Chapter 61 - **THE USANS INSTRUMENT**

In order to achieve much lower Q ranges, an entirely different instrument concept is used. Instead of choosing long wavelengths and long flight paths (as done in conventional SANS instruments), thermal wavelength neutrons and perfect single crystals are used in the USANS instrument. The USANS instrument uses the Bonse-Hart method for achieving very narrow collimation through multiple bounce monochromator (and analyzer) reflections.

1. THE USANS INSTRUMENT COMPONENTS

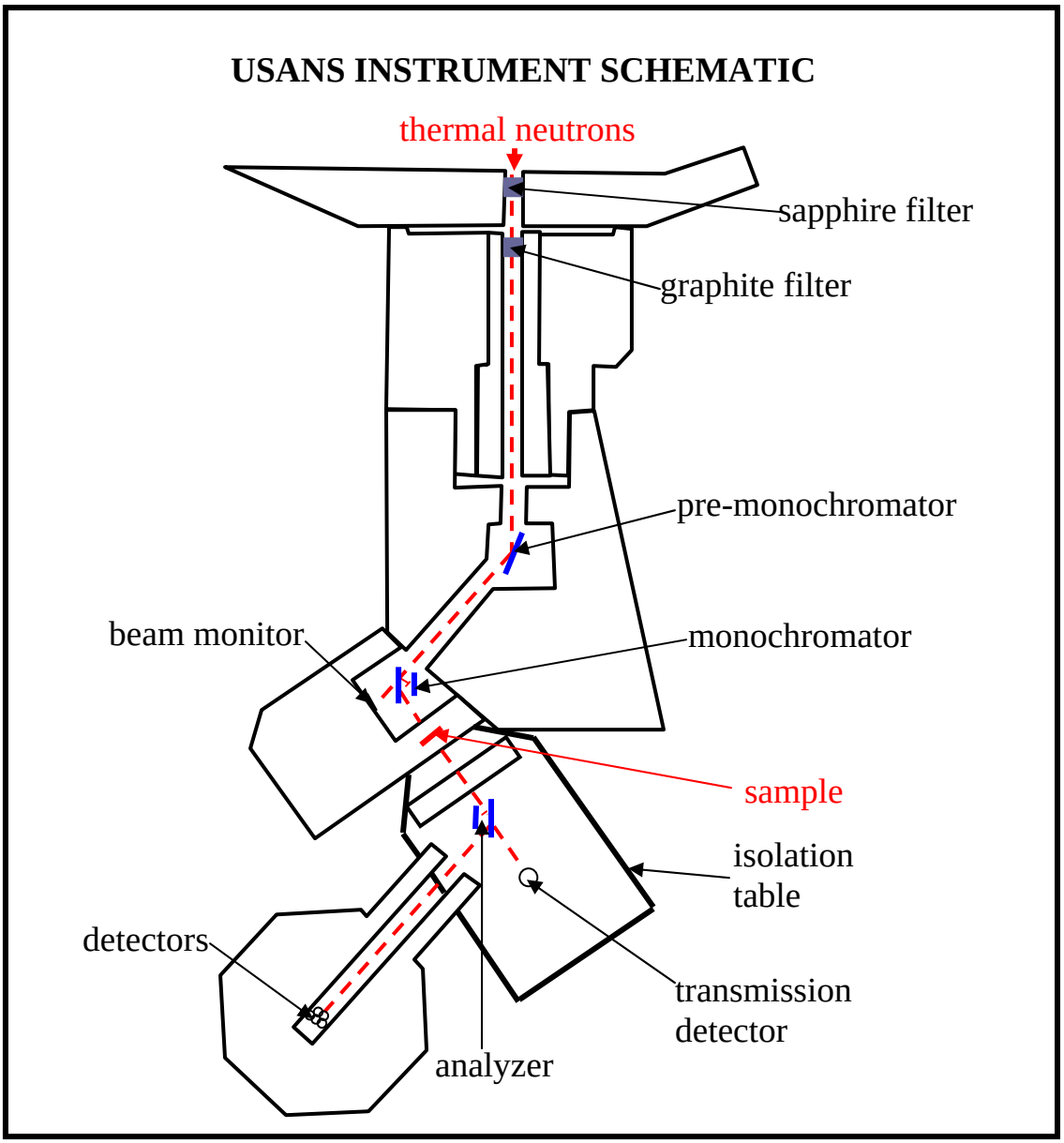

Figure 1: Schematic representation of the USANS instrument at the NIST CNR.

