SANS and USANS Investigation
of
Oil Uptake by Micellar Gels

Summer School on Small Angle Neutron Scattering and Neutron Reflectometry
NIST Center for Neutron Research

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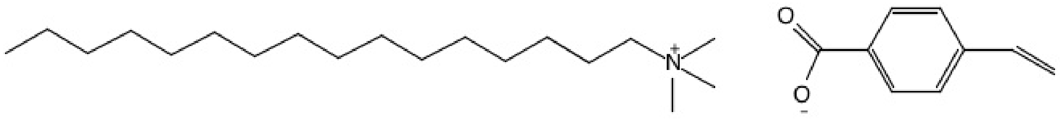
1 Introduction

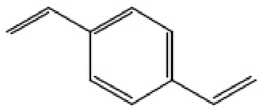
Surfactants are molecules that have both hydrophilic ("water loving") and hydrophobic ("water hating") components. In aqueous solvents such molecules self-assemble into structures that minimize contact between the solvent and hydrophobic segments. Micelles are one of a family of possible structures, with spherical, ellipsoidal, rod-like and disk-like micelles all being possible. A characteristic of micellar systems is the ability to solubilize oil through uptake into the hydrophobic micelle core - this is how your dish soap gets the grease off your plate.

This experiment will consider a surfactant with a polymerizable counterion and the uptake of oil by gels formed by cross-linking of micelles.

The surfactant in question is cetyltrimethylammonium 4-vinylbenzoate (CTVB) (figure 1), which forms rod-like micelles at a concentration of 10 mg/ml. The vinylbenzoate counterion can then be polymerized such that each micelle becomes a poly-electrolyte counterion around an alkyl core. These rod-like micelles form a viscoelastic solution that can be further covalently cross-linked using divinylbenzene (DVB) to form a space-filling gel.



(a) cetyltrimethylammonium 4-vinylbenzoate



(b) 1,4-divinyl benzene

Figure 1: Components of the micellar gel

SANS/USANS measurements (figure 2) show that the gel retains the locally cylindrical structure of the original micelles. Thus the material is effectively a "macro-micelle" with overall dimensions of centimeters.

As with a regular micellar solution, various organic materials can be solubilized in these micellar gels, with a solubilization capacity far greater than the unpolymerized micelles. The micellar gel also has the distinct advantage that the gel and solubilized material can be simply removed from solution.

Hence, we will consider the uptake of toluene by a micellar gel of CTVB and the variation in gel structure seen upon uptake.

