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Ion-specific effects in polyelectrolyte solutions: chain-chain interactions, chain rigidity and dynamics

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Abstract. Ion-specific effects in aqueous solutions of polyelectrolytes are addressed here. We focus on ionene cationic chains, featuring simple structure, absence of side-groups and very regular chain charge density. Ion-specific effects in ionene solutions are demonstrated using a series of monovalent (halide) counterions. The study combines both static and dynamic measurements by small angle neutron scattering, neutron spin echo and PFG-NMR. Ion-specific effects are a phenomenon at high polyelectrolyte concentration and the nature of the counterion is seen to influence drastically the ionene chain-chain interactions. The origin lies in the closer approach of large, highly polarisable counterions to the chain backbone, leading to more constricted counterion clouds. Equally affected is the local chain rigidity, as well as collective and self-diffusion coefficients at larger scales. Small, non-polarizable, strongly hydrating counterions, here F⁻ ions, lead to locally rigid chains. For such chains, the nm-scale collective dynamics as seen by neutron spin echo, is the fastest, while the self-diffusion seen at μm scale by PFG-NMR is the slowest. In other words, the loss of charge on the chain due to ion-specific counterion "condensation" has the opposite effect on collective diffusion and self-diffusion of the chains.

Keywords. polyelectrolytes, ion-specific effects, inter-chain interactions, self-diffusion, collective diffusion, PFG-NMR, neutron scattering, neutron spin echo.

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1. Introduction

Charged polymer chains, also referred to as "polyelectrolytes", are omnipresent among natural compounds, e.g. polysaccharides, nucleic acids etc., or indeed among the many synthetic substances used in food, cosmetic and packaging industries as well as in water treatment and several other fields [1]. The behaviour of charged polymer chains in solution, and we shall restrict ourselves here to aqueous solutions, is a world of its own. Two possible reference situations can be thought of as systems of departure: (a) electrolyte solutions and (b) uncharged polymer chains in solution. In the first case, we depart from a solution of atomic or molecular ions, both positive and negative, and we add connectivity between one type of these ions, be it positive or negative. This creates significant charge density inhomogeneities in the solution. This is by now not the common way of thinking about polyelectrolyte solutions, but it was indeed the point of departure for Fuoss et al back in the 1950s [2]. In the second case, we start with the already quite complex case of a macromolecular chain in solution, where the quality of the solvent (good/theta/bad) decides the chain conformation. Next we add charge to a fraction of the monomers on the chain, but importantly we also need to introduce a population of counterions into the surrounding solution (and partially condensed onto the chain, if the necessary conditions are met). Either way, the transition (adding connectivity or adding charge) is far from trivial and the consequences in terms of the structure, interactions and dynamics of the (macro)molecular species present in such a solution are considerable. This is naturally reflected in the very different properties of the solution on the macroscopic scale, its phase diagram, rheology, osmotic pressure, heats of dilution and other thermodynamic properties etc. [1].

Historically, it is indeed through the macroscopic properties that the peculiar behaviour of polyelectrolyte (PE) solutions was uncovered and the rheological studies of Fuoss et al (the Fuoss law) remain a reference in this respect, e.g. [3]. Tremendous progress has been made since the Fuoss studies and we recommend two reviews, dating from very different times, to trace this progress [4,5]. A breakthrough came in the 1970s, with the advent of scattering techniques, in particular neutron scattering, and the seminal experimental work of Cotton, Jannink et al [6,7], and the accompanying theoretical developments of de Gennes, Pfeuty et al (the scaling approach) [8–10]. From this point onwards, the molecular level description of solutions of neutral polymers and later on polyelectrolyte solutions indeed began to emerge.

Overall, the scaling-based theory of PE solutions is highly successful, especially when dealing with the interpretation of neutron and X-ray scattering experiments. There, it predicts correctly the scaling of the PE chain correlations probed via the universally observed maximum in the scattering data, the so-called *polyelectrolyte peak*. This feature of the scattering curves is completely absent for solutions of neutral polymers and reflects the electrostatic repulsion present in solutions of *charged* chains. De Gennes' theory of polyelectrolyte solutions was later broadened by Dobrynin and Rubinstein, to include all cases of solvent quality and concentration regimes [11]. The initial picture of dilute and semi-dilute concentration regimes was enriched (entangled and non-entangled sub-regimes) and extended, especially in the high concentration range [12–14]. The competition between electrostatic repulsion along a PE chain and hydrophobic (solvophobic) collapse has led to the prediction of the so-called *pearl-necklace* conformation of PE chains for the case of bad solvent [15] and these have indeed been observed experimentally [16,17] and by simulations [18].

Both the conformation of individual chains (the chain form factor) and the chain-chain correlations (the structure factor) modify the scattering curves. These individual contributions often cannot be distinguished easily, contrary to solutions of inorganic colloids for example. Polymer/PE solutions pose two problems in this respect: 1) the conformation of polymer/PE chains changes as a function of concentration and 2) polymer chains are penetrable objects, i.e. individual chains can get entangled. A very elegant method, the zero-average contrast (ZAC) method, is accessible in neutron scattering to highlight each of the contributions, for cases

where deuteration of the polymer/PE chains is possible [19]. In the absence of such measurements, the main features to account for in the scattering spectra remains the position of the scattering peak. As follows from the above paragraphs, the position of the PE peak depends on the PE concentration, but also on the chain conformation (consequence of the effective chain charge and the solvent quality).

