New opportunities for Anomalous Small-Angle X-Ray Scattering to characterize Charged Soft Matter Systems

M. Sztucki, E. Di Cola, and T. Narayanan
European Synchrotron Radiation Facility, B.P. 220, 38043 Grenoble, France.

E-mail: sztucki@esrf.eu

Abstract. This article presents a quantitative analysis of charged Soft Matter system using Anomalous Small-Angle X-ray Scattering (ASAXS). Specific experimental requirements and data reduction are described. The simultaneous analysis of data sets recorded below and above the absorption edge provides valuable constraints in data modelling. The merit of the method is illustrated by an example involving cationic surfactant micelles. The counterion profile around the micelle is deduced in a self-consistent manner and the results reveal the strong condensation of counterions on to the micellar surface.

1. Introduction
Deeper understanding of charged soft matter systems is of direct relevance to many applied areas of research including biophysical processes [1]. Examples include charge stabilized colloids, polyelectrolytes, surfactant micelles and membranes, DNA, proteins, etc. An important issue in the detailed description of such systems is the spatial distribution of counterions around a macroion [2]. In this context, quantitative Anomalous Small-Angle X-ray Scattering (ASAXS) offers a direct method for the structural characterization of charged systems [3-8]. The spatial distribution of counterions can be deduced with high precision by tuning the energy in the vicinity of the absorption edge of the counterions [5,9]. This information is not readily accessible by conventional scattering techniques as the contributions of the counterions and the macroions superimpose and thus cannot be distinguished. However, the stability and radiation sensitivity of the specimens as well as relatively low concentration of anomalous species in typical soft matter systems put high demands on the instrumental setup. The technical requirements for accurate data recording and the theoretical background for quantitative analysis of anomalous small-angle X-ray scattering data have recently been summarized [10].

This article focuses on new opportunities offered by detecting and ideally discriminating the contribution of fluorescence, which plays an important role in the energy range close and above the absorption edges. It will be demonstrated that quantitative simultaneous fitting of the scattering curves recorded not only below [10], but also above the corresponding absorption edge is feasible and helps to determine the spatial distribution profile of the counterions with high accuracy. This is illustrated by a micellar surfactant system (Tetradecyl-trimethylammonium bromide, TTAB) near the bromine K-edge (13474eV).

2. Anomalous small-angle X-ray scattering
The scattered intensity, \( I(q) \), from a suspension of centrosymmetric particles as a function of the modulus of the scattering vector, \( q = \frac{2\pi}{\lambda} \sin(\frac{\theta}{2}) \), (with \( \theta \) being the scattering angle and \( \lambda \) the wavelength of the incident radiation), can be expressed as

\[
I(q) = NP(q)S(q)
\]
with \( N \) the number density of particles, \( P(q) \) the single particle scattering function, and \( S(q) \) the structure factor of interactions. The single particle scattering function, \( P(q) \) is given by

\[
P(q) = F(q)F^*(q)
\]

(2)

\( F(q) \) being the scattering amplitude, and \( F^*(q) \) its complex conjugate. In the case of spherical particles

\[
F(q) = 4\pi \int \Delta \rho(r) \frac{\sin(qr)}{qr} r^2 dr
\]

(3)

with \( \Delta \rho(r) \) the relative scattering length density, \( \Delta \rho(r) = \rho(r) - \rho_m \), where \( \rho(r) \) is the radial scattering length density profile and \( \rho_m \) is the scattering length density of the background.

For dilute non-interacting systems, \( S(q) \approx 1 \), but for concentrated samples a polydisperse effective hard-sphere structure factor will be used.

Anomalous small-angle X-ray scattering uses the energy dependence of the X-ray scattering factor \( f \) of a given element when the energy of the incident X-ray beam is varied near the absorption edge of that element [see Fig. 1(a) for bromine]. In this case, the number of excess electrons per ion immersed in a medium becomes a function of energy of the incident beam

\[
\Delta f(E) = \Delta f_0 + f'(E) + if''(E)
\]

(4)

where \( \Delta f_0 \) denotes the scattering contribution of a single ion, \( f' \) and \( f'' \) are the real and imaginary parts of \( f \). The energy dependence of the radial scattering length density profile \( \Delta \rho \) can be determined as

\[
\Delta \rho(r, E) = \Delta \rho_0(r) + v(r) \delta \left[ f'(E) + if''(E) \right]
\]

(5)

with \( \Delta \rho_0(r) \) being the non-resonant scattering length density, \( v(r) \) being the spatial distribution of anomalous scattering units and \( r_e = 2.818 \times 10^{-15} \text{m} \) the classical electron radius. For further details see [10].