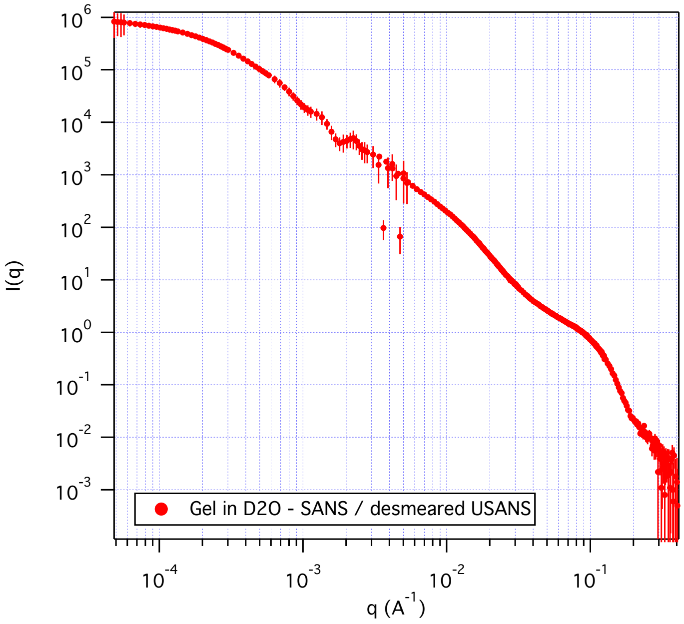


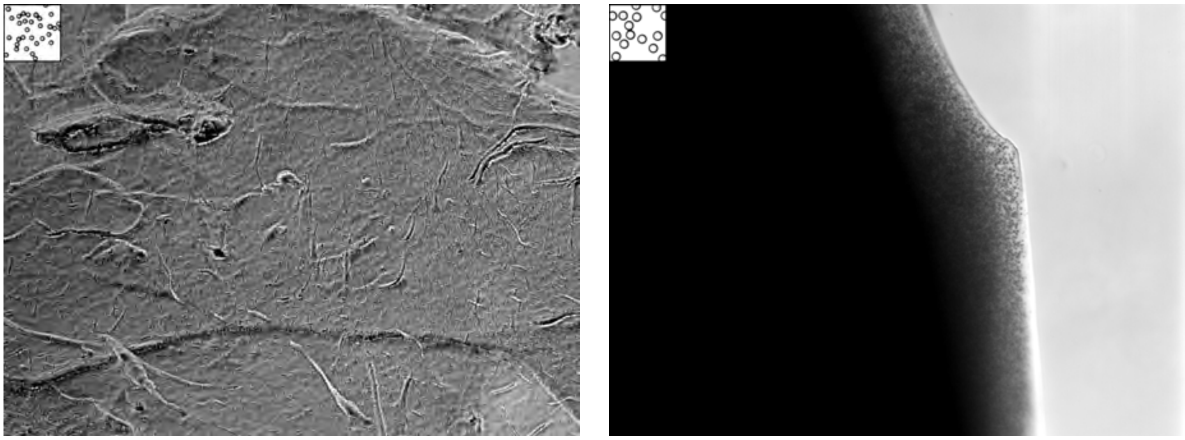
Figure 2: SANS/USANS measurement of gel in D_2O

Figure 3 shows optical micrographs of four oil-loaded gel samples after differing time periods. In each case the disk of gel was placed in a saturated solution of toluene in water for a number of days before being placed in a SANS/USANS sample cell. The micrographs shown in Figure 3 were taken in-situ in the cells.

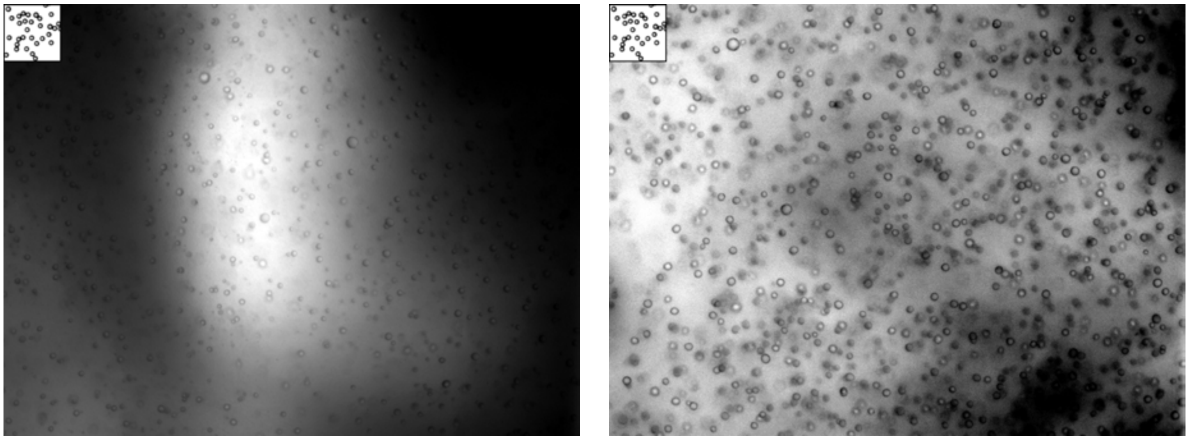
As can be clearly seen, there are micron sized "droplets" of something forming in the gel. This may be the source of the enhanced uptake seen for the gel system over the micellar system, but optical microscopy does not reveal what the "droplets" are - they are most likely oil, but could be voids where the presence of oil has broken down the gel structure.

1.1 Why use SANS?

Generally, static light scattering and small angle X-ray scattering (SAXS) provide the same information about the sample as neutron scattering *i.e* measurement of macroscopic scattering cross-section $d\Sigma/d\Omega(q)$. The contrast in light scattering arises from the difference in the light's refractive index between the particle and water. The wavelength of light limits q < 0.002 Å^{-1} and thus the size range probe to $>\sim$3000Å. Furthermore, in order to measure the light scattering the sample needs to be dilute and here we wish to study a concentrated network structure. The contrast in X-ray scattering arises from the variation in electron density within the sample. However USAXS does not generally reach as low q as USANS and with many samples x-rays (particularly at synchrotron sources) can cause damage to the sample as a result of the large amount of energy imparted. In the case of SANS the contrast arises from variations in the density and chemical composition within the sample. This allows for isotopic substitution to alter the scattering - a powerful technique known as "contrast variation".



