

**A SANS Experiment to Understand the Nature of Surfactant stabilization in  
Suspensions of Spherical Colloidal Silica Particles**

Summer School on Neutron Scattering and Reflectometry  
from Submicron Structures  
NIST Center for Neutron Research  
June 6, 10-12, 2004

**Abstract**

Small-angle neutron scattering (SANS) will be used to determine the structures formed by a surfactant additive to a system of spherical silica particles dispersed in water. The measurements will illustrate the advantage of neutron scattering using contrast variation technique.

All aspects of the experiment, from the sample preparation and instrument setup through to the data treatment and interpretation will be briefly described and references given for more in-depth study.

## I. INTRODUCTION

The mesoscopic nature of colloids, with its attendant energetic implications, along with their optical characteristics makes them ubiquitous in everyday activities and applications as well as highly useful systems for fundamental scientific studies. Blood, ink, coatings (paint, paper, etc.), foods, detergents, and personal care products are just a few examples of commonly encountered colloidal suspensions. In industrial applications they are extensively used in such things as liquid transport (particularly in processing stages), catalysis, mineral floatation, and enhanced oil recover. Finally, highly monodisperse colloidal model systems can be used to probe fundamental equations involving interfacial energies and flow fields, or used as probes of microenvironments such as in microrheology to name just a couple of examples. The stability of these nanosize objects is often critical and not always well controlled. In order to enhance their stability in dispersions against flocculation and settling, addition of surfactant and polymer to the formulation is often used. We propose in this experiment to characterize the size and structure of a silica particle dispersion in which small amount of surfactant is added in order to increase its stability. By a series of measurements we will detect and quantify the surfactant structure responsible for this enhanced stability.

Monodisperse  $\text{SiO}_2$  nanocolloids in size range of 80-100 nm were synthesized following the Strober method i.e. by hydrolyzing tetraethyl orthosilicate (TEOS) in ethanol in the presence of ammonium. The  $\text{SiO}_2$  nanoparticles have a polydispersity  $<10\%$ , are negatively charged with an isoelectric point of  $\sim 2.5$ , and are stable over a wide range of pH varying from 5 to 11. The surface charge density can be tuned by modifying the pH of the solution, with a surface charge of zero at the isoelectric point. A cationic surfactant (CetylTrimethylAmmonium Bromide or CTAB) is added at a concentration  $\sim \text{CMC}$  (critical micellar concentration). CTAB is expected to electrostatically attach to the silica surface to give an extended thickness of the order of 2-3nm [figure 1].

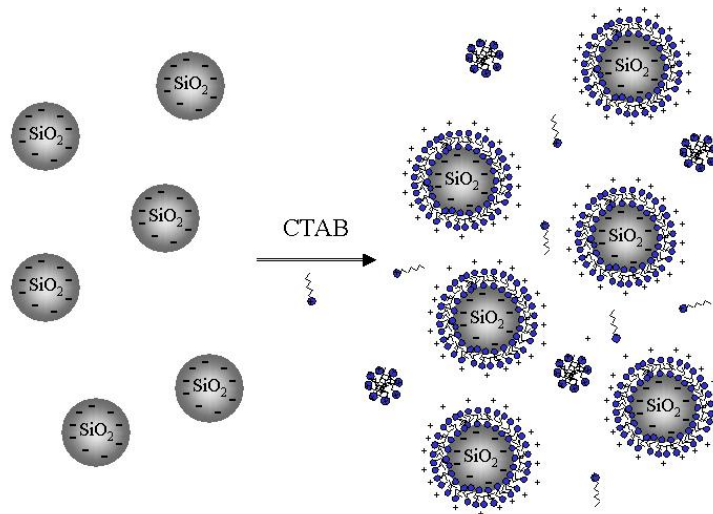


Figure 1: Schematic of CTAB absorption onto silica

To determine the particle size and polydispersity, a diluted solution of dispersed silica particles (at 0.1 wt%) in D<sub>2</sub>O will be measured. The surfactant structure, presumably an adsorbed organic bi-layer on SiO<sub>2</sub> will be characterized using the contrast match technique, after accurate determination of the scattering length density of the colloidal SiO<sub>2</sub>.

**The Objectives of the Experiment are:**

- **To determine the shape and average dimensions of the dispersed particles.** This information will be derived from the shape, i.e. the Q-dependence, of the scattering pattern. Since the particles are anticipated to be spherical, it will be necessary in order to characterize the size to measure the intensity over a Q-range that encompasses Q-values up to  $2\pi/D$ , where D is the average diameter of the particles.
- **Determine the volume fraction of the dispersed particles.** This information may be derived from the  $Q \rightarrow 0$  limit of the scattering curve having scaled the data to absolute units of cross section per unit volume and from the Porod's Invariant. This will require a wide Q range in order to properly integrate the area under the scattering curve
- **Determine, possibly, the presence or absence of interparticle self-organization effects.** This will be done by identifying and analyzing deviations in the Q-dependence of the scattering from that expected for a non-interacting, dilute suspension of particles.
- **Determine the surface area from the Porod regime.** This will be done by analyzing the high Q regime requiring measurements at Q well out in the tail of the scattering
- **Determine the scattering length density of the silica particle.** This will be done by dispersing SiO<sub>2</sub> in different D<sub>2</sub>O/H<sub>2</sub>O solvent mixtures, and by recording the total scattering intensity as a function of D<sub>2</sub>O content.
- **Determine the structure, presumably the thickness of the adsorbed surfactant layer (using both a solvent contrast matched to the silica and one that is not).** This will be done by analyzing the scattering curves of silica with and without surfactant (either in D<sub>2</sub>O or in contrast matched conditions)

