hydrogels.

Introduction

Hydrogels have widespread applications in the medical, pharmaceutical, and related fields.[1] In recent years, particular interest has been devoted to gels exhibiting phase transitions (i.e., volume collapse) in response to changes in external conditions. Since the first reported observation of gel collapse,[2] collapse phenomena have been intensely investigated[3] and novel applications have been proposed in a variety of areas, including solute recovery,[4] controlled release,[5] and environmentally sensitive membranes.[6]

A thermodynamic framework has long existed for interpreting gel-swelling equilibria in terms of gel and solution properties;[7] this framework, however, is often unsuitable for hydrogels. Aqueous solutions (e.g., hydrogels) are characterized by strong, orientation-dependent interactions (hydrogen bonds), which can dramatically influence phase (swelling) equilibria. Random-mixing polymer-solution models (e.g., Flory–Huggins theory) do not account for specific interactions and thus often fail to describe correctly phase behavior in aqueous solutions. For example, observed lower critical solution behavior in aqueous poly(*N*-isopropylacrylamide) gels cannot be explained using Flory–Huggins theory unless the Flory interaction parameter is given an unrealistic temperature dependence. This behavior can, however, be explained using a lattice model which accounts for hydrogen bonding by distinguishing between different types of interaction sites.[8]

In addition to polymer/solvent compatibility, gel phase behavior depends on gel structure. Network elasticity theories prescribe relationships between gel structure and gel deformational and swelling properties. Model networks of known structure[9-11] have been investigated to quantify the effects of structure (in particular, molecular weight between cross-links) on elastomer properties. However, for gels prepared in solution the effect on elastic and swelling properties of monomer concentration at preparation is not well understood.[12,13]

Additional complications in describing hydrogel properties arise when fixed charges are incorporated on the polymer network. A small degree of polyelectrolyte character can affect dramatically gel-swelling properties, including the extent of volume collapse and the conditions under

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which collapse occurs.[3,14] The effect of gel ionization on swelling behavior has been studied systematically for hydrogels containing weakly dissociating electrolytes (e.g., acrylic acid) in mixed solvent (acetone/water) systems.[15-17] For highly ionized gels, deformational and swelling behaviors have been studied in water and in aqueous salt solutions.[18-21] However, few studies have investigated systematically swelling in water and aqueous salt solutions for hydrogels containing strongly dissociating electrolytes at low degrees (<5%) of ionization.

At present, we do not have a relationship for describing (and predicting) simultaneously the effects of gel ionization, gel structure, and solution conditions on hydrogel swelling equilibria. For development of new models (and for testing existing models), systematic data are needed that isolate the effects of individual gel and solution properties on swelling equilibria. In this work we report such data for an ionized hydrogel copolymer system; experimental results are then used to evaluate the ability of a model (discussed below) to correlate and predict swelling equilibria in this system.

We examined the effects of gel composition and solution conditions on swelling properties of positively ionized acrylamide hydrogels at low degrees of ionization. Swelling equilibria are reported for polyacrylamide gels and for gels containing acrylamide copolymerized with small amounts of [(methacrylamido)propyl]trimethylammonium chloride (MAPTAC). MAPTAC, a quaternized ammonium salt, strongly dissociates in aqueous solution, rendering the degree of gel swelling relatively insensitive to pH. Thus, the solution variable of primary interest is the ionic strength, or salt concentration. Gel-composition parameters (charge density, cross-link content, and monomer concentration at preparation) were varied systematically; the equilibrium properties of the gels were measured in water and in NaCl solutions varying from 10^{-5} to 1.0 M.

We interpret and correlate gel-swelling properties within the framework of a recently proposed polymer-solution model,[8] extended here to describe swelling equilibria for polyelectrolyte gels. Our goal is to evaluate the ability of this model to predict swelling equilibria for ionized gels as a function of gel and solution properties. Network elasticity effects are described using the theory of Flory and Erman;[22] in this model, junction fluctuations are constrained to a greater or lesser extent depending on network interpenetration and degree of swelling. The contributions of charged comonomer and added electrolyte to gel swelling are estimated using ideal Donnan equilibria.[7] The only adjustable parameters in the resulting swelling model appear in the polymer/solvent mixing expression; these parameters are obtained from swelling equilibria in water for uncharged polyacrylamide gels. Predictions of swelling equilibria for ionized networks (using parameters obtained from polyacrylamide gel-swelling data) are compared with the measured swelling properties for acrylamide/MAPTAC copolymer gels in aqueous salt solutions.

Swelling Model

Swelling equilibria between a gel (phase, single prime) and surrounding solution (phase, double prime), must fulfill the criteria

$$\mu_i' = \mu_i'' \tag{1}$$

where μ_i is the chemical potential of species i. Equation 1 holds for all components (including ions) that exist both in the gel and in the surrounding solution (i.e., all *diffusible* species). When i represents the solvent (water), it is common[3,7,23] to write eq 1 in the form

$$\Pi = -\Delta\mu_1/V_1 = 0 \tag{2}$$

where Π is the osmotic-pressure difference between the gel and the external solution, V_1 is the molar volume of component 1 (the solvent), and $\Delta\mu_1 = \mu_1' - \mu_1''$.

The swelling pressure, Π, can be written as a sum of three contributions[3,23]

$$\Pi = 0 = \Pi_{mix} + \Pi_{elas} + \Pi_{ion} \tag{3}$$

where Π_{mix} represents the contribution from polymer/solvent mixing, Π_{elas} represents the elastic contribution from deforming the network chains from their reference state, and Π_{ion} represents the contribution due to the presence of mobile and bound ions (i.e., ion/solvent mixing effects and specific ion–segment interactions). Equation 3 assumes that the various contributions to the free energy of swelling are additive, i.e., that the partition function for swelling can be factored into independent contributions.[24] While this assumption has been questioned,[25] there exists (as yet) no tractable alternative for describing swelling equilibria.