(a) 0 Days (b) 1 Day



(c) 6 Days (d) 17 Days

Figure 3: Optical micrographs of gel samples after exposure to a saturated solution of toluene in water for differing time periods. The insets show micrographs of 10μm latex spheres on the same scale as the main image.

USANS also overlaps in length scale with optical microscopy. Here the advantage is that bulk samples can be studied and system averages of structure can be obtained as opposed to the localized measurements provided by microscopy.

SANS/USANS is therefore an ideal probe for the structure of these systems for two reasons. Firstly, the chemical sensitivity of neutron scattering and contrast variation allow us to determine the identity of the "droplets" where microscopy cannot. Secondly, the combination of SANS and USANS allows measurement of bulk samples over the whole relevant size range with no risk of damage to the sample.

2 The Objectives of the Experiment

To determine the the gel structure with and without oil The scattering data obtained under various contrast conditions with and without oil will be analyzed using model independent and non-linear model fitting techniques to identify the structure of the gel over a wide length scale.

To determine the identity of the "droplets" The scattering from the droplets will be identified and compared to predictions of scattering from possible droplet compositions.

3 The USANS Instrument

Fundamentally, the SANS experiment consists of measuring the number of neutrons scattered per incoming neutron as a function of scattering angle. Since the size probed is inversely proportional to angle, to examine larger objects we need to measure scattering at smaller angles. In the case of a "pinhole" SANS instrument this is achieved by moving a 2 dimensional detector relative to the sample such that a detector element subtends a smaller angle the further the detector is from the sample.

The SANS instruments at the NCNR can measure down to $8\times10^{-4}\text{Å}^{-1}$ at their maximum sample to detector distance and using lenses to focus the neutron beam. This implies a maximum size of measurable object of approximately 500nm. One can imagine simply making longer and longer instruments to study larger and larger objects, however there a limitations to that approach. Firstly neutrons have mass and so are affected by gravity. Hence they fall through a parabolic path as they travel from source to detector. Secondly, the collimation required as the instrument gets longer reduces the flux of neutrons on the sample and counting times increase. Indeed, the count rate at the detector varies with the fourth power of the resolution.

There is an alternative to the pinhole instrument and that is to use crystal diffraction to produce a monochromatic beam of neutrons with very good angular collimation and to then use an identical crystal to analyze the scattered beam. This instrument design is known as a Bonse-Hart type or Double-Crystal diffractometer.

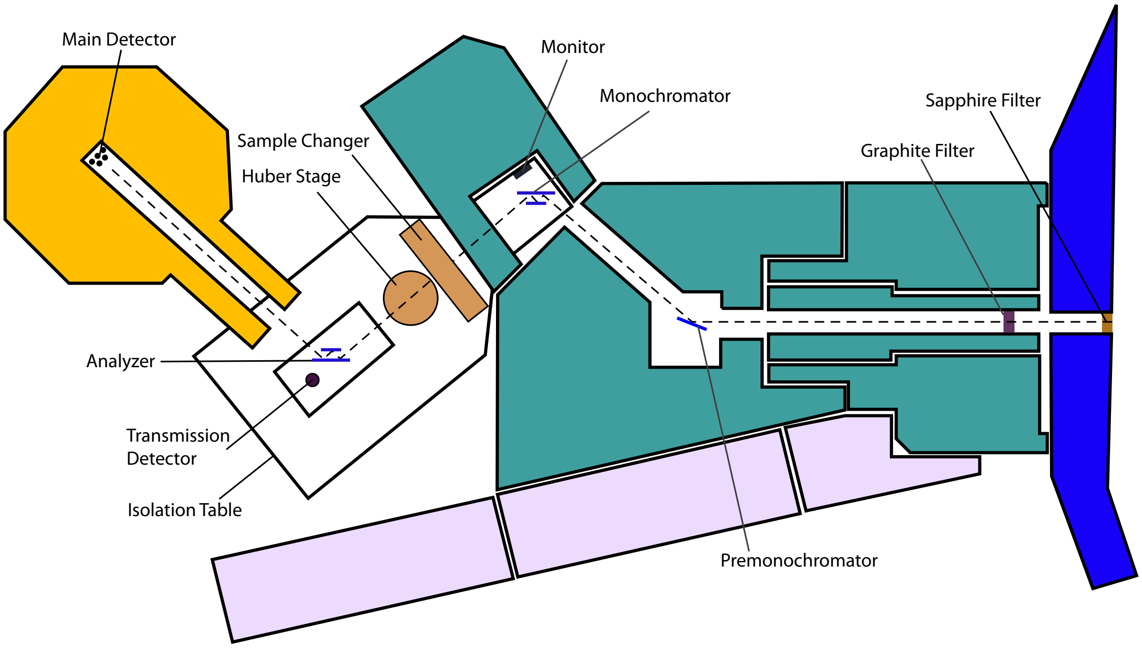


Figure 4: Schematic layout of the BT-5 USANS instrument. The dashed line indicates the beam path. The measured scattering angle, or momentum transfer q, is determined by rotation of the analyzer crystal.