## II. PLANNING THE EXPERIMENT

### Why use SANS?

Generally, static light scattering and small angle X-ray scattering (SAXS) provide the same information about the sample: measurement of the macroscopic scattering cross-section  $d\Sigma/d\Omega(Q)$ . The contrast in light scattering arises from the difference in the light's refractive index for each phase in the sample. The contrast in light scattering is typically much stronger than in SANS, requiring very dilute concentration of particles to avoid multiple light scattering. In addition, the wavelength of light limits  $q < 0.002 \text{ \AA}^{-1}$ . Thus light scattering can be used to estimate the diameter of silica particle in dilute solution, but can not resolve the thickness of the adsorbed surfactant layer. The contrast in X-ray scattering arises in the variation in electron density between the phases. The contrast is again stronger for X-rays than neutrons, but thinner samples often mitigate any multiple scattering. X-rays are strongly absorbed by most samples, requiring thin walled glass capillaries to contain the sample. Also, intense X-rays beams can cause irreversible sample damage altering the structure and chemistry of the studied solution. This is especially the case for organic compounds such as polymer, lipids and surfactant. In the present case, SAXS can be used to measure the data over the entire Q-range needed for this experiment and determine the size and shape of the silica particle, but again, characterization of the adsorbed surfactant layer would be difficult and would require a more complex model.

Given the stated objectives of the experiment and the decision to use neutrons, how do we go about preparing for the experiment to maximize our chances of success? Here we discuss some of the issues that bear on this question.

### II.1 Scattering Contrast

In order for there to be small-angle scattering, there must be scattering contrast between, in this case, the silica particles and the surrounding water. The scattering is proportional to the scattering contrast,  $\Delta\rho$ , *squared* where

$$\Delta\rho = \rho_p - \rho_w \quad \leftarrow \text{Scattering Contrast}$$

and  $\rho_p$  and  $\rho_w$  are the **scattering length densities (sld)** of the particles and the water, respectively. Recall that **sld** is defined as

$$\rho = \frac{\sum_{i=1}^n b_i}{V} \quad \leftarrow \text{Scattering Length Density}$$

where  $V$  is the volume containing  $n$  atoms, and  $b_i$  is the (bound coherent) **scattering length** of the  $i^{\text{th}}$  atom in the volume  $V$ .  $V$  is usually the molecular or molar volume for a homogenous phase in the system of interest.

The **sld**'s for the two phases in the present case, silica and water, can be calculated from the above formula, using a table of the scattering lengths (such as Ref. 1) for the elements, or can be calculated using the interactive *SLD Calculator* available at the NCNR's Web pages (<http://www.ncnr.nist.gov/resources/index.html>). The **sld**'s for silica, CTAB and water (both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ ) are given below in Table 1.

**Table 1.** The scattering length densities (SLD's) for the silica, CTAB, light water and heavy water.

Material	Chemical Formula	Mass Density (g/cc)	SLD ( $\text{cm}^{-2}$ )
Silica	$\text{SiO}_2$	$\sim 2.2$	$3.4 \times 10^{10}$
CTAB	$\text{C}_{19}\text{H}_{42}\text{BrN}$	1	$-.24 \times 10^{10}$
Light water	$\text{H}_2\text{O}$	1.0	$-.56 \times 10^{10}$
Heavy water	$\text{D}_2\text{O}$	1.1	$6.38 \times 10^{10}$

From Table 1 we see that scattering contrast for silica in  $\text{H}_2\text{O}$  [proportional to  $(3.4 - (-0.56))^2 = 15.7$ ] is  $\sim 2$  times greater than in  $\text{D}_2\text{O}$  [ $(3.4 - 6.38)^2 = 8.8$ ]. However, this is not the only factor to consider. One should also consider the concomitant incoherent scattering from each phase<sup>1</sup>. The incoherent scattering contributes to an isotropic background that can obscure weak coherent scattering from the smaller structural features in a material. Here we are interested in both small-scale structure and much larger scale structure. Since the incoherent scattering from  $\text{H}_2\text{O}$  is about 30 times greater than that from  $\text{D}_2\text{O}$ , we elect to do the experiment using  $\text{D}_2\text{O}$  as the solvent. The contrast in  $\text{D}_2\text{O}$  is quite adequate and the lower incoherent scattering background will make it easier to distinguish the  $Q$ -dependent coherent signal from the  $Q$ -independent incoherent background. In addition, the lower incoherent scattering from  $\text{D}_2\text{O}$  allows us to use a thicker sample, as we shall see next, which compensates for the lower coherent scattering contrast vis-à-vis  $\text{H}_2\text{O}$ .