Mixing Contribution. As a result of the Flory–Rehner assumption (eq 3), we can determine Π_{mix} using a molecular-thermodynamic model for an un-cross-linked polymer/solvent system. The well-known polymer-solution theory of Flory[26] and Huggins[27] has been used extensively for describing the polymer/solvent mixing contribution to gel swelling.[3,7,23] However, Flory–Huggins theory is based on a random-mixing lattice model which assumes that interaction potentials for solvent and polymer segments are homogeneous over the segment surfaces. This theory can describe successfully phase equilibria (including swelling equilibria) for nonpolar polymers in nonpolar solvents (e.g., polystyrene gel swollen in benzene). However, random-mixing models do not account for orientation-dependent interactions (i.e., hydrogen bonds) which dramatically influence the behavior of aqueous systems, including hydrogels.

Recently we proposed a quasi-chemical lattice model for aqueous solutions which accounts for hydrogen bonding by distinguishing between different types of interaction sites on a segment.[8] In this model, each solvent molecule or polymer segment may have one, two, or three types of interaction sites: hydrogen-bond donating sites (α sites), hydrogen-bond accepting sites (β sites), and sites that interact through dispersion forces (D sites). Because the solvent molecules or segments contain different types of interaction sites, their surface potentials are nonhomogeneous, and their energetics with neighboring sites are orientation-dependent. This model can account for the large, orientation-dependent nonrandom-mixing effects which occur in aqueous polymer solutions and in aqueous gels.

Prange et al.[8] present the partition function (and corresponding chemical potential expressions) for a binary system containing hydrogen-bonding components. The partition function is derived using Guggenheim's quasi-chemical approximation[28,29] extended to segments containing three types of interaction sites. We present here only the expression for the osmotic pressure contribution due to polymer/solvent mixing:

$$\Pi_{mix} = -\frac{RT}{V_1}\left[\ln\phi_1 + \phi_2 - \frac{1}{2}z_1{}^{\alpha}q_1 \ln\frac{[\Gamma_{11,pure}^{\alpha\alpha}]}{[\Gamma_{11,mix}^{\alpha\alpha}]} - \frac{1}{2}z_1{}^{\beta}q_1 \ln\frac{[\Gamma_{11,pure}^{\beta\beta}]}{[\Gamma_{11,mix}^{\beta\beta}]} - \frac{1}{2}z_1{}^{D}q_1 \ln\frac{[\Gamma_{11,pure}^{DD}]}{[\Gamma_{11,mix}^{DD}]}\right] \tag{4}$$

Here, R is the gas constant, T is temperature, ϕ_1 and ϕ_2 represent (respectively) the volume fraction of solvent and polymer in the gel; q_1 and the z_1's are structural parameters of the solvent (denoting, respectively, the solvent surface area and the number of contacts per unit surface area), and the Γ_{11}'s are factors representing the extent of nonrandom mixing around each type of contact site on the solvent. Equation 4 reduces to the athermal Flory–Huggins[7] result when all nonrandom factors (Γ_{11}) are set equal to unity.

The first two terms in the brackets of eq 4 give the random combinatorial contribution to the chemical potential (osmotic pressure). The last three terms represent contributions from nonrandom mixing and from (pairwise-additive) interactions between contact sites. The structural parameters in these terms are readily specified from molecular structure (i.e., they do not require binary experimental data). However, the nonrandom factors (the Γ_{11}'s) depend on temperature, on composition, and on the energetics that characterize different types of contacts in the mixture.

The expressions that relate the nonrandom factors to temperature, composition, and energetic interactions are known as the *quasi-chemical* equations. To solve these equations for the nonrandom factors (needed in eq 4), we must specify the exchange energies for the different contact pairs that can form between segments. These exchange energies are the adjustable parameters in the model. As explained by Prange et al.,[8] using reasonable simplifying assumptions, we reduce to 3 the number of independent exchange energies that must be obtained from experimental data. These parameters are the following: ω^{DD}, the exchange energy for dispersion–force interactions between unlike segments; $\omega^{\alpha\beta}$, the exchange energy for hydrogen-bonding interactions between unlike segments; ω^{D*}, the exchange energy for interactions between a hydrogen-bond-donating or -accepting site with a dispersion–force contact site. One additional exchange-energy parameter (which characterizes hydrogen-bonding interactions between like segments) has been set to a constant value for all systems and is, thus, not adjustable.[8]

Elastic Contribution. The two most common statistical theories for networks consider the idealized cases of the *affine* network[7] and the *phantom* network.[30] In the phantom network, junction points (cross-links) fluctuate freely, unaffected by the presence of neighboring chains or by the state of deformation. The resulting expression for the solvent chemical potential change (for isotropic swelling of a perfect tetrafunctional network) is[13,30]

$$\Delta\mu_{1,\text{elas}}^{\text{phantom}} = \frac{1}{2}RT(\phi_2^0/x_c)\lambda^{-1} \tag{5}$$

Here, x_c denotes the average number of segments per network chain (where a segment is defined as having the same volume as that of a solvent molecule), ϕ_2° represents the volume fraction of the gel in the reference state (i.e., at preparation), and the dilation ratio $\lambda = (\phi_2^\circ/\phi_2)^{1/3}$.

In the affine network, junction point fluctuations are totally suppressed and components of each chain vector transform linearly with macroscopic deformation. The resulting chemical potential expression (for a perfect tetrafunctional network) is[7,13]

$$\Delta\mu_{1,\text{elas}}^{\text{affine}} = \frac{1}{2}RT(\phi_2^0/x_c)\lambda^{-1}(2-\lambda^{-2}) \tag{6}$$

The primary difference between the affine and phantom network models is the leading constant in the chemical potential expression (1/2 in eq 5 and unity in eq 6). The second term in eq 6 accounts for the dispersion of the embedded junctions over space.[7]

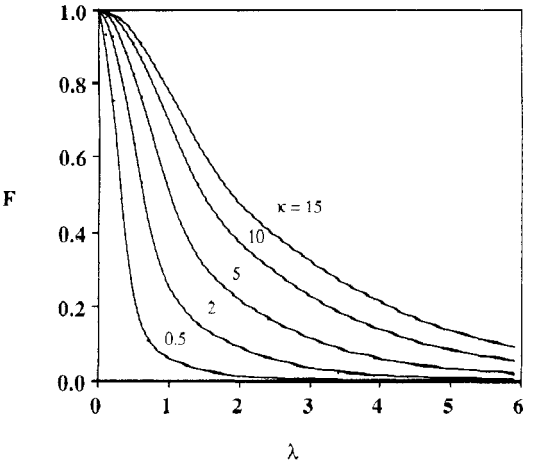

Figure 1. Dependence of interpolation function F in eq 7 on degree of swelling (dilation ratio) for different values of κ.

