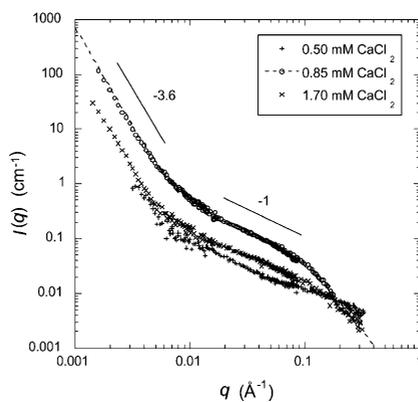**Full Paper: Calcium ions are introduced to sodium polyacrylate gels swollen in sodium chloride solutions** and the volume transition is measured by osmotic and small-angle neutron-scattering. The osmotic pressure is found to depend on the sodium chloride concentration, indicating that calcium preferentially replaces condensed sodium ions, a result supported by a Flory–Huggins analysis. At low scattering vectors q, the neutron-scattering response displays power-law behavior with a slope of approximately -3.6 (see Figure), consistent with scattering from surfaces of large objects. At larger q, a region with slope -1 is observed, characteristic of rigid linear structures.
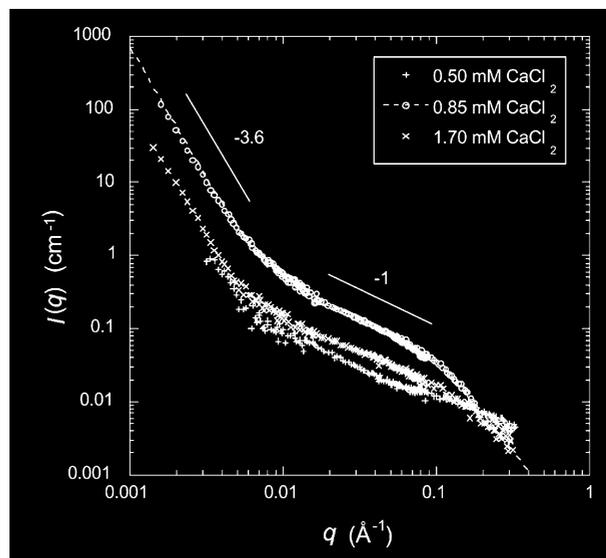

Calcium-Induced Volume Transition in Polyacrylate Hydrogels Swollen in Physiological Salt Solutions

F. Horkay,* P. J. Basser, A.-M. Hecht, E. Geissler

Full Paper: Osmotic and small-angle neutron-scattering measurements are performed to study the volume transition that occurs in sodium polyacrylate gels swollen in sodium chloride solutions when calcium ions are introduced. In the presence of calcium ions, the osmotic pressure depends sensitively on the sodium chloride concentration, indicating that calcium preferentially replaces condensed sodium ions. This substitution modifies the effective attractive interaction between polymer chains. Analysis of the osmotic data in terms of the Flory–Huggins theory reveals a sharp increase in the third-order ternary thermodynamic interaction parameter upon introduction of calcium ions. The neutron-scattering response at low scattering vectors q displays power-law behavior with a slope of approximately -3.6, consistent with scattering from surfaces of large objects. These results are in agreement with the development of dense polymer-rich regions dispersed in a soft polymer matrix. At larger q, a region with slope -1 is observed, characteristic of rigid linear structures.

Small-angle neutron-scattering spectra of polyacrylate hydrogels swollen by 40 mM sodium chloride solutions containing different amounts of $CaCl_2$ (+: 0.5 mM, ○: 0.85 mM, ×: 1.7 mM). The dashed curve shows the least squares fit of the 0.85 mM $CaCl_2$ data to Equation (5) in which the first term is replaced by Equation (8), and the second term is approximated by a simple power law.

Calcium-Induced Volume Transition in Polyacrylate Hydrogels Swollen in Physiological Salt Solutions

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Introduction

The understanding of the effect of different factors on the phase behavior of synthetic and natural polyelectrolyte gels is of great importance in a variety of different contexts, notably in explaining the mechanism of biological processes related to tissue excitation.[1,2] In addition, it is of considerable practical significance in areas such as controlled drug release, water retention and purification.[3,4] Most previous studies have been performed on weakly charged polyelectrolytes in which the local structure is governed by the hydrophobic interactions of the polymer backbone.[5–7] These structures give rise to a correlation peak, detected by small-angle neutron scattering (SANS), which depends on the ionic strength and the charge density of the polyelectrolyte. No systematic studies have been preformed on

strongly charged, fully neutralized polyelectrolyte gels under nearly physiological conditions in which scattering and thermodynamic methods are combined.