Since the USANS instrument at the NIST CNR uses thermal neutrons, it is located inside the confinement building (not in the guide hall). It uses the silicon (220) reflection peaked at a neutron wavelength of $\lambda = 2.4$ Å. Neutron filters (sapphire and pyrolitic graphite) are used to filter out higher components of the energy spectrum. These eliminate neutrons with fractional wavelengths ($\lambda/2$, $\lambda/3$, etc). A pre-monochromator is used to reduce the radiation level on the monochromator and other components. Channel cut perfect silicon crystals are used for monochromator and analyzer. The three crystals (for the triple bounce) are cut from the same large silicon ingot. A set of five end-window counters are used as neutron detectors to step-scan the angular range (Barker et al, 2005).

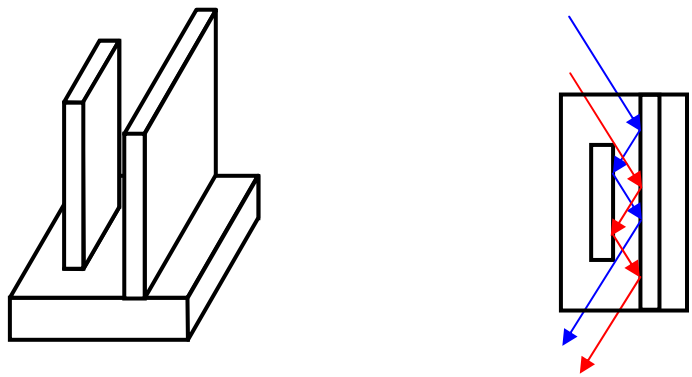

Figure 2: Triple bounce monochromator and analyzer single crystals. The three pieces are carved in the same single crystal silicon ingot.

2. THE USANS INSTRUMENT CHARACTERISTICS

The USANS instrument uses triple reflections from the single crystal silicon monochromator and analyzer in order to achieve very narrow $\Delta\lambda/\lambda$ and very high collimation (by reducing the beam angular divergence). It uses the slit geometry whereby the Q resolution is very tight in the horizontal direction and opened up in the vertical direction. The standard deviation of the Q resolution function is of order:

$$\sigma_Q^{hor} = 2.25*10^{-5}\ \text{Å}^{-1} \qquad (1)$$
$$\sigma_Q^{ver} = 0.022\ \text{Å}^{-1}.$$

The coarse vertical instrumental resolution allows the use of large sample sizes (5 cm diameter) and therefore large neutron beam currents.

The silicon (220) reflection is characterized by the λ = 2.4 Å (operating) USANS wavelength. Silicon has very narrow mosaic spread (a few arcsec FWHM). This low wavelength minimizes multiple scattering so that standard (1 mm or 2 mm) sample thickness can be used. Low wavelength also minimizes gravity effects on the neutron trajectories.

The reflectivity profile from one silicon piece drops out like $R(Q) \sim 1/Q^2$. For three reflections in a row (triple bounce), $R(Q) \sim 1/Q^6$. The wings of the beam profile are substantially depressed making the Bonse-Hart adequate for ultra small-angle measurements.

The USANS instrument covers an ultra low-Q range: $4*10^{-5}$ Å^{-1} < Q < 0.01 Å^{-1}. This corresponds to the size range 7.8 μm > d-spacing > 628 Å that overlaps with optical microscopy. Microscopy measurements are performed in real space whereas scattering measurements are performed in reciprocal space. Optical methods do not work on opaque samples whereas neutron scattering can measure opaque samples.