In our past publications, we have showed that for identical PE concentration, solvent quality and valence of the counterions, the *chemical nature* of the counterion by itself can also influence the shape of the scattering curve, the position and shape of PE peak and the extent to which this peak is indeed visible or not [20,21]. The origin lies in the hydration of the given ion, which influences its condensation onto the PE chain and thus modifies the effective chain charge. When the chemical nature of an ion is to “blame” for a given observation, biochemists and physical chemists refer to such instances as *ion specific effects* [22–27]. It has been observed that ion-specific effects manifest themselves more strongly for anions than cations [28,29]. Solutions and gels based on cationic chains with compensating *anions*, such as ionenes [20,21,30], show indeed stronger ion specific effects than anionic PEs, such as the widely studied polystyrene sulfonate [16,31–34]. Needless to say, any purely electrostatic theory, such as the scaling-approach of de Gennes, Manning theory of counterion condensation [35,36] or indeed the Poisson-Boltzmann approach [32] cannot account for these effects, as hydration properties of solvated ions do not come into consideration. One attempt in what seems the correct direction are theories accounting for local dielectric heterogeneities around the ions and the PE chains [37]. The orientation of the dipole moment of water molecules is indeed closely linked to the hydration and the polarizability of the hydrated species.

Ionenes, the focus of this study, are a group of water soluble cationic polyelectrolytes with pH independent charge, based on quaternary ammonium charged centres linked by simple hydrocarbon chains. Ionenes have already several applications including ion exchange resins, [38] water treatment in oil industry, [39] humidity sensors, [40] organic templates in the synthesis of mesoporous silica, [41] or anti-microbial agents. [42] The dramatic *ion specific effects* in ionene aqueous solutions mentioned earlier, have been initially observed in thermodynamic properties [43–45] and later on the micro-scale by scattering for the particular case of two halide ions, F^- and Br^- [20,21]. In this contribution, we show how this generalises for an entire series of halide counterions and what consequences it has for the dynamics of the PE chains. We bring information on the chain dynamics at the microscopic (nm) scale, by the neutron spin echo (NSE) technique, and also on the mesoscopic (μm) scale, by pulsed field gradient NMR (PFG-NMR).

2. Experimental methods

2.1. Ionenes: synthesis and structural overview

Ionenes and their precursors were synthesized using a procedure adapted from those described previously [20,21,45]. The details of the synthesis are provided in the SI file. The synthetic route leads invariably to ionenes with bromide counterions. Molecular weight of ionenes were determined by size exclusion chromatography (SEC) as described in ref [46]. The range of molecular weights is 20 000 - 60 000 g/mol, which corresponds to 100-300 nm in terms of chain length. SEC measurements on cationic polyelectrolytes are very difficult [47] and, for us, were successful only for 6,9-ionenes. In the following we consider that the above range of molecular weights applies also to ionenes of other charge densities, which were synthesized under identical conditions. We have indeed confirmation that the molecular weights of ionenes with different charge densities are of the same order of magnitude, from the NMR signal of amine end groups, which allow estimation of the degree of ionene polymerisation [48].

Counterion exchange was performed by dialysis starting from Br-ionenes. Dialysis tubes (Sigma-Aldrich, MWCO = 12000 g mol⁻¹) were filled with 0.02 M solutions of Br-ionenes and first dialyzed against 0.05 M solution of the desired NaX (3 weeks) to exchange anion and then dialyzed against water (2 weeks) to remove sodium ions. All ionene solutions for neutron scattering and NMR measurements were prepared gravimetrically. Deuterated water (Euriso-top, 99.9 %D) was used for neutron scattering samples as well as NMR samples.

The pH of the solutions was close to neutral and thus we estimate the effects of any dissolved carbonic acid as very small.

The general chemical formula of ionenes is $[-(\text{CH}_3)_2\text{N}^+-(\text{CH}_2)_x-(\text{CH}_3)_2\text{N}^+-(\text{CH}_2)_y-]_n$ for an x, y -ionene chain, with Br^- or other counterions (Figure 1). Ionenes with X^- counterions are referred to as X-ionenes in the rest of the manuscript. Values x and y represent the number of $-\text{CH}_2-$ (methylene) units between adjacent charged centres (quaternary ammonium centres) and can be varied accurately by synthesis. [49–51] By increasing x and y the ionene chain is less charged. In this manuscript we shall discuss ionene chains for which $x, y=3,3$ and $6,9$ (referred to as 3,3-ionenes and 6,9-ionenes). The simple structure (absence of bulky side-groups) and finely tuneable and *regular* charge density are very interesting structural features of ionenes. Other PEs, including styrene, present often charge on (bulky) side groups and charged monomers are distributed statistically along the chains. In order to make a parallel between ionenes on one side and polystyrene based and other PEs on the other, we may consider the structure of ionenes as a sequence of charged and uncharged "monomers" as depicted in Figure 1.

