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Ionic distribution and polymer conformation, near phase separation, in sodium polyacrylate/divalent cations mixtures: small angle X-ray and neutron scattering

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Abstract. Anomalous small angle X-ray scattering experiments show that before demixion in sodium polyacrylate/cobalt and sodium polyacrylate/calcium mixtures all the divalent counterions are in the close vicinity of the polyacrylate chain. The present results are consistent with previous UV/VIS spectroscopy, which have shown that all cobalt ions are chemically associated with acrylate groups. The chemical association dehydrates the acrylate monomers. However, the hydrophobicity of the complexed monomers is not strong enough to induce a collapse of the polymer chain at small spatial scale before the demixion. Indeed, the scattered intensity (X-ray and neutron scattering) decreases with the scattering vector q as q^{-x} with $x \approx 2$ for $q > 0.1$ nm^{-1} which indicates that the local conformation of the chain is Gaussian.

PACS. 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 61.20.Qg Structure of associated liquids: electrolytes, molten salts, etc.

1 Introduction

In order to elucidate the nature of the interactions which control the stability of highly anionic polyelectrolytes in the presence of multivalent cations, strong polyelectrolytes and weak polyelectrolytes were compared recently [1]. It was found that the precipitation of polyelectrolyte depends essentially on the chemical nature of the charged side groups. For sulfonate groups SO_3^- or sulfate groups OSO_3^-, phase separation occurs only with cations of valency larger or equal to three with a resolubilization at high salt concentration. The phase diagrams are weakly dependent on the chemical nature of the polymer backbone; the interactions with multivalents cations are purely electrostatic [2]. For acrylate groups (C_2H_3–COO^-), however, the demixion was observed with cations of valency larger or equal to two without resolubilization at high salt concentration. For mixtures of sodium polyacrylate with cobalt ions, the results obtained with different techniques (UV/VIS spectroscopy, EXAFS) [1] showed that demixion is due to a chemical association between cations and acrylate groups of two neighboring monomers of the same chain. The similarity of the phase diagrams with cobalt or calcium ions allows us to expect that in both systems the precipitation is due to the chemical association.

This paper is devoted to the determination of the distribution of the divalent counterions and of the local conformation of the polyacrylate chain near the demixion line. The systems studied are composed of sodium polyacrylate (weak polyelectrolyte) and cobalt or calcium salt. After describing the experimental conditions, we report the results obtained by X-ray (anomalous and "normal") and neutron small angle scattering techniques. X-ray scattering experiments give information on the structure of ions and polymer chains whereas neutron scattering probes only the structure of the polymer chains.

Table 1. Characteristics of polymers. N_w is the weight average degree of polymerization, of poly(acrylic acid) and N_w/N_n is the polydispersity index. τ represents the weight fraction of carboxylic groups.

	N_w	N_w/N_n	τ (wt%)
PAA1	39	≈ 2	77–78
PAA2	8.3×10^3	≈ 2	100

2 Experiments

2.1 Materials

The two poly(acrylic acid) used, purchased from Aldrich, were characterized by light scattering and gel permeation chromatography. Potentiometric titrations were also carried out to determine the degree of carboxylation τ

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Table 2. Characteristics of the different solutions studied. C is the weight fraction of polymer and α its degree of ionization. C_s^* represents the salt concentration at which the polyelectrolyte begins to precipitate (cloud point). RXL and RXS mean that the samples were studied by X-ray scattering on spectrometer D22 at Lure or on spectrometer of Saclay, respectively. N means that sample was studied by neutron scattering.

Sample Number	Systems PAAX/Y_2O/MCl_2 X/Y/M	C (wt%)	α (%)	[COO^-] (M)	[Salt] (M)	C_s^* (M)	Exp.
1	1/H/Co	10.9	95	1.11	0.34	0.34	RXL
2	2/H/Co	1.80	0.9	≈ 0	0.25	–	RXL
3	1/H/Co	10.5	95	1.07	0.235	0.34	RXL
4	1/H/Ca	10.5	95	1.07	0.24	0.34	RXL
5	1/H/–	10.8	0	0	0	–	RXL
6–10	2/H/Ca	2.00	100	0.278	0–0.075	0.07	RXS
11	2/H/Ca	0.475	100	0.066	0.024	0.022	RXS
12	2/H/Ca	2.00	100	0.278	0.028	0.07	RXS
13	2/D/Ca	2.00	100	0.278	0.028	0.07	RXS
14	2/D/Ca	2.00	100	0.278	0.093	0.07	N

(weight fraction of carboxylic groups). The different characteristics of the polyelectrolytes are given in Table 1.

For the poly(acrylic acid) of low molecular weight the degree of carboxylation is less than 1 because the chain end groups have no carboxylate groups. Indeed when this sample is fractionated by ultrafiltration and chains of lowest molecular weight are eliminated the degree of carboxylation increases. More quantitatively we have: $\tau = m(N_n - 2)/\big(m(N_n - 2) + 2m_D\big)$ where N_n is the mean number degree of polymerization, m and m_D are the molecular weight of the acrylic acid monomer and of the two end groups of the chains, respectively. From the numerical values given in the Table 1 we estimate that $m_D \approx 2.7m$.

