Silver behenate and silver stearate powders for calibration of SAS instruments

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Abstract. The possibilities of calibrations by silver behenate [CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{20}COOAg] and silver stearate [CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{16}CO\textsubscript{2}Ag] for the small angle scattering (SAS) technique are considered. It was shown that the long-period spacing of the silver compounds allow us to check the parameters of time-of-flight (TOF) method. Results of the data obtained from small angle neutron scattering (SANS) measurements performed with the silver behenate and the silver stearate powders are presented and compared with small angle X-ray scattering (SAXS) measurements.

1. Introduction

Small angle scattering of X-rays (SAXS) and neutrons (SANS) are two techniques that provide essential information about the structural properties of materials. The nature of the scattering in case of SAXS and SANS techniques are different (electron cloud interaction in case of SAXS and nuclei interaction in case of SANS), but nevertheless, the small angle scattering data treatment is similar. The module of q-vector is determined by the scattering angle and the wavelengths.

The traditional way of determining the wavelength and the resolution of the primary neutron beam produced by the monochromator of a SANS instrument is the time-of-flight (TOF) method, which is based on the principle to calculate the wavelength using the neutron speed given by the flight time of the neutrons. It is known that the TOF technique has high requirements for checking all of the parameters, such as the delay time (i.e. the time interval between the electronic start of the reactor and the real neutron pulse).

Therefore, we need a method for precise determination (checking) of the delay time (i.e. calibrations). One of the ways is the usage of known materials with ordered structure and long-period of the repetition distance. The methods for calibration of the SAXS and SANS instruments by using these materials, which can be so-called calibration standards, have been successfully tested [1-4]. In particular, silver behenate [CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{20}COOAg] and silver stearate [CH\textsubscript{3} (CH\textsubscript{2})\textsubscript{16}CO\textsubscript{2}Ag] were used.
for the calibrations of the instruments, because these silver compounds are the most suitable for observing the Bragg peaks in the small q range.

In this paper, we present the results of the comparison of the data obtained by the SAXS and the SANS technique with using the silver behenate and silver stearate, as well as proposing a measurement time gaining method by using a mixed silver behenate and silver stearate sample.

2. Materials and methods
The silver behenate and silver stearate are known silver salts of the long-chain fatty acids. The long-period spacing of $d_{001} = 58.378 (8)$ Å for silver behenate and $d_{001} = 48.68$ Å for silver stearate are known according to previous studies [1]. Silver behenate and silver stearate powders used in our study were purchased from Alfa Aesar, a Johnson Matthey Company [5].

SAXS experiments were performed using a pinhole camera Molecular Metrology SAXS System attached to a microfocused X-ray beam generator (Osmic MicroMax 002) that operates at 45 kV and 0.66 mA (30 W). The camera was equipped with a multiwire, gas-filled area detector with an active area diameter of 20 cm (Gabriel design). Two experimental setups were used to cover the q range of 0.0045 - 1.1 Å\(^{-1}\) ($q = (4 \pi / \lambda) \sin \Theta$, where $\lambda$ is the wavelength and $2 \Theta$ is the scattering angle).

The neutron experiments were performed at YuMO spectrometer by two-detector system mode with ring wire detectors [6,7]. The beam was collimated to a diameter of 14 mm on the sample. The data treatment was performed by SAS program [8] with smoothing mode [9]. The control of devices for the YuMO spectrometer was performed using the SONIX Software Package [10]. For this measurements a standard thermobox and sample environment were used [11].

3. SAXS measurements
The first experiment was performed by SAXS in order to demonstrate that in our experiments no sample degradation was observed during the neutron scattering experiments even with the high intensity gamma flux [12].

Fig. 1 shows a scattering pattern of silver behenate. Background was fitted by nonlinear curve and was subtracted from the scattering pattern; we had obtained a picture for the Bragg peaks of silver behenate, as can be seen in Fig. 2.
Figure 1. Scattering pattern from silver behenate obtained by SAXS.