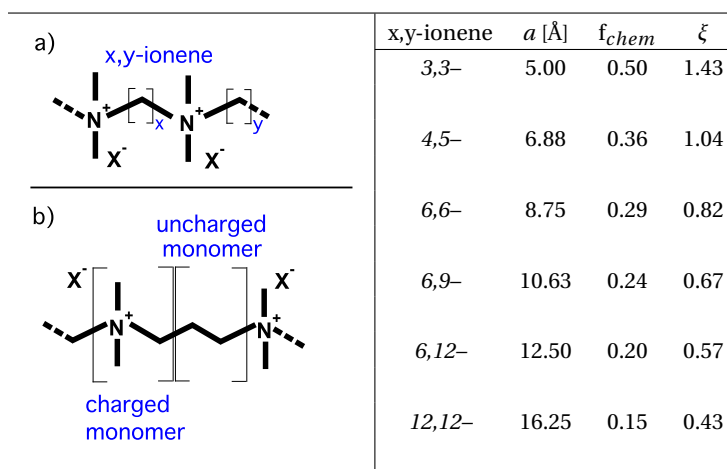


Figure 1. *Left:* (a) Schematic view of an x, y -ionene chain. (b) Schematic view of a 3,3-ionene ($x=3, y=3$) chain, showing the definition of a charged and uncharged monomer. *Right:* Ionene structural parameters: a is the charge separation on the chain, f_{chem} the fraction of charged monomers, ξ the Manning charge density parameter, defined as $\xi = L_B/a$, where L_B is the Bjerrum length (7.14 Å in water at room temperature). While 4,5- ionenes are at the $\xi = 1$ limit (onset of Manning-type condensation), only 3,3- ionenes have sufficient charge density to induce significant condensation ($\xi > 1$) and decrease the chemical charge (f_{chem}) to an effective charge (f_{eff}).

2.2. Neutron scattering

Small angle neutron scattering (SANS) measurements were carried out on the PACE spectrometer at LLB-Orphée, Saclay, France. Using up to three different combinations of incident neutron wavelength (λ) and sample to detector distance, a wave-vector (q) range of 0.01 to 0.45 Å⁻¹ was covered ($q=4\pi \sin(\theta/2)/\lambda$). The detector efficiency was taken into account by normalisation of data with flat (incoherent) signal from bulk light water. Ionene solutions were loaded into quartz cells with path length of 1 or 2 mm. Due to the isotropic nature of our samples, data were grouped in concentric rings, each corresponding to a given q value. The measured scattered intensities were corrected for transmission, sample thickness, incoherent and solvent background to yield the coherent scattered intensity, I_{coh} . We checked the reproducibility of neutron scattering spectra, by measuring samples from different synthesis batches.

Neutron Spin Echo (NSE) [52] experiments were carried out on the IN15 spectrometer in ILL, Grenoble, France. Samples were measured in 1 mm or 2 mm flat quartz cells. Using a combination of two neutron wavelengths, 6 Å and 9 Å, and detector angles of 3, 5, 7, 10, 13 and 19° at 6 Å and 3 and 6° at 9 Å, we achieved an accessible q range of 0.04 \AA^{-1} to 0.5 \AA^{-1} and time range of 0.07 ns to 11 ns at 6 Å and 0.25 ns to 36 ns at 9 Å. Both static, I_{coh} , and dynamic data, $I(q, t)$, in NSE was corrected for contributions from the quartz cell and the solvent (D_2O) background.

2.3. Pulsed field gradient NMR

The single pulse 1H NMR spectra were recorded using a Bruker Avance III 300 MHz NB spectrometer, operating at 7.05 T. The lock was obtained with a sealed 2 mm capillary filled with D_2O inserted inside the NMR tube. The chemical shift was referenced to $CFCl_3$. Pulsed field gradient NMR experiments were performed using a BBFO probe equipped with 55 G.cm^{-1} gradient coil. We used a NMR pulse sequence combining bipolar gradient pulses and stimulated echo. This sequence was repeated with 16 gradients of increasing strength from 2 to 50 G.cm^{-1} during 1.5 ms. The diffusion time was approx. 200 ms, which corresponds to a diffusion over a length scale of $1.5 \mu\text{m}$. The self-diffusion coefficients are obtained by nonlinear least-square fitting of the echo attenuation, using the Bruker Topspin software. All PFG-NMR data were measured at room temperature on ionene solutions in D_2O .

3. Results and Discussion

Small angle neutron scattering data of 3,3 X-ionenes with four different halide counterions ($X^- = F^-, Cl^-, Br^-, I^-$), at a moderate and high monomer concentration, is shown in Figure 2. From our previous studies, we know that both of these concentrations are in the semi-dilute regime, the overlap concentration for ionenes synthesized using our protocols was estimated to be below $c_p=0.07\text{M}$ [20]. In the semi-diluted regime, the position of the peak reflects the mesh-size formed by the interpenetrating chains. At 0.4M monomer concentration, the spectra of all systems show a well-defined polyelectrolyte peak (a clear maximum) at an almost identical position in the wave-vector q (a slight shift towards higher q values is noticed for the F-ionene, see later). At high monomer concentration (2M), the four systems feature very different scattering curves. Note that the increase of intensity in the small q region ($q < 0.03 \text{ \AA}^{-1}$) is due to large-scale heterogeneities in the system – a repeatedly-observed feature for PE solutions/gels, which remains poorly understood. The changes that interest us most are thus confined to the q region roughly between 0.03 \AA^{-1} and 0.4 \AA^{-1} . In this central region, a clear polyelectrolyte peak remains visible only for the F-ionene. Its position is shifted to higher q values in comparison to data at 0.4M, as expected, due to a denser mesh size at this higher concentration. In the sequence $F^- \rightarrow Cl^- \rightarrow Br^- \rightarrow I^-$, the central part of the spectrum gains in intensity and the intensity dip to the left of the PE peak seen for F-ionene gradually disappears. As a consequence the peak becomes highly asymmetric (the case of Cl-ionene, still a slight maximum observed). The peak disappears completely for the Br-ionenes and I-ionenes and instead a plateau is seen in the spectra, resembling a signal we would expect from a neutral polymer.

