SANS BASICS

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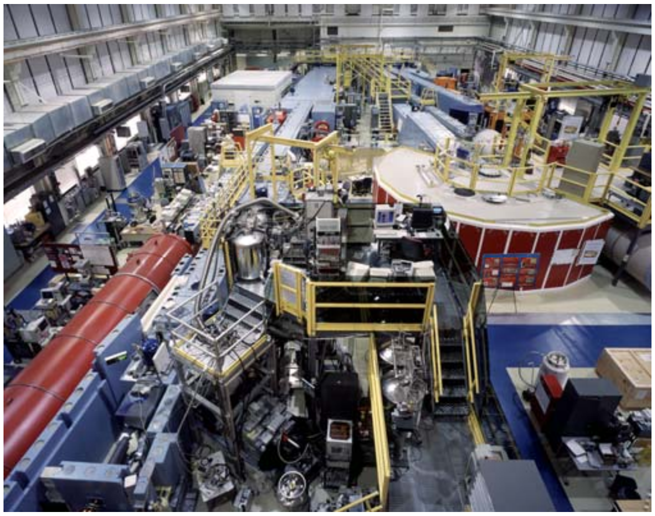
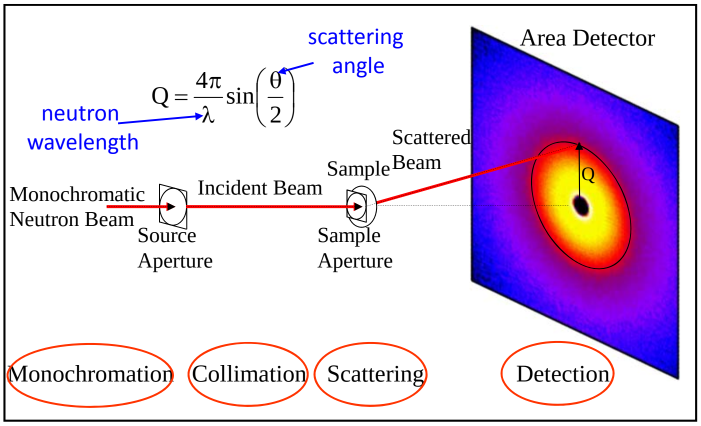
1 – The SANS Technique

