ANALYSIS OF THE CORRELATION OF COUNTERIONS TO MACROIONS BY ANOMALOUS SMALL-ANGLE SCATTERING

Matthias Ballauff[1], Mushtaq Patel[1], Sabine Rosenfeldt[1], Nico Dingenouts[2], Theyencheri Narayanan[3], Axel Müller[4], and Felix Plamper[4].

[1]*Physikalische Chemie I, NW I, University of Bayreuth, 95440 Bayreuth, Germany*

[2]*Polymer-Institut, Department of Chemistry, University of Karlsruhe, 76128 Karlsruhe, Germany*

[3]*European Synchrotron Radiation Facility, B. P. 220 F-38043 Grenoble Cedex, France*

[4]*Makromolekulare Chemie II, NW II, University of Bayreuth, 95440 Bayreuth, Germany*

INTRODUCTION

Polyelectrolytes are highly charged macroions that may dissociate into a macroion and a concomitant number of counterions when dissolved in water or other solvent with a high dielectric constant.[1] A central question in this field is the correlation of the counterions to the macroion in solution. Because of the strong electric field of the macroion in solution, a marked correlation of the counterions to the macroion is expected. In case of linear macroions, this correlation is by now well-understood in terms of the concept of "counterion condensation" first introduced by Manning.[2,3] Counterion condensation leads to a certain fraction of the counterions that is highly correlated to the macroion, i.e., the correlation persists up to high dilution. For typical polyelectrolytes as e.g. poly(styrene sulfonic acid) this fraction amounts to 20 to 30 % of the counterions.[1,3] For polyelectrolytes with a more complicated architecture as e.g. star polyelectrolytes a much stronger correlation of the counterions to the macroion is predicted.[4,5] For these polyelectrolytes theory and simulations come to the conclusion that most of the counterion are confined within the volume explored by the macroion.

Small-angle X-ray scattering (SAXS) and small-angle Neutron scattering (SANS) are uniquely suited to test these predictions.[6] However, a meaningful analysis by SAXS or SANS requires that the signal of the macroion can be distinguished from the signal of the counterions. In case of SANS this can be achieved by using deuterated counterions.[7] In case of SAXS exchange of weakly scattering counterions (as e.g. Cl⁻) by strongly scattering counterions (as e.g. I⁻) may be used for this purpose.

Recently, we could demonstrate that anomalous small-angle X-ray scattering (ASAXS) presents a more elegant way to distinguish between the scattering signals of the macroion and the counterions.[9-13]. ASAXS uses the anomalous dispersion of the counterions near their absorption edge where the scattering factor f becomes a complex quantity:[14]

$$f = f_0 + f'(E) + if''(E) \qquad (1)$$

the first term f_0 is the non-resonant term which equals the atomic number of the element.[13] The second and the third term of eq.(1) are the real and the imaginary part, respectively, that describe the anomalous dispersion near the absorption edge, and i is the complex unity. Fig. 1 displays f' and f'' as the function of energy E for rubidium. The absorption edge is localized at an energy of 15199.7 eV. Hence, the resonant terms become an explicit function of the energy E of the beam if E is slightly below this value. Using the effect of anomalous dispersion allows one to change the contrast in a systematic fashion and to distinguish between the signal of the counterions and the one of the macroion.[9-13]
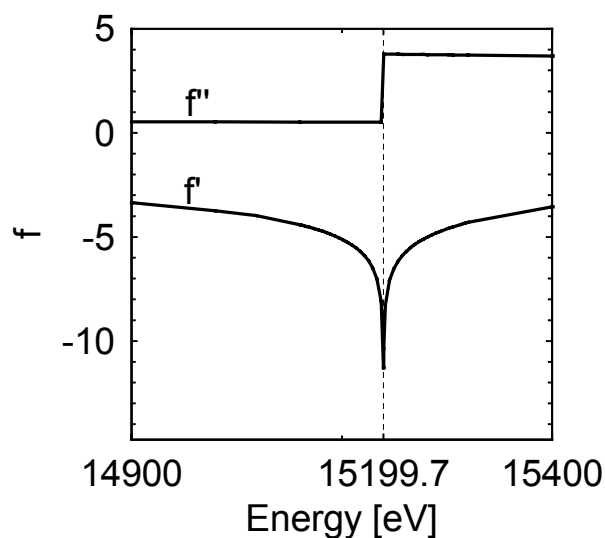

Figure 1. Dispersion of rubidium near the K-edge: The real and the imaginary parts f' and f'' (see eq. (1))are plotted as a function of the energy E of the incident radiation. The dashed line marks the energy of the K_α-edge of rubidium.