## II.2 Sample Thickness

The next decision we face is how thick should the sample be? Recall that the scattered intensity,  $I_s(Q)$ , is proportional to the product of the sample thickness,  $d$ , and the sample transmission,  $T_s$ , where  $T_s$ , the ratio of the transmitted beam intensity to the incident beam intensity, is given by

$$T_s = e^{-\Sigma_t d}, \quad \Sigma_t = \Sigma_c + \Sigma_i + \Sigma_a$$

<sup>1</sup> Incoherent neutron scattering has no counterpart in x ray or light scattering. It arises from the interaction of the neutron with the nucleus, which is described by a scattering length that depends on the particular nuclear isotope and its nuclear spin state.

where the total cross section per unit sample volume,  $\Sigma_t$ , is the sum of the coherent, incoherent and absorption cross sections per unit volume. The absorption, or neutron capture, cross section,  $\Sigma_a$ , can be computed accurately from the tabulated absorption cross sections of the elements (and isotopes) if the mass density and stoichiometry of the phase is known.  $\Sigma_a$  is wavelength dependent, being linearly proportional to  $\lambda$  for nearly all elements. The incoherent cross section,  $\Sigma_i$ , can be *estimated* from the cross section tables for the elements as well, but not as accurately because it depends somewhat on the atomic motions and is, therefore, temperature dependent. The coherent cross section,  $\Sigma_c$ , can also only be estimated since it depends on the details of both the structure and correlated motion of the atoms in the material.

The computations involved in estimated sample transmission are straightforward but tedious. The task is made easier using the NCNR's Web-based *sld calculator* which computes not only scattering length density, but also estimates the incoherent and absorption cross sections per unit volume. Table 2 gives some of these results for silica, H<sub>2</sub>O and D<sub>2</sub>O.

**Table 2.** Macroscopic cross sections (i.e. cross sections per unit volume) computed with the *sld calculator* on the NCNR's Web site for the solute and solvents in the experiment. The values for the absorption cross sections are for a wavelength of 6 Å.

	$\Sigma_c$ (cm <sup>-1</sup> )	$\Sigma_i$ (cm <sup>-1</sup> )	$\Sigma_a$ (6 Å) (cm <sup>-1</sup> )	$\Sigma_t$ (cm <sup>-1</sup> )	1/ $\Sigma_t$ (cm)
SiO <sub>2</sub>	0.234	0.000124	0.0126	0.2467	4.053
H <sub>2</sub> O	0.260	5.37	0.0741	5.70	0.175
D <sub>2</sub> O	0.518	0.136	0.000135	0.654	1.53

The sample to be measured consists of approximately 0.1 % silica (by weight) in D<sub>2</sub>O, or ~0.05 % silica by volume. Hence the total cross section per unit volume for the suspension is  $.9995 (0.654 \text{ cm}^{-1}) + 0.0005 (0.2467 \text{ cm}^{-1}) = 0.6538 \text{ cm}^{-1}$ , and  $1/\Sigma_t = 1.53 \text{ cm}$ . Hence the optimal sample thickness<sup>2</sup>, the 1/e thickness, is 1.53 cm. The corresponding thickness for the same volume fraction of silica in H<sub>2</sub>O is 0.175 cm. Hence the large incoherent cross section of hydrogen not only contributes a significant Q-independent background, it also limits the optimal sample thickness.

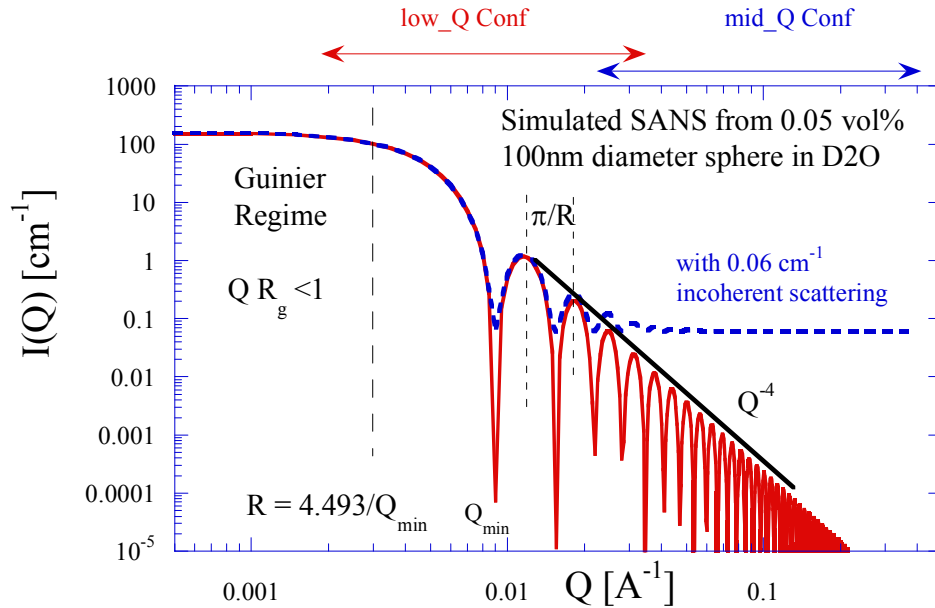
### II.3 Required Q-Range

For this experiment we know we will need to measure the intensity over a wide Q-range since the information we are looking for is distributed in the low and high Q regime. To get a better idea of the required Q-range, we can use the *SANS Data Simulator* (<http://www.ncnr.nist.gov/resources/simulator.html>) to calculate the Q-dependence of the scattering for the case of non-interacting and randomly oriented monodisperse spherical particle. From among the 20 different particle models currently included in the *SANS*

<sup>2</sup> The scattered intensity is proportional to  $d \exp(-\Sigma_t d)$  which has a maximum at  $d = 1/\Sigma_t$ . However, if  $\Sigma_i$  and  $\Sigma_a$  are small compared with  $\Sigma_c$ ,  $d$  should be chosen to make  $T \sim 0.9$  rather than  $1/e = .37$  to avoid multiple scattering.