In a recent paper[8] we reported measurements on polyacrylate hydrogels swollen in aqueous solutions containing both sodium chloride and calcium chloride. It was found that increasing the calcium content induces an abrupt and reversible volume transition. It was demonstrated that the elastic modulus of these gels shows no effect of the calcium chloride concentration, being governed primarily by the polymer concentration. Furthermore, analysis of the osmotic swelling pressure in the framework of the Flory–Huggins theory indicates that the addition of calcium chloride is accompanied by a jump-like increase in the third-order interaction term, while the second-order term varies only slightly. These results clearly indicate that the transition is governed by thermodynamic effects, which could be related to changes in the electrostatic interaction due to the difference in binding strength of calcium and sodium ions. Preliminary SANS experiments[9] also indicated that these gels exhibit enhanced static concentration fluctuations at small scattering vectors, which are due to the presence of superstructures having a characteristic length scale in excess of 1000 Å. No correlation peak was observed. These features distinguish the behavior of neutralized gels from weakly charged polyelectrolytes, and neutral gels.[10–13]

The aim of the present article is to investigate the osmotic properties of a neutralized polyacrylate hydrogel swollen in sodium chloride solution as a function of the calcium content and compare these respectively with the Flory–Huggins, virial and scaling expressions. The reason that we base our approach on the standard theories of neutral polymer solutions is that polyelectrolyte theories give little guidance about the behavior of neutralized polyelectrolyte gels in the presence of added salt. Our choice of acrylic acid gel as a model system is that its chemical structure is simple and its properties have been widely studied by other authors under different ionic conditions as a function of the degree of neutralization.[5,6] In this work, moreover, SANS measurements are made on the samples to identify the characteristic length scales that govern the osmotic response.

Theoretical Considerations

Osmotic Properties of Gels

The free energy of a swollen gel can be expressed as a sum of three terms,[14] corresponding to the mixing, the elastic and the ionic contributions, respectively. Thus

$$\Delta F = \Delta F_{mix} + \Delta F_{el} + \Delta F_{ion} \tag{1}$$

The driving force for the swelling process is the mixing of the polymer chains with the solvent molecules. The contribution of the elastic term in lightly crosslinked gels can be described satisfactorily by the Gaussian theory of rubber elasticity.[14] In fully neutralized (i.e., strongly charged) polyelectrolytes in salt solutions, in which counterion condensation[15] may occur, the ionic term is not expected to play a significant role. It is, however, reasonable to assume that changes in the ionic interactions primarily modify the mixing contribution.

In neutral polymer solutions, three alternative theoretical approaches are commonly employed to estimate the osmotic pressure, $\Pi_{mix} = \partial \Delta F_{mix}/\partial n$, where n is the number of moles of solvent in the gel. ($\Pi_{mix} = \omega + G$, where ω is the swelling pressure and G is the shear modulus.)

1) The Flory–Huggins approach,[14] based on the lattice theory of solutions, expresses the mixing pressure as

$$\Pi_{mix} = -(RT/v_1)[\ln(1-\varphi) + \varphi + \chi_0\varphi^2 + \chi_1\varphi^3] \tag{2}$$

where φ is the volume fraction of the polymer, v_1 is the molar volume of the solvent, R is the gas constant, T is the absolute temperature and χ_0 and χ_1 are constants that depend on the strength of the interactions.

2) In the scaling approach,[16] which assumes that the polymer chains are a sequence of infinitely thin elements, the equivalent expression is given by

$$\Pi_{mix} = A\varphi^m \tag{3}$$

where the exponent m depends on the thermodynamic quality of the solvent and the prefactor A is a non universal constant depending on the particular polymer solvent system. In good solvent conditions, i.e., where excluded volume interactions prevail, the theoretical value of $m = 2.31$.

3) The virial theory, based on the model of hard spheres, yields the following expression

$$\Pi_{mix} = b_2\varphi^2 + b_3\varphi^3 + \ldots \tag{4}$$

where b_2 and b_3 are the second and third virial coefficients, respectively.

