

Ion Condensation in a Polyelectrolyte Gel

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Summary: Anomalous small angle X-ray scattering is used to determine the distribution of divalent ions in a neutralized polyelectrolyte gel of sodium polyacrylate in the vicinity of the volume transition. At the five different energies of the incident beam used to vary the contrast, the scattering curves have similar shapes, and are separated only by constant multiplying factors. This result, in conjunction with SANS results from the same sample, indicates that the divalent ion (strontium) is confined on the polymer backbone.

Keywords: anomalous; gel; polyelectrolyte; scattering; volume transition

Introduction

The interactions between mobile ions and charged macromolecules govern a variety of phenomena ranging from simple ion exchange to complex biological processes. A striking example of such interactions is the phenomenon of volume transition in polyelectrolyte gels, whereby, under certain changes in the ionic composition of the surrounding aqueous solution, the swollen network collapses by expelling solvent. It has been observed that lightly cross-linked sodium polyacrylate (NaPAA) gels swollen in nearly physiological salt solutions undergo a volume transition in the presence of high valence cations.^[1] Introduction of alkali earth metal ions such as calcium or strontium, at 40 mmol/l of NaCl, yields a reversible volume transition when the concentration of calcium or strontium chloride exceeds 0.9 mmol/l in the external reservoir (Fig.1). This mechanism has been considered as a simple model of nerve

excitation,^[2] in which the nerve membrane displays a variation of volume during information transfer.

To investigate the underlying mechanism of this transition anomalous small angle X-ray scattering (ASAXS) may be used. This technique yields information simultaneously on the distribution of ions and on the polymer within the gel. This paper reports an ASAXS investigation into NaPAA in the presence of strontium at the volume transition ($c_{\text{SrCl}_2}=0.9$ mmol/l in the surrounding bath).

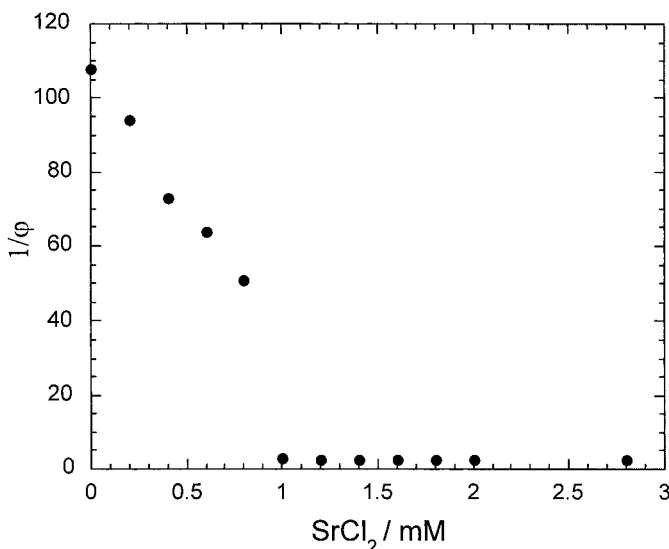


Fig. 1. Variation of the equilibrium swelling ratio of PAA hydrogel in 40 mmol/l NaCl with SrCl_2 concentration (Ref. 1). The swelling ratio is $1/\phi$, i.e., the inverse of the polymer volume fraction.

Experiments

To define the role of the ions in such systems, it is important to make measurements of the structure both of the ions and of the polymer. Contrast variation using the principle of anomalous scattering^[3,4] provides a unique technique for probing these two structural components. Such measurements are based on the fact that in the vicinity of an absorption edge the number of electrons participating in the scattering depends sensitively on the incident energy E . Strontium was used for the present investigation because of its large number of

electrons and because its absorption edge (16.1 keV) lies in a conveniently accessible energy range for synchrotron radiation measurements. The total scattering can be defined as

$$I_{\text{tot}}(q, E) = K_{\text{Sr}^{++}, \text{solv}}^2(E) S_{\text{Sr}^{++}, \text{Sr}^{++}}(q) + K_{\text{pol}, \text{solv}}^2 S_{\text{pol}, \text{pol}}(q) + K_{\text{Sr}^{++}, \text{solv}}(E) K_{\text{pol}, \text{solv}} S_{\text{Sr}^{++}, \text{pol}}(q) \quad (1)$$

where $K_{\alpha, \text{solv}}$ defines the electron density contrast between component α and the solvent and $S_{\alpha, \beta}(q)$ is the partial structure factor for which α and β represent either the polymer or the divalent ion cloud. On varying the energy of the incident photons, the effective electron number $f(E)$ of the strontium changes: the contrast between the strontium atoms and the solvent ($K_{\text{Sr}^{++}, \text{solv}}$) is varied, while that between polymer and solvent is constant, thus making it possible in principle to separate the structure factor of the polymer from that of the ion cloud.