Figure 3 summarizes the position of the PE peak for the four 3,3 X-ionenes seen in their SANS spectra. If up to 0.1M concentration the position of the peak is very close between for all systems, for $c_p > 0.1\text{M}$, the situation changes. Only the F-ionene follows the predicted $c_p^{1/2}$ law and the three other systems depart significantly from this description. Combining information from Figure 2 and 3 we observe that at 0.4M the PE peak position for 3,3 F-ionene is already somewhat higher than for all other systems, all curves present a well defined PE peak. For higher concentrations, the *strong* departure from the $c_p^{1/2}$ law in Figure 3 for Cl-, Br- and I-ionenes is mainly a consequence of the PE peak *disappearing* from the scattering signal. For a badly defined, asymmetric peak, the determination of its position is increasingly difficult (refer back to Figure 2 right). Overall, clearly the ion-specific effect is a high concentration phenomenon and we can place the critical concentration at around 0.1M. This corresponds to a charge concentration in the system of 0.05M, according to $c(X^-) = c(N^+) = c_p f_{chem}$.

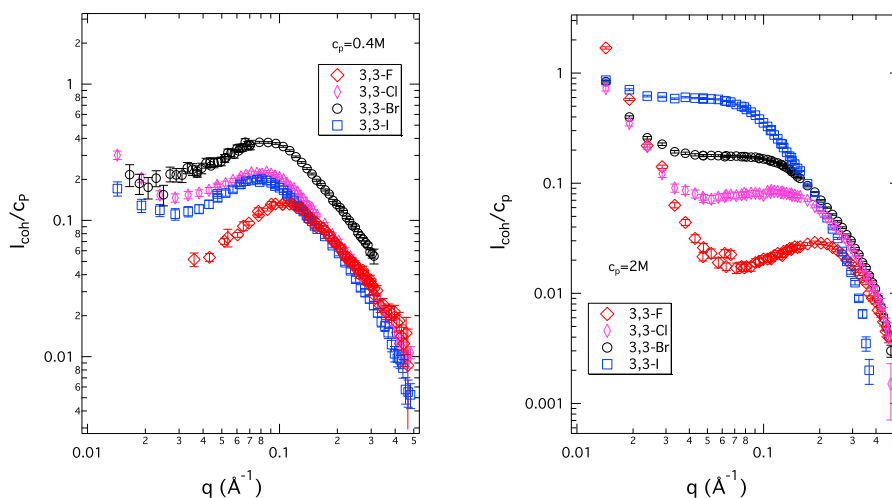


Figure 2. Coherent neutron scattering intensity normalised by ionene monomer concentration (I_{coh}/c_p), in arbitrary units, versus scattering wave-vector (q) for room temperature aqueous solutions (in D_2O) of 3,3 X-ionenes at two monomer concentrations, 0.4M (left) and 2M (right). These monomer concentrations correspond to volume fractions around 2% and 10% respectively.

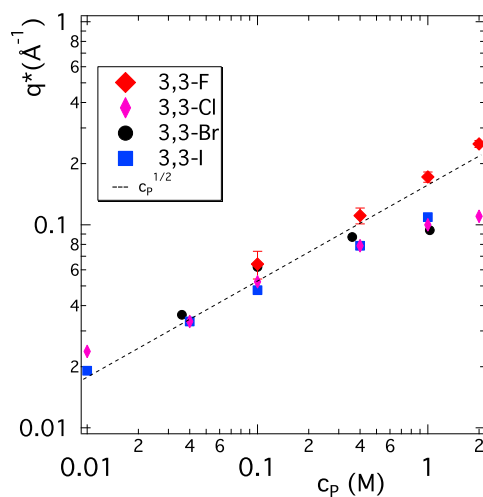


Figure 3. Position of the polyelectrolyte peak in SANS spectra (q^*) versus ionene monomer concentration (c_p) for 3,3 ionenes with different counterions. Typical error bars are represented on the 3,3-F data set. Dashed line is a guide to the eye representing a $c_p^{1/2}$ scaling law, expected in the semi-dilute concentration regime.

In order to further investigate the ion-specific effect and its consequence on the scattering spectra, we carried out measurements for a series of ionenes with mixed counterion clouds at a constant monomer concentration. This was done for ionene of different charge densities (3,3-, 6,9- and 12,12-). The most striking changes in the spectra are observed for the most highly charged chains (3,3-ionenes) and this system is shown in Figure 4. Additional data for 6,9-Br/F and 12,12-Br/F systems are included in the SI file. The two extreme

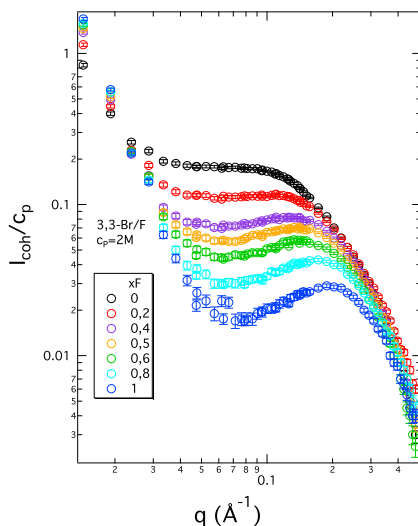


Figure 4. Coherent neutron scattering intensity normalised by ionene monomer concentration (I_{coh}/C_p), in arbitrary units, versus scattering wave-vector (q) for room temperature aqueous solutions (in D_2O) of 3,3 ionenes with mixed Br-F counterion clouds. The fraction of F^- counterions (x_F) is shown in the legend. All systems are at 2M monomer concentration.