Figure 4 show the schematic layout of the NCNR USANS instrument which is located on beam tube 5 (BT-5). A channel cut silicon crystal (monochromator) provides the neutron beam onto the sample, where the neutrons are scattered. A second identical channel cut crystal (analyzer) is then placed in the scattered beam path and rotated to select the scattering angle to be analyzed and diffract the neutrons scattered at that angle into the detector. An experiment consists of rotating the analyzer to a series of angles and counting the number of neutrons that reach the detector.

The intensity of scattering on the detector after background correction in a USANS experiment is given by

$$I_{cor}(q)_s = \varepsilon I_{beam} \Delta\Omega_A d_s T(\frac{d\Sigma_s(q)}{d\Omega}) \tag{1}$$

where

ε is the detector efficiency

I_{beam} is the number of neutrons per second incident on the sample

d_s is the sample thickness

T is the sample transmission

$\Delta\Omega$ is the solid angle over which scattered neutrons are accepted by the analyzer

$\frac{d\Sigma_s(q)}{d\Omega}$ is the measured scattering cross section, which is the true cross section modified by the instrumental resolution function.

The aim of the experiment is to obtain the differential macroscopic scattering cross section $\frac{d\Sigma}{d\Omega}$ from I_{meas}. How we can go about that process is described later, but first we need to decide how to prepare our sample for the measurement.

4 Planning the Experiment

Given the stated objectives of the experiment and knowledge of the instrument, 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.

4.1 Scattering Contrast

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

$$\Delta\rho = \rho_t - \rho_g \tag{2}$$

and ρ_t and ρ_g are the *scattering length densities* (SLD) of the toluene and the gel matrix , respectively. Recall that SLD is defined as

$$\rho = \frac{1}{V}\sum_{i}^{N} b_i \tag{3}$$

where V is the volume containing n atoms, and b_i is the (bound coherent) *scattering length* of the ith atom in the volume V. V is usually the molecular or molar volume for a homogenous phase in the system of interest.

The SLDs for the phases in the present case, surfactant, oil and water, can be calculated from the above formula, using a table of the scattering lengths (such as Sears,1992 [1]) for the elements, or can be calculated using the interactive SLD Calculator available at the NCNR's Web pages [2]. The SLDs for the components in this experiment are given below in Table 1.

Material	**Chemical Formula**	**Mass Density (g cm^{-3})**	**SLD (Å^{-2})**
Toluene	C_7H_8	0.867	0.94×10^{-6}
d8-Toluene	C_7D_8	0.943	5.66×10^{-6}
CTVB	$C_{16}H_{33}N(CH_3)_3^+C_9H_9O_2^-$	1.0	0.23×10^{-6}
DVB	$C_{10}H_{10}$	0.913	1.23×10^{-6}
Light Water	H_2O	1.0	-0.52×10^{-6}
Heavy Water	D_2O	1.0	6.32×10^{-6}

Table 1: The scattering length densities for Toluene, d8-Toluene, CTVB, DVB and, heavy and light water

Whilst the above gives the scattering length density of the individual components, we are most interested in the various combinations of components that actually make up the gel. It is often difficult to predict what the effective volume of a material will be when it self-assembles and so whilst the scattering length density of the gel can be calculated it is often more useful to measure it. This can be done by making gels in various mixtures of solvent across the composition range from pure H_2O to pure D_2O. Since

$$I(q) \propto (\Delta\rho)^2 \tag{4}$$

and

$$\rho_{solvent} = \phi_{D_2O}\rho_{D_2O} + (1 - \phi_{D_2O})\rho_{H_2O} \tag{5}$$

where ϕ_{D_2O} is the volume fraction of D_2O in the solvent and ρ is the relevant scattering length density, we can plot $\sqrt{I(0)}$ vs ϕ_{D_2O} and there will be a minimum where $\sqrt{I(0)} = 0$ corresponding to the *contrast match point*. This is the point where the SLD of the solvent matches that of the micellar gel.