The radius of gyration $R_{g\theta}$ of the largest poly(acrylic acid) (PAA2), which was used to determine the conformation of the polymer chain, was measured by light scattering close to the θ-condition (dioxane, $T = 25\,°C$) and found to be 40 nm. The overlap concentration C_θ^* is estimated to be of the order of 2–3 wt%.

Solutions were prepared in deionized H_2O water upon passing it through MilliQ Millipore system of pore size 0.22 μm (resistivity of 18 MΩcm) or in D_2O water. Poly(acrylic acid) is a weak acid, its ionization degree, α, defined as the ratio of the number of carboxylate groups (C_2H_3–COO^-) to the total number of carboxylate (C_2H_3–COO^-) and carboxylic groups (C_2H_3–COOH), is very low in pure water. Typically at a COOH concentration of 0.25 M, α is of the order of 0.01. Lower ionization degrees were obtained by addition of HCl to the poly(acrylic acid) solutions. Higher degrees of ionization were obtained by neutralization of the poly(acrylic acid) with sodium hydroxide ($\alpha = [NaOH]/[COOH]$ for $\alpha > 0.2$). In the presence of cobalt ions, α was fixed to 0.75 then pH was lower than 7 and cobalt cations were not hydrolyzed [3]. All the measurements were performed at room temperature and the characteristics of the solutions investigated are given in Table 2.

2.2 Small angle neutron scattering

Neutron scattering experiments were carried out on the small angle spectrometer PAXE in Laboratoire Léon Brillouin of Saclay (Laboratoire commun CEA-CNRS). The wavelength of the incident neutrons was 0.5 nm and the sample-detector distance was 5 m. The sample cells were quartz cells of inner thickness 5 mm (or 1 mm for H_2O sample). The intensity scattered by the solutions were determined according to the following formula: $I_{sol}(q) = [I_s/l_sT_s]/[I_w/l_wT_w]$. The subscript i = s or w corresponds to the mixture polyelectrolyte/salt/D_2O sample and to the H_2O sample, respectively. T_i is the transmission of the sample having a thickness l_i and I_i represents the scattered intensity corrected by subtraction of the parasitic intensity measured with an empty cell. It was checked that the intensities scattered by the added salts are negligible compared to that of the polyelectrolytes in the investigated salt regime. The coherent intensity scattered by the polyelectrolyte, $I(q)$, is obtained by subtracting the intensity scattered by the solvent and the incoherent scattering due to the polymer itself: $I(q) = I_{sol}(q) - I_B$. To evaluate the background intensity, I_B, a scattering measurement was done on a glutaric acid/D_2O solution which contained the same number of protons per unit volume as the polyelectrolyte sample.

2.3 Small angle X-ray scattering

X-ray scattering experiments were performed at LURE (Orsay) on the spectrometer D22 and at the laboratory of Chimie Moleculaire (Saclay).

A detailed description of LURE spectrometer D22 was given elsewhere [4]. The monochromator used was a Ge(2, 2, 0) crystal which allows to cover the 5–15 keV energy range. The monochromator of this spectrometer presents the advantage to select a well defined energy with a beam which remains at the same location whatever is the energy selected. The cross-section of the incident beam is of the order of 0.3×2 mm^2 at the sample level. Samples were contained in a fixed capillary tube of external diameter ≈ 1.3 mm (thickness of the capillary glass ≈ 10 μm). The capillary is open at both ends and samples were introduced in the capillary by sucking the solutions with a syringe. In this way for all the measurements, the scattering cell was the same and remained at the same position in the incident beam. The scattering intensities were recorded with a two-dimensional gas detector located at a distance of 1.5 m from the sample cell.

The Saclay apparatus is a Small Angle X-ray Scattering camera with pinhole geometry. The X-ray source was a copper rotating anode (energy 8 keV). A detailed description of this camera was given elsewhere [5]. The samples were contained in cells of thickness $l_s \approx 0.7$ mm, with planar kapton windows. The scattered intensity was detected by a two-dimensional gas detector located at a distance of 2.1 m from the sample.

The procedure used to determine the scattered intensities by the solution $I_{\rm sol}(q)$ is similar to the one used in neutron scattering measurements. The intensity scattered by the polyelectrolyte plus salt, $I(q)$, is obtained by subtracting the water contribution: $I(q) = I_{\rm sol}(q) - 1$.

2.4 Anomalous small angle X-ray scattering (ASAXS)

Experiments were carried out on the spectrometer D22, using the same experimental set up as the one used for "normal" small angle X-ray scattering (see Sect. 2.3). Samples investigated were mixtures of poly(acrylic acid) and cobalt chloride salt.

A detailed description of the contrast variation technique in X-ray scattering can be found in references [6,7], here we give the main features necessary to define the experimental conditions. When the photon energy E, is close to the energy E_e at the absorption edge of the cobalt (E_e of K edge = 7 709 eV), the scattering length of the cobalt ion, b_c, varies [6,7]:

$$b_c = \big(Z_c + f'(E) + {\rm i}f''(E)\big)b_o. \qquad (1)$$

Z_c is the number of electrons in the cobalt ion, and b_o represents the scattering length of a free electron ($b_o = 2.8 \times 10^{-13}$ cm). f' and f'' are the anomalous dispersion factors of free cobalt atom [8] (Fig. 1a), they are related to each other through the Kramers-Kronig relation. The factor f'' is linked to the atomic absorption cross-section of the cobalt ion, $\sigma_c(E)$, by [9]

$$\sigma_c(E) = 2b_o hcf''(E)/E, \qquad (2)$$

with h Plank's constant, and c the velocity of the light.

