

# On the crossroads of current polyelectrolyte theory and counterion-specific effects

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## SUPPLEMENTARY INFORMATION

### Additional neutron and X-ray scattering data

Figure S1 features the neutron scattering spectra of 3,3-Br and 3,3-F ionenes, showing again the clear disappearance of the PE peak in the case of Br-ionenes. This attests to the universality of the F-Br counter ion specific effect, across the entire range of ionene chain charge densities.

Figure S2 features the effect of additional electrolyte (NaF) on the scattering data of 12,12-F ionene. The disappearance of the PE peak under these conditions features two notable differences with respect to the *salt-free* Br-ionene solutions, as is explained.

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Figure S3 shows the X-ray scattering data on 3,3-ionenes with three different halide counter ions ( $F^-$ ,  $Br^-$ ,  $I^-$ ), showing a clear correlation between the extent of the counterion atmosphere and the position of the PE peak, as seen by this particular technique. These SAXS results confirm the differences in the spread of the counter ion atmosphere around the ionene backbone as was inferred also from the SANS data. Very similar behaviour has already been observed in a SAXS study of the poly(styrenesulphonic) acid salt solutions.<sup>1</sup> Interestingly 3,3-ionenes were the only samples in the present study that showed a detectable excess SAXS signal. For ionene samples of a lower chain charge density, the counterion atmosphere was not dense enough to yield a sufficient SAXS signal. This is in accordance with the results for the Manning charge density parameter presented in Figure 1 of the article.

*SAXS-Experimental:* Small angle X-ray scattering (SAXS) spectra were measured with an in-lab modified Kratky compact camera (Anton Paar KG, Graz, Austria) equipped with Osmic MAX-FLUX focusing multilayer optics as the monochromator and position sensitive detector PSD-50M (Mbraun, Garching, Germany). The camera was attached to a conventional PW 3830/00 X-ray generator (Philips- PANalytical B.V., EA Almelo, The Netherlands) equipped with a sealed X-ray tube (Cu  $\alpha$  K X-rays,  $\lambda = 0.154$  nm) operating at 40 kV and 50 mA. SAXS results were corrected for the background scattering and put to absolute scale using water as a secondary standard.

## References

- (1) Tomšič, M.; Bešter Rogač, M.; Jamnik, A. *Acta Chem. Slov.* **2001**, *48*, 333–342.
- (2) Combet, J.; Isel, F.; Rawiso, M.; Boué, F. *Macromolecules* **2005**, *38*, 7456–7469.
- (3) Combet, J.; Lorchat, P.; Rawiso, M. *Eur. Phys. Journal - Special Topics* **2012**, *213*, 243–265.