Small-Angle Neutron Scattering in Polymer Gels

For gels composed of flexible polymer coils the scattering intensity can be described as a sum of dynamic and static components[10–13,17–19]

$$I(q) = I_{dyn}(q) + I_{stat}(q) \tag{5}$$

in which the first term is governed by the osmotic concentration fluctuations, while the second may include a variety of structures frozen in by the crosslinks. The amplitude of the scattering vector q is given by

$$q = (4\pi/\lambda)\sin(\theta/2) \tag{6}$$

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

For neutral polymer gels, the first term in Equation (5) can be described by an Ornstein–Zernike function,[16] i.e.,

$$I_{\mathrm{dyn}}(q) = \Delta\rho^2(kT\varphi^2/M_{\mathrm{os}})/(1 + q^2\xi^2) \tag{7}$$

where $\Delta\rho^2$ is the contrast factor between polymer and solvent, M_{os} is the osmotic compression modulus, ξ is the thermal correlation length and k is the Boltzmann constant. For fully neutralized polyelectrolyte gels it is found that the osmotic fluctuations are described by[20]

$$I_{\mathrm{dyn}}(q) = \Delta\rho^2(kT\varphi^2/M_{\mathrm{os}})(1 + qL)^{-1}(1 + q^2\xi^2)^{-1} \tag{8}$$

where L is a persistence length.

In many gels, the random crosslinking process gives rise to a feature that can be described by a single Debye–Bueche expression[19,21,22] of the form

$$I_{\mathrm{star}}(q) = \Delta\rho^2\, kT\, 8\pi\Xi^3\langle\delta\varphi^2\rangle/(1 + q^2\Xi^2)^2 \tag{9}$$

where Ξ is the spatial range of the static concentration fluctuation and $\langle\delta\varphi^2\rangle$ its mean square amplitude. Systems containing star-like polymers exhibit a term similar to Equation (9), but with a different power dependence in the denominator,[23] where the exponent may vary between 3/2 and 2.7.

Experimental Part

Gel Preparation

Sodium polyacrylate gels were prepared according to a method described previously.[8] The samples were synthesized by free-radical copolymerization of partially neutralized acrylic acid and N,N'-methylenebis(acrylamide) in aqueous solution. The monomer concentration at crosslinking was 30% (wt./wt.) and ammonium persulfate was used as an initiator. After gelation the samples were fully neutralized in sodium hydroxide, washed in deionized water and then swollen in salt solution.

Osmotic and Mechanical Measurements

Gels were equilibrated with polymer solutions (polyvinyl pyrrolidone, molecular weight: 29 kDa) of known osmotic pressure.[24,25] The gels were separated from the polymer solution by a semipermeable membrane to prevent penetration of the polymer into the network. The concentration of both phases was measured when equilibrium was reached. This procedure gives for each gel the dependence of ω upon the polymer volume fraction, φ.

Prior to the osmotic measurements the polymer volume fraction in the gels was determined in aqueous solutions containing 40 mM NaCl and increasing amount of CaCl$_2$ (Figure 1).[8] It can be seen that polyacrylate gels exhibit a volume transition when CaCl$_2$ is added. In the present system the transition occurs at approximately 1 mM CaCl$_2$ concentration.

Shear modulus measurements were performed on cylindrical gel specimens prepared in a special mold.[8] Swollen
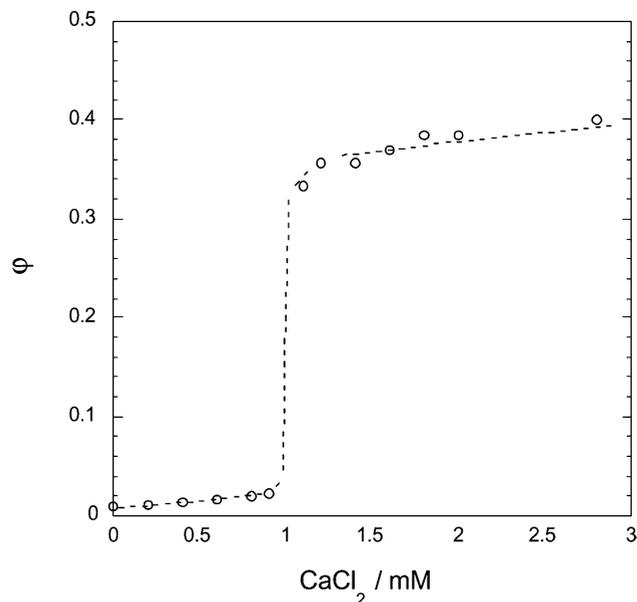

Figure 1. Variation of the polymer volume fraction in a sodium polyacrylate hydrogel swollen in 40 mM NaCl solution as a function of the CaCl$_2$ concentration in the surrounding liquid.

networks were uniaxially compressed (at constant volume) between two parallel flat plates using a TA.XT2I HR Texture Analyser (Stable Micro Systems, UK). The absence of volume change and barrel distortion was checked by determining the dimensions of the deformed and undeformed gel cylinders.