In the phantom and affine networks, constraints affecting junction fluctuations are, respectively, nonexistent and total. Real networks conform to neither of these limiting cases.[13] We use here a network theory[22,31] in which junction fluctuations are permitted, but the extent of these fluctuations depends on the constraints of neighboring chains. The chemical potential expression for this model (known as *constrained junction* theory) can be written

$$\Delta\mu_{1,\text{elas}} = \Delta\mu_{1,\text{elas}}^{\text{phantom}}(1-F) + \Delta\mu_{1,\text{elas}}^{\text{affine}}F \tag{7}$$

where F varies between 0 (no constraints on junctions) and 1 (complete constraints on junctions). Constrained junction theory thus interpolates between the limits of phantom and affine network behavior. The elastic contribution to eq 3 is determined from eq 7 by $\Pi_{\text{elas}} = -\Delta\mu_{1,\text{elas}}/V_1$.

The interpolation function in eq 7 depends on the degree of swelling (and on the extent of junction constraints) through the expression

$$F = K(\lambda,\kappa)/(1-\lambda^{-2}) \tag{8}$$

where $K(\lambda,\kappa)$ is given by eq 16 (and related equations) in Erman and Flory.[32] Parameter κ is a measure of constraints on junction fluctuations; it is related to the degree of network interpenetration through[34]

$$\kappa = (1/4)P\phi_2^\circ x_c^{1/2} \tag{9}$$

Dimensionless number P is determined by the type of polymer and the molar volume of the solvent; for polyacrylamide in water, we estimate $P = 3.0$.[33] For a specific polymer/solvent (gel) system, P remains constant and κ depends only on network composition (cross-link density and monomer concentration at preparation).

Figure 1 shows the dependence of interpolation function F on degree of swelling (dilation) for several values of κ. At low dilation ratios (small λ) and high degrees of network interpenetration (large κ), F approaches 1 and the network approaches affine behavior. At high degrees of swelling and/or small values of κ, F approaches 0 and the network is described by the phantom limit. Equation 8 does not have a singularity at $\lambda = 1$ because $K(\lambda,\kappa)$ also contains a factor that approaches zero as λ approaches unity.

In this work, we are primarily concerned with networks at high dilution. Based on the discussion above (and on Flory and Erman[22]), the behavior of these net-

works should be close to that of the phantom limit. However, we are also interested in the effect of gel composition at preparation (i.e., gel structure) on equilibrium swelling properties. In constrained junction theory, network elasticity depends on the degree of network interpenetration (characterized by parameter κ), which, in turn, is related to the gel composition at preparation through eq 9. Thus, in principle, this theory accounts for the effects of cross-link density and monomer concentration at preparation on gel elastic properties.

Ionic Contribution. Fixed charges on a network are confined (along with an equal number of counterions) to the gel phase, resulting in an unequal distribution of unbound ions between the gel and surrounding solution and an osmotic pressure difference between the two phases.[7] This osmotic pressure difference introduces an additional mixing contribution (of ions with solvent) to the swelling free energy and therefore to the solvent chemical potential. Donnan equilibria for describing this contribution[7] explain some basic features of polyelectrolyte gel swelling, often with semiquantitative success.[35]

A complete description for the effect of ions on gel swelling would require expressions for ion–ion, ion–solvent, and ion–polymer interactions; these interactions are ignored in the ideal Donnan approach. Some workers[18,36,37] have proposed a contribution to the solvent chemical potential (osmotic pressure) due to repulsions of fixed charges along the polymer chains (interchain repulsions are not considered). This contribution, while significant for highly ionized gels,[36] is likely be a second-order correction to the Donnan approach for gels with low degrees of ionization.

As an initial step toward extending our swelling model to polyelectrolyte gels, we consider here only the ion-mixing contribution (i.e., the ideal Donnan theory) for describing the effects of gel charge density and solution salt concentration on gel swelling. The osmotic contribution due to the ions is then given by[7]

$$\Pi_{ion} = RT\sum_j (c_j^{gel} - c_j^{ext}) \tag{10}$$

where c_j^{gel} and c_j^{ext} represent, respectively, ion concentrations within the gel and in the surrounding solution. The summation over j includes all mobile (unbound) ions. Equation 10 assumes that ion concentrations are small and that the solvent osmotic coefficient is unity.

The concentration of ions in the solution bathing the gel is typically fixed by experimental conditions. The concentration of ions within the gel is calculated according to Donnan equilibria, i.e., by applying eq 1 to the diffusible ions. For a gel in solution containing a single salt (where all ion valences are unity) we have[7]

$$\left(\frac{c_s^{gel}}{c_s^{ext}}\right) = \frac{c_s^{ext}}{c_s^{gel} + \frac{i\phi_2}{V_u}} \tag{11}$$

where c_s refers to the concentration of added salt within the gel (c_s^{gel}) or in the surrounding solution (c_s^{ext}), i represents the fraction of monomer units containing bound charges, and V_u denotes the molar volume of a monomer unit. Equation 11 assumes that the mean ionic activity coefficient of the diffusible salt is approximately the same in the gel phase as that in the surrounding solution.