The ASAXS experiments reported here were done on the BM2 beamline at the European Synchrotron Radiation Facility (ESRF). The sample detector distances were 1.50 m and 0.30 m, the detector being a 2D CCD camera (Princeton) with a resolution of 42.5 μm . The transfer wave vector range is between $0.008 \text{ \AA}^{-1} \leq q \leq 0.45 \text{ \AA}^{-1}$. Sequences of exposure times of 50 s were programmed. To minimise radiation damage in the gel, the position of the beam in the sample was successively changed for each energy measured. Corrections were made for the resonant Raman scattering background as well as for the coherent scattering from the solvent. Small angle neutron scattering (SANS) measurements were made on the D22 instrument at the Institut Laue Langevin, Grenoble (ILL), with incident wavelength 8 $\text{\AA}$. The sample-detector distances used were 5 m and 17 m, with an explored wave vector range $0.002 \text{ \AA}^{-1} \leq q \leq 0.15 \text{ \AA}^{-1}$. The gels were swollen in solutions of NaCl in D_2O of concentration 40 mmol/l and containing appropriate amounts of SrCl_2 . After radial averaging of the SANS spectra, corrections for incoherent background, detector response and cell window scattering were applied. Using D_2O instead of H_2O for SANS measurements does not change either the phase transition or the scattering.

Results

Figure 2 shows the ASAXS spectra of a polyacrylate gel close to the volume transition ($c_{\text{Polymer}} \approx 1 \text{ mol/l}$) for five different energies, ranging between 15.8 keV, ($f(E) = 32.5$) and 16.097 keV (where $f(E)=29$). The Kratky representation is chosen to make the intensity shift more visible between the five curves at high q . The insert in figure 2 shows the same curves, but where each is now multiplied by a constant factor $F(E)$, where $F(E) \geq 1$, such that all the curves are normalised to the response at 15.8 keV. It is apparent that the shape of the total signal is independent of the energy.

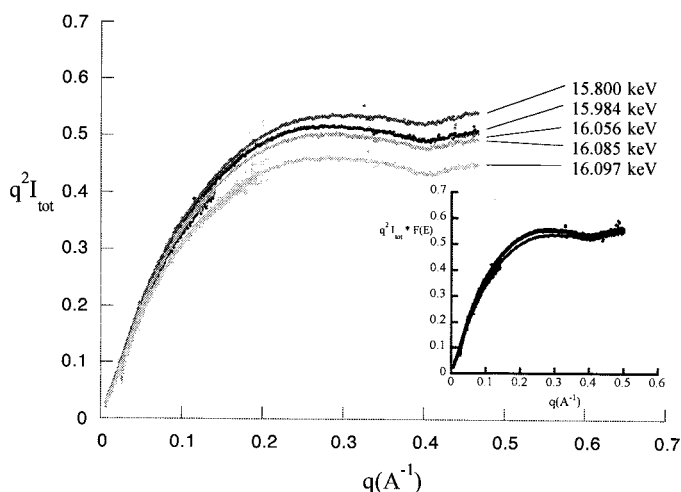


Fig. 2. Kratky plot at 5 energies as a function of q . Insert: Same curves multiplied by $F(E)$.

The spectra obtained from SANS (which is only weakly sensitive to the presence of small ions) from a polyacrylate gel under the same conditions as the gel at concentration $c_{\text{SrCl}_2} = 0.9 \text{ mmol/l}$ show that within the experimental uncertainty SANS and SAXS yield the same response (Figure 3). The SAXS measurement, which is principally sensitive to the scattering of the strontium, is thus the same as that of the simple polymer chains. This finding indicates that all the structure factors $S_{\alpha,\beta}(q)$ in equation 1 are identical and the scattering response of this gel can be treated as a binary system. Eq. 1 therefore becomes

$$I_{\text{tot}}(q, E) = K_{\text{pol, solv}}^2(E) S_{\text{pol, pol}}(q) \quad (2)$$

In this expression, it is not specified whether the strontium ions are located on the polymer or in the surrounding solution.

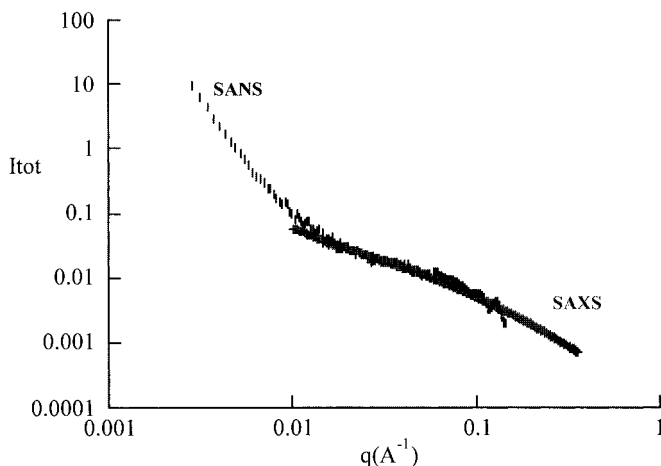


Fig. 3. SAXS (+) and SANS (○) scattering as a function of momentum transfer q . The SAXS response has been shifted vertically to coincide with the SANS intensity scale.