All measurements were carried out at $25 \pm 0.1\,^\circ$C.

Small-Angle Neutron-Scattering Measurements

The SANS measurements were performed at the Institut Laue Langevin, Grenoble, on the D22 instrument with incident wavelengths 8 Å and 14 Å. The sample-detector distances used were 2 m, 6 m and 17 m, corresponding to an explored wave vector range 0.001 Å$^{-1} \leq q \leq 0.32$ Å^{-1}. SANS measurements were also made on the NG3 instrument at NIST, Gaithersburg MD, using a wavelength of 8 Å. Two sample-detector distances were used, 3 m and 13.1 m, corresponding to an explored wave vector range 0.003 Å$^{-1} \leq q \leq 0.15$ Å^{-1}. The sample temperature during the experiment was maintained at $25 \pm 0.1\,^\circ$C. The gels were swollen in solutions of heavy water. After radial averaging, corrections for incoherent background, detector response and cell window scattering were applied. The neutron-scattering intensities were calibrated using water.[26]

Results and Discussion

In Figure 2 are plotted the values of Π_{mix} obtained from measurements of the swelling pressure ω and the elastic modulus G on gel samples containing 100 mM sodium chloride (a), and 100 mM sodium chloride plus different amounts of calcium chloride (b). Also shown are the fits of Equation (2)–(4) to the data from calcium-free sample and from the gel with the highest calcium content. In the
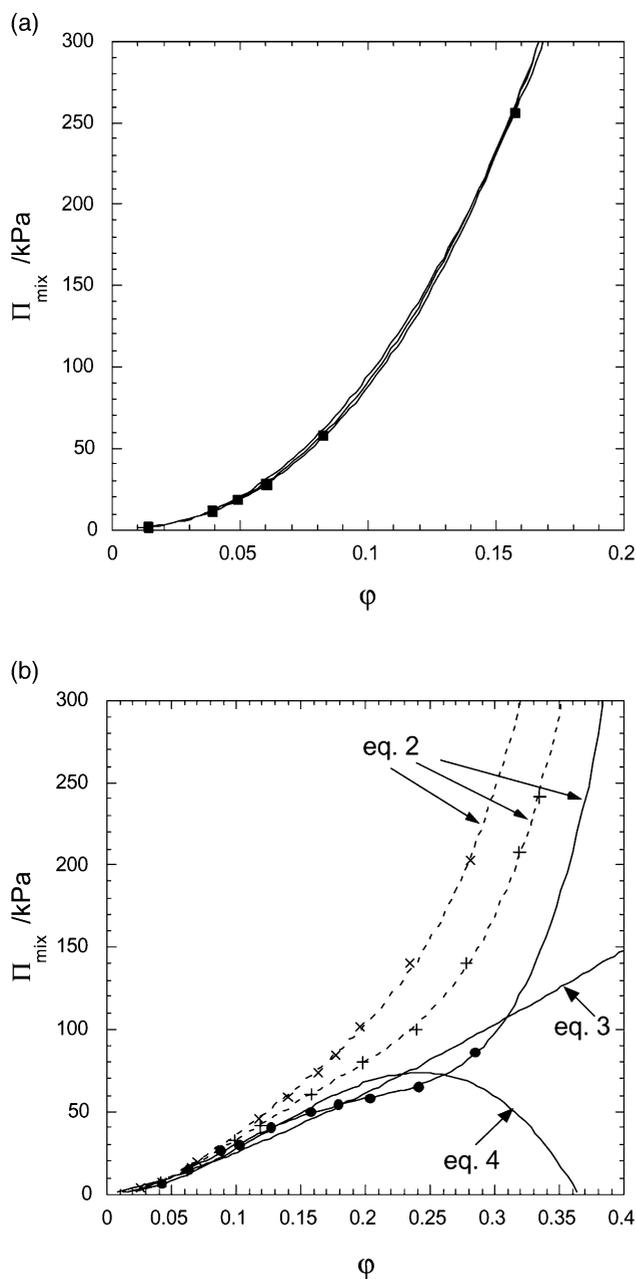
(a)