The main drawback of using slit geometry is the introduction of slit smearing of the data. The slit smearing integration of the scattering cross section (scattering intensity) is as follows:

$$\left(\frac{d\Sigma(Q)}{d\Omega}\right)_{smeared} = \frac{1}{\Delta Q_{ver}} \int_0^{\Delta Q_{ver}} dQ_y \, \frac{d\Sigma(\sqrt{Q^2 + Q_y^{\,2}})}{d\Omega}. \qquad (2)$$

Here the vertical integration window ΔQ_{ver} is proportional to the Q resolution in the vertical direction σ_Q^{ver}. Integrating up to 2 or 3 standard deviations is reliable.

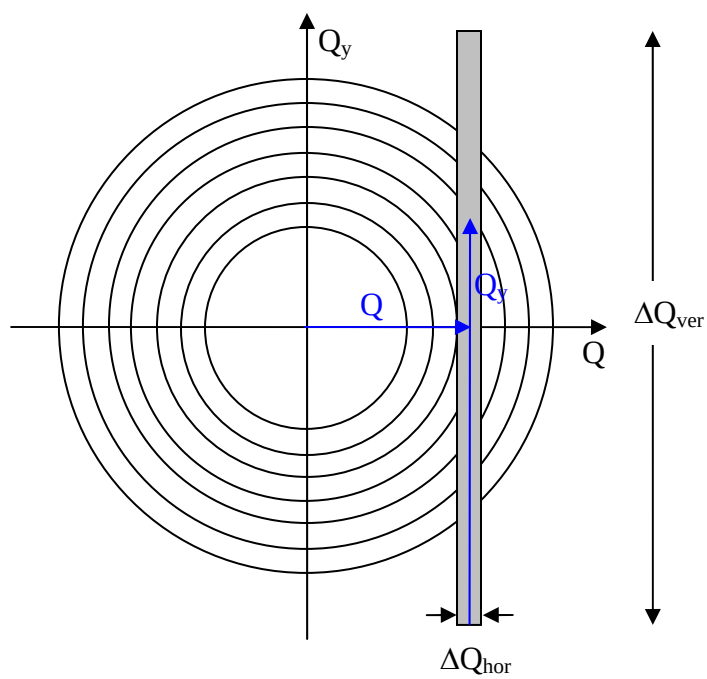

Figure 3: Rectangular binning for the slit geometry and the spherical symmetry of the scattered neutrons. Scattered intensity is summed up over the rectangular bin.

Two other figures of merit are the neutron current and the signal-to-noise ratio to insure low (acceptable) background level. The neutron current is Φ = 25,000 n/sec for a vertical sample slit size of Δy_2 = 5 cm. The signal-to-noise ratio is fairly low $5*10^5$ despite the fact that the USANS instrument at the NCNR is located inside the confinement building.

Assuming a Guinier-type function as a simple model for the scattering cross section at low-Q:

$$\frac{d\Sigma(Q)}{d\Omega} = \frac{d\Sigma(0)}{d\Omega} \exp\left(\frac{-Q^2 R_g{}^2}{3} \right). \qquad (3)$$

Here R_g is a characteristic radius of gyration. The smearing integral becomes:

$$\left(\frac{d\Sigma(Q)}{d\Omega} \right)_{smeared} = \frac{1}{\Delta Q_{ver}} \int_0^{\Delta Q_{ver}} dQ_y \, \frac{d\Sigma(0)}{d\Omega} \exp\left(\frac{-(Q^2 + Q_y{}^2) R_g{}^2}{3} \right). \qquad (4)$$

The following variable change is made $t = Q_y R_g / \sqrt{3}$ and the following integral is used:

$$\int_0^\infty dt \exp \exp\left(-t^2\right) = \frac{\sqrt{\pi}}{2}. \qquad (5)$$

Assuming that the resolution window is wide-enough, one obtains the following low-Q limit.

$$\left(\frac{d\Sigma(0)}{d\Omega} \right)_{smeared} = \frac{d\Sigma(0)}{d\Omega} \frac{\sqrt{3\pi}}{2\Delta Q_{ver} R_g}. \qquad (6)$$

