Combined SANS and SAXS in studies of nanoparticles with core-shell structure

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Small angle neutron scattering (SANS) and small angle X-ray scattering (SAXS) are essentially diffraction experiments involving small (~1°) scattering angles. Unlike conventional diffraction experiments (XRD or neutron diffraction) where one examines the specimen with an atomic resolution (~0.2 nm), SANS/SAXS are used to investigate structures on a length scale of ~10 nm. Hence, SANS / SAXS are ideal techniques for studying the sizes and shapes of nanoparticles. At times, because of differences in contrast for neutrons and X-rays, a combined SANS and SAXS study provides information about the core and the shell structure of nanoparticles. This paper gives an introduction to the techniques of SANS and SAXS and their applications in material science. Recent results on study of core-shell structure of a micelle (nanoparticle of organic material) are presented.

Keywords: Neutron scattering, Nanoparticles, Core-shell structure, Neutron diffraction

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1 Introduction

Nanoparticles are the particles (crystalline or amorphous) of organic or inorganic materials having sizes in the range 1-100 nm. In general, these particles could exist in a powder form or dispersed in some medium. They are usually stabilized against aggregation by a ligand shell (referred to as capping) present at the surface of the particle. For example, suspensions of gold particles in solvent such as toluene are prepared by capping the Au particles by alkylamines, alkanethiols or phospholipids. In short, nanoparticles usually consist of a core of material A and an outer shell of material B as shown in Fig. 1. Thioglycerol coated nanoparticles of CdS, gold coated nanoparticles of gold-sulphide, silver oxide coated silver particles and silver coated silica spheres are some examples of core-shell structures of nanoparticles.

An important area of nanotechnology concerns the development of reliable processes and techniques for synthesis and characterization of nanoparticles over a range of sizes and shapes. Several techniques such as Scanning Tunneling Microscope (STM), Transmission Electron Microscope (TEM), X-Ray Diffraction (XRD), Dynamic Light Scattering (DLS), Small Angle X-Ray Scattering (SAXS) and Small Angle Neutron Scattering (SANS) etc. have been used for determining the sizes and shapes of nanoparticles and it is not surprising that all these techniques have their merits and demerits2. This paper deals with the use of SANS and SAXS in the study of nanoparticles. It is shown that a combined SANS/SAXS study is an ideal method for determining the sizes of the core and the shell of a nanoparticle.

2 Nanomaterials

Nanocrystals cover a size range that is intermediate to the molecular size regime on one hand and the macroscopic bulk on the other. The top-down approach of preparing nanoparticles involves breaking of bulk particles to nanosizes (e.g. ball milling) and the bottom-up approach involves atom-atom or molecule-molecule assembling of nanoparticles. Micelle [Fig. 1(b)], for example, is a nanoparticle of organic molecules, which is formed by self-association of surfactant molecules in water.

In general, one can have nanoparticles of metals, semiconductors, dielectrics, magnetic materials, polymers or other organic compounds. It is seen that properties of these particles are quite sensitive to their sizes3. It is seen that reactivity of nanoparticles increases with decrease in size, melting temperature of nano phases is considerably lower than their bulk counterparts and the colour of a nanoparticle (especially semiconductors) changes with its size. At times a particle size-dependent magnetic properties that range from ferromagnetic to paramagnetic to super-paramagnetic with decreasing size. Similarly, the
properties (e.g. Meissner effect) of superconductors also depend on particle size.

Hence, to understand the physico-chemical and optoelectronic properties of nanoparticles and to exploit them for commercial applications, it is important to have dependable techniques for determining the sizes and shapes of nanoparticles. Depending on the chemical composition of the nanoparticle and the matrix in which they reside, SANS or SAXS can be used for this purpose.

3 SANS and SAXS

The SANS and SAXS are the techniques for obtaining structural information of a material on length scale of 1-100 nm and hence these techniques are routinely used for studying sizes and shapes of nanoparticles. The experiment involves scattering of a monochromatic beam of neutrons (or X-rays) from the sample and measuring the elastically scattered neutron (or photon) intensity as a function of the scattering angle. The magnitude of wave vector transfer \( Q \) in SANS/SAXS experiments is typically in range \( 0.01-1 \) nm\(^{-1} \). To obtain such low \( Q \) values, SANS/SAXS experiments involve small scattering angles. In short, SANS or SAXS are diffraction experiments corresponding to small scattering angles. Unlike conventional diffraction experiments, where the structure of a material is examined at atomic resolution (~0.2 nm), SANS/SAXS experiments involve small scattering angles. In short, SANS or SAXS are diffraction experiments corresponding to small scattering angles. Unlike conventional diffraction experiments, where the structure of a material is examined at atomic resolution (~0.2 nm), SANS/SAXS experiments involve small scattering angles. In short, SANS or SAXS are diffraction experiments corresponding to small scattering angles. Unlike conventional diffraction experiments, where the structure of a material is examined at atomic resolution (~0.2 nm), SANS/SAXS experiments involve small scattering angles.