(b)

Figure 2. Mixing pressure Π_{mix} vs. polymer volume fraction φ for a polyacrylate hydrogel swollen in (a) 100 mM NaCl solution. The continuous lines show the least squares fits to Equation (2)–(4); (b) 100 mM NaCl solutions containing different amounts of $CaCl_2$ ($\times$ 0.2 mM, $+$ 0.4 mM, $\bullet$ 0.6 mM). The continuous lines show the least squares fits of the 0.6 mM $CaCl_2$ gel data to Equation (2)–(4). The dashed lines are the fits of the 0.2 mM and 0.4 mM $CaCl_2$ gel data to Equation (2).

calcium-free gel all three fits provide reasonable agreement. For the gel with calcium, however, only the Flory–Huggins expression satisfactorily describes the osmotic response over the entire range of concentration explored. The scaling formalism of Equation (3) is unable to account for a deviation from simple power-law dependence that becomes more prominent with increasing calcium content.
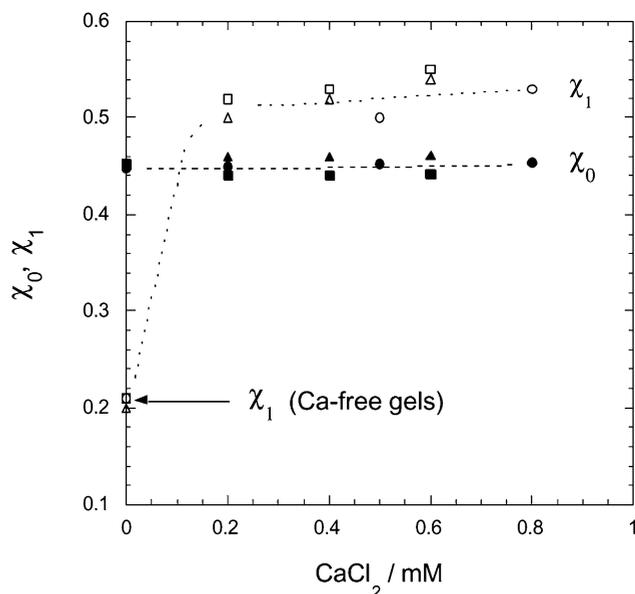

Figure 3. Values of χ_0 (filled symbols) and χ_1 (open symbols) as a function of the $CaCl_2$ concentration for polyacrylate hydrogels swollen in sodium chloride solutions (squares: 10 mM NaCl, circles: 40 mM NaCl, triangles: 100 mM NaCl).

The virial approach, on the other hand, underestimates the experimental data at higher polymer concentration where the concentration dependence of the osmotic pressure is weaker than quadratic.

Figure 3 shows the variation of the Flory interaction parameters χ_0 and χ_1 as a function of calcium content for gels swollen in solutions of sodium chloride at various concentrations. It is clear that χ_0 is virtually independent of the calcium content, while χ_1, after an initial jump, exhibits a weak, nearly linear increase with increasing calcium concentration. This behavior indicates that the main effect of the calcium ions below the transition is to increase the value of χ_1, thereby bringing the system close to the transition condition. This is consistent with previous studies[27,28] which showed that the majority of the monovalent counterions must be replaced before the volume transition occurs. The continuous increase in the interaction parameter in the Flory model leads to a volume transition that is consistent with the data shown in Figure 3.

The role of the ions in the transition on further increasing the calcium content, however, remains unclear. If the calcium ions bind strongly to the negatively charged groups of the polyanion, several consequences can be envisaged due to alteration of the structure of the polymer. One obvious effect is the change in the electrostatic screening between the residual charged groups. It is expected that replacement of monovalent by divalent ions induces a redistribution of the charges in the ion cloud and reduces the number of osmotically effective counterions and may also modify the effective charge of the polymer. In addition, at high overall polymer concentration strong ion binding may result in the

formation of bridges between different polymer chains. Clearly, these effects are not independent; for example, strong ion binding implies a chemical change that modifies the polymer–solvent interaction.