Another simple function to model the scattering cross section is the Lorentzian function:

$$\frac{d\Sigma(Q)}{d\Omega} = \frac{d\Sigma(0)}{d\Omega} \frac{1}{1 + Q^2 \xi^2}. \qquad (7)$$

Here also, making the variable change $t = Q'_y \, \xi$ and using the normalization integral:

$$\int_0^\infty dt \frac{1}{1+t^2} = \frac{\pi}{2}. \qquad (8)$$

The following result is obtained for the low-Q limit:

$$\left(\frac{d\Sigma(0)}{d\Omega} \right)_{smeared} = \frac{d\Sigma(0)}{d\Omega} \frac{\pi}{2\Delta Q_{ver} \xi}. \qquad (9)$$

3. THE FRAUNHOFFER DIFFRACTION

Fraunhoffer diffraction appears when aperture sizes become small. A circular aperture of radius R yields the following fringe pattern:

$$I(Q) = I(0)\left[\frac{2J_1(QR)}{QR}\right]^2. \qquad (10)$$

Here J_1 is the cylindrical Bessel function or order 1 and I(0) constitutes the diffracted beam intensity through the aperture. Fraunhoffer fringes start at the edge of the direct beam on the detector bank. A slit aperture of width L yields the following fringe pattern:

$$I(Q) = I(0)\left[\frac{\sin(QL/2)}{QL/2}\right]^2. \qquad (11)$$

These fringes constitute unwanted background when their Q range becomes comparable to the scattering features from the sample. This is the case of the USANS instrument whereby sub-millimeter slits are used and multi-micron size scales are probes.

Recall that $\left[\frac{2J_1(QR)}{QR}\right]^2$ and $\left[\frac{\sin(QL/2)}{QL/2}\right]^2$ are the form factors for a scattering disk of radius R and of a slab of width L provided that they are oriented perpendicular to the neutron beam. It is to be expected that the scattering from a particle of a specific shape be the same as the scattering from a sample of uniform density (think solvent) but with a beam defining mask of the same shape as the particle. This holds provided that the mask dimension is comparable to the size of the particle (nanometer to fraction of a micrometer scale).

4. TYPICAL USANS DATA

SANS and USANS data were taken from a 4 % poly(ethylene oxide) in d-ethanol. PEO crystallizes into lamellae that form a sponge-like structure. No Guinier region was observed in the SANS data, but its onset is visible in the USANS data. The scattering cross section is very large at low-Q, which yields good statistics. At intermediate-Q, the cross section is lower and the statistics are poor. It took 30 minutes to acquire the SANS data and 5 hours to acquire the USANS data.

