Osmotic and SANS Observations on Sodium Polyacrylate Hydrogels in Physiological Salt Solutions

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ABSTRACT: The volume transition induced by the addition of calcium into lightly cross-linked fully neutralized sodium polyacrylate hydrogels, swollen in 40 mM NaCl solutions, is investigated by osmotic swelling pressure and small-angle neutron scattering (SANS) measurements. In this reversible transition, the polymer volume fraction φ changes by more than an order of magnitude. The longitudinal osmotic modulus M_{os} deduced from macroscopic measurements shows an abrupt increase at the transition. The intensity of the scattered radiation can be decomposed into a static and a dynamic component. The former exhibits Porod scattering behavior, while the latter obeys an Ornstein−Zernike relation. The observed intensity of the dynamic part has a maximum at the transition and exhibits a functional dependence on the calcium concentration, which is similar to that of the osmotic susceptibility φ^2/M_{os}, determined from direct osmotic measurements.

Introduction

Until recently, the majority of investigations into polyelectrolyte networks has been devoted to weakly charged systems in which the characteristic length scales, and therefore the overall physical properties, are governed by the degree of ionization.[1−4] Less attention has been paid to fully neutralized gels, in which the ionic interactions in the backbone are negligible. Understanding the behavior of polyelectrolyte gels in salt solutions is likely to provide insight into the mechanisms of certain biological processes such as nerve excitation, muscle contraction, and cell locomotion. Tasaki[5−7] has shown that synthetic polyanionic gels (e.g., polysulfonic acid gels, poly(methacrylic acid) gels, poly(acrylic acid) gels) exhibit discontinuous volume changes at physiological conditions by using a biologically plausible mechanism of monovalent−divalent cation exchange.

In this paper we investigate the variation in the osmotic properties of fully neutralized polyacrylate gels swollen in sodium chloride solutions using experimental techniques that explore different characteristic length scales. The volume transition in these gels is induced by addition of calcium chloride to the surrounding liquid. If calcium chloride is added to a gel swollen in pure water, an immediate volumetric contraction is observed. When, however, the gel is first swollen in solutions of alkali metal salts, introduction of calcium causes first a gradual reduction in volume, followed by an abrupt contraction. In the particular case of a fully neutralized sodium polyacrylate gel swollen in a 40 mM NaCl solution, this transition occurs at a $CaCl_2$ concentration of about 1 mM in the surrounding liquid which is in a physiological range. The transition is reversible.[8]

The aim of the present work is to gain better insight into the nature of this transition, using macroscopic osmotic swelling pressure measurements along with small-angle neutron scattering (SANS). The specific aspects we address are the following: How can the volume transition be described in terms of macroscopic variables? How do the longitudinal osmotic modulus M_{os}, the scattering intensity $I(q)$, and the polymer−polymer correlation length ξ depend on calcium concentration? Are the macroscopic results consistent with those obtained from scattering measurements? These questions have not been investigated previously in relation to transitions induced by ion exchange in polyelectrolyte gels.

Theoretical Considerations

Osmotic Properties of Gels. Swelling equilibrium is attained when the swelling pressure of the gel, ω is equal to zero, where[9,10]

$$\omega = \Pi_{mix} + \Pi_{ion} - G \qquad (1)$$

Here, Π_{mix} and Π_{ion} are the mixing and ionic contributions to the osmotic swelling pressure, and G is the shear elastic modulus.

For networks made of flexible chains the elastic modulus is obtained from the theory of rubber elasticity[10]

$$G = G_0 \varphi^{1/3} \qquad (2)$$

where G_0 is a constant and φ is the volume fraction of the polymer.

The osmotic pressure, Π_{mix}, due to the mixing of network chains and solvent molecules can be expressed as[9]

$$\Pi_{mix} = -(RT/v_1)[\ln(1 - \varphi) + \varphi + \chi\varphi^2] \qquad (3)$$

where v_1 is the molar volume of the solvent, R is the gas constant, T is the absolute temperature, and χ is

the Flory−Huggins interaction parameter. Usually χ depends on polymer concentration, i.e., $\chi = \chi_0 + \chi_1\varphi + \ldots$.