*Data Simulator*, we choose the *Sphere* model. The documentation for this model can be found on the Web site at <http://www.ncnr.nist.gov/resources/sansmodels/sphere.html>. A plot from the *SANS Data Simulator* for monodispersed, randomly oriented sphere is shown in Fig. 2.

Notice in Fig. 2 that the scattering at larger  $Q$  is dominated by the solvent scattering from the  $D_2O$ . It will be necessary to correctly subtract this scattering curve in order to reveal the  $Q^{-4}$  power law characteristic of sharp interfaces.

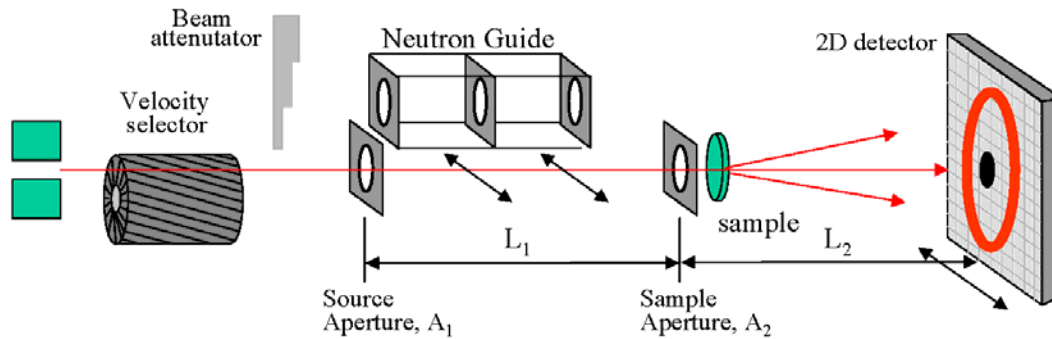


**Figure 2.** The simulated SANS from monodispersed, randomly oriented sphere with diameter  $D = 100$  nm. The dash curve includes the incoherent scattering from the  $D_2O$  solvent.

### III. COLLECTING THE DATA

#### III.1 How to Configure the SANS Instrument

Now that we know we want to cover as wide a  $Q$ -range as possible, we must decide how to configure the SANS instrument to do so efficiently. Here again we can use a computational tool, called SASCALC, as a guide. A schematic of the NCNR's 30-m SANS instruments is shown in Fig. 3, and the instrument configuration parameters, and their allowed range for the NG-7 30-m SANS instrument, are listed in Table 3.



**Figure 3.** Schematic diagram of the components of the NCNR's 30-m SANS instruments.

**Table 3.** The instrument configuration parameters, and their range of allowed values, for the NG-7 30-m SANS instrument.

Variable	Allowed Values
Neutron wavelength	5 – 20 Å (determined by the rotational speed of the velocity selector)
Wavelength spread (FWHM)	0.09, 0.11 or 0.22 (determined by the inclination of the velocity selector axis with respect to the beam direction)
Number of neutron guides, Ng	0 – 8 (determines the beam collimation by changing the distance of the source aperture from the sample)
Source aperture diameter	1.43, 2.20 or 3.81 cm for Ng=0; 5.08 cm for Ng=1-8
Sample-to-detector distance (SDD)	100 – 1530 cm
Detector offset	0 – 25 cm (detector translation perpendicular to beam to extend the Q-range covered at a given SDD)
Sample aperture diameter	0 – 2.5 cm
Beamstop diameter	2.54, 5.08, 7.62 or 10.16 cm
Beam Attenuator	10 choices of beam attenuator thickness to reduce beam intensity for sample transmission measurements

For a given set of allowed parameters, SASCALC computes the corresponding Q-range and the beam intensity (n/sec) on the sample. The Q-range for a particular configuration is determined by the choice of wavelength, detector distance and detector offset. To reach the largest-Q limit of the instrument, the shortest available wavelength, 5 Å, the shortest sample-to-detector distance, 100 cm, and the maximum detector offset, 25 cm have to be used. The number of neutron guides affects primarily the beam intensity on the sample. In general, we choose the largest number of guides, to maximize the beam intensity on the sample, consistent with the desired Q-range. In the present case, because of sample polydispersity and instrument resolution, the beam divergence in the high Q regime is not very important and we will use the following SASCAL choice:



### Instrument Configuration for large-Q portion of measurement range

Wavelength:	6.0 Å $\Delta\lambda/\lambda$ : 0.11 (FWHM)
Number of guides:	8
Sample-to-Detector distance:	150 cm
Detector Offset:	20.00 cm
Intensity at sample:	2.987E+006 Counts/sec
Qmin:	<b>0.0212</b> Å <sup>-1</sup> Resolution: 23.4%
Qmax:	<b>0.4023</b> Å <sup>-1</sup> Resolution: 4.7%
Horizontal Qmax:	0.3478 Å <sup>-1</sup>
Vertical Qmax:	0.2197 Å <sup>-1</sup>
Source aperture diameter:	5.08 cm
Sample Aperture diameter:	1.2 cm
Beam diameter at detector:	4.00 cm
Beamstop diameter required:	5.08 cm, (2.0 in)
Attenuator for transmission measurements:	No. 8
Source aperture to sample aperture distance:	387.0 cm

Next we consider how to configure the instrument to reach the low-Q end of the desired measurement range. In this experiment we want to reach the low Q-values required to see at least the tail of the Guinier region. We also require an instrumental resolution that will allow us to observe the minima of the form factor. The Q-range and other parameters for this configuration is as follow:

### Instrument Configuration for low-Q portion of measurement range

Wavelength:	6.0 Å $\Delta\lambda/\lambda$ : 0.11 (FWHM)
Number of guides:	0
Sample-to-Detector distance:	1530 cm
Detector Offset:	20 cm
Intensity at sample:	6 E+4 Counts/sec
Qmin:	<b>0.0021</b> Å <sup>-1</sup> Resolution: 28.2%
Qmax:	<b>0.0418</b> Å <sup>-1</sup> Resolution: 4.7%
Horizontal Qmax:	0.0356 Å <sup>-1</sup>
Vertical Qmax:	0.0219 Å <sup>-1</sup>
Source aperture diameter:	2.22 cm
Sample Aperture diameter:	1.2 cm
Beam diameter at detector:	4.8 cm
Beamstop diameter required:	5.08 cm, (2.0 in)
Attenuator to use for transmission measurements:	No. 4
Source aperture to sample aperture distance:	1627.0 cm

## III.2 What Measurements to Make

In addition to measuring the scattering from the sample for the three instrument configurations described in the previous section, additional measurements are needed to

correct for “background.” Counts recorded by the detector with the sample in place can come from 3 sources: 1) neutrons scattered by the sample itself (the scattering we are interested in); 2) neutrons scattering from something other than the sample, *but which pass through the sample*; and, 3) everything else, including neutrons that reach the detector *without passing through the sample* (stray neutrons or so-called room background) and electronic noise in the detector itself. To separate these three contributions, we need three measurements:

- i) Scattering measured with the sample in place (which contains contribution from all 3 sources listed above), denoted  $\mathbf{I}_{\text{sam}}$ ;
- ii) Scattering measured with the empty sample holder in place (which contains contributions from the 2<sup>nd</sup> and 3<sup>rd</sup> sources listed above), denoted  $\mathbf{I}_{\text{emp}}$ ; and,
- iii) Counts measured with a complete absorber at the sample position (which contains only the contribution from the 3<sup>rd</sup> source listed above), denoted  $\mathbf{I}_{\text{bgd}}$ .

In addition to these three ‘scattering’ measurements, the transmission of the sample (the fraction of the incident beam intensity that passes through the sample without being scattered or absorbed) and that of the sample cell must also be measured in order to correctly subtract the contributions to the background and to calibrate the scattering on an absolute cross section scale (the procedure is discussed in Section IV - Data Reduction). The transmission is measured by inserting a calibrated attenuator in the incident beam (to reduce the direct beam intensity to an accurately measurable level) and measuring the direct beam intensity with and without the sample (or the sample cell) in position. The ratio of these two short measurements (typically 1-2 minutes each) is the sample (or sample cell) transmission.

How the scattering and transmission measurements are used to reduce the data to a quantity, called the differential scattering cross section that is intrinsic to the sample, is described in Section IV (Data Reduction).

### III.3 How Long to Count

A SANS experiment is an example of the type of counting experiment where the uncertainty, or more precisely the standard deviation,  $\sigma$ , in the number of counts recorded in a time  $t$ ,  $I(t)$ , is  $\sigma = \sqrt{I(t)}$ . If the scattering is roughly evenly distributed over the SANS detector, then a good rule of thumb is that one should accumulate about 500,000 total detector counts per sample measurement (assuming minimal background). If the accumulated counts are circularly averaged, one obtains about 50 data points when plotting  $I(Q)$  versus  $Q$ . This amounts to about 1000 counts per data point with a standard deviation of  $\sqrt{1000} \sim 30$  or an uncertainty of about 3 %, which is good enough for most purposes.

A related question, is how long should the background and empty cell measurements be counted relative to the sample measurement. The same  $\sigma = \sqrt{I(t)}$  relationship leads to the following approximate result for the optimal relative counting times

$$\frac{t_{background}}{t_{sample}} = \sqrt{\frac{Count\ Rate_{background}}{Count\ Rate_{sample}}}$$

Hence if the scattering from the sample is weak, the background should be counted for as long (but no longer!) as the sample scattering. However, if the sample scattering count rate is, say, 4 times greater than the background rate, the background should be counting only half as long as the sample scattering.

#### IV. DATA REDUCTION

Data reduction consists of correcting the measured scattering from the sample for the sources of background discussed in Section III.2, and multiplying the corrected counts by a scaling factor (to remove incidental differences between measurements such as the counting time and sample thickness) that puts the data on an absolute scale of scattering cross section per unit volume. The measured neutron counts,  $I(Q)$ , recorded in a detector pixel in a time interval  $t$  are related to absolute cross section,  $d\Sigma(Q)/d\Omega$ , through the expression

$$I(Q) = \phi A \Delta\Omega \varepsilon t d T (d\Sigma(Q)/d\Omega) + I_{bgd}, \quad (1)$$

Where:

$\phi$  = the neutron flux (neutrons/cm<sup>2</sup>-sec) at the sample

$A$  = the area of the beam incident on the sample

$d$  = the sample thickness

$T$  = the transmission of the sample (and its container, if there is one)

$\Delta\Omega$  = the solid angle subtended by one pixel of the detector

$\varepsilon$  = the detector efficiency, and

$t$  = the counting time.