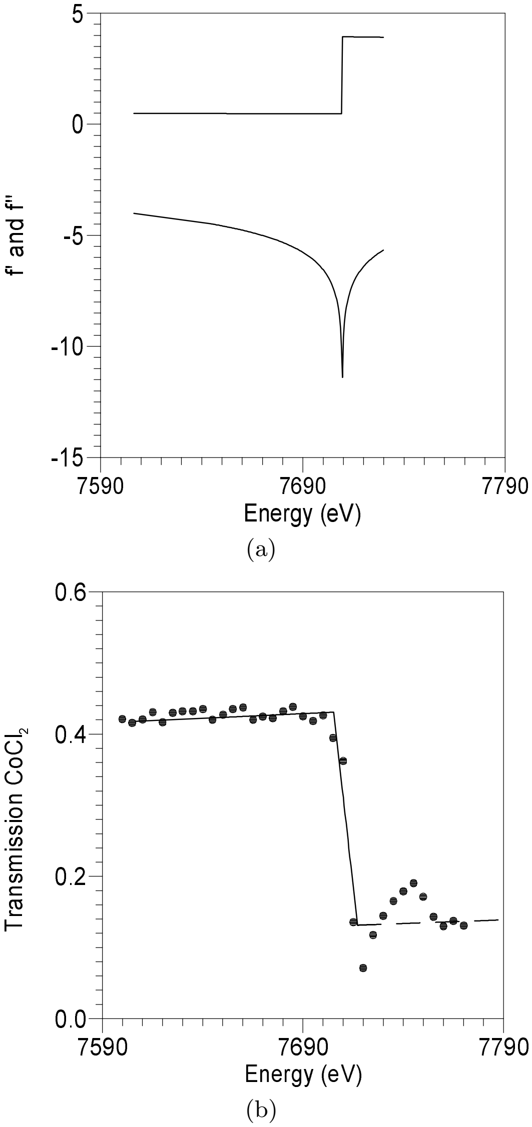

Fig. 1. (a) Energy dependence of anomalous dispersion factors f' (lower line) and f'' (upper line) for cobalt element [8]. (b) Energy dependence of the transmission coefficient of the cobalt chloride. The points are the experimental values and the line is the best fit (see Sect. 2.4). The oscillations of the experimental data at high energies are due to the EXAFS spectrum.

The effective contrast of cobalt ions cannot be simply calculated by using expression (1) and the numerical value of factors f' and f'' given in Figure 1a. In fact as the cobalt is surrounded by water molecules the position of the absorption edge, E_e, is displaced from its free atom value given in Figure 1a. Moreover due to the non zero bandwidth, ΔE, in the energy of the incident beam, average values of f' and f'' must be used. Experimentally E_e and ΔE were determined from the transmissions of a solution of cobalt chloride 0.5 M and of pure water measured as a function of the energy (7 600–7 770 eV). From the ratio of the two measured transmissions the intrinsic transmission of cobalt and chloride ions, T_m, was deduced. T_m can be written as

$$T_m(E) = 1/2\Delta E \int_{E-\Delta E}^{E+\Delta E} T(E'){\rm d}E'. \qquad (3)$$

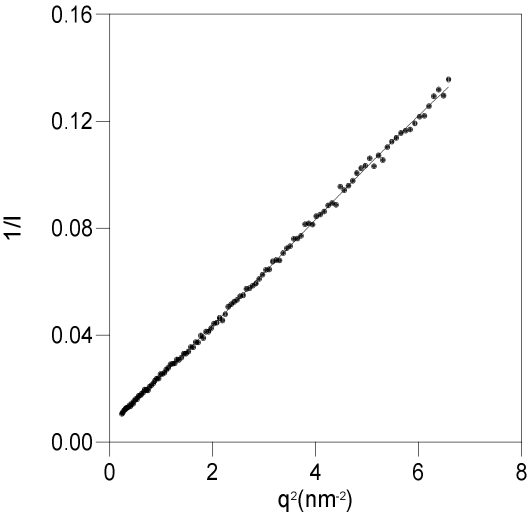

Fig. 2. Inverse of the intensity scattered by the mixture NaPA1/Co (sample 1) *versus* q^2. The energy of the incident X-ray beam was 7 600 eV.

$T(E')$ is the transmission at the energy E':

$$T(E') = \exp\{-\rho_c(\sigma_c + 2\sigma_{\mathrm{Cl}})l\}. \tag{4}$$

ρ_c is the number of cobalt ions per unit volume, σ_{Cl} represents the atomic absorption cross-section of the chloride ions[1], and l is a mean thickness of the solution contained in the capillary. Using expressions (2–4), and the values of f'' reported in Figure 1a, we found that the measured transmission was correctly described for an energy bandwidth $\Delta E = 6$ eV and a displacement of the absorption edge of +2 eV (see Fig. 1b).