Here we give a discussion of the analysis of polyelectrolytes by ASAXS. In particular, we discuss the application of this technique to star polyelectrolytes. We demonstrate that the strong correlation of the counterions to the macroion predicted by theory[4,5] can be seen indeed from the ASAXS-data. Hence, ASAXS has become a highly efficient tool for the study of polyelectrolytes as envisioned by Stuhrmann some 20 years ago.[14]

EXPERIMENTAL

A poly(acrylic acid) star with 21 arms was prepared by atom transfer radical polymerization, using a macroinitiator based on β-cyclodextrin. The number-average degree of polymerization of the arms is 125. Details of the synthesis and molecular characterization will be given elsewhere.[15]

All ASAXS measurements were performed at the beamline ID2 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.[16] Two sample-to-detector distances were used (2 and 10m). The detector was an image-intensified CCD-camera. The energy of the incident beam was varied between 12460eV and 15200eV.

All data have been corrected for detector response, efficiency, incident flux and normalized to an absolute scale. The normalized data were azimuthally averaged and corrected for the background of the water solvent and the empty cell.

In situ measurement of the extinction as a function of energy was done for each sample studied here. The concentration of the star polyelectrolyte was 5.75 g/L.

THEORY

An comprehensive account on the theory and the evaluation of ASAXS-data was given recently.[12,13] Therefore it suffice to delineate the main points here.

The star polyelectrolytes under scrutiny here have in average a spherically symmetric conformation.[4,5] However, the scattering amplitude $F(q)$ (q: magnitude of scattering vector; $q = (4\pi/\lambda)\sin(\theta/2)$; λ: wavelength of the radiation, θ: scattering angle) is a complex quantity because of the complex scattering factor f (see eq.(1)). Hence, the scattering intensity $I_0(q)$ follows as
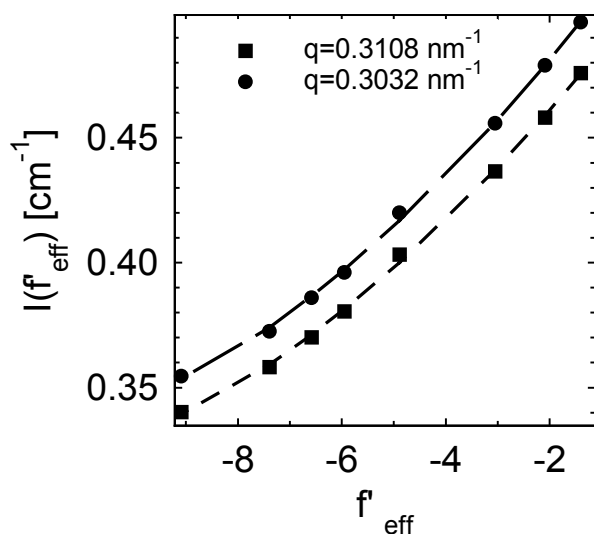
$$I(q) = F(q)F^*(q) \qquad (2)$$

Figure 2 Decomposition of the ASAXS-intensities according to Eq.(4): The intensity measured for a given q-value indicated in the graph is plotted against f'. The quadratic fit then leads to the three partial intensities enumerated in E.(4).

As mentioned above, only the rubidium counterions have a resonant part. The contrast Δf_{ion} hence becomes a complex quantity[12]

$$\Delta f_{ion} = f_0 - \rho_m V_{ion} + f'(E) + if''(E) \qquad (3)$$

where V_{ion} is the volume of a single ion and ρ_m is the electron density of the medium. From eq.(2) and eq.(3) it can be derived that the intensity I(q) measured near the edge consists of three terms:[9-14]

$$I(q) = F_0^2(q) + 2F_0(q)v(q) + (f'(E)^2 + f''(E)^2)v^2(q) \qquad (4)$$

where $F_0(q)$ is the scattering amplitude of the non-resonant scattering units in the system and $v(q)$ is the scattering amplitude related solely to the resonantly scattering units. In this way ASAXS gives access to v^2(q) which is the scattering intensity of just the resonantly scattering units, i.e. the counterions.

Eq.(4) is the basis of the analysis of the data inasmuch it demonstrates that three partial intensities may be derived from ASAXS. Moreover, it suggests to plot I(q) as the function of f' for all q-values under consideration.[12,13] This way of analyzing the data can be argued from the fact that below the absorption edge f'' is much smaller than f' (see Fig. 1). Hence, I(q) becomes a quadratic form of f' and the three partial intensities can be derived from this fit in a secure manner.[12,13]

RESULTS AND DISCUSSION

As mentioned above, Eq.(4) suggests to plot I(q) for each *q*-value as the function of f'. Fig. 2 shows this plot. As lined out in Ref.[12,13], the finite width of the primary beam must be taken into account by definition of an effective value of f' termed f'_{eff}. The correction thus effected is small unless very near to the edge.