Figure 2. Bragg peaks from silver behenate obtained by SAXS.

These peaks were fitted by Gaussian peak functions. The fitting procedures and calculations were performed for the first five peaks corresponding to 1-5\textsuperscript{th} order of long-period spacing. An overview of the results of Bragg peaks of silver behenate powder is shown in Table 1.
Table 1. Bragg peaks of silver behenate measured by SAXS

| Number of Bragg peaks | $Q_{\text{peak}}$ [Å$^{-1}$] | $d_{hkl}$ [Å] | $\Delta d/d$ [%] | $\Delta d$ [Å] | FWHM |
|-----------------------|------------------|-------------|-----------------|-------------|------|
| 1st                   | 0.1086           | 57.9        | 0.9             | 0.5         | 0.016|
| 2nd                   | 0.2151           | 58.4        | 0.8             | 0.5         | 0.021|
| 3rd                   | 0.3222           | 58.5        | 0.2             | 0.1         | 0.023|
| 4th                   | 0.4307           | 58.4        | 0.4             | 0.2         | 0.023|
| 5th                   | 0.5399           | 58.2        | 0.3             | 0.2         | 0.027|

Fig. 3 shows also a scattering pattern of silver stearate as another candidate sample for calibration standard. Typical picture of diffraction peaks of silver stearate is presented in Fig. 4. We should note that we have used same reduction procedure for silver stearate as before for silver behenate. Table 2 shows an overview of the results of Bragg peaks from the silver stearate powder.

![Figure 3](Image)

**Figure 3.** Scattering pattern from silver stearate obtained by SAXS.
Figure 4. Bragg peaks of the silver stearate obtained from SAXS measurement.

Table 2. Bragg peaks of silver stearate measured by SAXS

| Number of Bragg peaks | Q_{peak} [Å^{-1}] | d_{hkl} [Å] | Δd/d [%] | Δd [Å] | FWHM  |
|-----------------------|-------------------|-------------|-----------|--------|-------|
| 1st                   | 0.1351            | 46.5        | 4.5       | 2.1    | 0.025 |
| 2nd                   | 0.2656            | 47.3        | 2.8       | 1.3    | 0.023 |
| 3rd                   | 0.3998            | 47.1        | 3.2       | 1.5    | 0.028 |
| 4th                   | 0.5341            | 47.1        | 3.3       | 1.6    | 0.028 |
| 5th                   | 0.6717            | 46.8        | 3.9       | 1.8    | 0.034 |

4. SANS measurements

SANS patterns of silver behenate and silver stearate obtained from the SANS YuMO spectrometer are shown respectively in Fig. 5 and Fig. 6. To provide the Bragg peak analysis on the SANS patterns, we have used Gaussian functions. Table 3 shows the results of the first and second Bragg peaks for silver behenate. For silver stearate, it is presented in Table 4.
Figure 5. Neutron diffraction pattern from: A. silver behenate sample; B. silver stearate sample.

From the typical SANS diffraction pattern of silver behenate (see Fig. 5. A.) we can see that the first Bragg peak has sufficient intensity and second peak has lower intensity. Third, fourth and fifth peaks disappear in the incoherent background. However, to determine the wavelength from the Bragg reflections in the neutron diffraction pattern just one Bragg peak is enough [2, 3]. This statement is also valid for the silver stearate (Fig. 5.B).

