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New experiments for the quantification of counterion condensation

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ABSTRACT

The condensation of counterions is an important aspect of charged macromolecules. Therefore an experimental characterization of the condensation of counterions is desirable. In this contribution two experimental techniques for the characterization of counterion condensation are introduced and compared: Anomalous Small Angle X-Ray Scattering (ASAXS) is able to probe the spatial distribution of counterions and electrophoresis nuclear magnetic resonance (NMR) measures counterion condensation via the effective charge obtained from the dynamic behaviour of molecules and complexes in an electric field.

1. Introduction

Electrostatic effects play an important role in nature as well as in many artificial materials. Often a large number of charges is located on a single object like a colloid or a macromolecule (polyelectrolyte behaviour) resulting in an electrostatic potential so strong that the counterions do not have sufficient thermal energy to escape it [1,2]. The individual groups remain charged (dissociated or protonated), the counterions however are located in the vicinity of the macromolecule. The charges remaining on the polyelectrolyte affect the morphology of the polyelectrolyte and its response to environmental changes. A better understanding of the processes of counterion capturing by polyelectrolytes therefore is an important issue in fundamental science and at the same time is highly relevant to the development of new functional materials.

Only few methods are known, which permit to measure and quantify the condensed counterions. An indirect measure of condensation is the activity of counterions in the solution containing the polyelectrolyte. This can be probed either by potentiometry [3–6] or conductometry [7], where the difference of the measured effect between the total number of ions and the active number is attributed to condensed counterions. The activity of chloride anions for instance in the presence of poly(dimethyldiallylammoniumchloride) has been measured by chloride ion selective electrodes [3]. More effort has been devoted to the investigation of metal cations in the presence of polyanyions [4–7]. By means of the latter contributions, specific binding of alkaline earth cations could well be distinguished from classical counter ion condensation observed with alkali metal cations. An approach similar to the electrochemical methods is the measurement of the osmotic pressure [8] because only the non-condensed counterions are osmotically active and contribute to the osmotic pressure. In neutron scattering experiments the distribution of counterions in the vicinity of dendrimers has been evaluated and attributed to the condensation of counterions [9]. The interaction of polyelectrolytes with paramagnetic counterions has been observed both in the mobility as manifested in the EPR lineshape [10] and the spin exchange broadening of the spectra from distance-dependent interaction [11].

There are also numerous theoretical works and simulations on the subject of counterion condensation. Holm and coworkers discussed different estimators for the effective charge of macromolecules derived from simulations [12]. These nicely correspond to criteria found in different experiments

The subject of the present paper is to present two recent experimental developments giving a direct access to the condensation of counterions and probing the local distribution of the counterions within the domain of the hosting polyelectrolyte. Anomalous X-Ray Scattering reveals scattering curves with element selectivity and thus offers information on the spatial distributions of the "selected element". Herewith, clustering of counterions on a macromolecule can be observed and quantified. The combination of diffusion and electrophoresis NMR inherently provides chemical selectivity from the NMR-spectroscopic information. Via the electrophoretic mobility and the self diffusion coefficient the effective charge of macromolecules and counterions is determined.

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2. Anomalous Small Angle X-Ray Scattering

2.1. Evolution of the Field

Despite the fact that the work which applies ASAXS on the investigation of counterion distribution in polyelectrolyte solution is still sparse, some significant progress has been achieved in the field which is only partially covered by a more recent article on the benefit ASAXS offers to an investigation of the behaviour of dilute polyelectrolyte solutions [13]. Progress in the field includes the successful isolation of the scattering pattern of the counterions and the quantification of the amount of counterions bound to the domain of the polyelectrolyte chains. Along this line, the following notes extend former reports [14••,13] and at the same time intend to convince a broader audience on the potential ASAXS bears for the investigation of counterion binding by polyelectrolyte chains in solution.

The scattering contrast of a SAXS experiment in general is determined by the excess electron density $\Delta\rho$ of the dissolved polyelectrolyte salt with respect to the electron density of the solvent. Accordingly, the scattering amplitude from the polyelectrolyte $A(q)$ is represented as a function of the momentum transfer q as follows

$$A(q) = \int_V \Delta\rho\left(\vec{r}\right) \exp\left(-i\,\vec{q}\,\vec{r}\right) d^3r \qquad 1$$

with the momentum transfer q corresponding to the value of the scattering vector written as a function of the wavelength λ of the x-ray beam, and of the observation angle θ.

$$q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

Once the scattering sample includes an absorbing species, the amplitude $A(q)$ in Eq. (1) can be subdivided as follows

$$A(q) = \int_V \Delta\rho_{nr}\left(\vec{r}\right) \exp\left(-i\,\vec{q}\,\vec{r}\right) d^3r + \int_V \Delta\rho_r\left(\vec{r}\right) \exp\left(-i\,\vec{q}\,\vec{r}\right) d^3r \qquad 2a$$

$$A(q) = A_{nr}(q) + A_r(q) \qquad 2b$$

In Eq. (2b), the first term comprises the entire non-resonant scattering $A_{nr}(q)$ from all species of the polyelectrolyte including the polymer chains and the counterions and the second term captures the additional resonant scattering contribution $A_r(q)$, which exclusively stems from the counterions as the absorbing species.

