Solid Alkane Reverse Micelles (SARMS): Size Distribution Determined X-Ray Scattering

Ali Surage and Joseph DiVerdi*

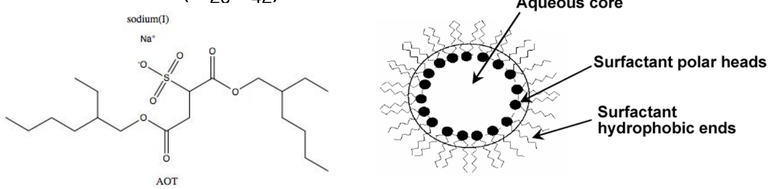
Department of Chemistry, Colorado State University

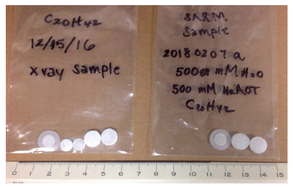
Purpose

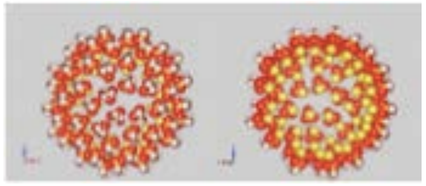
Use of X-ray diffraction analysis in determination of size and shape of SARMS.

Solid Alkane Reverse Micelles (SARMs)

Nanometer-sized water droplets inside alkanes due to the surfactant sodium bis(2-ethylhexyl)-sulfosuccinate (AOT) in alkane icosane ($C_{20}H_{42}$)







Basics of X-ray Diffraction

X-ray beam scatters off the inner shell electrons of the molecules in the sample in which the angles are calculated using Bragg's Law (1), where, θ = incident angle, d = inter-planar spacing, λ = incident wavelength.

$$\lambda = 2d\sin\theta \qquad (1)$$

Interactions of X-rays with Matter

Both SAXS and X-ray crystallography exploit coherent (Thomson) X-ray scattering. In coherent scattering, electrons oscillating under the influence of the electric field of the X-ray beam act as secondary sources, emitting X-rays with the same wavelength as the incident beam, but 180° out secondary sources, emitting X-rays with the same wavelength as the incident beam is proportional to (1 + $\cos^2 2\Theta$), reaching a maximum when the scattering is parallel to the incident X-ray beam (2Θ = 0°) and falling off at large 2Θ angles. Atomic scattering have been accurately calculated for all of the elements and are influenced by the number of electrons for the atom and the orbitals the electrons occupy. In general, the intensity of coherently scattered X-rays decreases with increasing X-ray energies (decreasing X-ray wavelength). This decrease is discontinuous at energies near atomic orbital-binding energies unique to each atom. The atomic-scattering factors at theses energies are described by additional terms accounting for this behavior. Use of this 'anomalous scattering' has become an important method for solving protein crystal structures (section 2.2.5).

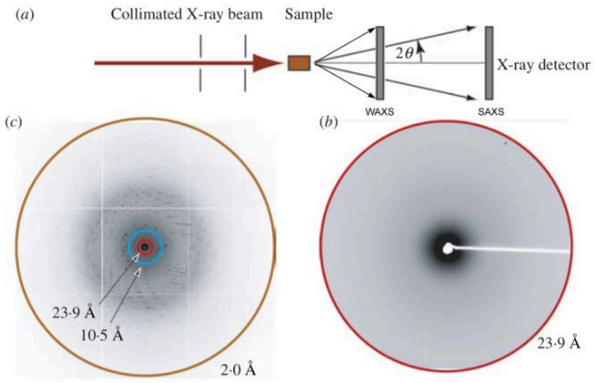
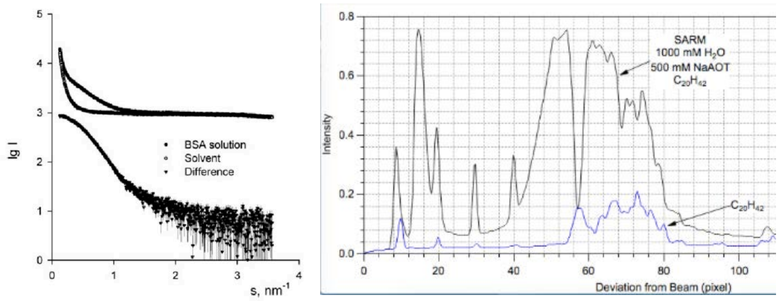
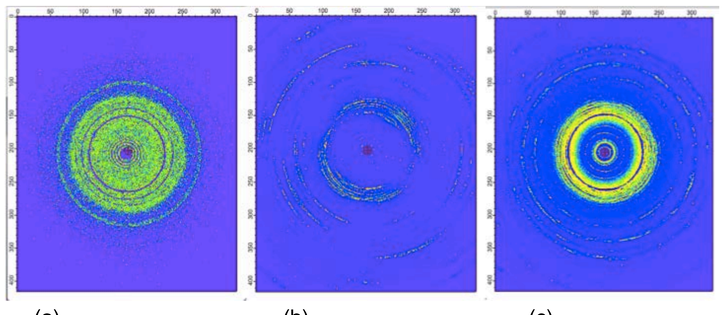