When we perform this analysis for these micellar gels (Figure 5) we find that the contrast match point for the gel is at 17 % by weight D_2O in H_2O. Note that here we did not have a value for I(0), so have approximated it with I(Q=0.0041) which is acceptable as there is no change in the shape of the scattering curve with D_2O content at that Q value.

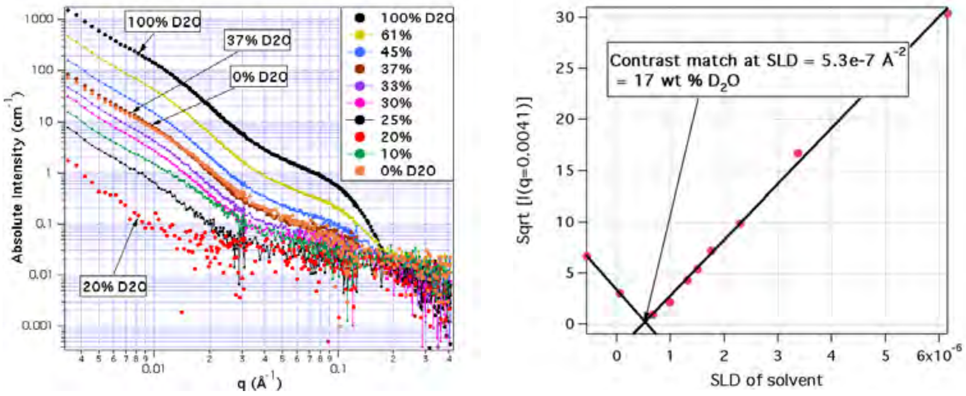


Figure 5: Contrast match point determination for a micellar gel swollen with toluene.

4.2 Sample Thickness

Given the calculated sample contrast, how thick should the sample be? Recall that the scattered intensity is proportional to the product of the sample thickness, d_s and the sample transmission, T. It can be shown that the transmission, which is the ratio of the transmitted beam intensity to the incident beam intensity, is given by

$$T = e^{-\Sigma_t d_s} \tag{6}$$

where $\Sigma_t = \Sigma_c + \Sigma_i + \Sigma_a$, i.e. the sum of the coherent, incoherent and absorption macroscopic cross sections. The absorption cross section, Σ_a, can be accurately calculated from tabulated absorption cross sections of the elements (and isotopes) if the mass density and chemical composition of the sample are known. The incoherent cross section, Σ_i, can be *estimated* from the cross section tables for the elements as well, but not as accurately as it depends on atomic motions and is therefore temperature dependent. The coherent cross section, Σ_c, can also only be estimated since it depends on the details of both the structure and the correlated motions of the atoms in the sample. This should be no surprise as Σ_c as a function of angle is the quantity we are aiming to measure!

The scattered intensity is proportional to $d_s T$ and hence

$$I_{meas} \propto d_s e^{-\Sigma_t d_s} \tag{7}$$

which has a maximum at $d_s = 1/\Sigma_t$ which implies an optimum transmission, $T_{opt} = 1/e = 0.37$. The sample thickness at which this occurs is known as the "1/e length".

The NCNR web based SLD calculator provides estimates of Σ_i and Σ_a and gives an estimate of the 1/e length as well as calculating the SLD.

4.3 Multiple Scattering

The analysis of small angle scattering data assumes that a neutron is scattered only once on passing through the sample and thus that the scattering angle is simply related to structure of the sample. However, if the small angle scattering is strong enough to result in multiple scattering, then the shape of the scattering curve will become distorted [4] and analysis essentially impossible. Thus when Σ_c is significantly larger than $\Sigma_i + \Sigma_a$ the thickness should be chosen such that $T > 0.9$ rather than 0.37 to avoid problems with multiple scattering.

In this experiment, the optimum sample thickness has been determined to be 1mm.

4.4 Required q range

The q range that is routinely accessible using the BT-5 USANS instrument is 5×10^{-5}Å^{-1} to 5×10^{-3}Å^{-1}. Both low q and high q limits are in practice determined by whether there is measurable scattering above background since the analyzer can be set to count at any q. The high q value chosen for an experiment is usually determined by the length scales of relevance to the sample and whether overlap with the SANS measurement regime is required. Figure 6 shows the accessible q ranges of the SANS and USANS instruments.

In this experiment we will be measuring to approximately 3×10^{-3}Å^{-}1.

5 Collecting data

As discussed earlier, the experiment consists of scanning the analyzer through a series of angles and counting the scattered intensity on the detector. The first step before collecting the scattering data, therefore, is to decide which angles to measure at and how long to count at each.