ASAXS measurements were performed at 3 energies (7 600, 7 695, and 7 708 eV) and the mean values of f' used to compute the scattering length of the cobalt ion were −3.90, −5.98, and −7.95[2]. These values were obtained using the values of f' given in Figure 1a with a shift in energy of +2 eV and averaged over an energy range of ±6 eV. Note that the same experiments are not possible with calcium ion because its K edge energy is too low for D22 spectrometer at LURE.

3 Results and discussion

In order to determine the region where cobalt ions are located, anomalous X-ray scattering experiments was done on charged polyacrylate PA1 in the presence of cobalt near the demixion (sample 1, Tab. 2). The spectra obtained at different energies of the incident beam are smoothed with a polynomial expression before being compared (Fig. 2). The increase of the energy leads to a decrease of the scattering length and of the scattered intensity. In Figure 3 are reported in a log-log scale the intensity scattered at 7 600 eV, $I(E = 7\,600, q)$, and the differences of scattered intensities at different energies: $I(7\,600, q) - I(7\,695, q)$ and $I(7\,600, q) - I(7\,708, q)$. All the curves are parallel to each other which means that the intensities measured at the three energies are proportional. We conclude that the cobalt ions are in the close vicinity of the backbone of the polyacrylate[3]. The same type of experiment was done on the weakly charged poly(acrylic acid) PAA2 in the presence of $\mathrm{CoCl_2}$ (sample 2, $\alpha = 9\times10^{-3}$) and on a solution of pure cobalt chloride with the same concentration in cobalt as in sample 2. The variations of the scattered intensities with the energy were identical for both systems. As no association occurs between cobalt ions and COOH groups, the intensity scattered by sample 2 is the superposition of the intensities scattered by the polymer and the solvent $\mathrm{H_2O}$-$\mathrm{CoCl_2}$. These results show that the technique is sensitive enough to detect if the cobalt ions are in the vicinity of the polymer chain or uniformly distributed in the solution.

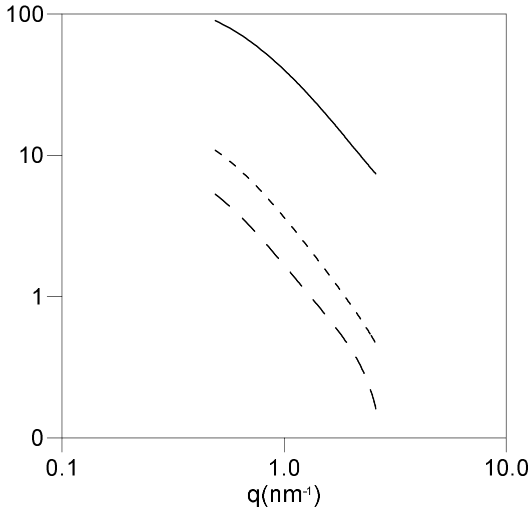

Fig. 3. Variation of the scattering intensity as a function of the energy of the incident X-ray beam (sample 1). The solid line represents the smoothed scattered intensity at 7 600 eV, the dashed lines are the difference of the scattered intensity at the 3 energies: long dash $I(7\,600, q) - I(7\,695, q)$ and short dash $I(7\,600, q) - I(7\,708, q)$.

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[1] The atomic absorption cross-section of chloride σ_{Cl} is computed using expression (3) and the f''_{Cl} values given in reference [9].

[2] As f'' is negligible with respect to $Z_c + f'$ we suppose that $b_c = \big(Z_c + f'(E)\big)b_o$.

[3] The amplitude scattered by $N - n$ bare monomers and n monomers with associated counterion is $A(q) = \sum_{i=1}^{N-n} b_m \exp(\mathrm{i}qr_i) + \sum_{i=N-n+1}^{N} b_m \exp(\mathrm{i}qr_i) + b_c \exp\big(\mathrm{i}q(r_i + d_i)\big)$, where d_i is the distance between the monomer and the counterion. If $qd_i \ll 1$ then the intensity scattered is the intensity scattered by N monomers partially labelled

$$I(q) \sim \sum_{i=1}^{N}\sum_{j=1}^{N}\langle b_j b_i \exp\big(\mathrm{i}q(r_i - r_j)\big)\rangle$$

$$\sim \langle b^2\rangle \sum_{i=1}^{N}\sum_{j=1}^{N}\langle \exp\big(\mathrm{i}q(r_i - r_j)\big)\rangle \sim \langle b\rangle^2 \sum_{i=1}^{N}\sum_{j=1}^{N}\langle \exp\big(\mathrm{i}q(r_i - r_j)\big)\rangle$$

with $\langle b\rangle = b_m + nb_c/N$.