Various theoretical models describe the ionic contribution, Π_{ion}, to network swelling pressure.[11-13] In general, the effect of the counterions is governed by the structure and composition (e.g., ionic strength, degree of ionization) of the system. In gels swollen in a salt solution, the short-range polymer−solvent interactions dominate the long-range repulsive electrostatic forces. Beyond a threshold salt concentration and ionization degree, the ions condense on the polymer chain, and Π_{ion} no longer contributes directly to the measured osmotic pressure.[11] In the neutralized poly(acrylic acid) system investigated here, the salt concentration lies well beyond this critical value, i.e.

$$\omega = \Pi_{mix} - G \tag{4}$$

Thus, the longitudinal osmotic modulus governing the scattering properties of the gel is then given by[14]

$$M_{os} = \varphi \ \partial\omega/\partial\varphi + {}^4\!/_3 G$$

$$= \varphi^2(RT/v_1)\{1/(1 - \varphi) - 2\chi_0 - 3\chi_1\varphi\} + G_0\varphi^{1/3} \tag{5}$$

SANS in Polymer Gels. For gels composed of flexible polymer coils the scattering intensity can be described by a sum of dynamic and static components[15-19]

$$I(q) = I_{dyn}(q) + I_{stat}(q)$$

$$= \Delta\rho^2\left[\frac{kT\varphi^2}{M_{os}}\frac{1}{1 + q^2\xi^2} + \frac{A}{(1 + q^2\Xi^2)^2}\right] \tag{6}$$

where $\Delta\rho^2$ is the contrast factor between the solvent and the polymer, k is the Boltzmann constant, A is a factor describing the amplitude of the static concentration fluctuations, and ξ and Ξ are respectively the dynamic and static correlation lengths. The amplitude of the scattering vector q is given by

$$q = (4\pi/\lambda) \sin(\theta/2) \tag{7}$$

where λ is the wavelength of the incident neutrons and θ is the scattering angle.

The Ornstein−Zernike expression (first term) in eq 6 corresponds to the thermal fluctuations in a semidilute polymer solution, where ξ is the mean distance between contact points.[20] The second term describes static concentration fluctuations, such as elastic constraints frozen-in by the cross-links or other structural features present in a particular gel. In many gels several correlation lengths may be necessary to describe the static scattering response.[21,22]

In systems undergoing a phase transition it is expected that the thermodynamic changes will be manifested in the first term of eq 6, through modifications both in M_{os}, i.e., in the amplitude of the dynamic scattering intensity, and in the correlation length ξ. At the transition point the osmotic pressure weakens, and correspondingly, ξ is expected to display a maximum.[20] Changes in the second term of eq 6, however, mainly reflect the redistribution of the polymer within the gel at large length scales.

Experimental Methods

Gel Preparation. The preparation of poly(acrylic acid) gels has been described previously.[8] The samples were synthesized
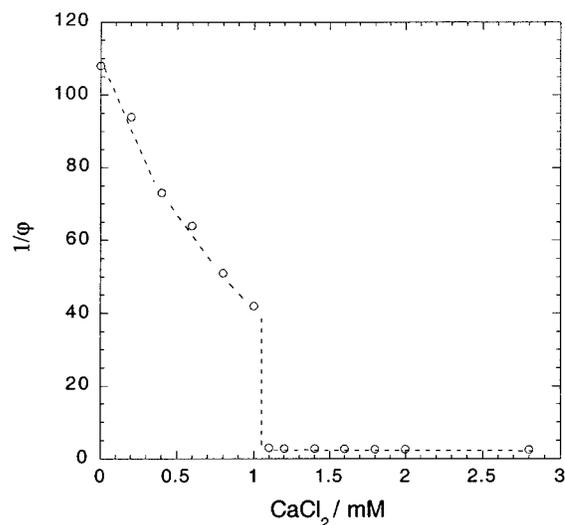
Figure 1. Variation of the equilibrium swelling ratio of sodium polyacrylate hydrogel in 40 mM NaCl with CaCl$_2$ concentration (ref 8).