In the ion concentration regime explored the counter-ions are condensed, since the distance between charged groups on the polymer backbone ($d = 2.5$Å) is smaller than the Bjerrum length (7.1 Å).

Although the assumptions of the Debye–Hückel theory are not valid for polyelectrolyte solutions, it may yield a qualitative estimate of the effect of calcium ions on the interaction range of charged groups. The Debye–Hückel screening length is given as

$$\frac{1}{\kappa} = \left[\frac{\varepsilon_r \varepsilon_o kT}{\sum_i \left(z_i e \right)^2 c_i} \right]^{1/2} \tag{10}$$

where ε_o and ε_r are the dielectric permittivity of free space and the dielectric constant of water, respectively, z_i is the ion valence of the ionic species i at concentration c_i, and e is the electron charge. Equation (10) predicts for the value of $1/\kappa \approx 15$ Å for the 40 mM sodium chloride solution. When calcium chloride is added, this value falls to ca. 5 Å close to the volume transition (assuming that no strong binding occurs). Even in the latter case the Debye–Hückel length exceeds that of the distance of charge separation, and consequently electrostatic effects cannot be ignored. Above the transition, however, the ion concentration is such that $1/\kappa$ drops to about 1 Å, which is less than the distance between adjacent charges.

The differences in the behavior of the calcium-free gel and those containing calcium are illustrated in Figure 4. In the absence of calcium ions the osmotic properties are practically unaffected by the sodium chloride concentration over the observed range, but the introduction of the divalent ion induces a significant decrease in mixing pressure. This result implies that the calcium ions preferentially replace the condensed sodium counterions. It follows therefore that the volume transition cannot be attributed entirely to the effect of ion screening. The replacement of loosely bound sodium ions by calcium ions is expected to reduce chain repulsion because divalent counterions compensate more efficiently the charge of the bare polyanion.[29] This effect gives rise to a relative decrease of the chain radius as observed in aqueous sulfonated polystyrene solutions with monovalent and divalent counterions, suggesting that chain rigidity may be influenced by counterion valence.[29] This picture is consistent with the present observations since the third-order thermodynamic interaction parameter is governed by chain flexibility.[16]

In polyacrylate solutions, addition of multivalent cations results in precipitation.[27,28] In gels, however, since the polymer molecules are connected to each other, macroscopic phase separation cannot occur. It is therefore rea-
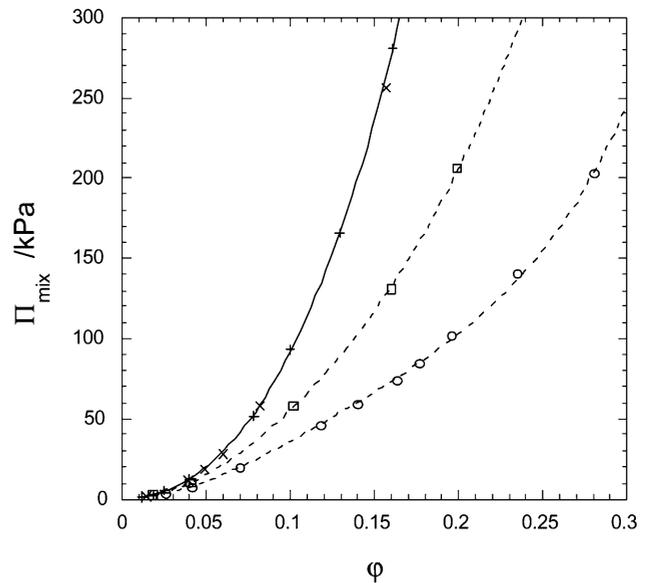

Figure 4. Comparison between the effect of sodium chloride concentration on the mixing pressure of polyacrylate hydrogels in the absence of CaCl$_2$ (+ 40 mM NaCl, × 100 mM NaCl) and in the presence of 0.2 mM CaCl$_2$ (squares: 40 mM NaCl, circles: 100 mM NaCl).

sonable to assume that in the present gels the increased effective attractive interaction favors the development of regions of higher polymer concentration. The reversible nature of the volume transition and the absence of measurable effect of calcium on the elastic modulus[8] indicate that calcium binding is not permanent. It therefore seems likely that calcium ions favor the formation of clusters that are present in the gel before the transition. Since these dense zones are dispersed in a continuous matrix, they must be connected through regions of lower polymer concentration, where the chains are stretched by the prevailing residual electrostatic interactions.