Swelling Equilibria Calculations. The equilibrium degree of swelling for given gel composition and solution conditions is determined by solving eq 3 for ϕ_2; all three contributions to eq 3 depend on ϕ_2 (or, equivalently, on λ), and an iterative solution is required. The elastic and ionic contributions to eq 3 do not require adjustable parameters; ϕ_2^o, x_e, and i are determined from the nominal gel composition; V_1 and V_u are estimated, respectively, as 18.0 and 62.8 cm^3/mol; and c_s^{ext} is determined from the external salt concentration (fixed in the experiments). The mixing contribution to the swelling pressure (eq 4) requires structural parameters for the polymer and solvent and three exchange-energy parameters. Structural parameters for water are the same as those used by Prange et al.[8] q_1 (=r_1) = 1.0, and $z_1^\alpha = z_1^\beta$ = 2.0; structural parameters for the polymer are estimated as $z_2^\alpha = z_2^\beta$ = 1.0.[38]

The three exchange-energy parameters (the only *adjustable* parameters in the model) must be obtained from experimental data. These parameters characterize polymer/water interactions in the absence of charged comonomer or dissolved electrolyte; they are obtained here from swelling equilibria for (uncharged) polyacrylamide gels in water, as explained in the Results and Discussion.

Experimental Section

Materials. Acrylamide (AAm) and *N,N'*-methylenebis(acrylamide) (BIS), both electrophoresis grade, were obtained from Eastman Kodak. MAPTAC (in 50% aqueous solution) was obtained from Monomer-Polymer and Dajac Laboratories; ammonium persulfate and dichlorodimethylsilane were purchased from Eastman Kodak; sodium metabisulfite was obtained from Sigma; toluene (reagent grade) and NaCl were purchased from Fisher. All monomers and reagents were used as received. Water for synthesis and for swelling measurements was distilled and filtered through a Barnstead Nanopure II system before use.

Gel Synthesis. Gels were prepared by free-radical solution copolymerization of AAm and MAPTAC, using BIS as the cross-linking monomer. Polymerization was initiated using the redox couple ammonium persulfate with sodium metabisulfite.[15] Gels were formed in 10 × 75 mm silanized test tubes; silanization was accomplished by immersing the glass tubes in a solution of dichlorodimethylsilane in toluene (2% v/v) for 2 min.[6]

All gels were prepared in aqueous solution. AAm and BIS (in amounts corresponding to a desired gel composition) were dissolved in 40 mL of water and degassed at room temperature under a 27-in.Hg vacuum for 90 min. Two initiator solutions containing, respectively, 0.030 g of ammonium persulfate and 0.030 g of sodium metabisulfide in 15 mL of water (for each solution) were also degassed for 90 min. The three solutions were transferred to a nitrogen-filled glovebox. Inside the glovebox a predetermined amount of MAPTAC, along with 5.0 mL of each initiator solution, was added to the monomer solution. The resulting solution was stirred with a magnetic stirrer until completely mixed and then poured into the gel molds. After 24 h, the gels were removed from the test tubes, sliced into disks (approximately 3 mm in width), and soaked in deionized water (refreshed periodically) for approximately 7 days.

The nominal gel composition is determined by the relative amounts of monomers and diluent (water) at preparation. The following three variables are convenient for defining this composition:[39]

$$\%\ C = \frac{\text{moles of cross-linking monomer in feed solution}}{\text{total moles of monomer in feed solution}} \times 100$$

$$\%\ T = \frac{\text{mass of all monomers (g)}}{\text{volume of water (mL)}} \times 100$$

$$\%\ MAPTAC = \frac{\text{moles of MAPTAC in feed solution}}{\text{total moles of monomer in feed solution}} \times 100$$

Three series of AAm/MAPTAC copolymer gels were prepared for this work; in each series one composition parameter was varied while the other two parameters were held constant. In addition, two series of gels were prepared without MAPTAC; for these gels % C and % T were varied independently.

Table I
Swelling Equilibria for Polyacrylamide Gels in Water[a]

variable % C gels[b]		variable % T gels[c]	
% C	swelling ratio[d]	% T	swelling ratio[d]
0.1	44.9 (1.7)	15.0	25.7 (0.50)
0.2	25.7 (0.50)	20.0	19.1 (0.12)
0.5	14.9 (0.04)	25.0	17.1 (0.27)
1.0	12.6 (0.41)		
5.0	7.14 (0.05)		

[a] Gels contain no MAPTAC; all measurements made at room temperature and atmospheric pressure. [b] Monomer concentration held constant at 15% T. [c] Cross-link concentration held constant at 0.2% C. [d] Swelling ratio given as grams of swollen gel/grams dry gel; results in parentheses indicate standard deviation.

To analyze for reaction completeness, we examined the concentration of solids (monomer or polymer) leached from gel samples into aqueous solution after equilibrating for 1 week. Negligible amounts of unreacted solids were found in solution. We thus conclude that the nominal % T provides a good measure of the monomer concentration in the gel at network formation. Unfortunately, we do not have an independent measure of the effective cross-link density within the gel (as can be determined from stress–strain measurements). The nominal cross-link density is used here for comparing experimental and calculated swelling equilibria.

Swelling Measurements. Following synthesis, gel disks were equilibrated in deionized water at room temperature (and atmospheric pressure). The approach to equilibrium (typically requiring 1 week) was followed by monitoring the diameters of the gel disks with a caliper. For every gel prepared, three equilibrated samples (each containing four or five gel disks) were blotted with laboratory tissue (to remove surface water), weighed, dried under vacuum at room temperature, and weighed again. The swelling capacity was determined as the mass ratio of swollen gel to dry gel.

Sodium chloride solutions were prepared in the concentration range 10^{-5}–1.0 M. Gel disks were transferred from the deionized water to each of the salt solutions and allowed to equilibrate. During the equilibration process, the solutions were refreshed daily and the diameters of the gel disks were recorded. After the disk diameters ceased to change (approximately 1 week), the swelling capacity was determined by drying the gels (as described above) or by converting the gel diameter change into a volume change. Assuming that the gel swells isotropically[15]

$$(V/V_0) = (D/D_0)^3$$

where V_0 and V denote, respectively, the volume of the gel disks in deionized water and in sodium chloride solution and D_0 and D represent the corresponding gel diameters. Knowing the swelling capacity of the gels in deionized water, we can determine their swelling capacity after a given volume (diameter) change. Gel capacities determined by volume change were in excellent agreement with those determined by drying and weighing;[40] thus, the former (simpler) method was used in most cases.