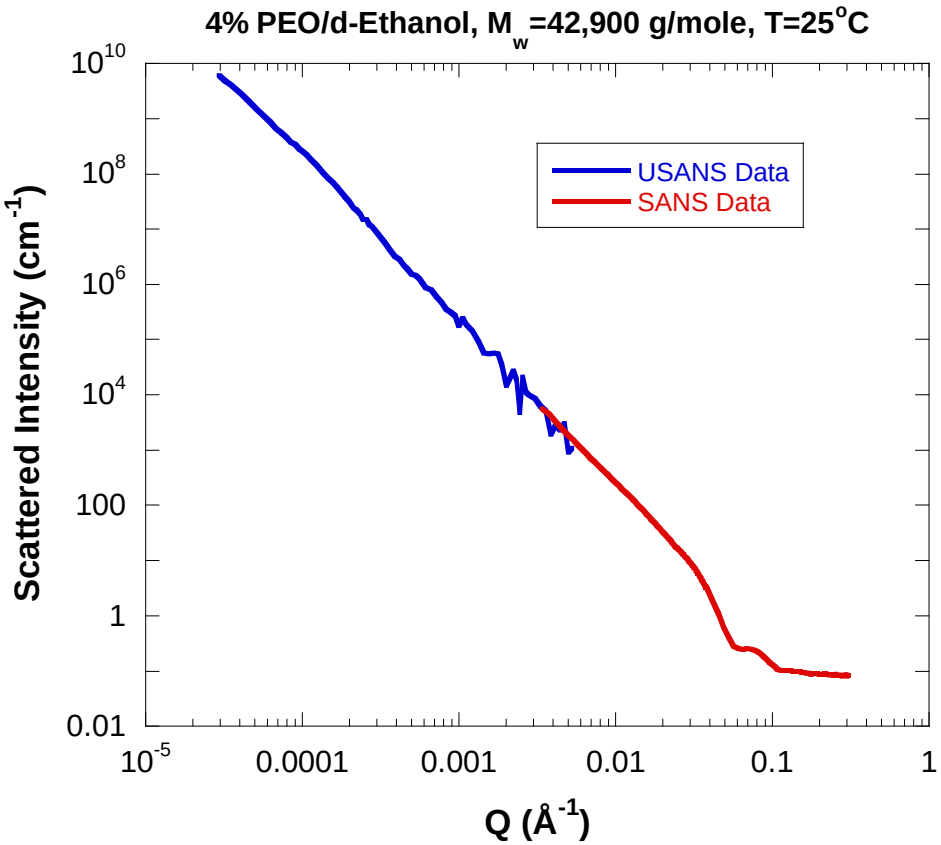

Figure 4: SANS and USANS data taken from a sample of 4 % poly(ethylene oxide) in d-ethanol.

More SANS and USANS data were taken from the PEO/d-ethanol at higher polymer weight fractions. The Guinier region is better defined and the high-Q oscillations from the lamellar structure occur at lower Q values (Ho et al, 2006). The high-Q Porod exponent is m = 3.5 which points to a mass fractal (sponge-like structure).

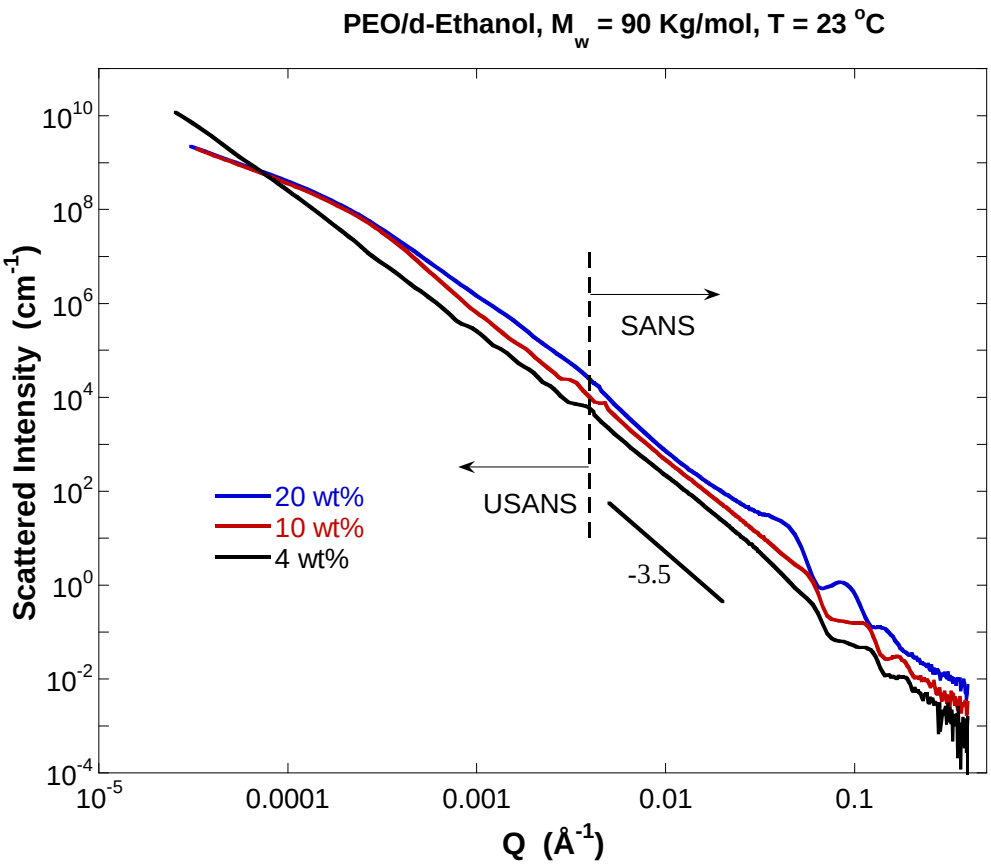

Figure 5: SANS and USANS data taken from crystalline PEO/d-ethanol. The incoherent background level has been subtracted.