Table 3. Bragg peaks of silver behenate measured by SANS

| Number of Bragg peaks | Q_{peak} [Å⁻¹] | d_{hkl} [Å] | Δd/d [%] | Δd [Å]   | FWHM |
|----------------------|----------------|------------|----------|----------|------|
| 1st                  | 0.1086         | 57.85      | 0.92     | 0.53     | 0.023 |
| 2nd                  | 0.2154         | 58.34      | 0.09     | 0.05     | 0.031 |

Table 4. Bragg peaks from the silver stearate measurements by SANS.

| Number of Bragg peaks | Q_{peak} [Å⁻¹] | d_{hkl} [Å] | Δd/d [%] | Δd [Å]   | FWHM |
|----------------------|----------------|------------|----------|----------|------|
| 1st                  | 0.1332         | 47.17      | 3.1      | 1.46     | 0.032 |
| 2nd                  | 0.2614         | 48.07      | 1.3      | 0.62     | 0.057 |

We have also measured using the YuMO spectrometer a mixed sample of two silver powders: silver behenate and silver stearate 50% + 50% wt%. The peak analyses of the mixture of silver behenate and silver stearate were carried out from the results of this measurement. Neutron diffraction patterns for the mixture of silver behenate and silver stearate powders are presented in Fig. 7 and Fig. 8. The difference between the two figures is that in the case of Fig. 7 the resulting curve was obtained by the measurement of the mixture of the compounds, while for the Fig. 8 we have combined the diffraction curves from pure silver behenate and silver stearate. In the Fig. 7 from the lower-to-higher q-range region in the neutron diffraction pattern, we can see the first peak Bragg peak from silver behenate, then first Bragg peak from silver stearate, then second Bragg peak from silver behenate and
the last one is the second Bragg peak from silver stearate in the mixture of silver compounds. One can see that there is an overlapping between the silver behenate and silver stearate peaks due to the fact that the two silver powders have long period spacing in nearby q-range. Another reason why the overlapping occurs is because the SANS spectrometer has low resolution and it produces wider diffraction peaks than the peaks produced by SAXS instruments. An overview of results from peak analysis for the SANS measurement for the sample mixture are presented in Table 5.

![Neutron diffraction pattern for mixture from the silver behenate and silver stearate.](image)

**Figure 7.** Neutron diffraction pattern for mixture from the silver behenate and silver stearate.
Figure 8. Neutron diffraction pattern for mixture from the silver behenate and silver stearate (combination of raw files).

Table 5. Results from the sample mixture measurement of silver stearate and silver behenate measured by SANS.

| Powder          | $Q_{\text{peak}}$ [Å$^{-1}$] | $d_{hkl}$ [Å] | $\Delta d / d$ [%] | $\Delta d$ [Å] | FWHM |
|-----------------|-------------------------------|---------------|--------------------|----------------|------|
| Silver behenate | 0.1075                        | 58.45         | 0.09$^a$           | 0.05$^a$       | 0.015|
| Silver stearate | 0.1343                        | 46.82         | 3.9                | 1.85           | 0.033|

$^a$ Uncertainty of delay time, only due to the delay time in accordance with lattice periodicity

From comparisons between full widths at half maximum (FWHM) results of the SAXS and the SANS measurements, we may conclude that the SANS YuMO spectrometer creates larger diffraction peak broadening than the SAXS instrument used in this study.

5. Conclusions
We considered the usage of the silver behenate and silver stearate sample measurements for the scattering vector or the wavelength calibration by the SAS technique. We have shown that the long-period spacing of the silver compounds allow us to check TOF method parameters. From comparisons between FWHM results of SAXS and SANS measurements, YuMO spectrometer has lower resolution than the pinhole camera Molecular Metrology SAXS System. For increasing the resolution of YuMO spectrometer we are planning to implement the new type of position sensitive detector with central hole in standard mode [13,14]. We have obtained some of the parameters of the YuMO spectrometer (namely: time of delay, correct wavelength etc.) using the measurements of silver behenate and silver stearate as calibrants. We suggest using a mixture of silver behenate and silver stearate for calibration of detectors on the YuMO spectrometer, because more peaks are visible in this case and in a single experiment we can obtain and check the calculation of the chosen parameters. The diffraction pattern of the mixture gives the same information with same accuracy as two separate measurements of silver compounds. SAXS and SANS measurement results of the silver behenate and the silver stearate powders are presented and compared.
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