by free-radical copolymerization of partially neutralized acrylic acid and N,N-methylenebis(acrylamide) in aqueous solution following the procedure described by Sugitani et al.[23] The monomer concentration at cross-linking was 30% (w/w). Ammonium persulfate was used as an initiator. After gelation the samples were fully neutralized, washed in deionized water, and then swollen in salt solution.

Osmotic and Mechanical Measurements. Gels were equilibrated with poly(vinylpyrrolidone) solutions (molecular weight: 29 kDa) of known osmotic pressure.[24,25] A semipermeable membrane was used to prevent penetration of the polymer into the network. When equilibrium was reached, the concentration of both phases was measured. This procedure gives for each gel the dependence of ω upon the polymer volume fraction, φ.

The shear modulus of the gels was determined using a TA.XT2I HR texture analyzer (Stable Micro Systems, UK). The measurements were performed under uniaxial compression on cylindrical specimens in equilibrium with the salt solutions at deformation ratios $0.7 < \Lambda < 1$. The shear modulus, G, was calculated from the nominal stress, σ (force per unit undeformed cross section), using the relation[10]

$$\sigma = G(\Lambda - \Lambda^{-2}) \tag{8}$$

The absence of volume change and barrel distortion during these measurements was verified.

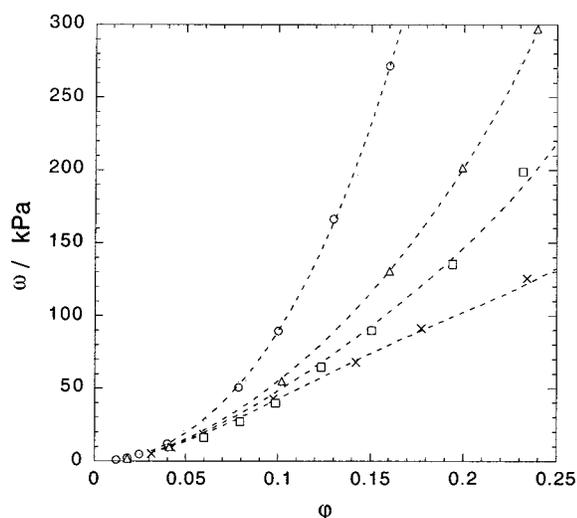Both the swelling and mechanical measurements were carried out at 25 ± 0.1 °C.

Small-Angle Neutron Scattering Measurements. The SANS measurements were performed at the National Institute of Standards and Technology (NIST), Gaithersburg, MD, on the NG3 instrument with incident wavelength of 8 Å. The sample−detector distances used were 3 and 13.1 m, corresponding to an explored wave vector range 0.003 Å$^{-1} \leq q \leq 0.15$ Å^{-1}. The ambient temperature during the experiments was 25 ± 0.1 °C. The gel samples were prepared in solutions of heavy water. Standard 2 mm NIST sample cells were employed. After radial averaging, corrections for incoherent background, detector response, and cell window scattering were applied. The neutron scattering intensities were calibrated using the absolute intensity standards available at NIST.[26]