Reproducibility and Results. Swelling measurements were performed in triplicate; Tables I–IV give mean values of the measurements and indicate mean deviations. In general, standard deviations of the measured swelling capacities were less than 3% of the mean capacity for a particular gel at a given solution concentration. Reproducibility of the synthesis procedure was verified by preparing a series of three gels having the same nominal composition and comparing measured swelling capacities for these gels in aqueous sodium chloride. In the range 10^{-5}–1.0 M, swelling capacities for the three gels agreed, on average, within 3%. The gels were also dried and subjected to elemental analysis; atomic compositions were essentially identical.

Results and Discussion

We discuss the effect of gel composition on swelling equilibria for polyacrylamide gels in water and for acrylamide/MAPTAC copolymer gels in aqueous NaCl; model calculations are compared with experiment. We first present results for uncharged polyacrylamide gels in water; for this system, exchange-energy parameters are optimized to fit the measured swelling equilibria, and calculated swelling curves are compared with experiment. Second, we present swelling equilibria for acrylamide/MAPTAC copolymer gels in aqueous NaCl; measurements for this system are compared with predictions based on exchange-energy parameters obtained from the polyacrylamide gel-swelling measurements.

We examine here two essential features of the gel-swelling model. First, we examine the ability of the model to represent the dependence of gel swelling on gel composition (i.e., structure) for an *uncharged* network. In this analysis, model parameters (exchange energies) are optimized to experimental data; these calculations are, thus, not regarded as predictions but as the best correlation of the measurements using this model. We then examine the ability of the model to *predict* the effect of adding charged comonomer to polyacrylamide gels. Here, exchange-energy parameters are *not* optimized to experiment; instead, we use parameters obtained from the uncharged polyacrylamide gel-swelling data. Predicted swelling equilibria are compared with measurements (in aqueous salt solutions) of ionized networks prepared with different compositions (structure) and charge densities (fraction charged comonomer). Thus, we test the ability of the model to predict simultaneously the effects of gel composition and solution conditions on swelling of ionized networks using parameters obtained from the corresponding uncharged networks.

Polyacrylamide Gels in Water. Table I presents swelling equilibria in water for polyacrylamide gels prepared with different nominal compositions. Two series of gels were prepared; in one series the cross-link density was varied holding % T constant while in the other series, the monomer concentration was varied holding % C constant. As indicated, standard deviations of measured swelling capacities were generally less than 3% of the mean values.

The three exchange-energy parameters in the gel-swelling model were adjusted to represent best the data in Table I. The sum of the squared residuals of eq 3 was minimized with respect to the energy parameters using a modification of the Levenberg–Marquardt algorithm.[41] Optimized parameter values are as follows: $\omega^{DD} = 324.8$, $\omega^{\alpha\beta} = -1117$, and $\omega^{D*} = -109.2$ (exchange energies have units of degrees Kelvin).

Figures 2 and 3 compare experimental swelling equilibria with calculations made using the optimized exchange-energy parameters. Calculated swelling capacities for gels with varying cross-link density (Figure 2) agree reasonably well with experiment; the decrease in gel capacity with increasing % C follows (approximately) an inverse-power relation over most of the investigated % C range. However, below (about) 0.2% C, measured swelling capacities increase more rapidly with decreasing % C than calculated capacities. Model calculations for gels with varying % T (Figure 3) are less sensitive to monomer concentration than those observed; predicted capacities are larger than experiment at high % T and smaller than experiment at low % T.

The monomer concentration at preparation affects network elasticity (and swelling behavior) by determining the average change dimensions in the reference state (and thus the value of λ for a given degree of swelling). Increasing the monomer concentration also increases the number of entanglements formed between network chains dur-

Table II
Swelling Equilibria in NaCl Solutions for Gels Prepared with Varying Amounts of Charged Comonomer[a]

% MAPTAC[c]	swelling ratio (g swollen gel/g dry gel)[b] for specified NaCl concn					
	1.0 M NaCl	10^{-1} M	10^{-2} M	10^{-3} M	10^{-4} M	10^{-5} M
0	28.2 (0.33)	23.7 (0.30)	22.7 (0.26)	22.9 (0.27)	24.1 (0.28)	24.8 (0.29)
1.0	25.7 (0.84)	21.3 (0.69)	25.2 (0.88)	54.8 (1.5)	104 (3.0)	125 (3.6)
2.0	24.9 (0.88)	22.4 (1.1)	35.4 (1.0)	106 (3.2)	223 (6.4)	273 (8.1)
3.0	28.3 (1.0)	26.0 (0.87)	53.8 (1.7)	173 (5.3)	356 (12)	425 (13)
4.0	35.8 (1.4)	33.9 (1.5)	83.3 (2.6)	282 (8.3)	606 (19)	729 (22)
5.0	31.2 (1.2)	33.6 (1.1)	90.9 (2.9)	322 (7.8)	719 (19)	878 (24)

[a] All measurements made at room temperature and atmospheric pressure. [b] Results in parentheses represent standard deviation. [c] All gels prepared with 15% T and 0.2% C.