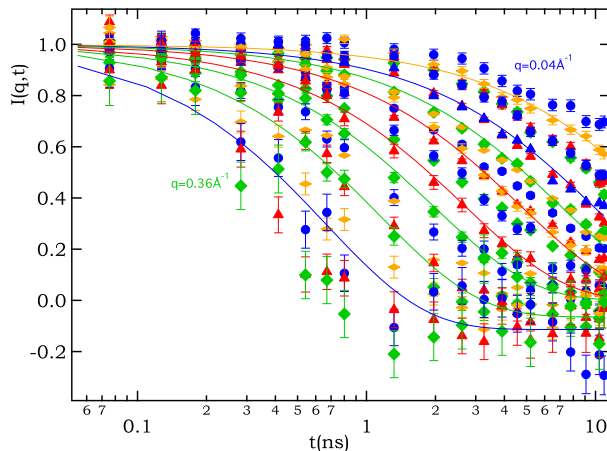
systems ($x_F=1$ and $x_F=0$) are naturally identical to the F^- and Br^- ionene data in Figure 2. All intermediate systems place themselves logically between the two extremes, with gradual changes with increasing/decreasing x_F . The complete disappearance of PE peak (absence of a maximum) is only present for the pure Br system. As expected, the intermediate curves *cannot* be obtained by a linear combination of the curves corresponding to the $x_F=1$ and $x_F=0$ extremes [53]. For a given x_F , each chain is surrounded by a mixed counterion cloud at the given ratio, there are no chains in a "pure F" or "pure Br" environment. Interestingly, as we decrease the charge density of the ionene chains (6,9- and 12,12-ionenes), the difference in scattered intensity between the pure F and pure Br extremes is diminished (see SI). This is probably due to a decreasing overall counterion concentration in the system, as we move from 3,3- to 12,12-ionenes.

Having scattering data for ionene solutions across a whole series of halide counterions gives a very strong argument for the previously suggested origin in terms of a decreased effective charge of the ionene chains as we move towards larger, more polarisable ions with a lower hydration energy, i.e. as we descend the halogen series in the periodic table. For completeness, radii of halide ions in solution, polarizability and hydration energies are summarized for the four halide ions used in Table 1. For the larger ions, the counterion atmosphere around the ionene backbone is more constricted, as has also been clearly shown by previous molecular dynamics simulations on ionene solutions [54]. As soon as counterion clouds of adjacent chains do not overlap, the repulsion between the chains is no longer present and the PE peak in the scattering spectra disappears. Counterions are however not necessarily condensed in the Manning sense of the word, as we have seen by osmotic pressure measurements in ionene solutions in the past [20] and as was equally observed for other systems [55]. The counterions still contribute to the osmotic pressure, unlike what has been seen for counterions in solutions of hydrophobic polystyrene-based polyelectrolytes, where counterions are condensed as part of the "pearls" in the pearl-necklace conformation [56].

In the following, we are interested in exploring the rigidity of the ionene chains as a function of the counterion condensation. We have explored this for the case of F^- and Br^- counterions using the neutron spin echo technique (NSE) [52]. Neutron spin echo gives access to the microscopic dynamics of the chain on the length-scale of nm and a ps-ns timescale. The measured data in neutron spin echo is the intermediate

Table 1. Ionic sizes in solution (R_s), polarizabilities (α) and hydration free energies (ΔG_{hyd}) for halide ions.

Ion	R_s [57] (Å)	α [58] (Å ³)	ΔG_{hyd} [58] (kcal/mol)	ΔG_{hyd} ($k_B T$ /ion)
F ⁻	1.24	1.20	-112.1	-189.3
Cl ⁻	1.80	3.65	-82.4	-139.1
Br ⁻	1.98	4.96	-76.1	-128.5
I ⁻	2.25	7.30	-67.0	-113.1

**Figure 5.** Intermediate scattering function, $I(q, t)$, measured for 6,9-Br ionene at $c_p=0.4M$, as measured by NSE. Each curve corresponds to a given q value in the range from 0.04 to 0.36 Å⁻¹. Lines are mono-exponential fits for a selection of the curves.

scattering function, $I(q, t)$, which is formally the spatial Fourier transform of the van Hoff correlation function, $g(r, t)$. We measure the dynamic data on the coherently scattered signal arising from the contrast between hydrogenated ionene chains in a deuterated solvent (D₂O), the same systems as those used previously for the small angle scattering experiments. The NSE data was collected for ionene chains with intermediate chain charge densities, 6,9-ionenes, at 0.4M and 2M monomer concentrations.

An example of NSE data is shown in Figure 5, where a series of $I(q, t)$ curves for 6,9-Br ionene at 0.4M is presented, each curve corresponding to a given q value. Following a standard analysis, the data was modelled using a mono-exponential decay to obtain a value of a characteristic relaxation time, τ , at a given q value. Under a simple diffusion model, this characteristic time is converted into an effective diffusion coefficient, D_{eff} , following the relation $1/\tau = D_{eff}q^2$. Note that for large q values, the background corrections (quartz cell and solvent) lead to an unphysical long-time asymptote of slightly less than 0. For these cases the fitting parameters were relaxed to allow for a non-zero (slightly negative) constant background.

Figure 6 summarizes the coherently scattered intensity (as measured by polarization analysis on NSE) and the effective diffusion coefficients, D_{eff} , resulting from the mono-exponential fitting of the $I(q, t)$ curves. Data for all four systems studied by NSE is shown: 6,9-Br and 6,9-F ionenes, each at 0.4M and 2M monomer concentration. The position of the PE peak in the coherently scattered intensity observed by NSE (Figure 6, left) reflects what has been observed already by SANS (Figures 2 and 4), the data for Br- and F-ionenes at low monomer concentration show a peak at the same q position, while at high concentration the scattered intensity is radically different.