5.1 Configuring the instrument

We need to measure over a range of angles spanning two orders of magnitude in q and an appropriate q spacing for around q=0 would lead to a huge excess of data points at around q=1×10^{-3}Å$-$1.

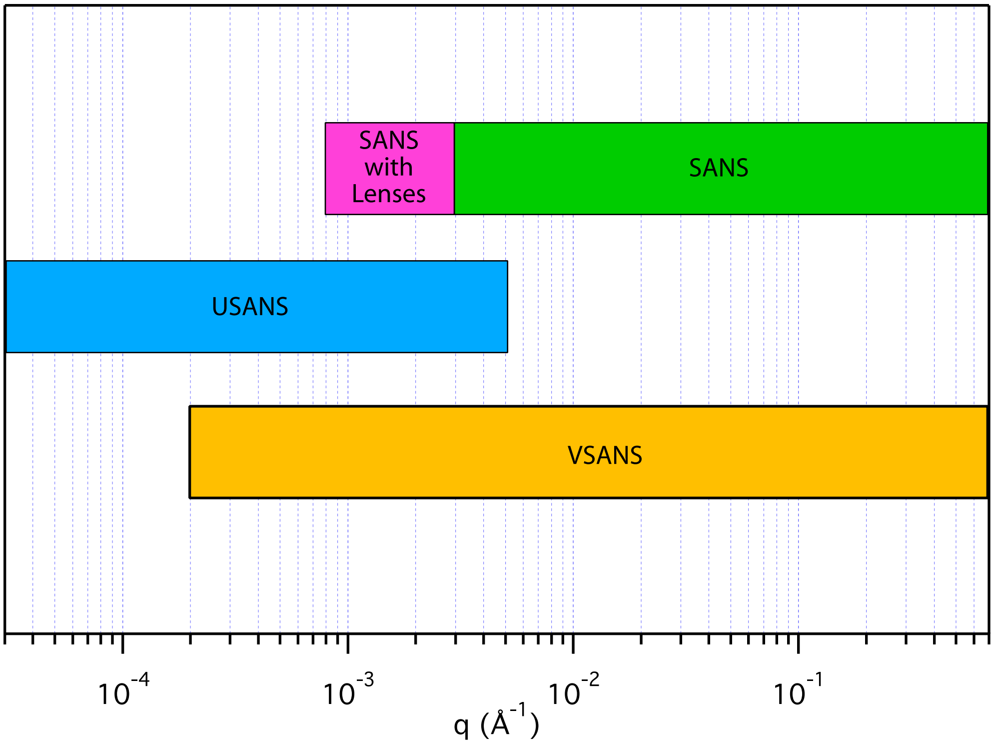


Figure 6: Comparison of the accessible q ranges of the BT-5 USANS instrument, NG-3 and NG-7 SANS instruments and the proposed VSANS instrument

Thus we divide the data collection into six separate equally spaced scans, with each scan having roughly double the q spacing of the previous one. The first scan spans the main beam and the peak intensity from that scan is used to determine the q=0 angle, to scale the intensity into absolute units and to determine the sample transmission.

5.2 What measurements to make

To correct for instrument "background" measurement of scattering without the sample is needed. Counts recorded on the detector can come from three sources: 1) neutrons scattered by the sample itself; 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.

In order to separate these contributions we need to make three separate measurements:

1. Scattering measured with the sample in place (which contains contributions from all three sources listed above), $\mathbf{I_{sam}}$
2. Scattering measured with the empty sample holder in place (which contains contributions from sources 2 and 3 above), $\mathbf{I_{emp}}$

3. Counts measured with a complete absorber at the sample position (which contains only the contribution from source 3 above), $\mathbf{I_{bgd}}$

The $\mathbf{I_{bgd}}$ on the USANS instrument is predominantly due to fast neutrons. This background is independent of instrument configuration as the fast neutrons are not coming along the beam path. It has been measured and is $0.018\mathrm{s}^{-1}$, which equals 0.62 counts per 10^6 monitor counts. Thus we do not usually measure a blocked beam run on USANS but use a fixed value for $\mathbf{I_{bgd}}$

5.3 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, σ, in the number of counts recorded in time, $I(t)$ is given by $\sigma = \sqrt{I(t)}$. Thus increasing the counting time by a factor of four will reduce the relative error, σ/I by a factor of two. If there are 1000 total counts per data point, the standard deviation is $\sqrt{1000}$ which is approximately 30, giving a relative uncertainty of about 3%, which is good enough for most purposes.