Table III
Swelling Equilibria in NaCl Solutions for Gels Prepared with Varying Amounts of Cross-Linking Monomer[a]

% C[c]	swelling ratio (g swollen gel/g dry gel)[b] for specified NaCl concn					
	1 M NaCl	10^{-1} M	10^{-2} M	10^{-3} M	10^{-4} M	10^{-5} M
0.1	47.8 (4.3)	40.6 (3.8)	64.7 (5.9)	203 (20)	526 (48)	741 (70)
0.2	28.1 (1.8)	23.5 (1.2)	39.9 (2.0)	120 (9.6)	241 (13)	274 (19)
0.5	15.6 (0.25)	13.4 (0.39)	19.6 (0.29)	44.0 (0.53)	60.4 (1.0)	65.4 (1.6)
1.0	11.2 (0.67)	10.1 (0.53)	15.4 (0.68)	30.0 (1.3)	36.4 (1.6)	37.1 (1.6)
5.0	6.70 (0.13)	5.84 (0.13)	7.16 (0.40)	9.02 (0.18)	9.66 (0.22)	9.64 (0.19)

[a] All measurements made at room temperature and atmospheric pressure. [b] Results in parentheses represent standard deviation. [c] All gels prepared with 15% T and 2% MAPTAC.

Table IV
Swelling Equilibria in NaCl Solutions for Gels Prepared with Different Monomer Concentrations[a]

% T[c]	swelling ratio (g swollen gel/g dry gel)[b] for specified NaCl concn					
	1 M NaCl	10^{-1} M	10^{-2} M	10^{-3} M	10^{-4} M	10^{-5} M
10	56.7 (4.1)	52.4 (2.3)	72.7 (2.8)	221 (9.0)	641 (24)	1070 (58)
15	28.1 (1.8)	23.5 (1.2)	39.9 (2.0)	120 (9.6)	241 (13)	274 (19)
20	16.5 (1.8)	14.4 (0.85)	24.4 (0.97)	61.4 (2.3)	94.7 (3.4)	114 (4.8)
25	11.7 (0.75)	11.7 (0.50)	20.0 (0.86)	43.0 (1.9)	59.2 (3.2)	64.4 (2.8)

[a] All measurements made at room temperature and atmospheric pressure. [b] Results in parentheses represent standard deviation. [c] All gels prepared with 0.2% C and 2% MAPTAC.

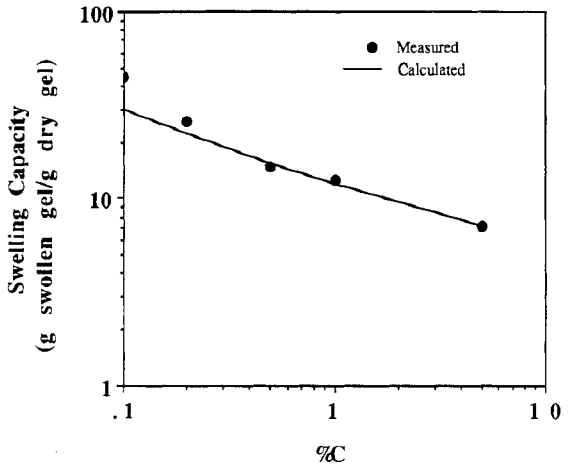

Figure 2. Experimental and calculated swelling equilibria in water for polyacrylamide gels prepared with 15% T and with varying cross-link densities (% C). Error bars for measured swelling capacities are smaller than the symbols used.

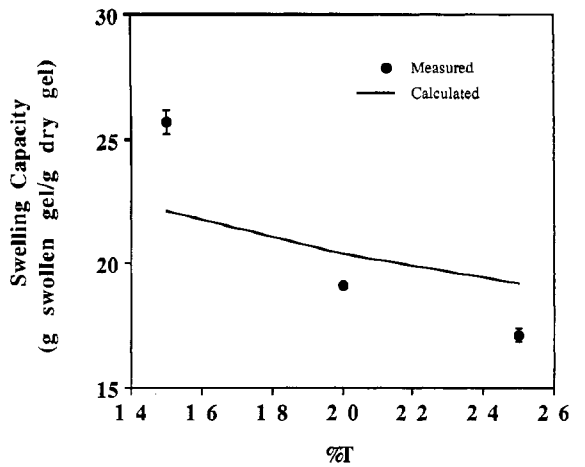

Figure 3. Experimental and calculated swelling equilibria in water for polyacrylamide gels prepared with 0.2% C and with varying monomer concentrations (% T). Error bar for 20% T measurement is smaller than the data symbol.

ing polymerization. In constrained junction theory, entanglements contribute to elasticity only by suppressing junction fluctuations. Increasing the monomer concentration at preparation gives larger values of κ (eq 9) and increased values of interpolation function F, thereby shifting network behavior closer to the affine limit (eq 7). Several authors[9,42] have suggested that entanglements not only suppress junction fluctuations but also contribute to elasticity further by acting as additional network cross-links; the free energy of deformation then depends on the number of entanglements and does not have affine behavior as the upper limit (as in constrained junction theory).

We do not attempt to resolve the controversy concerning the effect of entanglements on network elasticity. Figure 3 indicates that, for describing our measurements, constrained junction theory is not sufficiently sensitive to monomer concentration (entanglement density). In their analysis of stress–strain isotherms for networks formed in solution, Erman and Mark[12] obtained good agreement with experiment using constrained junction theory; they allowed κ to vary with ϕ_2° to a larger degree

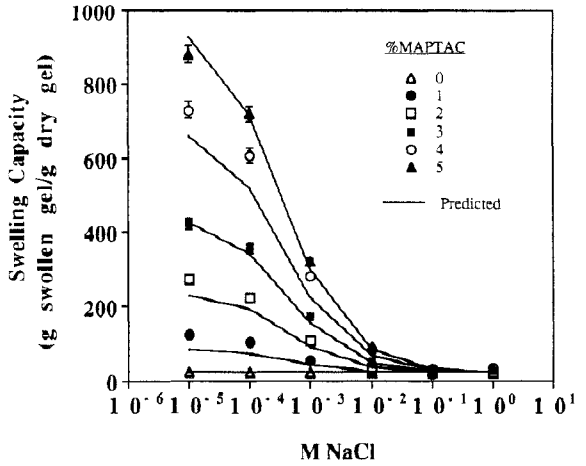

Figure 4. Comparison of measured and predicted swelling equilibria for acrylamide/MAPTAC copolymer gels prepared with 15% T, 0.2% C, and varying concentrations of charged comonomer (% MAPTAC). Predictions are based on known composition and structure parameters and on exchange energies determined from polyacrylamide gel swelling in water (Figures 2 and 3).

