



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

Claire Hotton ^a, Yasmine Sakhawoth ^a, Anne-Laure Rollet ^a, Juliette Sirieix-Plénet ^a,
Lingsam Tea ^a, Sophie Combet ^b, Melissa Sharp ^c, Ingo Hoffmann ^d, Frédéric Nallet ^e and
Natalie Malikova ^{*,a}

^a Laboratory of Physical Chemistry of Electrolytes and Interfacial Nanosystems (PHENIX), Sorbonne Université, CNRS, 75005 Paris, France

^b Laboratoire Léon-Brillouin (LLB), UMR12 CEA-CNRS, Université Paris-Saclay, F-91191 Gif-sur-Yvette CEDEX, France

^c European Spallation Source (ESS) AB, Box 176, S-22100 Lund, Sweden

^d Institut Laue Langevin (ILL), Grenoble F-38042, France

^e Centre de Recherche Paul-Pascal, UMR Université de Bordeaux-CNRS 5031, 115 Avenue du Dr Albert Schweitzer, 33600 Pessac, France

E-mails: claire.hotton@universite-paris-saclay.fr (CH), yasmine.sakhawoth@gmail.com (YS), anne-laure.rollet@sorbonne-universite.fr (ALR), juliette.sirieix-plenet@sorbonne-universite.fr (JSP), lingsam.tea@sorbonne-universite.fr (LT), sophie.combet@cea.fr (SC), melissa.sharp@ess.se (MS), hoffmann@ill.fr (IH), frederic.nallet@u-bordeaux.fr (FN), natalie.malikova@sorbonne-universite.fr (NM)

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1. Synthesis of ionenes

The synthesis builds upon the original synthetic routes of Rembaum and Noguchi [1–3]. In general, Br-ionenes are synthesized from the corresponding equimolar amounts of *N,N,N',N'*-tetramethyl-1,*x*-alkane and 1,*y*-dibromoalkane (Aldrich) by a polyaddition reaction in dimethylformamide (methanol in the case of 6,12- and 12,12-ionene) at room temperature and under argon atmosphere for a duration of 7 days.

Preparation of dimethylamine (DMA) aqueous solution. Dimethylamine hydrochloride (86.0 g, 1.05 mol) was transferred in to a two-necked, 500mL round-bottom flask equipped with a magnetic stirrer. One neck was connected to a dropping funnel containing NaOH aqueous solution at 23 M (50 mL, 1.15 mol) and the other one to the tube immersed in ice-cold water (18 mL). NaOH solution was added dropwise to dimethylamine hydrochloride (DMA.HCl) while stirring at 10 °C. The mixture was warmed to its initial boiling point (55 °C)

* Corresponding author.

and then slowly further on up to 90 °C. Vapours of DMA were condensed/dissolved while passing through the ice-cold water. The procedure yielded an aqueous solution (57%, 51.7 g, 0.63 mol) of DMA.

Synthesis of N,N,N',N'-tetramethyl-1,12-dodecanediamine. 1,12-Dibromododecane (8.35 g, 25 mmol) was dissolved in tetrahydrofuran (70 mL) into a 250 mL round-bottom flask. The solution was cooled to -78 °C and an aqueous solution of DMA (57%, 39.5 g, 0.5 mol) was added. After being stirred for 30 min at the same temperature, the reaction mixture was allowed to warm to room temperature and stirred for 24h. Volatile components were removed under reduced pressure, and the resulting white residue was dissolved in 2 M NaOH aqueous solution (200 mL). Thereafter the liquid phase was extracted with diethyl ether several times. The combined organic layers were collected and concentrated to obtain a yellow oil. The crude product was purified via vacuum distillation (100 °C and 1 mbar) from CaH₂ to provide a clear colourless liquid product (4.5 g, 90% yield).

Synthesis of 12,12-Ionene Bromide. N,N,N',N'-tetramethyl-1,12-dodecanediamine (4.5 g, 22.5 mmol) was added to a solution of 1,12-Dibromododecane (5.77 g, 22.5 mmol) in methanol (55 mL). The reaction mixture was stirred for 3 days at 45 °C. The solution was then concentrated and the residue was precipitated with diethylether. After the decantation, the supernatant was eliminated. The solid was dissolved in water and washed with diethylether. After elimination of water by freeze-drying, the 12,12-ionene was obtained as white solid (12,49 g, 95%).