Results and Discussion

Figure 1 shows a typical example of the variation of the gel swelling degree as a function of calcium concentration in the external liquid. Calcium chloride was added to the solvent surrounding each specimen, which
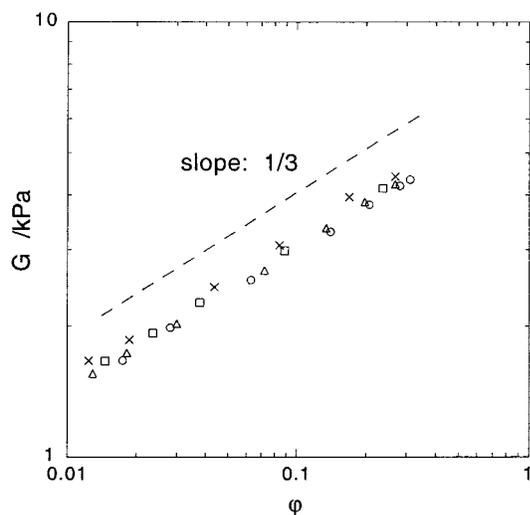
Figure 2. Measured values of the shear modulus G as a function of polymer volume fraction φ in 40 mM NaCl solutions containing different amounts of $CaCl_2$ (○, 0 mM $CaCl_2$; △, 0.2 mM $CaCl_2$; □, 0.5 mM $CaCl_2$; ×, 0.8 mM $CaCl_2$).

Figure 4. Plots showing the variation of χ_0 and χ_1 as a function of $CaCl_2$ concentration. The arrows indicate the corresponding values in 40 mM NaCl solution without $CaCl_2$.
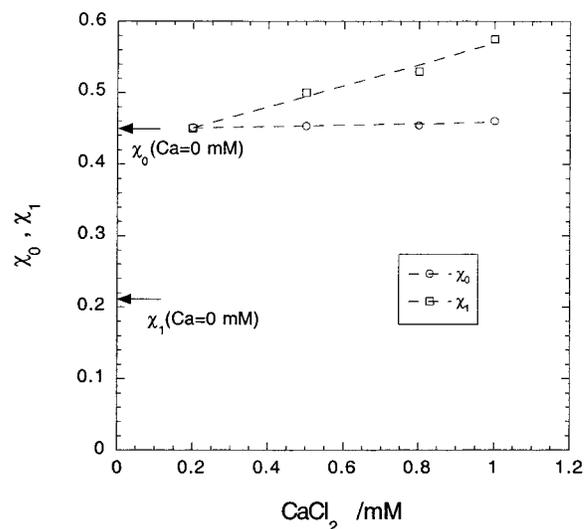

Figure 3. Dependence of the swelling pressure ω on the polymer volume fraction φ in 40 mM NaCl solutions containing different amounts of $CaCl_2$ (○, 0 mM $CaCl_2$; △, 0.2 mM $CaCl_2$; □, 0.5 mM $CaCl_2$; ×, 0.8 mM $CaCl_2$).

Figure 5. Dependence on $CaCl_2$ concentration of the longitudinal osmotic modulus M_{os} calculated from eq 5.
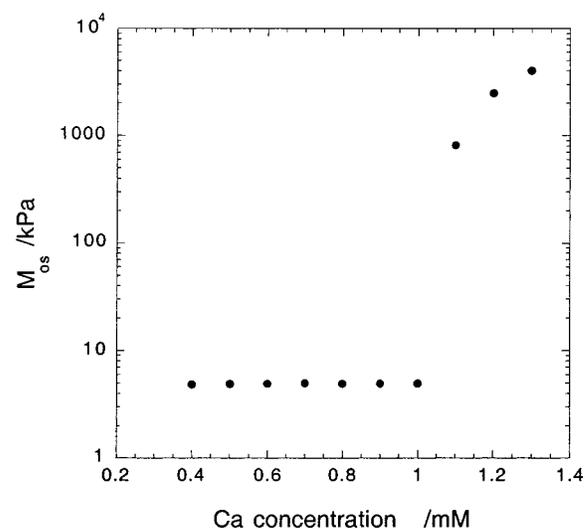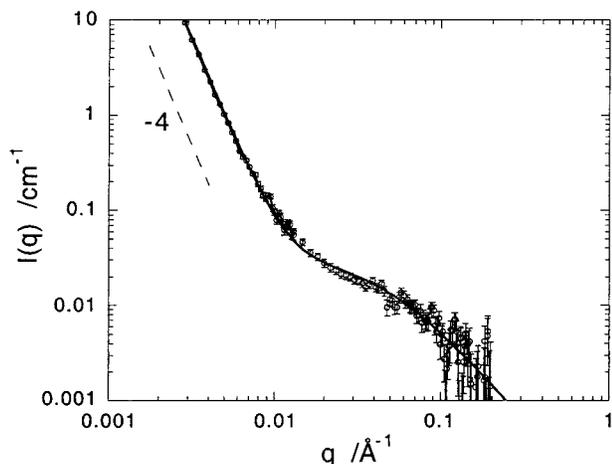
had been previously allowed to swell in a 40 mM NaCl solution. At low calcium concentrations the network volume gradually decreases, while at approximately 1 mM a sharp contraction of the specimen is observed. Although similar volume transitions have been reported for several different hydrogels containing charged acrylic monomers,[1,27,28] the nature of this transition is not clearly understood.