The small-angle intensity \( I(Q) \) as a function of scattering vector for a dispersion of nanoparticles can be expressed as

\[
I(Q) = nP(Q)S(Q)
\]

where \( n \) is the number density of the particles, \( P(Q) \) is the intraparticle structure factor and depends on the shape and size of the particle, \( S(Q) \) is the inter-particle structure factor and is decided by the spatial distribution of the particles. \( P(Q) \) is given by the integral:

\[
P(Q) = \left| \int (\rho(r)-\rho_s)\exp(iQr)dr \right|^2
\]

In the simplest case of a monodispersed system of spherical particles with a radius \( R \), \( P(Q) \) is given by:

\[
P(Q) = (\rho - \rho_s)^2 V^2 \left[ \frac{3j_1(QR)}{QR} \right]^2
\]

where \( V = (4/3)\pi R^3 \), \( \rho_s \) is the scattering length density of the solvent, \( \rho \) is the mean scattering length density of the particle and \( j_1(QR) \) is spherical Bessel function. Similar expressions for \( P(Q) \) for different geometrical shapes e.g. (cylinder, disk, ellipsoid etc.) and for a system of polydisperse spheres are available in the literature (Ref. 8).

The intraparticle structure factor \( P(Q) \) for a spherical particle having core-shell structure is given by:

\[
P(Q) = (\rho - \rho_s)^2 V^2 \left[ \frac{3j_1(QR)}{QR} \right]^2
\]
where \( R \) is the radius and \( V \) is the volume of the particle. \( R_i \) and \( V_i \) in Eq. (4) are the radius and the volume of the inner core of the particle, respectively. The thickness of spherical shell around the core is given by \( R_s = R - R_i \). The \( \rho_1, \rho_2 \) and \( \rho_s \) in Eq. (4) stand for mean scattering length densities for the core, shell and solvent, respectively.

The expression for \( S(Q) \) depends on the relative positions of the particles. In case of homogenous and isotropic system, \( S(Q) \) can be written as.

\[
S(Q) = 1 + 4\pi n \int (g(r) - 1) \frac{\sin Qr}{Qr} r^2 dr \quad \ldots \quad (5)
\]

where \( g(r) \) is the radial distribution function. \( g(r) \) is the probability of finding another particle at a distance \( r \) from a reference particle centered at the origin. The details of \( g(r) \) depend on the interaction potential \( U(r) \) between the particles. Usually, \( S(Q) \) exhibits a few peaks in the small \( Q \) range corresponding to pairwise correlation between scattering particles; therefore, these peaks are, specifically the first one is, known as the correlation peak. In very dilute systems, \( S(Q) \) tends to unity because the extremely small \( Q \) range is not accessible in experiments. In such cases, the scattering intensity mostly represents \( P(Q) \).

### 4 Concept of Contrast Factor in SANS/SAXS Experiments

Scattered neutron (or X-ray) intensity in SANS or SAXS experiment depends on \((\rho - \rho_s)^2\) — the square of the difference between the average scattering length of the particle and the average scattering length density of the solvent. \((\rho - \rho_s)^2\) is referred to as the Contrast Factor. The values of \( \rho \) and \( \rho_s \) depend on the chemical composition of the particle and the solvent and is different for neutrons and X-rays. The differences in \( \rho \) values for neutrons and X-rays arise from the fact that while neutrons are scattered by the nucleus of an atom, the X-rays are scattered by the electron clouds around the nucleus\(^5\). It is seen that as one goes across the periodic table, the neutron scattering lengths vary in a random way and the X-ray scattering lengths increase linearly with the atomic number of the atom. The value of \( \rho \) or \( \rho_s \) for X-ray will be small for hydrogenous materials (organic compounds) as compared to that for heavier elements such as Au, Br etc. This is not the case with neutrons.

Further, the fact that scattering length of hydrogen is negative (\(-0.3742 \times 10^{-12} \text{ cm}\)) and that for deuterium is positive (\(0.6674 \times 10^{-12} \text{ cm}\)), the value of \( \rho \) for neutrons changes significantly on deuteration of a hydrogenous sample. It is, in fact, possible to mix the hydrogenous and the deuterated species and thus vary the contrast in a continuous way in a neutron experiment.

It is because of the properties of X-rays and neutrons that one is able to determine the core and shell structure of nanoparticles. For example SAXS experiments on gold nanoparticles will give information about the size of the core. X-rays will not see the hydrogenous capping material. However, neutrons are largely scattered from hydrogenous material of the capping which constitutes the outer shell of the Au nanoparticles. For neutrons, the above particles will appear as hollow spherical shells. Micelles, which are nanoparticles of the hydrogenous materials, behave differently. In this case, neutrons see the core of the micelle and X-rays give information about the shell of counterions around the micelle.

