

Experimental evidence for two thermodynamic length scales in neutralized polyacrylate gels

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The small angle neutron scattering (SANS) behavior of fully neutralized sodium polyacrylate gels is investigated in the presence of calcium ions. Analysis of the SANS response reveals the existence of three characteristic length scales, two of which are of thermodynamic origin, while the third length is associated with the frozen-in structural inhomogeneities. This latter contribution exhibits power law behavior with a slope of about -3.6 , reflecting the presence of interfaces. The osmotically active component of the scattering signal is defined by two characteristic length scales, a correlation length ξ and a persistence length L . © 2002 American Institute of Physics.
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INTRODUCTION

Recently there has been an increased interest in the properties and the underlying structural features of both synthetic and natural polyelectrolyte systems. The majority of previous studies have been directed to the understanding of the physics of weakly-charged polyelectrolytes in pure water or in the presence of monovalent ions.^{1–3} Few investigations have been devoted to neutralized polyelectrolyte solutions^{4,5} and gels containing multivalent ions.⁶ Such systems are of great significance, both theoretically and practically, e.g., in ion exchange resins and also in biological processes where, under physiological conditions, ion exchange plays a central role, e.g., in nerve excitation or in muscle contraction.^{1,7,8}

It has previously been found that the addition of multivalent cations to sodium polyacrylate gels is accompanied by a discrete volume transition, in which the solvent content of the gel at equilibrium undergoes an abrupt change.^{6–8} This transition, which occurs when the majority of the sodium counterions are replaced by calcium ions, is reversible. Such reversibility implies that the calcium ions are not strongly localized on the polyanion but rather form equilibrium dynamic associations. The greater electric charge associated with higher valence counterions increases the attractive interaction and modifies the counterion cloud. Addition of multivalent ions to polyelectrolytes may affect the electrostatic interactions between the charged groups and, in the case of strong binding, may also form bridges between neighboring

polymer chains. Furthermore, all these changes may modify the mixing pressure. It has been previously found, however, that addition of calcium ions to sodium polyacrylate gels swollen in sodium chloride solutions does not affect the equilibrium elastic modulus of the system and that the transition is reversible.⁹ Moreover, small angle neutron scattering (SANS) measurements indicate that there are significant structural differences between this neutralized polyelectrolyte gel and an analogous neutral counterpart, namely polyacrylamide.¹⁰

Simple binary solutions of neutral polymer consist of a polymer component and a low molecular weight solvent. The osmotic pressure of a semidilute polymer solution¹¹ is characterized by a correlation length ξ that can be measured by small angle scattering techniques. In the case of random thermal concentration fluctuations, this scattering response is given by an Ornstein–Zernike lineshape,¹¹

$$I_{\text{os}}(q) = \Delta\rho^2 \frac{kT\varphi^2}{\varphi \partial\Pi/\partial\varphi} \frac{1}{(1+q^2\xi^2)}, \quad (1)$$

where q is the transfer wave vector, $\Delta\rho^2$ is the contrast factor¹² between polymer and solvent, k is the Boltzmann constant, T is the absolute temperature, Π is the osmotic pressure of the system, while φ is the polymer volume fraction. The correlation length ξ defines the average spatial extent of the thermal concentration fluctuations and is the result of short-range van der Waals interactions.

In neutral gels, an analogous osmotic component is present but, to take account of the finite elastic modulus, G , the denominator $\varphi\partial\Pi/\partial\varphi$ in Eq. (1) must be replaced by the longitudinal osmotic modulus,¹³ $M_{os}(=\varphi\partial\Pi/\partial\varphi+4G/3)$. Moreover, in such gels, as well as in many polymer solutions, structural inhomogeneities, resulting either from crosslinking or from molecular associations, are observed, the characteristic size of which is generally much larger than the length scale ξ defining the osmotic properties. Owing to their size (and, in the case of gels, their fixed nature), these large objects make no significant contribution to the thermodynamics in spite of the fact that they contribute strongly to the scattering spectrum. Thus, in the case of neutral gels,^{14,15} it is generally found that the SANS intensity can be described by a function containing both an osmotic and a crosslinking contribution,

$$I(q)=I_{os}(q)+I_x(q). \quad (2)$$

The second term in Eq. (2) arises from concentration fluctuations frozen-in by the crosslinks and therefore depends upon the mechanism of the crosslinking process and on the particular polymer gel investigated.