The variation of the shear modulus as a function of the polymer volume fraction φ is shown in Figure 2. In the double-logarithmic representation all data points fall on a straight line, the slope of which is close to $^1/_3$, as predicted by eq 2. This result implies that in the swollen state the calcium ions make no significant contribution to the effective cross-link density: the static elastic properties of these gels are thus primarily governed by the density of the chemical cross-links and the concentration of polymer.

Figure 3 shows the swelling pressure as a function of the polymer volume fraction for a sodium polyacrylate gel in solutions containing both sodium chloride and
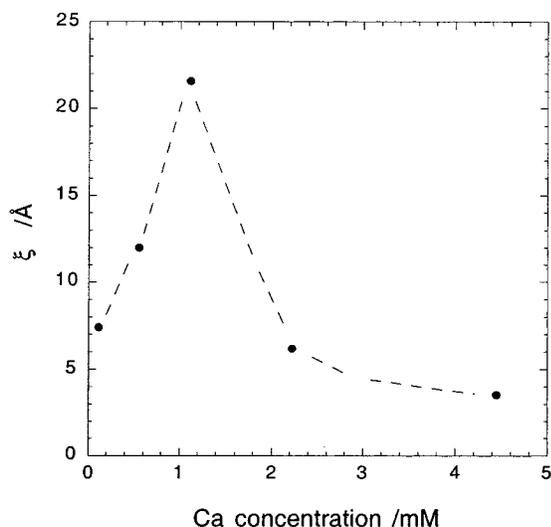
calcium chloride. These measurements were confined to the homogeneous region to the left of the transition in Figure 1. The continuous lines through the experimental points are the least-squares fits to eq 4 in which the fitting parameters χ_0 and χ_1 are allowed to vary. As shown in Figure 4, the addition of calcium causes an initial jump in the value of χ_1 and thereafter a slow increase, while the χ_0 displays a continuous, albeit weak, increase over the entire concentration range explored. The point at highest calcium concentration in Figure 4 is obtained by extrapolation, assuming that both χ_0 and χ_1 are continuous throughout the transition region.

The experimentally determined concentration dependence of χ_0 and χ_1 allows us to evaluate the polymer volume fraction at equilibrium swelling φ_0 as a function of the calcium concentration. Hence, the variation of the longitudinal osmotic modulus $M_{os}(\varphi_0)$ can be calculated from eq 5. The results, shown in Figure 5, indicate an abrupt change close to the calcium concentration at which the volume transition is observed.