In Figure 6 (left) we also indicate the high q intensity dependence. Assuming that the chain-chain correla-

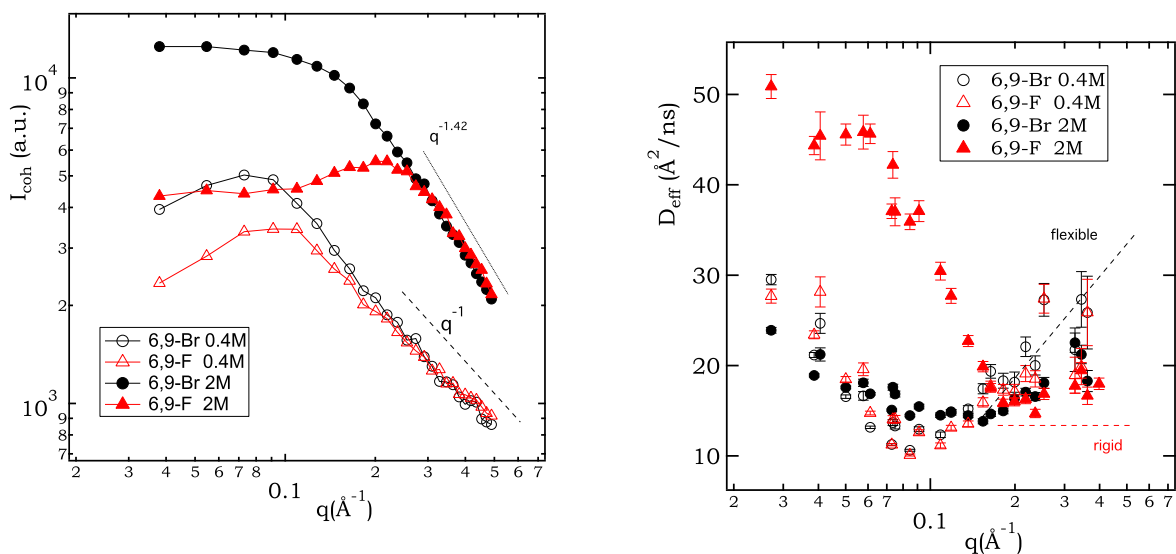


Figure 6. Coherently scattered intensity (polarisation analysis in NSE, left) and effective diffusion coefficient, D_{eff} , (right) as a function of the wave-vector, q , for all systems studied by NSE.

tions do not contribute in a significant way to the scattered intensity in the high q region (this is an approximation, as we are not working under the "zero average contrast" conditions here), the power law reflects the conformation of the individual chains. While a q^{-1} behaviour is characteristic of a rod-like conformation (and this is the case of the low concentration data for both Br- and F-ionenes), a q^{-2} behaviour corresponds to a signal of a Gaussian chain, in other words a neutral polymer in a Θ solvent ($q^{-1.7}$ indicates Gaussian chains with an excluded volume contribution). It is clear that compared to 0.4M data both 2M data sets have a higher decay exponent ($q^{-1.42}$) at high q values, which indicates a less rod-like conformation. At the same time we need to note that the high q dependence in the SANS spectra (Figures 2 and 4) does not agree with the NSE-determined decay exponents. The SANS data features much higher exponents (close to q^{-2} already for the 0.4M data sets and even higher for the 2M data sets). It is important to realise that the decay exponent at high q is very sensitive to the incoherent background subtraction. This is done in very different ways in SANS and in NSE. In SANS data reduction, the density of H atoms is first estimated from the concentrations of the hydrogenated chains in the deuterated solvent and compared to H atom density of pure water. The background constant to subtract is determined from the ratio of these two H atom densities. In NSE, the decomposition of the total scattered signal into coherent and incoherent contributions is measured *directly* using polarisation analysis, which relies on the spin flip of incoherently scattered intensity from H nuclei [59]. As a result, we consider the high q exponents determined from NSE as more reliable and we do not conclude on the chain conformation from the high q SANS signal.

There are several points to note regarding the effective diffusion coefficients in Figure 6 (right), all of the order of 10^{-10} m^2/s . We may consider the figure in two parts, below and above the q^* position or the high- q end of the observed plateau, depending on the given system. Both theory [60] and previous experiments [61–63] on polyelectrolyte solutions show a rapid decrease of D_{eff} for $q < q^*$ and then a constant value for $q > q^*$. The constant value at high q reflects the rod-like conformation of a charged chain. On the contrary, the signal in a semi-dilute solution of a neutral polymer chain should show D_{eff} increasing linearly with q in the high q region [64]. From the high q behaviour, the most rigid chain is indeed that of F-ionenes at 2M concentration, as this data set features the most constant values beyond q^* . The remaining three systems (Br 2M, Br 0.4M and

F 0.4M) all feature a more significant increase in D_{eff} beyond q^* . While both 0.4M data sets gave a clear rod-like behaviour in the coherently scattered intensity, Figure 6 (left), these chains do not show the highest rigidity as seen from the D_{eff} . One difficulty in the interpretation is probably the intra- and inter-chain correlations mixing in both the static and the dynamic signal. Measurements under ZAC would probably help disentangle the inter- and intra-chain correlations contributing to the scattered signal, at least for the static signal. NSE measurements under ZAC seem challenging.

We may view the trends in Figure 6 (right) as a demonstration of "de Gennes narrowing", where dynamics is suppressed (slowed down) for all wave-vectors close to the peak in the structural correlations [65]. The two 0.4M data sets indeed form a (inverse) bell-shaped curve, with a minimum in D_{eff} around the PE peak position at 0.08-0.09 \AA^{-1} . For the 2M data sets, the striking difference between Br and F is related to the very different scattered intensities: as q decreases below 0.2 \AA^{-1} (a) the 2M F system passes through a structural maximum and its dynamics increases very fast for all smaller q s; (b) the scattered intensity for 2M Br system continues to grow below 0.2 \AA^{-1} to reach a plateau, the dynamics in 2M Br is significantly suppressed in comparison to 2M F in the entire region below 0.2 \AA^{-1} , but begins to rise slowly, once the plateau is reached.