In polyelectrolyte systems, on the other hand, the most important difference from neutral polymers is the existence of longer range forces due to partially shielded electrostatic interactions. These forces, which may also include electric dipolar and quadrupolar interactions, coexist simultaneously with the short-range van der Waals forces. Recent neutron scattering measurements¹⁶ performed on semidilute poly(styrene sulfonate) solutions at larger ionic strength indicate that replacement of condensed monovalent ions by multivalent ions modifies the local conformation of the polymer chains. The experimental observations do not appear to be in agreement with the existing models.

It is reasonable to assume that osmotically relevant contributions are also modified due to varying the interactions between the components (polyion, counterions, added salt ions, solvent molecules). It is therefore expected that the local structure of a polyelectrolyte requires more than one length scale to describe its osmotic properties. None of the previous works has addressed the effect of structural changes induced by multivalent ions on the osmotic scattering response of polyelectrolyte gels.

The aim of this study is to identify the characteristic length scales of the different structural elements that define sodium polyacrylate gels in the course of the volume transition that accompanies the sodium–calcium ion exchange process. A comparison is made between the osmotic scattering response of these gels determined by small-angle neutron scattering and the results of direct osmotic swelling pressure measurements.

EXPERIMENTAL SECTION

Sodium polyacrylate gels were synthesized by free-radical copolymerization from their respective monomers and the crosslinker N,N' -methylenebis(acrylamide) in aqueous solution as described previously.⁹ The crosslink concentration was 0.3% by weight. The acrylic acid units were first neutralized in NaOH and equilibrated with aqueous solutions

of 40 mM NaCl. This salt concentration is well above that required to satisfy the Manning condensation condition. The concentration of CaCl₂ in the surrounding solution was then increased gradually up to 2.0 mM CaCl₂. At CaCl₂ concentrations higher than 1 mM a volume transition occurs in this system, probably due to associations induced by the Ca²⁺ ions.⁹

Osmotic swelling pressure measurements were made by enclosing the gel sample in a dialysis membrane and allowing swelling equilibrium to be established in a polymer solution of known osmotic pressure.^{17,18}

The shear modulus was determined from uniaxial compression measurements performed on cylindrical gel specimens using a TA.XT21 HR texture analyzer (Stable Micro Systems, UK).⁹

The SANS measurements were made on the D22 instrument at the Institut Laue Langevin, Grenoble with an incident wavelength of 8 Å and sample detector distances 17, 6, and 3m. Dry sodium polyacrylate network samples were swollen in 40 mM NaCl/D₂O solution, and then varying amounts of CaCl₂ (in D₂O) were added. The amount of solution used was adjusted so that the final polymer concentration for the gels below the transition was 0.05 gcm⁻³. Above the volume transition, however, the resulting polymer concentration of the gels was higher, owing to their limited swelling ability in the presence of calcium. The gel specimens were cut to fit into the circular sample holders.

RESULTS AND DISCUSSION

In a homogeneous polyelectrolyte solution,¹⁹ the osmotic pressure Π is usually taken to consist of two terms. The contribution of the counterions, Π_c , is proportional to the charge density φ/A (where A is the number of monomers between effective charges on the polymer and φ is the polymer concentration) and the polymer contribution Π_p , which scales like a neutral polymer solution. Thus,

$$\Pi/kT = \phi/A + 1/\xi^3, \quad (3)$$

where ξ is the correlation length between charged polymer subunits. The long-range interactions may be expected to lead to a different concentration dependence of ξ from that in neutral polymer solutions.¹¹

In order to determine the relative importance of the two terms in Eq. (3), the osmotic pressure of the sodium polyacrylate gels investigated here was determined as a function of polymer concentration, at three different calcium concentrations below the volume transition (Fig. 1). In the double logarithmic representation each of these curves is linear over the whole concentration range explored ($0.02 \leq \varphi \leq 0.2$), with slopes ranging from 1.5 to 1.8, indicating that for these gels the first term in Eq. (3) is negligible. Moreover, the decrease in power law exponent on approaching the volume transition is contrary to what is expected for a neutral gel when a phase separation is induced by decreasing the solvent quality. In the latter case, the value of the exponent increases from 2.25 (strong excluded volume condition) to 3 (theta condition).¹¹ The present results thus imply that the thermodynamic properties involve another length scale in addition to that mediated by van der Waals interactions.