SANS measurements (Figure 5) performed on gels containing various amounts of CaCl$_2$ support the above observations. The overall intensity scattered by the sample with 0.85 mM CaCl$_2$ is significantly greater than the other two concentrations. The composition of this sample is close to the volume transition (c.f. Figure 1). At low q all three spectra display a strong scattering response with a slope of approximately -3.6 in the double logarithmic representation. This feature is characteristic of scattering from rough surfaces.[23] At higher q a region of weaker q-dependence is visible, with a slope of approximately -1, as expected from rod-like structures.[30] Such regions of stretched polymer chains have also been observed in charged polymers.[31] This behavior terminates in a shoulder at the highest q values. It can also be seen that the curve for the 0.85 mM gel intersects the other two curves, i.e., the shoulder appears earlier. This finding indicates a thermodynamic correlation length ξ that is larger in this sample, as expected in a system close to the volume transition. The dashed line is the least
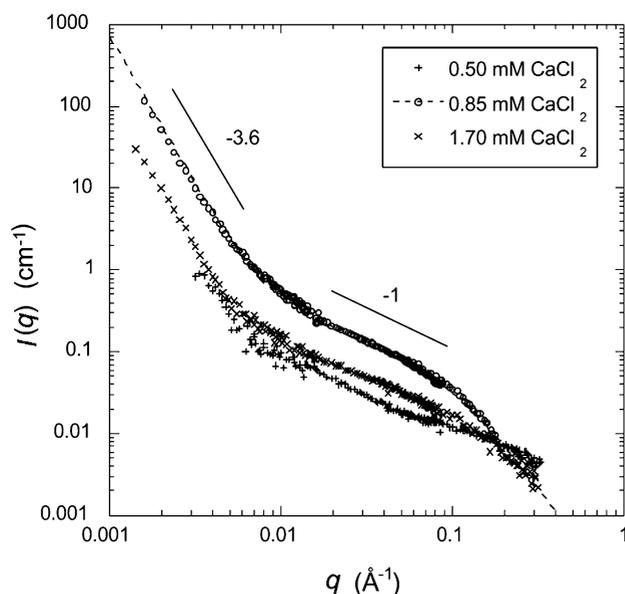
Figure 5. Small-angle neutron-scattering spectra of polyacrylate hydrogels swollen by 40 mM sodium chloride solutions containing different amounts of $CaCl_2$ (+: 0.5 mM, ○: 0.85 mM, ×: 1.7 mM). The dashed curve shows the least squares fit of the 0.85 mM $CaCl_2$ data to Equation (5) in which the first term is replaced by Equation (8), and the second term is approximated by a simple power law.

The neutron-scattering results indicate the presence of extended linear structures, which could correspond to stretched polymer chains connecting regions having different local concentrations. Large static inhomogeneities are also present, both below and above the volume transition, displaying power-law behavior with a slope of approximately -3.6, consistent with surface scattering. These large structures, however, do not contribute significantly either to the macroscopically measured osmotic pressure or to the dynamic concentration fluctuations.

squares fit of Equation (5) to the data of the 0.85 mM $CaCl_2$ sample, in which the first term is replaced by Equation (8), and the second term is approximated by a power law ($I_{stat}(q) = Aq^{-3.6}$, where A is a constant). This analysis yields the values $\xi = 9$ Å and $L = 70$ Å, respectively. Such a relatively large value of L indicates the presence of locally stretched regions of the polymer chains in the system, as observed previously for neutralized polyelectrolyte solutions in the absence of added salt.[31]

The presence of the -3.6 power-law behavior both below and above the transition indicates that the evolution in the overall structure is not directly related to the macroscopic volume transition, but is instead a continuous process.

Conclusions

The volume transition induced by calcium–sodium cation exchange in sodium polyacrylate gels swollen in sodium chloride solution has been investigated by both osmotic and neutron-scattering techniques. Of the three alternative expressions (Flory–Huggins, virial and scaling) only the Flory-Huggins formalism provides a straightforward description of the effect of calcium ions on the osmotic pressure both below and in the vicinity of the volume transition region. These ions primarily affect the third-order interaction parameter, which increases abruptly when calcium ions are introduced. The subsequent gradual increase of this parameter as calcium chloride continues to be added is then sufficient to create the conditions for volume transition.

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