### 5 Results of SANS and SAXS Studies on Micelles

Micelle is an associate of surfactant molecules such as sodium dodecyl sulphate (SDS), cetyltrimethylammonium chloride\(^7\) (CTAC) etc. These long organic molecules (~2.5 nm long) whose one end is hydrophobic and the other one hydrophilic, self-aggregate in water and these aggregates of surfactant molecules are referred to as micelles. It may be noted that ionic surfactant such as CTAC, ionizes in aqueous solution and the CTAC micelle is essentially an aggregate of \( \text{CTA}^+ \) ions. The \( \text{Cl}^- \) ions, known as counterions, tend to stay near the \( \text{CTA}^+ \) micellar surface. CTAC micelle thus mimics a nanoparticle of organic material around which there is outer shell of \( \text{Cl}^- \) ions. Aswal \textit{et al}.\(^10\) have carried out SANS and SAXS experiments to determine the size of the core and the shell of CTAC micelles.

Figure 2 shows the comparison of SANS and SAXS data on 100 mM CTAC micellar solution. Both these data show a correlation peak at \( Q \sim 0.6 \text{ nm}^{-1} \), which is due to a corresponding peak in the interparticle structure factor\(^11\) \( S(Q) \). The position of the correlation peak depends on the average distance between the micelles and is independent of the radiation used. The peak usually occurs at \( Q_m \sim 2\pi/d \), where \( d \) is the average distance between the micelles.
The hump in SAXS data at $Q \sim 1 \text{ nm}^{-1}$ arises from scattering of shell-like structure of the condensed counterions around the micelles. The analysis of SANS data using Eq. (1) as discussed in our earlier paper\textsuperscript{11} determines the shape and size of the core of the micelle. It is found that the CTAC micelles are prolate ellipsoidal with the semimajor axis $a = 2.92$ nm and semi minor axis $b = c = 2.3$ nm. The fractional charge on the micelle was found to be 0.28 suggesting 72% of Cl$^-$ counterions reside near the micelle surface. The thickness of the layer of these counterions, referred to as condensed counterions, was obtained from SAXS data\textsuperscript{10,12}. The thickness of the outer shell was the only unknown parameter in analysis of SAXS data, as all other parameters were already known from SANS data. The fitted value of the thickness over which the Cl$^-$ counterions are condensed is 0.46 nm. The fact that ionic radius of bare Cl$^-$ ion is 0.18 nm, this suggests that the thickness of shell of counter ions in CTAC micelles is about 30% larger than the mono layer thickness of Cl$^-$ ions.

It is known that as compared to Cl$^-$ ions, Br$^-$ ions have less affinity to water. Thus, one expects that Br$^-$ ions in CTAB micellar solutions will be less dispersed in water as compared to Cl$^-$ ions in CTAC solutions. To examine if SANS/SAXS data will be sensitive to the above, SANS and SAXS experiments were carried out on CTAB micellar solution\textsuperscript{12}. The results are shown in Fig. 3. Again, we see a correlation peak at $Q \sim 0.5 \text{ nm}^{-1}$ both in SANS and SAXS data. The prominent peak at $Q \sim 1 \text{ nm}^{-1}$ in SAXS data in Fig. 3 is arising from a corresponding peak in $P(Q)$. As already mentioned, $P(Q)$ relevant to SAXS is the one that corresponds to a hollow sphere of Br$^-$ ions. The fact that scattering power of Br is higher than that of Cl, the $P(Q)$ peak at $Q \sim 1 \text{ nm}^{-1}$ is more prominent in CTAB data as compared to that in CTAC data. Combined analysis of SANS and SAXS data showed that thickness of shell over which Br$^-$ ions are distributed is $\sim 0.42$ nm. The fact that ionic radius of bare Br$^-$ is 0.195 nm, suggests that most of the condensed Br$^-$ ions reside in a monolayer of counterions around the micelle. This shows that compared to Cl$^-$ ions, Br$^-$ ions tend to stay closer to the micelle. It is interesting to note that these experiments are sensitive to even small changes in the thickness of the shell. The CTAB micelles are much bigger in size as compared to CTAC micelles\textsuperscript{13}.

In summary, SANS and SAXS experiments on CTAC show that aggregate of CTAC surfactant molecules is nearly spherical (radius $\sim 2.5$ nm) and it has an outer shell (thickness $\sim 0.5$ nm) of Cl$^-$ ions. The fact that we are able to show that the outer-shell of Cl$^-$ ions around CTAC micelle is more diffused as compared to shell of Br$^-$ ions around CTAB micelles suggests that SANS / SAXS are ideal techniques for studying core-shell structures of nanoparticles.

**References**

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