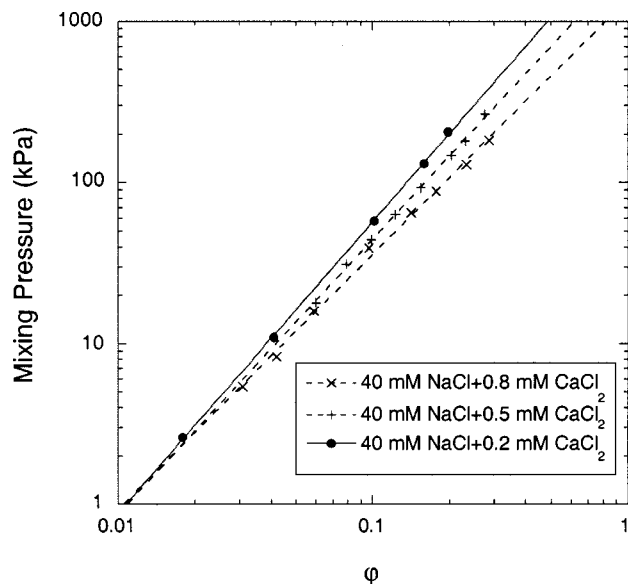


FIG. 1. Mixing pressure of polyacrylic hydrogels as a function of polymer volume fraction ϕ , in solutions containing 40 mM NaCl and different amounts of CaCl_2 . The slopes of the straight lines through the experimental data points are 1.81 (0.2 mM CaCl_2 : ●), 1.71 (0.5 mM CaCl_2 : +) and 1.59 (0.8 mM CaCl_2 : ×).

Figure 2 shows the scattering response for a polyacrylate gel slightly below the volume transition (0.85 mM CaCl_2). In this gel volume transition occurs at 1.0 mM CaCl_2 concentration.⁹ In this figure, for small values of q ($< 8 \times 10^{-3} \text{ \AA}^{-1}$) power law behavior can be seen with a slope $n = -3.6$, followed by a quasilinear region ($0.02 < q < 0.08 \text{ \AA}^{-1}$) and finally a shoulder at about 0.1 \AA^{-1} . The

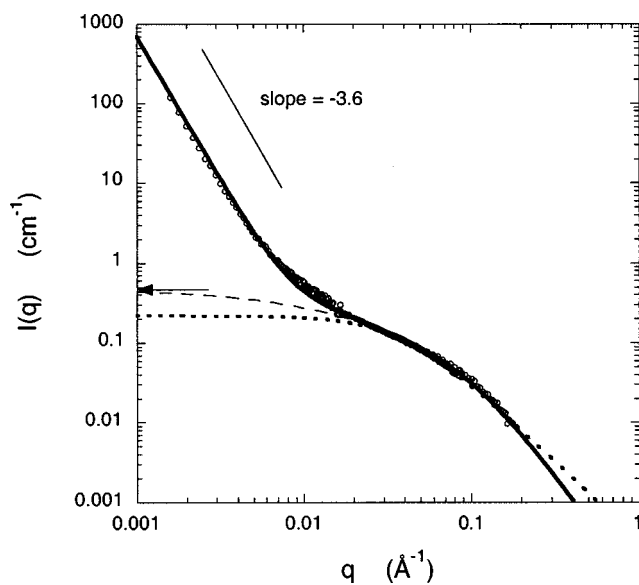


FIG. 2. SANS spectrum of a sodium polyacrylate hydrogel close to the volume transition at 0.85 mM CaCl_2 . Dotted line is the osmotic component [Eq. (1)] of the least squares fit of the data to Eq. (2). Continuous line is the least squares fit of Eq. (2) to the data, in which the osmotic component is replaced by Eq. (5), and M_{os} is calculated from the macroscopic swelling pressure and shear modulus measurements. Dashed line is the osmotic component [Eq. (5)] of this fit (the horizontal arrow indicates the numerical value of the intensity deduced from the macroscopic observations, using the neutron scattering contrast factor).