A confocal optical micrograph was taken from 4 % hPEO/h-ethanol at ambient temperature. The sponge-like structure can be readily observed.

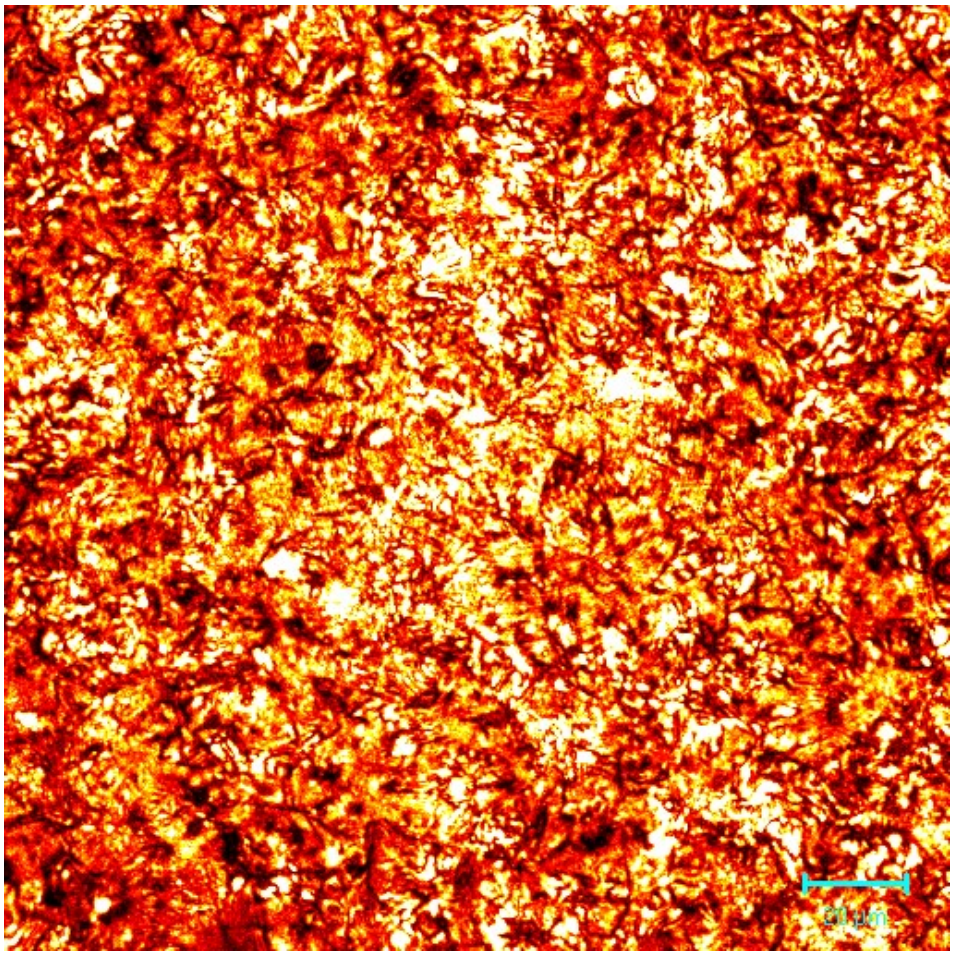

Figure 6: Confocal optical micrograph for a 4 % hPEO/h-ethanol sample. This picture represents data taken 28 μm underneath the sample surface. The scale bar represents a 20 μm length scale.