$I_{bgd}$  = counts from sources not traversing the sample

The incidental instrumental factors can be lumped together into one constant

$$K = \phi A \Delta\Omega \varepsilon t \quad (2)$$

and the intrinsic quantity,  $d\Sigma(Q)/d\Omega$ , the differential scattering cross section per unit volume, is obtained by scaling the recorded counts

$$d\Sigma(Q)/d\Omega = I(Q)/(K d T) \quad (3)$$

We now go over the specific steps involved in extracting  $d\Sigma(Q)/d\Omega$  from the raw data. Following equation (1), the raw scattered intensity measured from the sample,  $I_{sam}$ , and the empty cell,  $I_{emp}$ , can be written as

$$I_{sam} = K \, d \, T_{sample+cell} \left( \left( \frac{d\Sigma(Q)}{d\Omega} \right)_{sample} + \left( \frac{d\Sigma(Q)}{d\Omega} \right)_{emp} \right) + I_{bgd} \quad (4)$$

$$I_{emp} = K \, d \, T_{cell} \left( \left( \frac{d\Sigma(Q)}{d\Omega} \right)_{emp} \right) + I_{bgd}$$

where  $T_{sample+cell}$  and  $T_{cell}$  are the measured transmission of the sample (in its container) and the empty container, respectively. From the above, the background corrected scattering, denoted  $I_{cor}$ , is given by

$$I_{cor} = (I_{sam} - I_{bgd}) - \left( \frac{T_{sample+cell}}{T_{cell}} \right) (I_{emp} - I_{bgd}) \quad (5)$$

The corrected counts,  $I_{cor}$ , are proportional to the quantity of interest, namely the differential scattering cross section. From the above equations,

$$I_{cor} = K \, d \, T_{sample+cell} \left( \frac{d\Sigma(Q)}{d\Omega} \right)_{sample} \quad (6)$$

The instrumental scale factor,  $K$ , will be determined from a measurement of the attenuated direct beam intensity,

$$I_{direct} = T_{atten} \, \phi \, A \, \Delta\Omega \, \varepsilon \, t = T_{atten} \, K \quad (7)$$

where  $T_{atten}$  is the transmission of a calibrated attenuator.

## V. DATA ANALYSIS

The measured intensity (corrected for background and put on an absolute scale) for any ‘‘particulate’’ system can be expressed as

$$\frac{d\Sigma(Q)}{d\Omega} = (\rho_p - \rho_w)^2 V_p^2 N_p P(Q) S(Q), \quad (8)$$

where  $\rho_p$  and  $\rho_w$  are the sld’s of the silica particles and the  $D_2O$ , respectively;  $V_p$  is the mean particle volume, and  $N_p$  is the number of particles per unit volume.  $P(Q)$  is the scattering form factor for the particles,

$$P(Q) = \left| \frac{1}{V_p} \int_{V_p} e^{i\vec{Q}\cdot\vec{r}} d\vec{r} \right|^2, \quad (9)$$

the square of the Fourier transform of the particle shape. Finally,  $S(Q)$  is the structure factor (the inter-particle correlation factor) which is essentially the Fourier transform of  $g(r)$  the pair distribution function. Since the volume fraction of silica particles in our sample is about 0.0005, it is reasonable to analyze the scattering in terms of randomly oriented, non-interacting particles (i.e. we neglect the structure factor in this case and set  $S(Q) = 1$ ). In this so-called dilute limit, the particles scatter independently, and the total scattering is the sum of the scattered from each particle.

***Particle Volume Fraction Determined from Invariant or  $I(0)$ :***

- For all two phase systems having uniform scattering length densities in each phase, the volume fraction  $\phi$  can be determined from the integration of all the scattering

$$\phi(1 - \phi) = \frac{Q_I}{2\pi^2 \Delta\rho^2} \quad (10)$$

where the invariant is determined by

$$Q_I \equiv \int_0^\infty q^2 \frac{d\Sigma}{d\Omega}(q) dq \quad (11)$$

- For dilute systems, and for particle with a uniform scattering length density, the forward scattering is simply:

$$\frac{d\Sigma}{d\Omega}(0) = \phi V_p \Delta\rho^2 \quad (12)$$

where  $\phi$  is the volume fraction of particles ( $\phi = N_p V_p$ ),  $V_p$  is the average particle volume, and  $\Delta\rho^2$  is the scattering length density contrast squared.

***Determination of the specific surface area:***

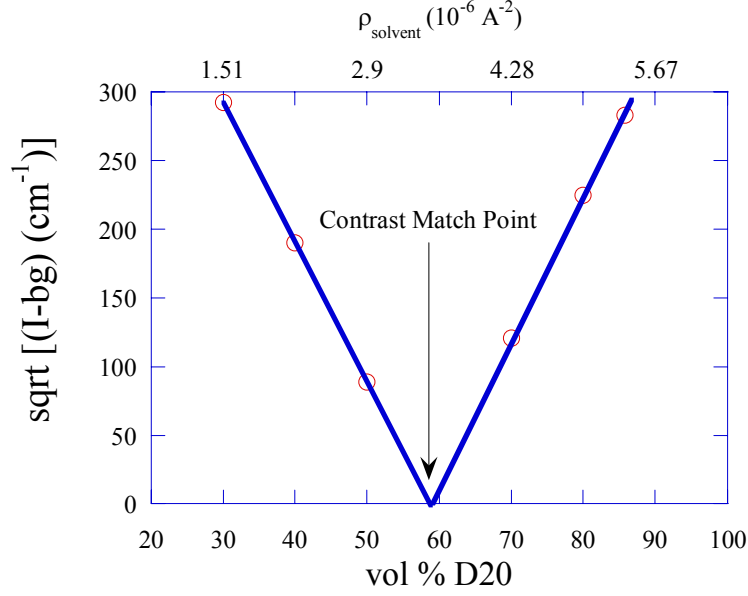
The specific surface area is determined from small angle scattering data using the Porod's approximation:

$$\lim_{Q \rightarrow \infty} I(Q) = 2\pi \Delta\rho^2 S / Q^4 \quad (13)$$

where  $S$  is the surface area per unit volume.