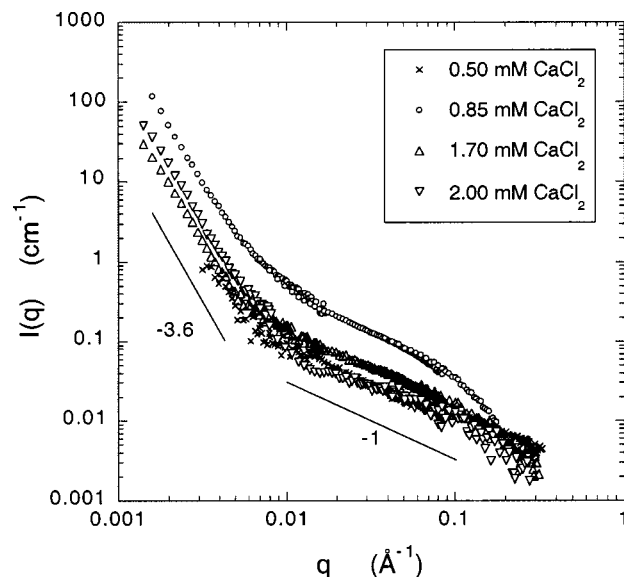


FIG. 3. Plot of SANS spectra for sodium polyacrylate gels in 40 mM NaCl containing various amounts of calcium indicated in box. Polymer concentration of the gels (in g cm^{-3}): × 0.05, ○ 0.05, △ 0.12, ▽ 0.15. The straight lines indicate slopes of -3.6 and -1 , respectively.

slope of the intensity increase at low q is characteristic of scattering from surfaces.^{20–22} The size of these objects exceeds 1000 \AA but, in the absence of any low- q plateau, no value can be attributed to this quantity. The dotted line in Fig. 2 is the osmotic term obtained from a least-squares fit to the data assuming a neutral gel system. In this fit, $I_{os}(q)$ is assumed to be the same as in Eq. (1), while $I_x(q)$ is approximated by

$$I_x(q) = Bq^{-3.6} \quad (4)$$

where B is a constant. In this figure the value of the scattering intensity at $q=0$, calculated from the measured osmotic pressure, is indicated by an arrow. It can be seen that the intensity of the osmotic term obtained from the fit of a single Lorentzian to the SANS data underestimates the osmotic contribution by a factor of approximately 2. Since the experimental error of the osmotic measurements is not more than 10% and that of the absolute intensity in the neutron measurements is better than 5%, this discrepancy confirms that the thermodynamic response of the gel is not completely described by Eq. (1), i.e., the structure factor is different from that of a neutral gel. In this fit, the value of the correlation length ξ is found to be 26 \AA .

Figure 3 shows the SANS spectra of a set of similar sodium polyacrylate gels containing different amounts of calcium. The scattering intensity increases as the transition is approached, displaying the highest intensity at 0.85 mM Ca concentration (the transition occurs at 1 mM Ca) and thereafter decreases again above the transition. This behavior is expected on the basis of the enhanced concentration fluctuations that develop around the volume transition, an effect that is much larger than that due to the increase in concentration beyond the transition. It is clear from the double logarithmic representation of Fig. 3 that the low q feature is practically independent of the CaCl_2 concentration, indicating that the

evolution in the overall structure is not directly related to the macroscopic volume transition, but is instead a continuous process. This term is the result of scattering from the surfaces of large ($>1000 \text{ \AA}$) structures (e.g., crosslink zones) formed before the volume transition.

It is also apparent that in the intermediate q -range relevant to the osmotic response all the curves display an intensity that varies approximately as q^{-1} . This behavior is characteristic of linear scattering arrays, as, for instance, may be expected from polymers that are locally stretched.²³ The simplest expression that maintains the observed features of the thermal correlation length as well as reproducing the q^{-1} dependence of the scattering intensity is that of a system described by a persistence length L . In this phenomenological approach, the osmotic scattering term becomes

$$I_{\text{os}}(q) = \Delta\rho^2(kT\varphi^2/M_{\text{os}})(1+qL)^{-1}(1+q^2\xi^2)^{-1}. \quad (5)$$

The fit of Eqs. (2), (4), and (5), in which φ^2/M_{os} is defined from the osmotic swelling measurements of Fig. 1, is shown as a heavy continuous line in Fig. 2. This fit yields 9 and 70 \AA , for ξ and L , respectively. The corresponding osmotic component in this fit, i.e., Eq. (5) is shown as a dashed line in Fig. 2.

CONCLUSIONS

The present SANS results indicate that the description of neutralized polyelectrolyte hydrogels in the presence of added salt requires at least three length scales, two of thermodynamic origin and one frozen-in. The thermodynamic properties are defined by two characteristic length scales, a persistence length L of locally stretched chains and the blob size ξ . The frozen-in inhomogeneities display power-law behavior with a slope of approximately -3.6 . This term is the result of scattering from the surfaces of large ($>1000 \text{ \AA}$) structures (e.g., crosslink zones) formed before the volume transition.

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