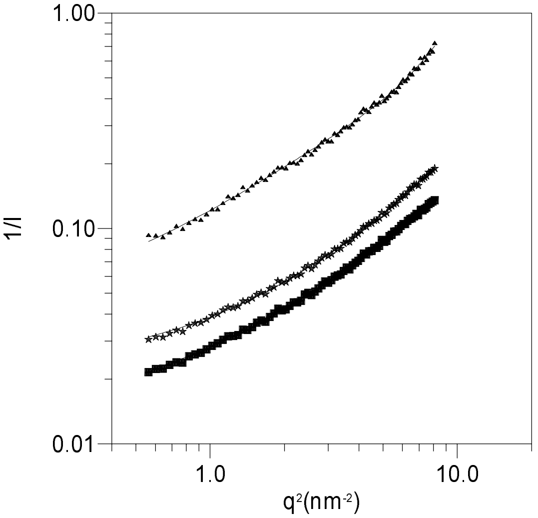

Fig. 4. Comparison of intensities scattered by uncharged PAA1 (triangles) and charged PAA1 in the presence of calcium (stars) and cobalt (squares) ions at 10 500 eV.

In addition, scattering experiments at the same polymer concentration with $CoCl_2$ and with $CaCl_2$ (samples 3 and 4) at an energy of 10 500 eV, where the transmission is higher, were carried out. At this energy the sample with cobalt ions produced fluorescence. The fluorescence intensity was estimated from measurements realized on a solution of cobalt chloride at different energies (10 500, 7 708, 7 695 and 7 600 eV) and then subtracted. For comparison, measurements were also done on neutral poly(acrylic acid) (sample 5). All the intensities scattered by the different systems are proportional (see Fig. 4). The variation of the scattering intensity comes from the variation of the contrast of the monomer dressed by cobalt or calcium ions which increases with the atomic number of the counterion. In agreement with UV/VIS spectroscopy and ion selective electrode measurements [1], the X-ray scattering measurements show that before the demixion calcium and cobalt counterions are near the polyelectrolyte backbone. By fitting the inverse of the scattered intensity as a function of q^2 to a polynomial expansion,

$$1/I(q) = [1/I(q \to 0)][1 + q^2 R_g^2/3 + a_2 q^4 + a_3 q^6], \quad (5)$$

we can determine the intensity scattered at low q values, $I(q \to 0)$, and a z-average radius of gyration R_g. We find that R_g is equal to 1.9 nm for the neutral poly(acrylic acid) and to 1.5 and 1.8 nm for the polyacrylate in the presence of calcium and cobalt ions. Thus conformation of this polyelectrolyte of low molecular weight is the same for the three different situations within the experimental uncertainty.

Let us first consider the case of the neutral poly(acrylic acid), the intensity $I(q \to 0)$ is proportional to the apparent contrast, K, of the monomer in water

$$K = b_m^2 \quad \text{with} \quad b_m = [Z_m - Z_{H_2O} V_m / V_{H_2O}] b_o. \quad (6)$$

Z_{H_2O} (= 10) and V_{H_2O} ($= 30 \times 10^{-3}$ nm^3) are the number of electrons and the partial volume of water molecule, respectively. Z_m and V_m are the number of electrons and the partial volume of the acrylic monomer (C_2H_3–COOH). If the interactions between polymers are negligible then

Table 3. Atomic numbers and partial volumes.

Compounds	Z	Partial volumes (10^{-3} nm^3)
Na^+	10	-11.0^a
Co^{++}	25	-58.0^a
Ca^{++}	18	-47.7^a
H, D_2O	10	30
C_2H_3–COOH	38	78^b
C_2H_3–COO^-	38	48.5^b

^{a} Values obtained from reference [16] and ^{b} from reference [17].

$$I(q \to 0) = K \rho N_w / \sigma'_w \quad (7)$$

where ρ, N_w, and σ'_w represent the number density of monomers, the mean weight average of degree of polymerization of PAA1 and the differential scattering cross-section of water per unit volume, respectively. As the partial volume of the acrylic monomer is known (see Tab. 3) its contrast can be easily calculated ($K = 1.13 \times 10^{-23}$ cm^2). Taking the differential scattering cross-section of water per unit volume[4] $\sigma'_w = 1.65 \times 10^{-2}$ cm^{-1} and for N_w the value measured by light scattering (see Tab. 1), we obtain $1/I(q \to 0) = 4.1 \times 10^{-2}$ which is close to the measured value of 5.5×10^{-2}. In this calculation, we have assumed that the contributions to the total scattering intensity of all the monomers are the same. However we know that it is not the case since the monomers at the two ends of the chains are bigger than the acrylic monomers (see Sect. 2.1). We estimate that doing this approximation the error is only of the order of 20% (see Appendix).

Let us now consider the case where the poly(acrylic acid) is charged and in the presence of divalent cations. The contrast can be written as in equation (6) but now V_m is the effective partial volume of the dressed monomers and Z_m is the mean number of electrons in the dressed monomers:

$$\begin{aligned} Z_m &= (1-\alpha) Z_{COOH} + \alpha Z_{COO^-} + \alpha\beta Z_{Na} + \alpha g Z_c \\ &= Z_{COO^-} + \alpha\beta Z_{Na} + \alpha g Z_c. \end{aligned} \quad (8)$$

Z_{COOH}, Z_{COO^-}, Z_{Na}, and Z_c are the number of electrons in the acrylic monomer (C_2H_3–COOH), the acrylate monomer (C_2H_3–COO^-), the sodium ion, and the divalent cation M^{++}, respectively. β is the fraction of acrylate groups which carries condensed sodium and g is the mean number of associated divalent cation per carboxylate group C_2H_3–COO^-. As all the divalent cation are in the vicinity of the polymer chain we have $g = [M^{++}]/[C_2H_3$–$COO^-]$ where $[M^{++}]$ is the concentration of the added

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[4] $\sigma'_w = (Z_{H_2O} b_0 / V_{H_2O})^2 kT \chi_T$ where χ_T is the compressibility of the water; in the temperature range 20–25 °C the quantity $T\chi_T$ is constant and equal to 1.35×10^{-7} deg/Pa.