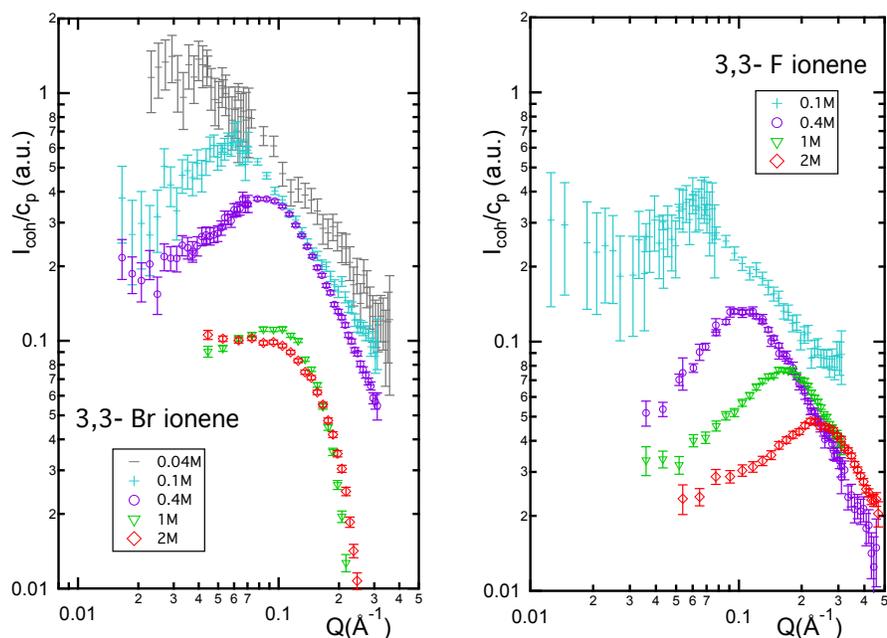


Fig. S 1: Coherent neutron scattering intensity normalised by ionene monomer concentration ( $I_{coh}/c_p$ ) versus scattering wave-vector ( $Q$ ) for room temperature aqueous solutions of 3,3-Br and 3,3-F ionenes (in  $D_2O$ ). Monomer concentrations as indicated in the legends.

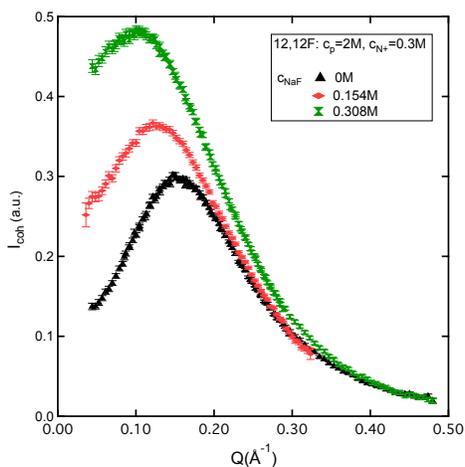


Fig. S 2: Coherent neutron scattering intensity ( $I_{coh}$ ) versus wave-vector ( $Q$ ) for 12,12-F ionenes at 2 M monomer concentration, with increasing concentration of added salt (NaF). All data are taken at room temperature. With respect to PE peak disappearance in *salt-free* Br-ionene solutions, we observe two notable differences: adding NaF to F-ionene solutions leads to a) the peak shifting significantly to lower  $Q$  values and b) the peak remaining symmetric and of an almost constant width.

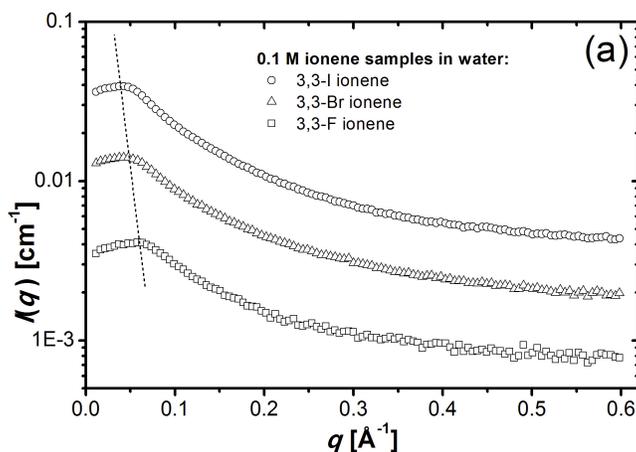


Fig. S 3: X-ray scattering intensity versus wave-vector ( $Q$ ) for aqueous solutions of 3,3-ionenes with three different halide counter ions, at  $c(\text{N}^+) = 0.1 \text{ M}$  (solutions in light water). Note that the position of the PE peak observed by SAXS and SANS for the 3,3-F and 3,3-Br systems is very close (within  $0.01 \text{ \AA}^{-1}$  of each other). Slight variations of PE peak position between SANS and SAXS have been observed before, as the two techniques are not sensitive to correlations involving the same species (SANS - backbone, SAXS - counter ions, in general).<sup>2,3</sup> The PE peak observed by SAXS shifts clearly to higher  $Q$  vectors as we move from large halide counter ions ( $\text{I}^-$ ) towards the smallest halide counter ion, with the most negative hydration energy ( $\text{F}^-$ ). There is thus clearly a correlation between the extent of the counter ion atmosphere (most extended in case of  $\text{F}^-$ ) and the position of the PE peak seen by SAXS. Note that SAXS measurements on ionenes with lower charge densities were unsuccessful due to insufficient scattering contrast.