The excess electron densities appearing in Eq. (2a) are determined by the density distributions $u(r)$ of monomeric units forming the polymers and by the density distribution of the counterions $v(r)$ via

$$\Delta\rho_{nr}(r) = \left[\left(f_{0,C} - \rho_S V_C\right)\right]\cdot v(r) + \left[f_M - \rho_S V_M\right]\cdot u(r) \qquad 3a$$

$$\Delta\rho_r(r,E) = \left[f'_C(E) + i f''_C(E)\right]\cdot v(r) \qquad 3b$$

In Eq. (3a, 3b), V_M and V_C are the volumes of a monomer within the polymer and of a counterion respectively. The electron density of the solvent is indicated as ρ_S. Further on, f_M and $f_{0,C}$ represent the number of electrons of a monomer and a counterion respectively. It has to be emphasized that the excess number of electrons of the counterion includes two extra terms, which depend on energy (wavelength) and which form the resonant term of Eq. (3b). These two energy dependent terms $f'_C(E)$ and $f''_C(E)$ and hence $\Delta\rho_r(r,E)$ only contribute significantly if experiments are performed close enough to the absorption edge of the absorbing species and decrease to zero a few percent beyond the value of the energy at the absorption edge. An illustrative example for the evolution of $f'_C(E)$ and $f''_C(E)$ is given in Fig. 1 for Sr^{2+} which act as counterions in an example indicated below. Due to this dependence of $f'_C(E)$ and $f''_C(E)$ on the energy the scattering contrast of the polyelectrolyte-counterion system can be varied by changing the wavelength of the primary x-ray beam close to an absorption edge. This variation in turn provides additional information on the internal structure of complex scattering species. To this end, the scattering pattern described as the differential scattering cross section is written as follows[14••],.

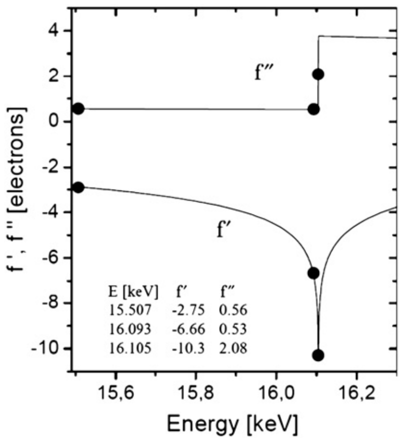
$$\frac{d\Sigma}{d\Omega}(q,E) = \left\langle A_{nr}(q)\cdot A_{nr}*(q)\right\rangle + 2f'_C(E)F_{nrC}(q) + \left[f'_C(E)^2 + f''_C(E)^2\right]S_{CC} \qquad (4)$$

where the first term represents the non resonant part also available with a conventional SAXS experiment, F_{nrC} corresponds to the cross term and S_{CC} is the normalised scattering contribution from the counterions addressed by ASAXS.

Publications where this concept has been applied for the first time to the investigation of polyelectrolyte systems refer to biological molecules and date back to the early seventies [15,16]. Here, the loose shell of Cs^+ counter ions condensed around the stiff backbone of anionic DNA chains had been addressed. Wavelength dependent SAXS measurements close to the L_3 absorption edge of Cs^+ indicated a decrease of the (apparent) cross section radius of the DNA strand upon approaching the absorption edge. The decrease was attributed to the dispersion of $f'_C(E)$, which, as an increasingly negative value, lowered the scattering contrast of the condensed counterions. The resulting decrease of the apparent cross section could only be made consistent with an adsorbed Cs^+ shell larger than the bare radius of the DNA strand.

It was only in 1999, when Sabbagh et al [17] presented another study on the condensation of Co^{2+} ions on sodium polyacrylate (Na–PA) chains. They performed an analysis of three scattering curves close to the K absorption edge of Co^{2+} revealing that the closer the wavelength gets to the edge, the lower the scattering curve lies. A suitable ASAXS reference experiment with weakly charged polyacrylic acid in the presence of Co^{2+} ions revealed the same scattering behaviour as a pure $CoCl_2$ solution and hence indicated the complete lack of correlations of Co^{2+} ions around the neutral polyacrylic acid coils. Although, this ASAXS experiment was a purely qualitative analysis, it showed that Co^{2+} condensation occurred onto anionic PA coils and that ASAXS is sensitive to ion specific scattering.

Further analysis of counterion condensation was propelled by the progress in preparing new model polyelectrolytes with well defined



E [keV]	f′	f″
15.507	-2.75	0.56
16.093	-6.66	0.53
16.105	-10.3	2.08

Fig. 1. Anomalous dispersion corrections obtained by Cromer-Liberman calculations [26,27]. The values at 16.105 keV result from the convolution with the energy resolution of the JUSIFA beamline [25•]. Reproduced with kind permission from Springer Science & Business Media: The European Physical Journal E-Soft Matter.