***Contrast matched point determination:***

As expressed in equation 8, the scattering intensity  $\frac{d\Sigma(Q)}{d\Omega}$  is proportional to the square of the scattering contrast  $(\rho_p - \rho_w)^2$ . To determine the scattering length density of the particles, we have to disperse them in different D<sub>2</sub>O/H<sub>2</sub>O solvent mixtures and record the square root of the total intensity as a function of the solvent scattering length density or equivalently, D<sub>2</sub>O content (Figure 4).



**Figure 4:** Square root of the intensity as the function of the solvent D2O content. The contrast match point is determined where the scattering intensity falls to 0.

### *Sphere form factor*

In the limit  $Q \rightarrow 0$  for randomly oriented particles expression (8) reduces to

$$I(Q) \propto \exp(-Q^2 R_g^2 / 3). \quad (15)$$

where  $R_g$  is the radius of gyration of the particle and is valid for any particulate system regardless of shape. Equation 15 is an example of Guinier's Law which is valid only for  $Q R_g \leq 1$ . **For a homogenous sphere it can be shown that  $R_g^2 = 3R^2/5$ .**

This expression is easy to use and allows one to quickly extract the radius of gyration of any particle from the low  $Q$  region by plotting  $\ln(I)$  versus  $Q^2$  without *any* knowledge of the particle morphology.

In the present case however the size of the silica particles ( $\sim 100\text{nm}$ ) is too large to be able to use the Guinier approximation in the SANS  $Q$  range defined above except as a rough estimate. To use that approximation, we would need a configuration using the lenses, and for much larger particles, USANS data would be required which can go to  $Q \text{ min} = 5 \cdot 10^{-5} \text{ \AA}^{-1}$ .

Thus, to analyze our data it will be necessary to use the full expression of the scattering from spheres. The general expression for the form factor of a sphere of diameter  $2R$ , is given by

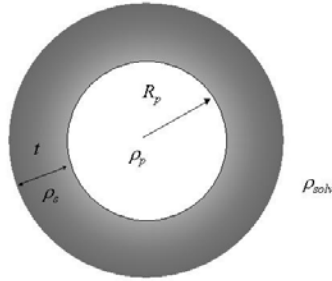
$$P(Q) = \left[ \frac{3(\sin QR - QR \cos QR)}{(QR)^3} \right]^2, \quad (14)$$

We will have to take into account the sample polydispersity, the instrumental resolution and the incoherent scattering from the sample, as pointed out in Section II.3. The later

will be done by including a constant as a fitting parameter since the incoherent scattering is a constant Q independent background term.

***Polydisperse spheres model:***

The schematic of our system consists on a sphere of radius  $R_p$  and scattering length density  $\rho_p$ , covered by a shell of thickness  $t$  with a scattering length density  $\rho_s$  (in the case of absorbed surfactant) in a solvent of scattering length density  $\rho_{solv}$ . (see figure 5)



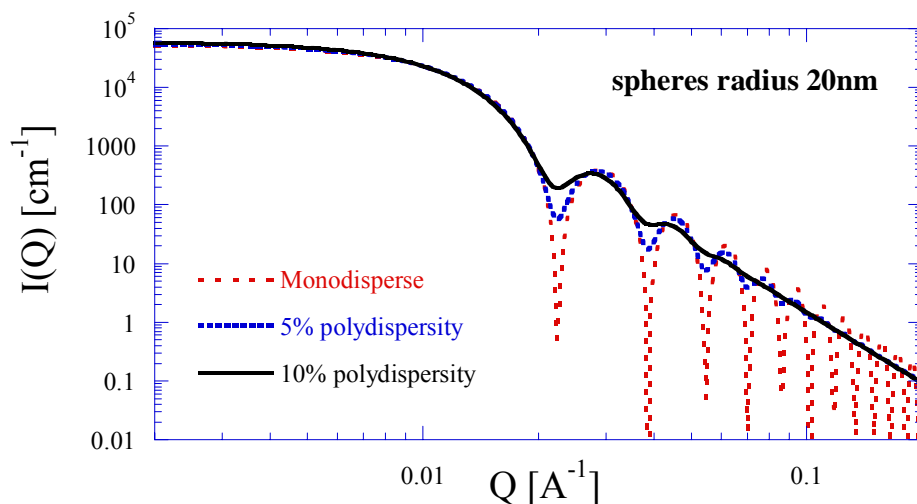
**Figure 5 :** Representation of the core shell model.