Synthesis of 6,6-, and 3,3-Ionene Bromides. These ionenes were prepared as described for 12,12-ionene bromide, with the appropriate dibromoalkanes and diaminoalkanes [4–7]. In the case of 3,3-ionene bromide, small amounts of water were repeatedly added into the reaction mixture, when it became white and very viscous, to ensure the solubility of all components.

2. Viscosity measurements on ionene solutions

Figure SI-1 features viscosity measurements for 6,9-Br and 6,9-F ionenes. Changes in slope occur at the same concentrations, which confirms the information from SANS that the two systems are in the same concentration regimes at 0.4M and 2M. Similar type data is obtained for 3,3-ionenes and 12,12-ionenes (data not shown).

3. Additional SANS measurements on 6,9- and 12,12-ionenes

Figure SI-2 shows the SANS intensity for ionene chains with mixed counterion clouds at moderate (6,9-ionenes) and low (12,12-ionene) chain charge densities.

4. Scattering length densities and contrasts for ionene PEs in water. Estimate of relative ion and ionene chain contributions.

Table SI-1 summarizes the scattering length densities of the different components in ionene halide PEs and their contrast with respect to the D₂O solvent. Table SI-2 presents an overall factor estimating the relative intensities of the ionene-ionene partial scattering function and the ion-ion partial scattering function. This estimation is based on the intensity being proportional to $(\Delta\rho)^2 * V^2$, where $\Delta\rho$ is the contrast and V the volume of the scattering object (ionene repeat unit or ion). This overall intensity factor in Table SI-2 is informative: (a) trivially, the ion contribution is more important as we move towards more highly charged ionene chains, (b) the most favourable case (i.e. with the weakest ion contribution) are solutions for F-ionenes, where even for the most highly charged chains, the ionene signal is 4-5 orders of magnitude higher than the ion signal. (c) the least favourable cases correspond to 3,3-Br and 3,3-I ionenes, where we are however still at one order of magnitude difference.

5. Decoupling of coherent and incoherent intensity in NSE via polarisation analysis

Figure SI-3 shows the decoupling of scattered intensity into its coherent and incoherent contributions, as obtained by polarisation analysis in NSE.

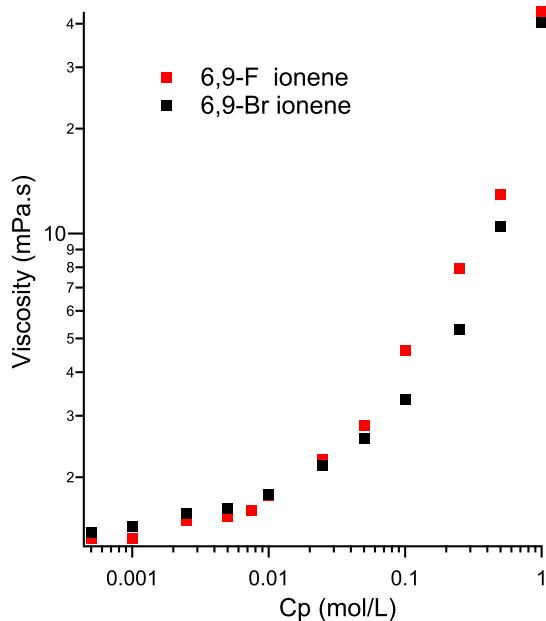


Figure 1. Viscosity measurements for aqueous solutions of 6,9-Br and 6,9-F ionenes.