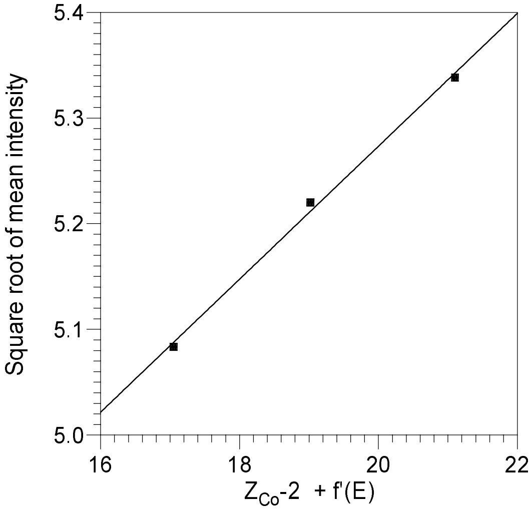

Fig. 5. Variation of the square root of the mean intensity $\langle I(E)\rangle$ $\big(=\sum_{i=1}^{n} I(E,q_i)/n\big)$ scattered by the mixture NaPA1/Co (sample 1) as a function of the cobalt ion apparent scattering length (in electrons unit).

divalent cation. In particular for anomalous scattering, we have

$$\sqrt{I(E)} \sim b_{\mathrm{m}} = [Z_{\mathrm{COO}^-} + \alpha\beta Z_{\mathrm{Na}} + \alpha g\big(Z_{\mathrm{Co}^{++}} + f'(E)\big) - Z_{\mathrm{H_2O}} V_{\mathrm{m}}/V_{\mathrm{H_2O}}]b_{\mathrm{o}}. \tag{9}$$

The variation of the square root of the mean intensity $\langle I\rangle(=\sum I(q_i)/n)$ as a function of $Z_{\mathrm{Co}^{++}} + f'(E)$ should be a linear function; which is well verified experimentally (see Fig. 5). At scattering vector lower than 2 nm^{-1}, the effective scattering entity is the monomer dressed by the cobalt ions, which are located in the close vicinity of polyacrylate. An additional information which can be deduced from the variation of the mean scattered intensity with energy is the partial volume V_{m}. If we assume that all sodium ions have been replaced by divalent cobalt ($\beta = 0$), as g is known ($= 0.306$), from the relative slope (slope/intercept) of the line of Figure 5 which is equal to $\alpha g/(Z_{\mathrm{COO}^-} - Z_{\mathrm{H_2O}} V_{\mathrm{m}}/V_{\mathrm{H_2O}})$ we can deduce the effective partial volume of the dressed monomer. The relative slope is equal to 1.57×10^{-2} which leads to $V_{\mathrm{m}} = 59 \times 10^{-3}$ nm^3. If some sodium ions remain near the polymer chain ($\beta \neq 0$) then $V_{\mathrm{m}} = 59 + \alpha\beta V_{\mathrm{H_2O}} Z_{\mathrm{Na}}/Z_{\mathrm{H_2O}}$, thus whatever is the value of β we have $V_{\mathrm{m}} \geq 59 \times 10^{-3}$ nm^3. The partial volumes of the monomers dressed with cobalt and calcium ions can be also deduced from the measurements done at an energy of 10 500 eV. As the contrast of the acrylic monomer (C_2H_3–COOH) is known, by comparing the mean scattering intensity of the neutral poly(acrylic acid) with the mean intensities scattered by the poly(acrylic acid) charged in presence of divalent cation, the contrasts of dressed monomers can be determined. Using expressions (6) and (8), the partial volumes of the dressed monomers can be also deduced. We find that V_{m} is larger than 54×10^{-3} nm^3 and 61×10^{-3} nm^3 in the presence of cobalt and calcium, respectively. At this stage, it is now interesting to evaluate the volume V_{m} when the charged monomers and the cations are supposed to remain completely hydrated. In these conditions the partial volume V_{m} is a linear function of the partial volumes of the different entities

$$V_{\mathrm{m}} = (1-\alpha)V_{\mathrm{COOH}} + \alpha V_{\mathrm{COO}^-} + \alpha\beta V_{\mathrm{Na}} + \alpha g V_{\mathrm{c}}. \tag{10}$$

V_{COOH}, V_{COO^-}, V_{Na}, and V_{c} are the partial volumes of uncharged monomers, charged monomers, sodium and divalent cations, respectively. Whatever is the β value, the experimental values are always larger than the calculated values using the measured partial volumes given in the literature (see Tab. 4). This is in favor of a partial dehydration of the charged monomers and cations when complexation between charged monomers and cations occurs. This point is in agreement with refractive index and density measurements which show that the chemical association induces a dehydration of monomer and cation [10,11].