Figure 6 shows the neutron scattering spectrum of the gel just above the transition. In all cases a strong signal is observed at small values of q. The observed

Figure 6. SANS intensity from sodium polyacrylate hydrogel in 40 mM NaCl solution containing 1.1 mM CaCl$_2$. Note at low values of q the intensity varies nearly as q^{-4}, characteristic of scattering from a surface (see text).
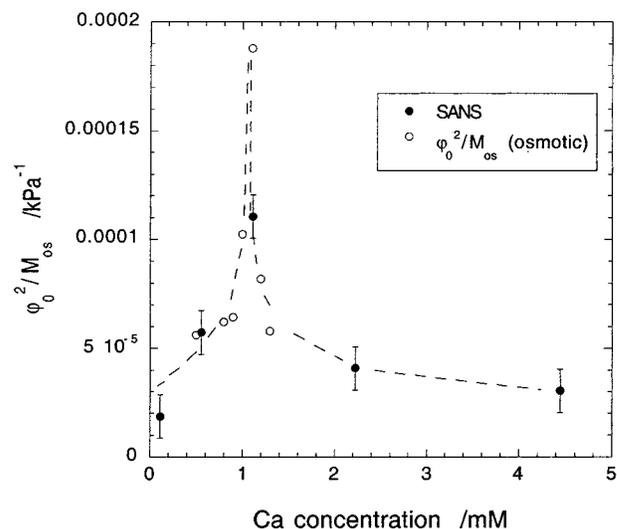

Figure 7. Variation of the thermal correlation length obtained from the dynamic component in eq 6.

Figure 8. Comparison between the osmotic susceptibility φ^2/M_{os} determined from the macroscopic measurements (open circles) and the amplitude of the dynamic contribution of the SANS spectrum (filled circles). The latter data have been multiplied by the factor 3.8×10^{-3}.

SANS (filled circles). The agreement between these results indicates that the effective molecular interactions that govern the volume transition are independent of the length scale of the observations; i.e., the large structures detected in the SANS experiment do not affect the thermodynamic properties of the gel.

Conclusions

The volume transition induced by monovalent−divalent cation exchange in sodium polyacrylate gels has been investigated by both osmotic and neutron scattering techniques. The macroscopic change in gel volume can be satisfactorily described by assuming a continuous variation in the interaction term through the transition region. The longitudinal osmotic modulus M_{os} exhibits an abrupt increase at the transition.

In this process, it is conceivable that calcium ions act as a cross-linker between neighboring chains. Such an increase in cross-link density would reduce the equilibrium swelling degree. The results of the measurements of the equilibrium shear modulus, however, demonstrate that G is governed by the polymer volume fraction and, within experimental error, varies according to the prediction of classical rubber elasticity theory. Moreover, as the value of the shear modulus is small, its contribution to M_{os} in the transition region is negligible. M_{os} displays a stepwise increase at the transition.

The neutron scattering response of these gels exhibits both a static and a dynamic component. The former shows Porod scattering behavior, characteristic of smooth interfaces. The latter displays an Ornstein−Zernike line shape from which the thermal correlation length of the gel can be deduced. Both the dynamic component of the scattering intensity and the corresponding correlation length exhibit a maximum at the transition. In addition, the dependence upon calcium concentration of the intensity scattered by the thermal fluctuations closely follows that of φ^2/M_{os} calculated from macroscopic observations.

slope in this region is close to -4, which is the asymptotic limit of the second term in eq 6 when $q\Xi \gg 1$. This feature characteristic of Porod scattering[29] is caused by smooth interfaces such as can occur in starlike structures.[30]

The plateau region at higher q implies that the gel is homogeneous on the corresponding length scale and exhibits solution-like properties described by the first term of eq 6: the continuous line through the neutron data points is the least-squares fit to eq 6 in the condition $q\Xi \gg 1$. For these samples we conclude therefore that a single static term together with a solution-like term satisfactorily describe the neutron scattering signal. The dependence of the thermal correlation length ξ on the calcium concentration is shown in Figure 7. As expected, this parameter displays a maximum in the vicinity of the transition.

According to eq 6, the intensity scattered by thermal fluctuations is proportional to φ^2/M_{os}. This quantity can be calculated independently from macroscopic measurements using eq 5. Figure 8 compares the dependence upon the calcium concentration of φ^2/M_{os}, calculated from macroscopic measurement (open circles) with the intensity of dynamic scattering component measured by

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