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

$$\frac{t_{bgd}}{t_{sam}} = \sqrt{\frac{\text{Count Rate}_{bgd}}{\text{Count Rate}_{sam}}} \tag{8}$$

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

Since the scattering usually becomes much weaker at larger q, the time spent per data point increases with angle and the high q scans dominate the overall counting time.

5.4 Sample Transmission

The sample transmission is determined in two ways.

5.4.1 Wide angle transmission

A separate transmission detector (see figure 4), located behind the analyzer, collects all neutrons not meeting the Bragg condition for the analyzer. When the analyzer is rotated to a sufficiently wide angle from the main beam orientation the transmission detector counts both the direct beam intensity and the coherently small angle scattered intensity. Thus the ratio of the count rate on the transmission detector with and without the sample is the sample transmission ($\mathrm{T_{wide}}$) due to attenuation from incoherent scattering and absorption.

5.4.2 Rocking curve transmission

Rotating the analyzer through the main beam allows the intensity at q = 0 to be measured. The ratio of this intensity with and without the sample gives the transmission of the sample ($\mathrm{T}_{\mathrm{rock}}$) due to attenuation from incoherent scattering, absorption and *coherent small angle scattering*.

5.5 Multiple scattering estimate

The ratio of these separate transmission measurements can be used to estimate the amount of multiple scattering by determining the scattering power ($\tau = \Sigma_{SAS} d_s$) by

$$T_{SAS} = \frac{T_{\mathrm{Rock}}}{T_{\mathrm{Wide}}} = e^{-\tau} \tag{9}$$

where ideally $T_{SAS} > 0.9$

5.6 Simulation of Scattering

Given enough information about the chemical composition of the sample and expected scattering properties we can simulate the scattering to help us optimize the experimental setup. The reduction and analysis package provided for Igor Pro [5] by NIST [6] contains tools to help you do this.

The simulation takes input about your sample and simulates the data you would expect to collect on the instrument. This can guide you in deciding many of the factors discussed above such as appropriate sample thickness, counting time, and amount of multiple scattering. Additionally it can help decide on the density of data points to be collected for USANS or the instrument configurations for SANS.

6 Data reduction

Data reduction consists of correcting the measured scattering from the sample for the sources of background discussed in section 5.2 and rescaling the observed, corrected data to an absolute scale of scattering cross section per unit volume. This is done via equation (1) presented previously and reproduced here for reference:

$$I_{cor}(q)_s = \varepsilon I_{beam} \Delta\Omega_A d_s T(\frac{d\Sigma_s(q)}{d\Omega}) \tag{10}$$

The beam intensity, εI_{beam}, is measured by rotating the analyzer through the direct beam at q = 0 with the empty cell in the beam path. The transmission, T, is measured by taking the ratio of the count rate observed on the transmission detector with and without the sample in the beam path. The solid angle of scattering accepted by the analyzer, $\Delta\Omega_A$, is given by

$$\Delta\Omega_A = \left(\frac{\lambda}{2\pi}\right)^2 (2\Delta q_v)\Delta q_h \tag{11}$$

where $2\Delta q_v$ is the total vertical divergence of the beam convoluted with the angular divergence accepted by the detector and Δq_h is the horizontal divergence accepted for diffraction by monochromator and analyzer crystals. The instrument accepts scattered neutrons with $\pm\Delta q_v = 0.117\text{Å}^{-1}$. The horizontal resolution Δq_h is measured from the full width at half maximum (fwhm) of the main beam profile obtained by rotating the analyzer through the direct beam. The fwhm when the crystal is properly aligned is 2.00 arcsec, equating to $\Delta q_h = 2.55 \times 10^{-5}\text{Å}^{-1}$. Thus the solid angle over which neutrons are accepted by the analyzer is $\Delta\Omega_A = 8.6 \times 10^{-7}$ ster.