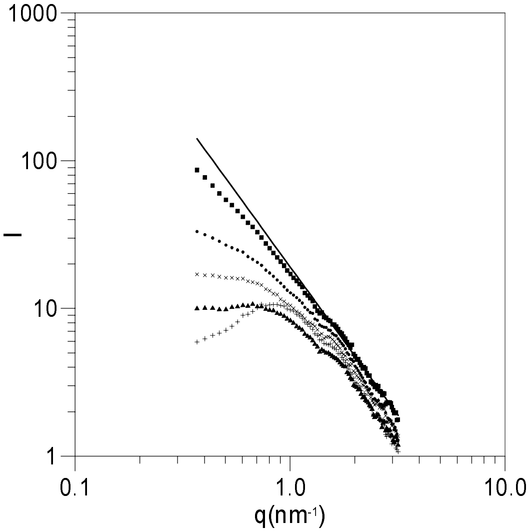

Fig. 6. Variation of the X-ray intensity scattered by mixtures of NaPA1 and Ca, up to precipitation (samples 6–10) as the salt concentration increases: (+-crosses) without salt, (triangles) 1.4×10^{-2} M, (×-crosses) 2.8×10^{-2} M, (dots) 5.2×10^{-2} M, (squares) 7.5×10^{-2} M. The full line represents a slope −2.

In Figure 6 is reported the variation of the X-ray scattering intensity when calcium chloride is added, the polymer concentration being constant (samples 6–10). Before addition of salt the scattered intensity presents a peak at 0.7 nm^{-1} in agreement with previous results [12]. As the salt concentration increases the peak is displaced toward lower q-values and disappears a fact which reveals a reduction of repulsive interactions. The increase of the overall scattering intensity, especially at high q values, is due to the increase of contrast of the dressed monomers. Just before the demixion the scattering intensity at high q-values can be described by a power law with an exponent close to −2. A similar power law behavior was already observed with a PAA weakly charged gel [13]. The experiments were repeated on a sample more diluted in polymer (sample 11) and a q-dependence of the scattered intensity close to q^{-2} was also obtained (see Fig. 7). In this figure are reported the scattered intensities divided by the polymer

Table 4. Partial volumes of the dressed monomers. $V_m^{(\mathrm{exp})}$ partial volumes deduced from anomalous and "normal" X-ray scattering measurements. K is the apparent contrast. $V_m^{(\mathrm{calc})}$ partial volumes computed using expression (10) and the measured partial volumes given in the literature (see Tab. 3).

Samples	g	Energy (eV)	K (cm^{-2}) × 10^{25}	$V_m^{(\mathrm{exp})} \geq$	$V_m^{(\mathrm{calc})} \leq$
1	0.306	Anomalous	–	59×10^{-3} nm^3	33×10^{-3} nm^3
3	0.220	10 500	504	54×10^{-3} nm^3	38×10^{-3} nm^3
4	0.224	10 500	369	61×10^{-3} nm^3	40×10^{-3} nm^3

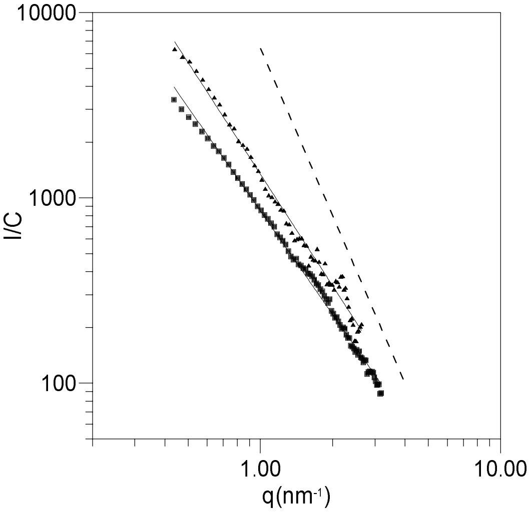

Fig. 7. X-ray scattering intensity, near the demixion, divided by the polyacrylate concentration: (squares) $C = 2$ wt% (sample 10) and [Ca] $= 7.5 \times 10^{-2}$ M; (triangles) $C = 0.475$ wt% and [Ca] $= 2.4 \times 10^{-2}$ M (sample 11). The dash line represents a slope -3.

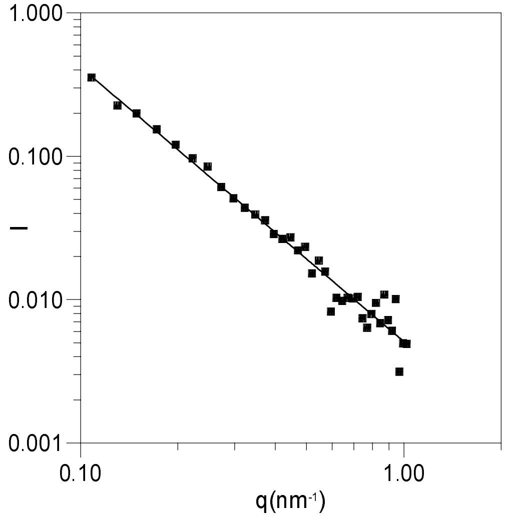

Fig. 8. Neutron scattering intensity measured in solution just at the cloud point (sample 14). The squares are the experimental points and the solid line the best fit which decreases as $q^{-1.9}$.

concentration for samples 10 and 11. At high scattering vector where the interactions are negligible we expect that the two curves coincide. There is a little discrepancy because the dressed monomers for the two samples have slightly different contrasts: the number of calcium per monomer is higher for sample 11. However, we can notice that at high q values the two curves are parallel which tends to indicate that the local conformation of the polymer is probed in this q-regime.