The total scattered intensity can be decomposed into three components,

\[
I(q) = N \{ F_0^2(q) + 2f'(E)F_0(q)v(q) + [f'^2(E) + f''^2(E)]v^2(q) \} \]

(6)

the energy independent normal SAXS \( F_0^2(q) \), a cross-term involving the amplitudes of normal SAXS and the resonant scattering of the counterions, and the pure resonant scattering term (self-term) due to counterions \( v^2(q) \). The Fourier transform of the self-term \( v^2(q) \) can directly yield the spatial distribution \( v(r) \) of the resonant atoms [7,9].

![Figure 1](image-url)

**Figure 1.** (a) Energy dependent real \( f' \) and imaginary \( f'' \) parts of the X-ray scattering factor \( f \) of bromine near its K-edge (13474eV) depicting the anomalous effect [11]. The vertical lines indicate the energies chosen in this study. (b) and (c) present a selection of the recorded ASAXS data at a sample concentration of 17mM and 50mM, respectively. The fluorescence background was subtracted from all data.

3. Experimental

Tetradecyl-trimethylammonium bromide [TTAB, C\(_{14}\)H\(_{29}\)N(CH\(_3\))\(_3\)Br] is a well-known cationic surfactant, which forms micelles above the critical micellar concentration (cmc) of about 3.6mM. TTAB
Aldrich 99%) solutions were prepared at different concentrations above the cmc: 10mM, 17mM and 50mM using MilliQ water. ASAXS measurements were performed at the High Brilliance Small-Angle X-ray Scattering beamline ID02 at the European Synchrotron Radiation Facility, Grenoble (France). Measurements of the samples with 17mM and 50mM concentration were recorded at a sample to detector distance of 0.9m by using the FReLoN CCD detector [10]. The following relative energies (\(E - 13474\) eV) near the bromine K-edge were used: -1000eV, -160eV, -54eV, -16eV, -10eV, -6eV, -4eV, -2eV, ±0eV, +2eV, +4eV, +8eV, +16eV, +46eV. As fluorescence detection plays an important role in the energy range close to and above the absorption edges, further data were recorded using an energy-resolving detector (Pilatus300K from Dectris). The sample to detector distance for these measurements was 2.0m. The investigated sample had a concentration of 10mM. The detector was first operated with a standard energy threshold of 50% of the working energy (i.e. ~6700eV). A second measurement was performed using an adjustable threshold of 12500eV as the fluorescence emission of Bromine is about 11.9keV (K\(\alpha\)).

![Figure 2. ASAXS measurement of a sample with 10mM concentration using an energy-resolving pixel detector (Pilatus300K). The scattering level of water is indicated to demonstrate the limit of detection. Fig. (a) shows the normalized scattering data recorded at two energies at and 12eV above the absorption edge of Br. Circles and squares represent data recorded with an energy threshold of 6700eV whereas the measurements marked by triangles and stars were recorded with maximum energy discrimination (threshold: 12500eV). In both cases a fluorescent background is detected which has to be subtracted. (b) After fluorescence correction, data recorded with and without energy discrimination are in good agreement.](image-url)

The ASAXS data were analysed by simultaneously fitting multiple scattering curves recorded below and above the absorption edge of Bromine. The obtained results demonstrate that the fluorescence background can be well handled. Fitting ASAXS data recorded below and above the absorption edge allows achieving better reliability of the simulated data as the full achievable range of \(f^+\) and \(f^-\) values are exploited. For data fitting, a spherical core double-shell model was used which is described in detail in [10]. Fig. 3(a) presents exemplarily 8 of the 14 fitted curves together with their best fits showing...
good agreement. Fig. 3(b) illustrates the model which uses a polydisperse core of radius $R$ with scattering contrast of the tetradecyl chains in the inner sphere (blue), followed by a first shell of closely packed trimethylammonium head groups (red, thickness $t$).

The most interesting fit parameter is the spatial distribution of the bromide ions $v(r)$ (black dots) within the outer shell (grey). For data fitting a unique set of structural parameters [$R$, $t$, $v(r)$] was used and only the scattering contrast of the counterion layer [Eq. (5)] was varied according to the effective values of $f'(E)$ and $f''(E)$.