In practice, colloidal particles are never identical in size, there is always a distribution in size due to synthesis methods. In order to take into account these “imperfections”, we will use the polydisperse core shell model (called polycoreshell model in the SANS fitting package) to fit our data. The form factor  $P(Q)$  of polydisperse core shell is given by:

$$P(Q) = \int_0^{\infty} Sch(r) P_1(Qr) dr$$

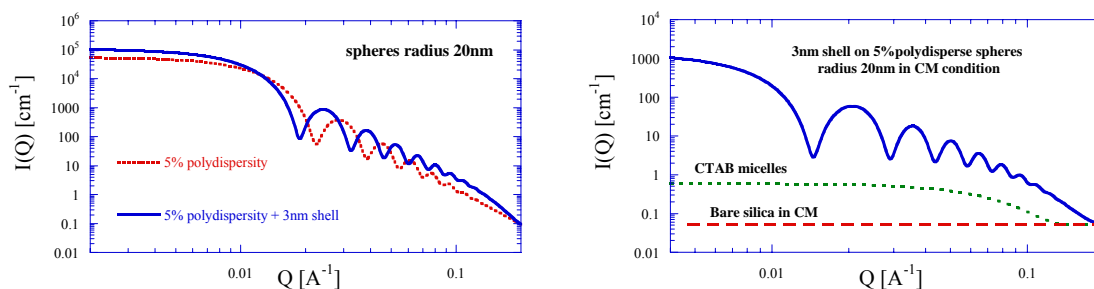
where  $Sch(r)$  is the Schultz distribution (polydispersity in size) which is both physically realistic as well as mathematically tractable, and where  $P_1(Qr)$  is the single form factor of a core shell. These analytical expressions can be found in reference 2. Note that the model assumes a distribution only in the particle core size while the shell thickness is fixed.

In figure 6, we give an example of how polydispersity in size affects the scattering data from an ideal sphere form factor (in this case we fix the shell thickness  $t = 0$ )



**Figure 6:** effect of size polydispersity on scattering curves from spheres

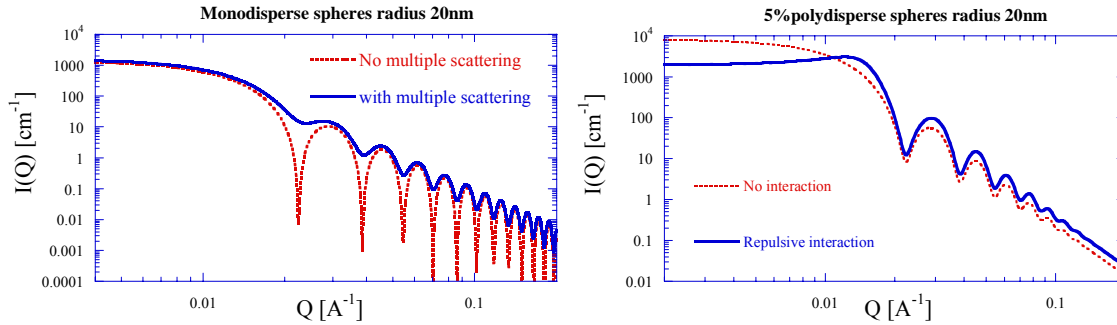
Using this polycore shell model, we can first simulate the scattering curves from silica particles covered or not by a surfactant layer. According to figure 7, characterization of a thin adsorbed layer should be possible especially in contrast match condition.



**Figure 7:** effect of a shell on scattering curves from polydisperse spheres

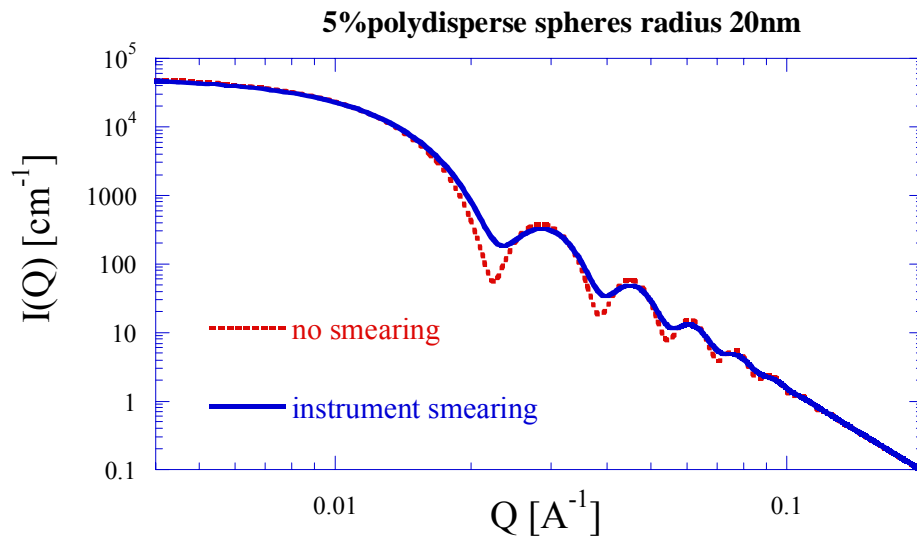
However, independently of the sample quality, other important aspects can considerably affect the validity of the data analysis. As explained in equation (8) the scattering intensity is proportional to the scattering contrast and particle volume fraction. So high scattering contrast and high particle content will lead to higher count rates and shorter accumulation times. However, multiple scattering (neutrons scattering more than once in the sample) and particle-particle interactions will dramatically alter the scattering curve (Figure 8), leading to inexact values for the radius of gyration and sample polydispersity.





**Figure 8:** effect of multiple scattering and particle-particle interactions on scattering curves from spheres

Another limiting factor in observing the minima of the form factor is the instrument resolution. Size and divergence of the beam, wavelength distribution and detector pixel size will contribute to smearing the ideal sample scattered intensity and will have a significant effect on the measured scattering data (Figure 9).



**Figure 9:** effect of instrumental resolution on scattering curves from polydisperse spheres

In conclusion, much care should be taken when performing a SANS experiment if one wants to quantitatively understand the measurements.

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