Two different ion distributions can give rise to this result:

- 1) the strontium counterion layer is closely associated with and is spatially indistinguishable from the polymer backbone.
- 2) the strontium ions are free and uniformly distributed in the solution surrounding the polymer.

From the tabulated values of the effective electron density $f(E)$ of strontium and the mass density d of the polymer, the electron density contrast K^2 between the solvent and the polymer can be calculated. The two possible distributions yield respectively

$$K_{\text{pol+Sr, solvent}}^2 = 3.2 \times 10^{21} [d(1 + 0.013 f(E)) - 1.68]^2 \text{ cm}^{-4} \quad (3)$$

$$K_{\text{pol, solvent+Sr}}^2 = 1.95 \cdot 10^{22} [1 - 0.00055 f(E)]^2 \text{ cm}^{-4} \quad (4)$$

where the mass density d of poly(strontium acrylate), although not known, is expected to be greater than that of un-ionized polyacrylic acid^[5] (1.49 g cm^{-3}) and/or of the acrylic monomer^[6]

(1.53 g cm^{-3}). For the ionized acrylic monomer in the second case, the mass density is known^[6] to be equal to 2.43 g cm^{-3} . The latter is the density assumed for the ionized polymer in calculating the contrast in eq 3.

The result of this calculation is inconsistent with the second hypothesis since it predicts a weak variation of intensity in the direction opposite to that observed experimentally. The first hypothesis, however, predicts the correct variation. Figure 4 shows the least squares fit, obtained by varying d in eq. 3, to the observed values of $1/F(E)$ (filled symbols). The resulting curve, exhibiting a decrease of intensity with increasing E , is obtained for $d = 1.83 \text{ g cm}^{-3}$ (continuous line). The contrast variation results thus show unambiguously that the strontium ions are confined along the polyanion.

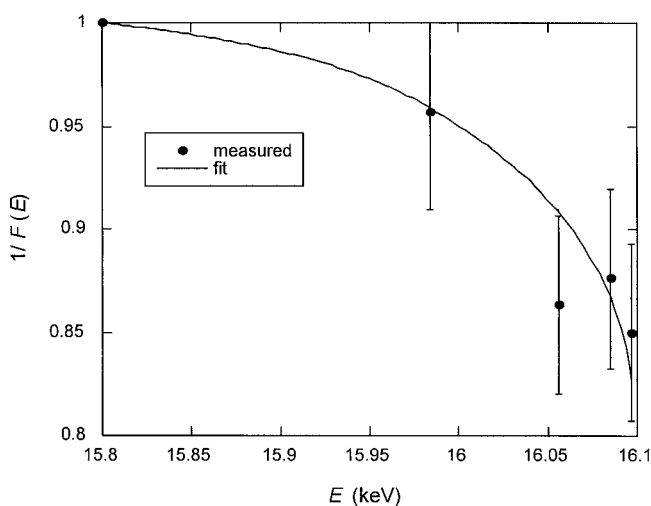


Fig. 4. The intensity ratio $1/F(E)=I(E)/I(E=15.8 \text{ keV})$ as a function of incident energy (filled symbols). Continuous curve is calculated contrast variation for PAASr in a NaCl solution, with mass density of the polymer $d_{\text{PAASr}}=1.83 \text{ g cm}^{-3}$.

In general, in ASAXS measurements^[4,7] owing to the large number of electrons, the dominant part of the ASAXS signal originates from the counterions, while the contribution of the polymer is only a small fraction of the total. Therefore in an ASAXS experiment, no significant energy dependence in the shape of the scattering response is expected. Thus, no firm

conclusion can be deduced about the form of the counterion cloud based on the similarity of the shapes of the scattering curves alone. The demonstration that the counterions are in intimate contact with the polymer backbone comes from two sources:

- 1) the similarity in shape between the SAXS and the SANS data, the latter of which is only weakly sensitive to the counterions;
- 2) the quantitative agreement between the observed energy dependence of the intensity of the ASAXS signal and expression (2) above, which requires a condensed counter-ion cloud.

Conclusion

ASAXS and SANS are used to study the distribution of divalent ions in a hydrogel of poly(sodiumacrylate) at the volume transition. It is shown that the structure factor of the strontium is similar to that of the polymer chain. Contrast variation indicates that the divalent ions are confined on the polymer backbone : no diffuse ion cloud is observed for this particular swelling ratio corresponding to the volume transition.

Measurements of these PAASr hydrogels in the fully swollen and in the collapsed state (before and after the transition) are currently in progress.

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