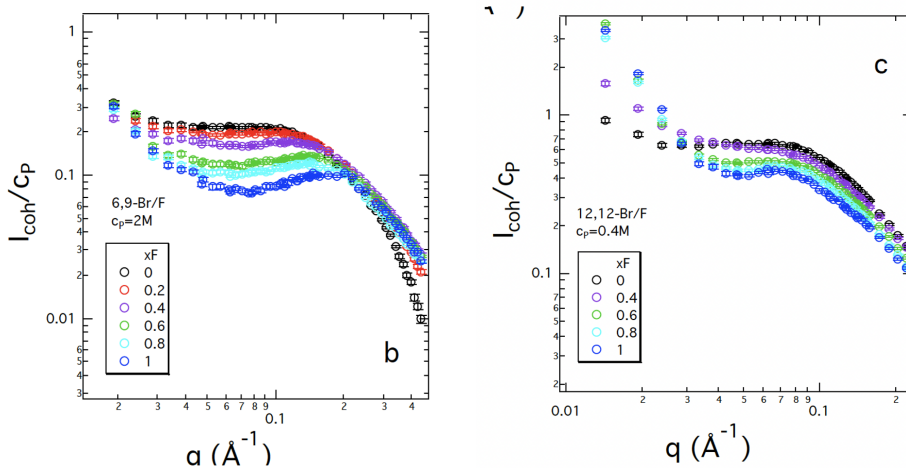


Figure 2. Coherent neutron scattering intensity normalised by ionene monomer concentration (I_{coh}/c_p), in arbitrary units, versus scattering wave-vector (q) for room temperature aqueous solutions (in D_2O) of 6,9- and 12,12-ionenes with mixed Br-F counterion clouds. The fraction of F^- counterions (xF) is shown in the legend. All systems are at 2M monomer concentration.

Table 1. Scattering length densities (SLD) of the different components in ionene halide polyelectrolytes (ionene repeat unit, counterions) and their contrast with respect to D₂O solvent.

Ionene, Ion, solvent	SLD (cm ⁻²)	(Δρ) ² in D ₂ O (cm ⁻⁴)
3,3-	-1.42*10 ⁹	4.20*10 ²¹
4,5-	-1.76*10 ⁹	4.24*10 ²¹
6,6-	-1.99*10 ⁹	4.27*10 ²¹
6,9-	-2.15*10 ⁹	4.30*10 ²¹
6,12-	-2.28*10 ⁹	4.31*10 ²¹
12,12-	-2.45*10 ⁹	4.33*10 ²¹
F ⁻	7.08*10 ¹⁰	5.49*10 ¹⁹
Cl ⁻	3.92*10 ¹⁰	5.84*10 ²⁰
Br ⁻	2.09*10 ¹⁰	1.81*10 ²¹
I ⁻	1.11*10 ¹⁰	2.74*10 ²¹
H ₂ O	-5.62*10 ⁹	-
D ₂ O	6.34*10 ¹⁰	-

Table 2. Overall factor estimating the relative intensities of the ionene-ionene partial scattering function and the ion-ion partial scattering function. Factors rounded to 2 significant figures.

	3,3-	4,5-	6,6-	6,9-	6,12-	12,12-
F-ionene	16000	25000	36000	50000	64000	100000
Cl-ionene	160	250	360	500	650	1000
Br-ionene	29	46	66	90	120	190
I-ionene	10	14	20	28	36	57

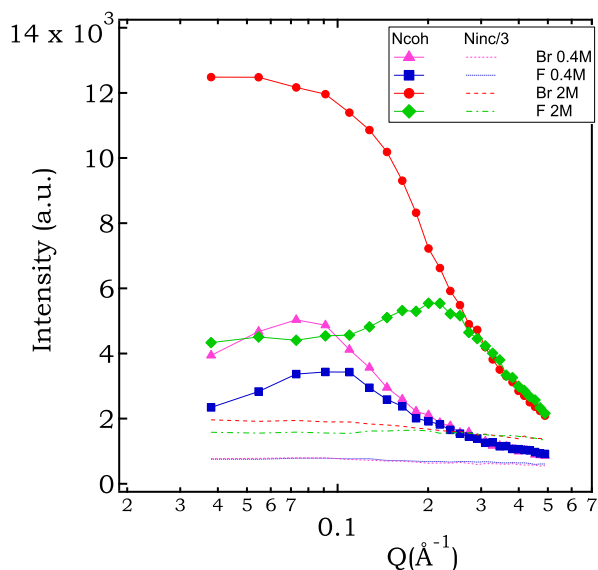


Figure 3. Scattered intensity as a function of the wave-vector Q, decoupled into the coherent (Ncoh) and incoherent (Ninc) contributions. The latter is presented with an intensity pre-factor of 1/3, to reflect its effective contribution in the dynamic signal measured by the neutron spin echo technique. Four samples are considered: ionene chains with F and Br counterions, each at a low and a high monomer concentration, 0.4M and 2M respectively.

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