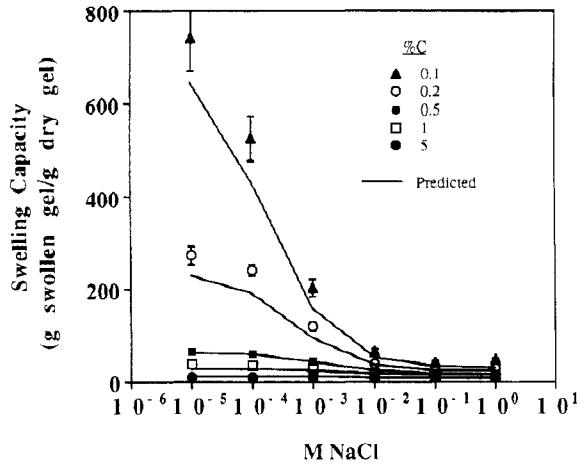

Figure 5. Measured and predicted swelling equilibria for acrylamide/MAPTAC copolymer gels prepared with 15% T, 2.0% MAPTAC, and varying cross-link densities (% C).

than suggested by theory, replacing the exponent on ϕ_2° in eq 9 from unity to (approximately) 1.7. We also attempted varying the exponent on ϕ_2° but found negligible improvement in representation of the swelling data when % T was varied. The leading factor of 1/4 in eq 9 is considered approximate;[32] we found that adjustment of this parameter gives little improvement toward agreement with experiment.

AAm/MAPTAC Gels in NaCl. Tables II–IV present swelling equilibria in aqueous NaCl for acrylamide/MAPTAC copolymer gels prepared with different compositions. The tables indicate the three series of gels prepared, varying, respectively, in % MAPTAC, % C, and % T. Figures 4–6 compare measured and calculated swelling equilibria for this system. The calculated swelling curves are determined using the exchange-energy parameters obtained from polyacrylamide gel-swelling data and from structural parameters based on the nominal gel composition. Thus, calculations shown in Figures 4–6 are *predictions* of swelling equilibria based on independently determined parameters.

Gels varying in % MAPTAC were studied to isolate the effect of charge density (and ionic strength) on swelling behavior; these gels were prepared with constant cross-link density and constant monomer concentration (0.2% C and 15% T, respectively). At low ionic strength, a large dependence of swelling capacity on % MAPTAC is observed (Figure 4) and the gels absorb large quantities of their weight in water (the 5% MAPTAC gel has a capacity of nearly 1000). As ionic strength rises, the gels deswell dramatically between 10^{-5} and 0.1 M NaCl and then become insensitive to ionic strength in the range 0.1–1.0 M NaCl.

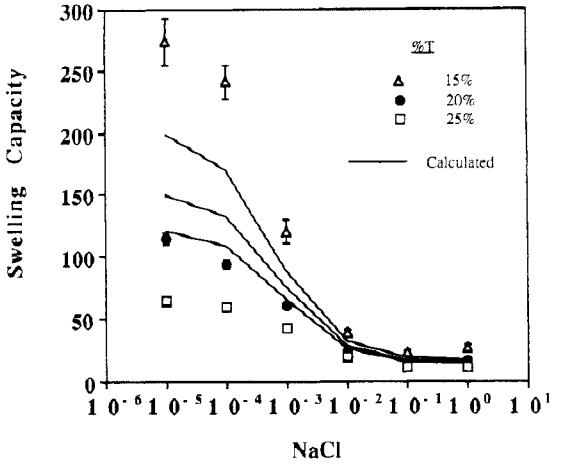

Figure 6. Measured and predicted swelling equilibria for acrylamide/MAPTAC copolymer gels prepared with 0.2% C, 2.0% MAPTAC, and varying monomer concentrations (% T).

The behavior observed in Figure 4 is readily explained (and expected) on the basis of simple physical arguments. At low ionic strength, the concentration of bound charges (and accompanying co-ions) within the gel exceeds the concentration of salt in the external solution; a large ion-swelling pressure causes the gel to expand, thereby lowering the concentration of co-ions within the gel. As the external salt concentration rises, the difference between the internal and external ion concentrations decreases and the gel deswells; the gel continues to deswell with rising external salt concentration until the mobile-ion concentrations within and surrounding the gel are approximately equal (here, at about 0.1 M NaCl). The swelling behavior in Figure 4 can also be explained on the basis of repulsions between fixed charged groups on the gel. At low ionic strengths (large Debye lengths), repulsions are long-range and the gel expands to minimize the repulsive free energy; as ionic strength rises (smaller Debye lengths), repulsions are shielded and the gel deswells.

The ionic contribution to gel swelling used here (eq 10) considers only the effect on swelling due to the differences in mobile-ion concentrations between the gel and surrounding solution; repulsions between fixed charges (in addition to other specific ion interactions) are not considered. Thus the reasonable agreement of predicted swelling equilibria with experiment (Figure 4) is impressive and confirms earlier work[35] suggesting that the ideal Donnan theory provides semiquantitative estimates of the ionic contribution to gel swelling. It is particularly encouraging to note that, using only information for uncharged polyacrylamide gels in water, we can predict the effect on swelling equilibria in *salt solutions* due to adding fixed charges to polyacrylamide gels.

Figure 5 compares measured and predicted swelling measurements in aqueous NaCl when % C is varied for gels with 15% T and 2.0% MAPTAC. These results are analogous to those presented in Figure 2; however, Figure 5 superimposes the effects of gel charge and salt concentration on the effect of % C. As in Figure 2, we see here a large dependence of swelling capacity on cross-

link density; this dependence is most apparent at low ionic strengths. Predictions agree reasonably well with experiment over the range of % C and NaCl concentration investigated. Again (analogous with the polyacrylamide gel studies), we see the largest discrepancy between experimental and calculated swelling capacities at low % C; these deviations are particularly apparent at low NaCl concentrations.