SANS and USANS data from a crosslinked gel are described next (Kim et al, 2006). Here also, the USANS data showed scattering information not observed by SANS. This system consisted of 1 % cetyltrimethylammonium 4-vinylbenzoate (CTVB) surfactant in d-water. Divinyl benzene crosslinker (0.8 mol crosslinker per 1 mol surfactant) was added to form a polymerized micelles soft gel. A slice of the gel was then equilibrated with excess oil (octane or toluene). The gel turns more opaque and white as it solubilizes oil. The USANS range shows that there are large "droplets" of oil present that can not be seen by SANS. Clearly, the gel can solubilize more toluene than octane.

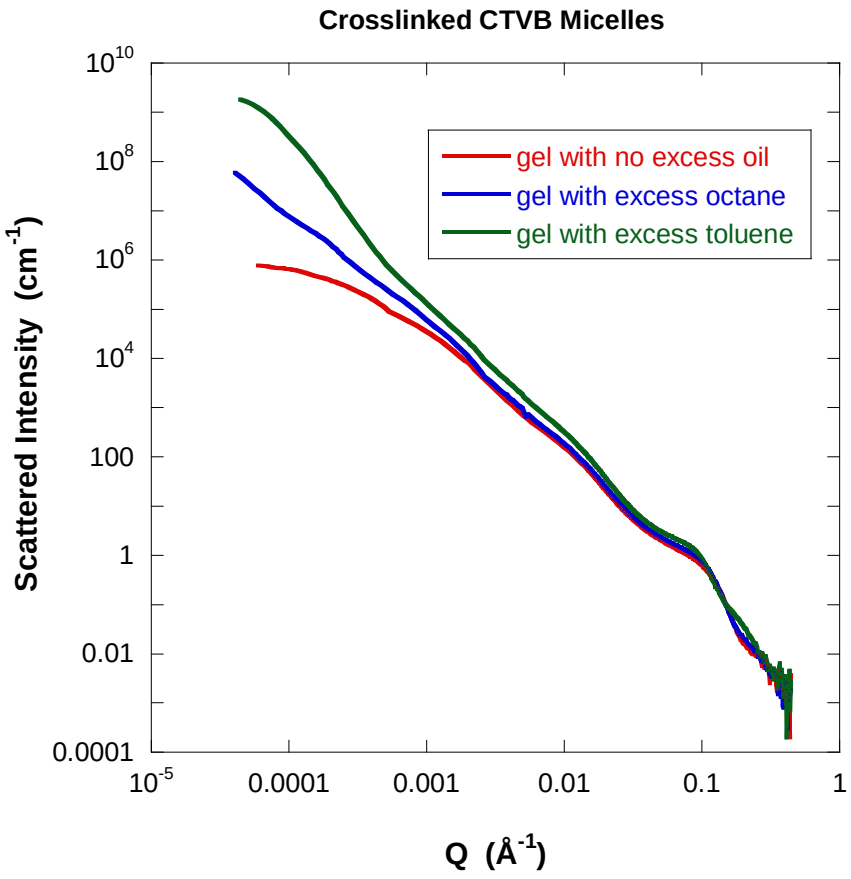

Figure 7: SANS and USANS data from CTVB wormlike micelles that were crosslinked to form a soft gel then swollen in oil.

REFERENCES

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QUESTIONS

1. Does the USANS instrument use cold or thermal neutrons?

2. What is the Q range for the USANS instrument? What is the corresponding d-spacing size range?
3. What is the main advantage of the USANS instrument?
4. What is the main difference between conventional SANS instruments and the USANS instrument?

ANSWERS

1. The USANS instrument uses thermal neutrons in order to avoid multiple scattering characterizing cold neutron wavelengths.
2. The USANS instrument covers the following Q range: $4*10^{-5}$ $Å^{-1} < Q < 0.01$ $Å^{-1}$. This corresponds to 7.8 μm > d-spacing > 628 Å.
3. The USANS instrument can observe structures in the optical (micrometer) size range in opaque samples. Optical methods can not probe opaque samples.
4. Conventional SANS instruments use velocity selectors for monochromation and long flight paths for collimation whereas the USANS instrument uses single crystal silicon for monochromation and triple bounce reflections (monochromator and analyzer) for improved resolution.