Fig. 2 demonstrates that there is a slight but finite curvature that is due to the third term v^2(q). Hence, all three terms enumerated in Eq.(4) can be derived from this analysis as shown previously for other systems.[12,13] Fig. 3 displays all partial intensities derived from this analysis. The term $F_0(q)$ is the intensity that would be measured in a conventional SAXS-experiment far below the absorption edge. The third term v^2(q) is the intensity of the cloud of counterions around the star macroion and presents a highly valuable information not accessible by the conventional SAXS-experiment.

Fig. 3 demonstrates that all terms including the cross term $F_0(q)v(q)$ run parallel to each other. This indicates that the counterions that determine v^2(q) decorate the macroion, that is, there is a strong correlation of the counterions to the macroion as predicted by theory.[4,5]
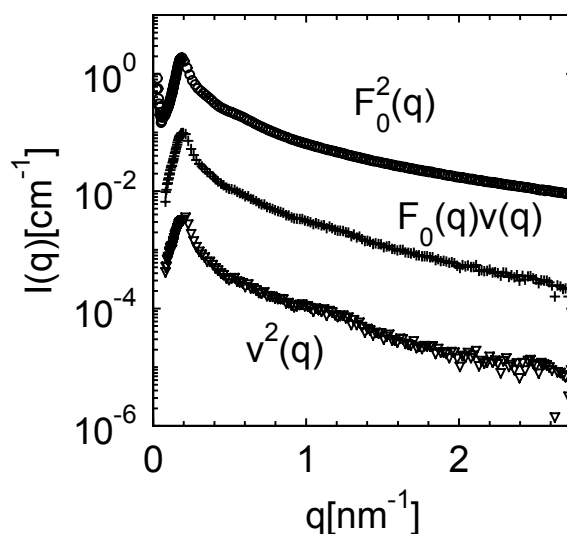

Figure 3 Partial intensities of the polyelectrolyte star as derived from the ASAXS-experiment according to eq.(4). Here $F_0^2(q)$ is the scattering intensity deriving from the non-resonant scattering factor f_0 (see eq.(1)). The terms $v^2(q)$ is the scattering intensity solely due to the resonantly scattering units, i.e., the counterions of the star polymer. Finally, $F_0(q)v(q)$ gives the cross term between the amplitudes $F_0(q)$ and $v(q)$.[9-13]

REFERENCES
1. Schmitz, K. S. *Macroions in solution and colloid suspension*, VCH-publisher, New York, 1993.
2. Manning, G., *Ann. Rev. Phys. Chem.* **1972**, *23* 117.
3. see the discussion in Deserno, M.; Holm, Ch., Blaul, J.; Ballauff, M.; Rehahn, M. *Eur. Phys. J. E* **2001**, *5*, 97.
4. Jusufi, A.; Likos, C. N.; Löwen, H. *Phys. Rev. Lett.* **2002**, *88*, 018301.
5. Jusufi, A.; Likos, C. N.; Löwen, H. *J. Phys. Chem.* **2002**, *116*, 11011.
6. Glatter, O.; Kratky, O., *Small-Angle X-Ray Scattering*, Academic Press, London, 1982.
7. Kassapidou, K.; Jesse, W.; Kuil, M.E.; Lapp, A.; Egelhaaf, S.; van der Maarel, J. R. C. *Macromolecules* **1997**, *30*, 2671.
8. see, e.g., Guilleaume, B.; Blaul, J.; Wittemann, M.; Rehahn, M.; Ballauff, M. *J Cond. Matter* **2000**, *12*, A245.
9. Guilleaume, B.; Ballauff, M.; Goerigk, G.; Wittemann, M, Rehahn, M. *Colloid Polym. Sci.* **2001**, *279*, 829.
10. Guilleaume, B.; Blaul, J.; Ballauff, M.; Wittemann, M, Rehahn, M.; Goerigk, G. *Eur. Phys. J. E* **2002**, *8*, 299.
11. Dingenouts, N.; Merkle, R.; Guo, X.; Narayanan, T.; Goerigk, G.; Ballauff, M. *J. Appl. Cryst.* **2003**, *36*, 578.
12. Dingenouts, N.; Rosenfeldt, S.; Pontoni, D.; Narayanan, T. Ballauff, M.; *Macromolecules.* **2004**, *37*, 8152.
13. Patel, M.; Rosenfeldt, S.; Ballauff, M.; Dingenouts, N.; Pontoni, D.; Narayanan, T. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2962.
14. Stuhrmann, H. B. *Adv. Polym. Sci.* **1985**, *67*, 123.
15. Plamper, F.; Müller , A. H. E., in preparation.
16. Narayanan, T.; Diat, O.; Boesecke, P. *Nucl. Instrum. Methods Phys. Res. A* **2001**, *467*, 1005.