Mesoscopic dynamics of ionene chains in D_2O solutions was measured by PFG-NMR. Figure 7 summarizes the D_{NMR} data for 3,3-ionenes with the four different halide counterions, as a function of monomer concentration, c_p . For comparison, this Figure also features data from sodium polystyrene sulfonate (PSS), measured by PFG-NMR in H_2O , from reference [66]. The ionene and PSS data fall into the same range of D_{NMR} , of the order of $10^{-11} \text{ m}^2/\text{s}$. At room temperature, the ratio of D_2O and H_2O viscosities is 1.25 and this conversion factor would have to be used for a detailed quantitative comparison of the two data sets. The ionene chains correspond to molecular weights of 20-60 kDa, which fall well within the range of molecular weights for the PSS data [66]. However, the size polydispersity (PID) of ionene chains (due to the poly-addition reaction as opposed to radical polymerisation for PSS) is significantly higher: $\text{PID}(\text{ionene})=1.8\text{-}2.0$ and $\text{PID}(\text{PSS})=1.25\text{-}1.5$. Given these differences, we do not dwell on a detailed quantitative PSS-ionene comparison. The general trend as a function of c_p is similar for the two types of PE chains, with a decrease in D_{NMR} for c_p above approximately 0.1-0.2M.

Let us concentrate on the D_{NMR} data in Figure 7, for different counterions, especially in the higher c_p region, i.e. above 0.1M. The ordering of D_{NMR} data for 3,3-ionenes does not follow in a simple way the halide anion series, contrary to what was seen in the SANS data. The order here is $D(\text{F}) < D(\text{Cl}) > D(\text{Br}) \gg D(\text{I})$. We see two phenomena behind this non-monotonous behaviour: (a) change of chain conformation (less rod-like as we move down the halide series towards larger anions) and (b) inter-chain aggregation (the system becomes less soluble as move down the halide series). A change from rod-like to globular chain conformation leads to an *increase* in the *self*-diffusion coefficient of the chain [67], the inter-chain aggregation leads to its *decrease* (larger objects diffusing). For the 3,3-I ionenes the inter-chain aggregation is indeed pronounced, 3,3-I ionene shows a significantly lower D_{NMR} than all the other systems (roughly a factor of 2 lower) throughout the entire concentration range. This scenario is consistent with the evolution of viscosity (η) of aqueous solutions of a neighbouring cationic PE, poly(diallyldimethylammonium), along the halide series [68]. Indeed, η decreases between Cl^- and Br^- solutions of this PE (chains change from a rod-like to a more globular conformation), and the system becomes insoluble with I^- (no F^- data are available in ref [68]). We attach importance to the fact that 3,3-F ionenes show somewhat lower D_{NMR} than Br- and Cl-ionenes, in the moderate to high c_p range. To ensure that this difference is real, we have explored changes in D_{NMR} for ionenes with mixed Br/F counterion clouds and the data is summarized in Figure 8, for two different ionene charge densities. Indeed, as we move from pure-Br to pure-F ionene chains, the chain dynamics clearly *decreases*.

4. Conclusion

The combination of small angle neutron scattering, neutron spin echo and PFG-NMR gives us here several pieces of information on the state of the counterion atmosphere around positively charged PE chains in aqueous solution, as a function of the counterion chemical nature, i.e. *ion specific effects*. A series of monovalent

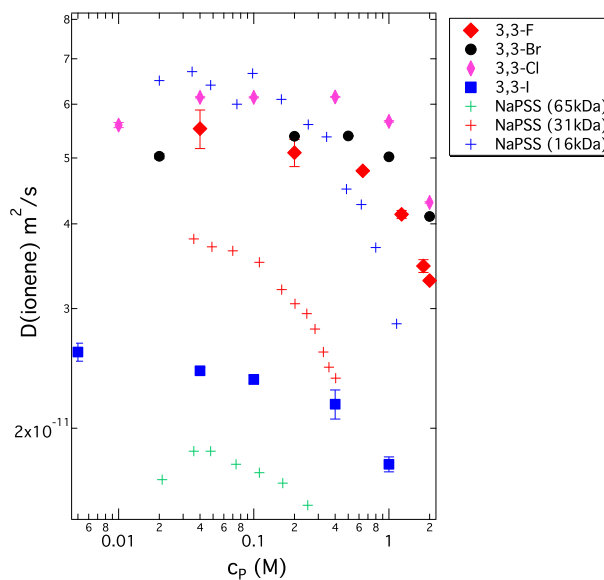


Figure 7. Self-diffusion coefficients of ionene chains for 3,3-ionenes with four different halide counterions as indicated, versus monomer concentration, c_p (solvent = D_2O) as measured by PFG-NMR. Crosses correspond to measurements for polystyrene sulfonate with Na^+ counterions (NaPSS) at three different molecular masses as indicated. NaPSS data from reference [66] (solvent = H_2O).

halide counterions is explored. The strong ion specific effect is observed clearly at high PE monomer concentrations and is consistent with the picture of an increasingly more compact counterion atmosphere around the PE chain, due to more substantial counterion "condensation" onto the chain. This is accentuated as we move along the halide series towards larger, more polarizable and more weakly hydrated counterions. This is demonstrated by a reduced chain-chain repulsion in the system, as shown by the disappearance of the PE structural peak in the scattering data. Importantly, the ion specific effect has consequences for the chain rigidity, local and mesoscopic chain dynamics, as shown further by NSE and PFG-NMR.