X-ray scattering measurements depend on the intensity scattered by the ions and the polyelectrolyte, in order to probe only the conformation of the polymer backbone, neutron scattering experiments were performed. D_2O was used as solvent to minimize incoherent scattering and to maximize the contrast. However, replacing H_2O by D_2O can eventually slightly modify the interactions and the conformation of the polymer. To check this point X-ray experiments were carried out on system PANa2/$CaCl_2$ dissolved in H_2O and D_2O (samples 12–13). The profiles of the scattered intensities are identical within experimental error; this is consistent with the fact that the salt concentration at which the polyelectrolyte precipitates is the same in both solvents. In Figure 8 are reported the neutron measurements on sample 14 just at the cloud point, the intensity decreases as $q^{-1.9}$ in agreement with the X-ray experiments. The accuracy in this neutron scattering experiment is less than with X-ray scattering experiment because the contrast becomes very poor when the poly(acrylic acid) is highly charged.

The precipitation of polyacrylate in the presence of $CaCl_2$ can be explained by the chemical association of two neighboring monomers by a divalent calcium ion which makes the monomers uncharged and thus hydrophobic [1] but this hydrophobicity is not sufficient to induce a collapse of the chain at small spatial scale $1/q < 10$ nm. In fact, when the concentration of added divalent counterions increases the repulsive interactions decrease and the conformation of the polymer is collapsed at large spatial scale as shown by viscosity measurements [1]. Thus short intermonomer spacings remain more or less Gaussian while distances between widely separated monomers shrink. Near the demixion, the chain contraction is very similar to the one encountered in neutral polymer before demixion as, for instance, in the polystyrene/cyclohexane system when the temperature is decreased below the theta-temperature [14,15].

4 Summary and conclusion

X-ray scattering experiments clearly show that the majority or possibly all the divalent counterions are in the close vicinity of the polyelectrolyte backbone. The change of the energy of the incident beam or of the nature of counterions lead to a variation of contrast which can only be explained by assuming that the partial volume of the dressed monomer is larger than the sum of the partial volumes of the charged group ($C_2H_3CO_2^-$) and of the divalent counterions in the isolated and hydrated state. This is a consequence of the chemical association between charged groups and divalent counterions which partially dehydrates both the negatively charged group and the divalent cation.

Close to the demixion line, at high scattering vectors $q > 0.1$ nm^{-1} where the local conformation of polymer chain is probed, the scattered intensity decreases as q^{-x} with $x \approx 2$. This exponent, smaller than 3, indicates that the local conformation of the chain (spatial scale $1/q <$ 10 nm) is not collapsed. Near demixion, when the chain collapses, a blob structure still exists as it is the case for neutral polymers.

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Appendix

Here, we compute the intensity scattered (at zero scattering vector) by a polydisperse sample where each polymer chain is composed of 2 end monomers of scattering length $b_\mathrm{d} = [Z_\mathrm{d} - Z_{\mathrm{H_2O}} V_\mathrm{d}/V_{\mathrm{H_2O}}]b_\mathrm{o}$ and $N_i - 2$ monomers of scattering length $b_\mathrm{m} = [Z_\mathrm{m} - Z_{\mathrm{H_2O}} V_\mathrm{m}/V_{\mathrm{H_2O}}]b_\mathrm{o}$. The intensity scattered by such system has the following form:

$$\begin{aligned} I &\sim \sum n_i \big(2b_\mathrm{d} + (N_i - 2)b_\mathrm{m}\big)^2 \\ &\sim \sum n_i \left(N_i^2 + 4\delta N_i + 4\delta^2\right) b_\mathrm{m}^2 \quad \text{with} \;\; \delta = b_\mathrm{D}/b_\mathrm{m} - 1. \end{aligned}$$

n_i is the number of polymers having N_i monomers. With a good approximation, for uncharged poly(acrylic acid), $b_\mathrm{D}/b_\mathrm{m} \approx m_\mathrm{D}/m$ (≈ 2.7, see Sect. 2.1) where m and m_D are the molecular weight of the acrylic acid monomer and of the two end groups of the chains, respectively.

The approximate form of the intensity used is

$$I_\mathrm{app} \sim \sum n_i N_i^2 b_\mathrm{m}^2.$$

Then the error in the approximation is

$$(I - I_\mathrm{app})/I_\mathrm{app} \approx 4\left(\delta^2 + \delta/N_n\right)/N_\mathrm{w}.$$

For the average molecular weights given in Table 1 ($N_\mathrm{w} \approx 40$ and $N_n \approx 20$) the error in taking b_m instead of b is estimated to be of the order of 20%. The small error reflects the fact that the scattering is dominated by the scattering of the largest polymers where end groups effect is small. We must notice that when monomers are charged and dressed by divalent cations the effective scattering length b_m increases; consequently δ will be lower than 1 and the error in the approximation will be smaller.

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