Fig. 1. X-ray interactions with sample for SAXS and crystallography. (a) Both SAXS and X-ray crystallography involve placing a sample (orange) into a highly collimated X-ray beam (red) and measuring the scattered X-rays. The angle of any scattered position with the direct beam is 2Θ. (b) Scattering from a solution of yeast PCNA with a maximum resolution of 23.9 Å. (c) Diffraction from a nickel superoxide dismutase crystal at 2.0 Å resolution. The equivalent position of the highest resolution of the SAXS experiment indicated (red circle). The blue circle indicates the highest resolution achievable (q = 0.6 Å^{-1}) for SAXS data collection at SIBYLS. Both images collected at beamline 12.3.1 (SIBYLS) at the Lawrence Berkeley National Laboratories. Diffraction image courtesy David Barondeau, Department of Chemistry, Texas A&M University.



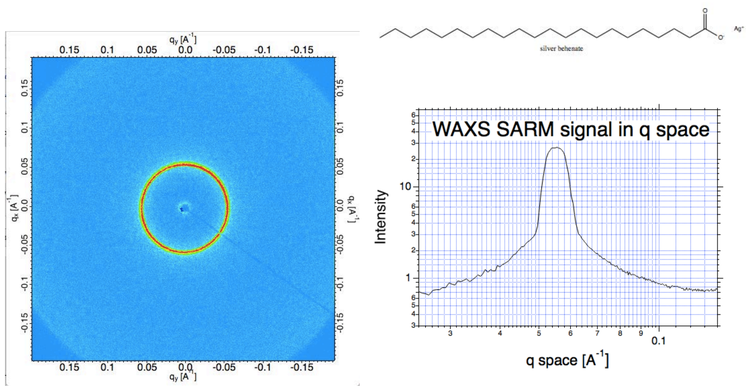
(a) (b)

Fig. 2. Typical X-ray scattering patterns from (a) solution of BSA in 50 m HEPES, pH 7.5, solvent scattering and the difference curve (pure scattering from the protein, scaled for the solute concentration, 5 mg ml^{-1}). Data recorded at EMBL beamline X33 (synchrotron DESY, Hamnburg); 25 µm mica cuvette, sample thickness 1 mm. (b) SARM sample comparison to icosane background.



(a) (b) (c)

Fig. 3. Earlier measurements of x-ray scattering images showing (a) silver behenate calibration data, (b) icosane background, (c) SARM data without correction for icosane.



(a) (b)

Fig. 4. (a) Scattering pattern obtained from SARM (W_0 = 2.0). (b) Intensity of scattered x-ray beam as a function of the q space, calculated using the corresponding angle 2Θ and sample to detector distance.

Fourier transform

Relates space and reciprocal space domains.

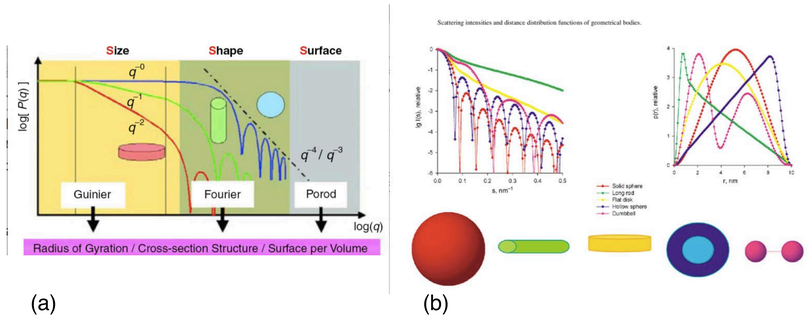
- P(q), form factor: electron density within a particle.
- S(q), structure factor: representing the spatial arrangement of particles.

Electron density

Function of r coordinate where P(r)dr is the number of electrons in volume dr. Computed from average mass density, p_m, multiplied by the electrons per gram, Z_m, given by Avogadro's number, N_A = 6.022 x 10^{23} mol^{-1}, the number of electrons per molecule or monomer unit, Z_M, and molecular weight of the molecule or monomer unit, M_M.

$$I(\mathbf{q}) = \left|\mathrm{FT}\left[\sum_n \delta(\mathbf{x}-\mathbf{x}_n)\right]\right|^2 |\mathrm{FT}[\rho_p(\mathbf{x})]|^2 = S(\mathbf{q})P(\mathbf{q}). \qquad (2)$$

$$\rho = Z_m \rho_m = \frac{Z_M N_A \rho_m}{M_M}, \qquad (3)$$



(a) (b)

Fig. 5 (a) Fourier Transform of the square of electron density, p, provides intensity in q space. Plotting log[P(q)] vs. log(q) derives information from the calculated slope bout size, shape, and surface of the sample, (b) log intnsity or electron density plotted versus the distance (nm) provides analysis of the shape of the molecules being examined. A solid sphere, long rod, flat disk, hollow sphere, and dumbbell all result in characteristic slope patterns.