In principal, it is important to distinguish between the *collective* effective diffusion coefficient of the PE chains as measured by NSE (arising from the coherently scattered signal at the nm-scale) and the *self* diffusion coefficient by PFG-NMR (by construction of the position encoding method via magnetic field gradients) at the μm scale. Further, within the nm-scale probed by NSE, different behaviour is observed on the very local scale, i.e. smaller than the typical mesh size of the interpenetrating PE chains, and on the nm-length scale above the typical mesh size. Let us look at these three scales in turn:

- (a) local scale below PE mesh size, probed by NSE: Here the notion of *collective* motion seen via the coherent signal in NSE no longer applies, the scale probed is too small. NSE probes the dynamics of individual chains and informs us on their rigidity. We observe that PE chains retaining a strong chain-chain repulsion (i.e. with F^- counterions) show increased chain rigidity of the PE chains, at high monomer concentration.
- (b) nm-scale, larger than the PE mesh size, probed by NSE: Here, NSE dynamic data indeed probe *collective* dynamics in the PE network, as the coherent signal is dominated by the *inter-chain* correlations at these length scales. For locally rigid chains (i.e. with F^- counterions), the *collective* dynamics at this scale is very fast. For more flexible chains (i.e. with Br^- or Cl^- counterions), the dynamics here is suppressed. We see this as a case of "de Gennes narrowing", as the Br^- or Cl^- systems show an intense scattering signal at this spatial scale. The effective *collective* diffusion coefficients at the nm-scale are

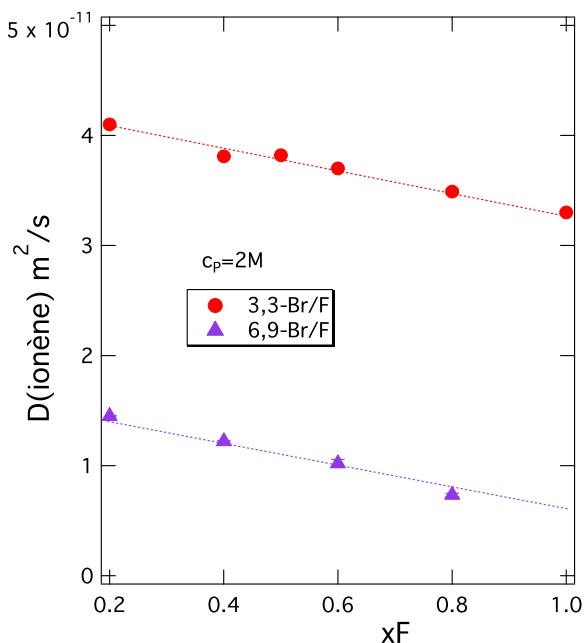


Figure 8. Self-diffusion coefficients of ionene chains for systems with mixed Br/F counterion atmospheres at a monomer concentration of 2M, as a function of the fraction of F^- counterion, xF , as measured by PFG-NMR. Two different ionene chain charge densities are presented.

- all of the order of $10^{-10} \text{ m}^2/\text{s}$.
- (c) μm -scale, probed by PFG-NMR: On this largest scale PFG-NMR probes the *self*-diffusion of the individual PE chains. Locally rigid charged chains, with fast collective dynamics seen at nm-scale (i.e. with F^- counterions) diffuse consistently slightly *slower* than locally more flexible chains with slow nm-scale dynamics. The *self*-diffusion coefficients at the μm scale are all of the order of $10^{-11} \text{ m}^2/\text{s}$.

Dynamics in PE solutions has been probed extensively by DLS [69]. In the semi-dilute PE concentration regime, this techniques gives access to the *collective* dynamics (D_{coll}) at the mesoscopic scale, the closest length scale would be the PFG-NMR scale above. Concentrating on the fast mode in the DLS signal, charged rigid PE chains show consistently *faster* collective dynamics compared to flexible neutral chains. This is again a demonstration of de Gennes narrowing, which leads to large values of D_{coll} for repulsive systems at length scales much larger than the PE mesh-size (i.e. $q < q^*$ in the scattering language, which is where DLS operates). For charged chains at high monomer concentration in the absence of salt, the order of magnitude for DLS-determined *collective* diffusion coefficients is $10^{-10} \text{ m}^2/\text{s}$ [69]. This is the same order of magnitude as the *collective* diffusion coefficients measured here by NSE. Also, the order of magnitude difference between *self*-diffusion and collective diffusion coefficients in PE solutions has been noted before ($D_{self} \ll D_{coll}$) [66,69]. Our new data sets (NSE, PFG-NMR) on ionene PE solutions are consistent with these observations. However, the effects of the counterion-specificity on D_{self} measured here by PFG-NMR suggest that D_{self} of charged chains is *lower* than that of neutral chains. In other words, the loss of charge on the chain, due to counterion-specific "condensation" onto the chain, has the opposite effect on D_{self} and D_{coll} . This seems to be indeed in line with very recent DLS and PFG-NMR data on PSS sulfonate [70]. Overall, the more strongly charged chains adopt a more extended conformation, resulting in a lower *self*-diffusion coefficient, while the *collective* diffusion in these more repulsive systems is enhanced due to de Gennes narrowing.

Conflicts of interest

The authors declare no competing financial interest.

Dedication

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Supplementary data

Supporting information for this article is available on the journal's website under article's URL or from the corresponding author.

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