The radial scattering length density profile $\Delta\rho(r)$ to the best fits presented before is shown in Fig. 4(a). The spatial distribution function of the Br counterions is presented in Fig. 4(b). The simultaneous fits of ASAXS data recorded below and above the Br $K$-edge confirm the derived fit results in [10]. The core radius is about $R = 1.55\text{nm}$ and the thickness of the shell representing the head groups is $t = 0.27\text{nm}$. The distribution of the counterions is concentrated in a layer of $\sim 0.34\text{nm}$ thickness with an exponential decay of the histogram to zero at a distance of $3.1\text{nm}$ from the center of the core, which is in agreement with the strong coupling of the counterions. The maximum number density of the ions is determined to be $3.8\text{nm}^{-3}$, which corresponds to about $1/10$ of the closest possible packing of the ions. The distribution function presented in Fig. 4(b) corresponds to about 72% of the bromide...
ions bound to the surfactant head groups. This result is consistent with the previous estimates of counterion association from neutron scattering [12] and electrochemical methods [13].

![Figure 5](image1.png)

**Figure 5.** Comparison of scattering curves calculated from a spherical and ellipsoidal form factor model. The fitted polydispersity is 45% and < 20% for the two models, respectively.

Regarding the fit model, it should be considered that micelles have strong shape fluctuations resulting in an elongated form. Hence, they should be ideally fitted by an ellipsoidal form factor, which, however, necessitates a double numerical integration to take into account for size distribution and orientation of the particles. Therefore, a spherical model was chosen for the simultaneous fitting routine. Fig. 5(a) illustrates exemplarily that both a spherical form factor model and an ellipsoidal model can fit the experimental data recorded at 13420 eV. In the latter case, the orientational averaging of the ellipsoids also results in a smearing of the form factor oscillations and a smaller polydispersity is sufficient to describe the data. Therefore the polydispersity of the investigated system is less than 20% as compared to 45%, which is overestimated by the spherical model. The axes in the ellipsoidal core have a dimension of 1.34nm and 1.99nm.

The sample with a concentration of 50mM [Fig. 1(c)] shows a pronounced structure factor. The interaction between the particles was analysed dividing the data measured at various energies by the corresponding simulated form factor as derived from fitting the 17mM data [Fig. 3(a)]. The averaged structure term was fitted using an effective structure factor for polydisperse hard spheres [14]. The derived fit parameters give an effective radius of interaction of 3nm and a polydispersity of 19% which is in good agreement with the form factor fits.

![Figure 6](image2.png)

**Figure 6.** Averaged structure factor derived from measuring the sample with 50mM concentration at various energies and dividing by the corresponding fitted form factor. The fit of an effective structure factor for polydisperse homogeneous spheres shows good agreement.

![Figure 7](image3.png)

**Figure 7.** Comparison of the three partial intensities of SAXS term, cross-term and resonant term as derived from splitting the ASAXS data (17mM) presented in Fig. 1(b) (open symbols) and the best fit results shown in Fig. 3(a) (lines).
The derived best fit model was also compared to the three partial intensities which include the energy independent normal \textit{SAXS term}, the \textit{cross-term} involving the amplitudes of normal SAXS and the resonant scattering of the counterions, and the weak \textit{resonant term} due to counterions. The splitted intensities were derived from the data recorded from the sample with 17mM concentration [Fig. 1(b)] according to Eq. (6) and numerically solving the corresponding system of equations. A routine implemented in the \textit{SAXSutilities} package [15] was used for this purpose. Figure 7 shows the corresponding results. Open symbols represent data derived from ASAXS measurements whereas the continuous lines originate from the best-fit model presented in Fig. 3(a). Although the curves were not directly fitted to the partial intensities, they show very good agreement.

4. Discussion
The results presented in the previous section illustrate the power of ASAXS to probe the spatial distribution of counterions when the corresponding atomic absorption edge is experimentally accessible to quantitative SAXS measurements. The simultaneous analysis of the data recorded below and above the absorption edge provides additional constraints in data modelling. The fluorescence contribution close to and above the absorption edge can be corrected accurately for particulate systems. The spatial distribution of anomalous atoms derived by the direct modelling of the scattering curves and that deduced from the decomposed partial intensities is in good agreement. Both results reveal strong condensation of counterions on to the micelles. The form factor of the micelles can be described by a core-multi shell sphere model with an overestimated polydispersity or an ellipsoidal form with more realistic polydispersity. The structure factor can be modelled by a polydisperse effective hard-sphere system. The anomalous effect in the structure factor of interactions is weak compared to that in the form factor.

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