Figure 6 presents the effect of % T on swelling equilibria for gels similar to those shown in Figure 3; here, however, the gels were prepared with 2.0% MAPTAC (and with 0.2% C) and are studied in NaCl solutions. Comparison of measured and predicted swelling capacities is similar to that observed in Figure 3; predicted swelling behavior is much less sensitive to % T than that observed. Adding bound charges to the gels increases dramatically their swelling capacity at low ionic strengths and amplifies the disagreement between measured and predicted swelling equilibria.

Finally, we note an unexpected (but consistent) anomaly in the swelling data in Tables II–IV. Virtually all ionized gels exhibit a *small* increase in capacity as salt concentration rises from 0.1 to 1.0 M NaCl. Because this trend is subtle, it is not easily noticed in Figures 4–6. Ideal Donnan equilibria cannot explain an increase in gel swelling with increasing ionic strength. The capacity increase occurs at moderate salt concentrations where specific ion–solvent and ion–polymer interactions (ignored in the ideal Donnan theory) may be important. We have not investigated a more elaborate theory for explaining the increase in gel swelling between 0.1 and 1.0 M NaCl.

Conclusions

We have demonstrated the ability of a swelling model to correlate and predict swelling equilibria for neutral and ionized polyacrylamide gels in water and in aqueous salt solutions. The effects on swelling equilibria of gel charge density and solution ionic strength were well-described using ideal Donnan theory, confirming earlier work in this area.[35] However, the effect of gel structure (particularly of monomer concentration at preparation) on swelling behavior was not quantitatively described.

The discrepancy between calculated and observed swelling behavior for gels varying in monomer concentration appears related to the dependence of chain entanglements on monomer concentration and to the absence of a contribution to elasticity resulting from entanglements in eq 7. However, definitive conclusions regarding the effect of entanglements (and monomer concentration) on network elasticity cannot be inferred from this work. Such conclusions are more appropriately obtained from independent elasticity measurements (i.e., stress–strain data) for model networks prepared with different monomer concentrations.[12] In such studies, different elasticity models may be compared directly, without the added complication of describing polymer/solvent mixing effects. (Deformational studies are typically conducted at constant volume.) In addition, mechanical measurements would allow for determination of an *effective* cross-link density for the networks under study. Due to the lack of such information, we have used the nominal gel composition for estimating this property.

Computer simulations of networks[43] may ultimately resolve questions regarding network structure/property relationships by providing "experimental" data for networks in which the structure is known exactly. However, for current applications of polyacrylamide hydrogels (of heterogeneous and ill-defined structure), we require additional experimental effort to obtain a quantitative swelling model valid for a wide range of gel and solution parameters.

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Registry No. (AAm)(MAPTAC)(BIS) (copolymer), 98587-56-5; (AAm)(BIS) (copolymer), 25034-58-6; NaCl, 7647-14-5.

Density and Concentration Fluctuations in Plasticized Poly(cyclohexyl methacrylate)

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ABSTRACT: Polarized photon-correlation functions of high molecular weight plasticized PCHMA samples have been studied in the temperature range from near T_g to T_g + 150 K. The time-correlation function can measure both the density fluctuations caused by primary segmental relaxation and concentration fluctuations due to cooperative diffusion. It is the first time in a dynamic light-scattering experiment that both concentration and density correlation functions have been observed within the time window of the technique at the same temperature for a range of temperatures. The average primary relaxation times exhibit a strong temperature dependence with activation parameters experimentally the same for all plasticizer (DOP) concentrations. On the contrary, the activation parameters for the slow relaxation process were found to decrease with increasing DOP concentration. The coupling model, which is applicable to both segmental relaxation and cooperative diffusion, can explain this difference together with all accessorial features of the present experimental data.

Introduction

Photon-correlation spectroscopy (PCS) has been extensively utilized to study diffusion constants in polymer solutions and local relaxation processes in bulk amorphous polymers near and above T_g and only recently in the glassy state.[1] The dynamics of density and concentration fluctuations were studied by PCS for the first time in polydisperse poly(phenylmethylsiloxane) (PPMS).[2] The fast primary relaxation associated with the density fluctuations and the much slower q^2-dependent (with q^{-1} being the probing wavelength) diffusional mode were found to display vastly different temperature and pressure dependence.[3] This difference could be accounted for by the coupling model of relaxation.[4] However, the time-correlation functions for the fast density and slow concentration fluctuations in that system were recorded at different not overlapping temperature and pressure ranges, as their separation exceeds the time range accessible in present day digital correlators.

In this paper, we report PCS measurements of the density and concentration time-correlation functions for three plasticized PCHMA samples in the temperature range from near T_g to T_g + 150 K. The additive used was dioctyl phthalate (DOP) (actually bis(2-ethylhexyl) phthalate) with concentrations 5, 10, and 15 wt %. For the present system both relaxation processes fall within the correlator time regime (10–10^{-6} s) for temperatures between 90 and 125 °C. It is the first time in a dynamic light-scattering experiment that both concentration and density correlation functions have been observed within the time window of the technique at the same temperature for a range of temperatures.[25] This observation is not easily accomplished because of difficulties in the choice of systems that have significant contributions to light scattering from concentration fluctuations and also not too large a separation in the time scales of the relaxation times so that concentration and density fluctuations can be fitted into the experimentally accessible time window.

On the theoretical side, the coupling model, which is valid for considerations of both the density fluctuations caused by primary segmental relaxation and concentration fluctuations due to cooperative diffusion (also the terminal region for shear viscoelasticity),[5] has already been applied to explain the occurrence of two different temperature dependences of the corresponding relaxation times.[4] Although one may rationalize this difference by other means, it will be shown that the coupling model can explain this difference together with all accessorial features of the present experimental data.

Experimental Section

The time-correlation functions $G(q,t)$ of the polarized light scattered intensity at different temperatures (338–483 K) were measured at scattering angles of θ = 45, 90, and 150°. The light source was an argon ion laser (Spectra Physics 2020) operating

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