As you may have noted above, the analyzer has very good resolution in the horizontal direction and very poor resolution in the vertical direction as depicted graphically in figure 7. This is referred to as "slit geometry" as opposed to the "pinhole geometry" of a standard SANS instrument - you may be familiar with this from using a Kratky camera for lab-based small angle x-ray scattering. The large difference between the horizontal and vertical resolutions means that the smearing can be treated as that from an "infinite" slit. The measured cross section, $d\Sigma_s/d\Omega(q)$, obtained from data reduction as described above is related to the true differential macroscopic cross section, $d\Sigma/d\Omega(q)$ by the relation [7]

$$\frac{d\Sigma_s}{d\Omega}(q) = \frac{1}{\Delta q_v}\int_0^{\Delta q_v} \frac{d\Sigma}{d\Omega}(\sqrt{q^2+u^2})du \tag{12}$$

Figure 8 compares the scattering from a 1 volume % dispersion of 2 μm silica particles with 5% polydispersity in D_2O using pinhole and slit geometries. Note the damping of the oscillations, the change in slope and reduction in intensity. Desmearing the data directly can be done by an iterative convergence method [8] but the desmeared result is very unstable, being sensitive to noise in the data. The preferred method is to make use of equation (12) to smear a model function and fit the smeared data *directly*. The latter is the method we will employ in the analysis of our data.

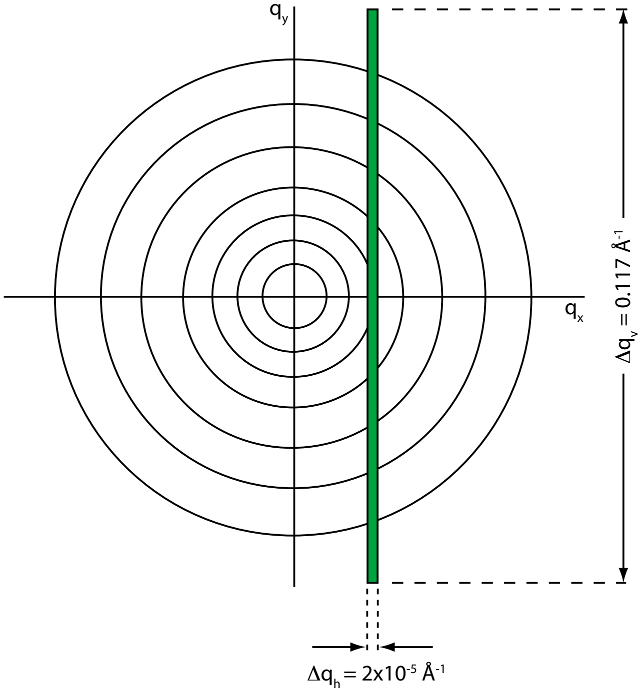


Figure 7: View of scattering with axes q_x and q_y collected by the analyzer on the BT-5 USANS instrument. The circles represent iso-intensity contours from isotropic small angle scattering. The narrow slit represents the scattering region collected by the analyzer.

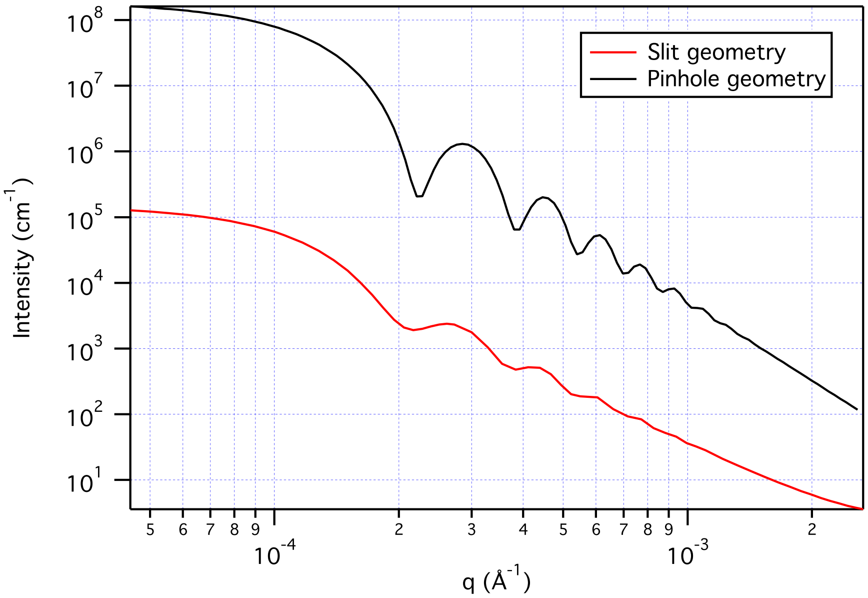


Figure 8: Comparison of the modeled scattering from a 1 volume % dispersion of 2 μm silica particles with 5% polydispersity in D_2O using pinhole and slit geometries

7 Data Analysis

At the summer school you will reduce and analyze data collected from samples of micellar gel before and after swelling with toluene to determine:

- The structure of the gel
- The oil content of the swollen gel
- The identity of the “droplets”
- The size of the “droplets”

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