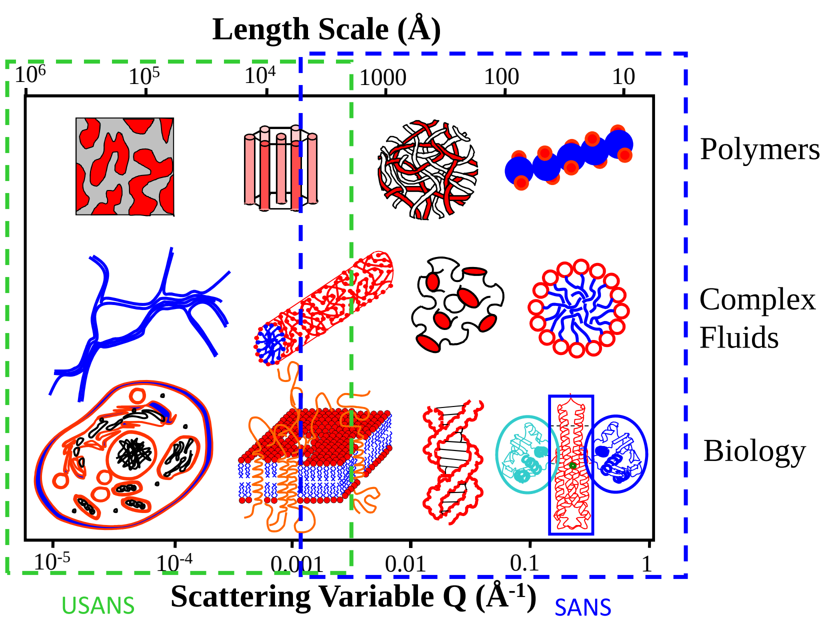
The NIST Center For Neutron Research



Small-Angle Neutron Scattering



Nanoscale Structures



SANS Cross Sections

$$I(Q) = \frac{d\Sigma_{coh}(Q)}{d\Omega} + \frac{d\Sigma_{incoh}}{d\Omega}$$

COHERENT

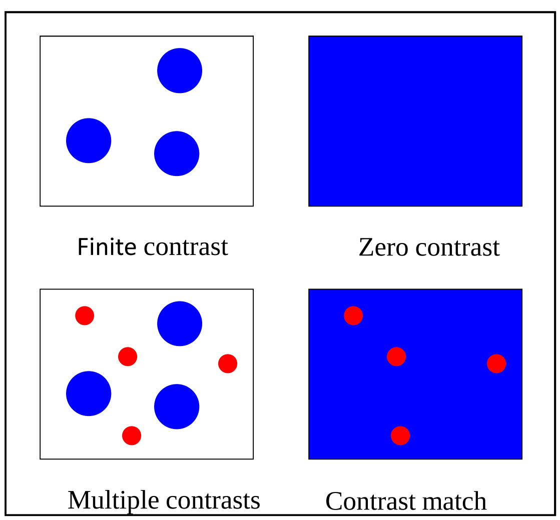
~ Contrast factor = $(\rho_A - \rho_B)^2$
- Info. about structure

INCOHERENT

- Q-independent
- no info. about structure

Scattering length density: $\rho_A = \frac{b_A}{v_A} = \frac{\text{scattering length}}{\text{volume}}$

The Contrast Match Method

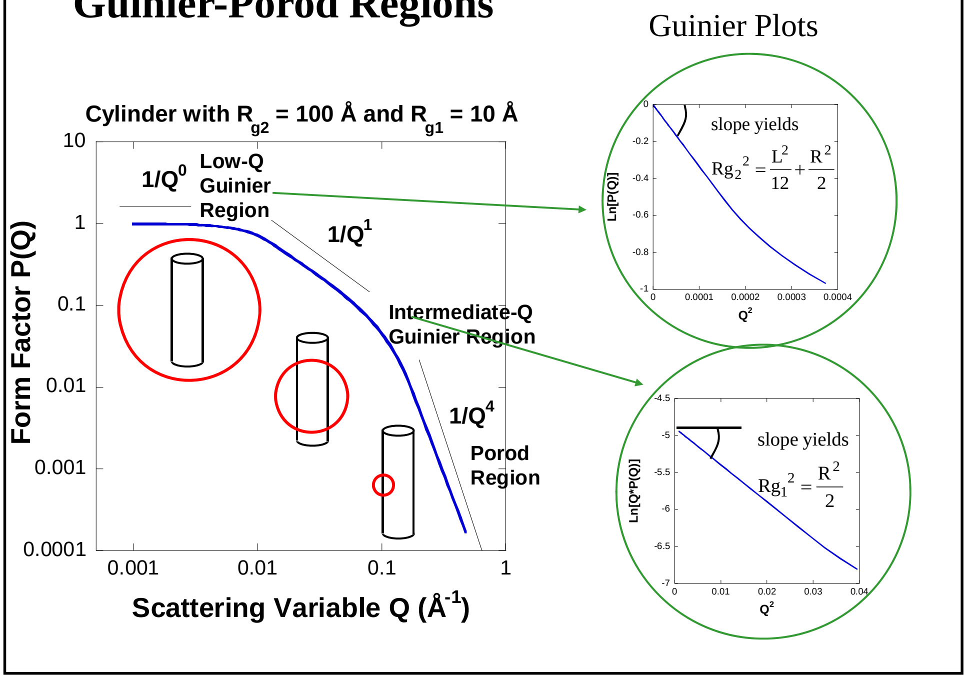


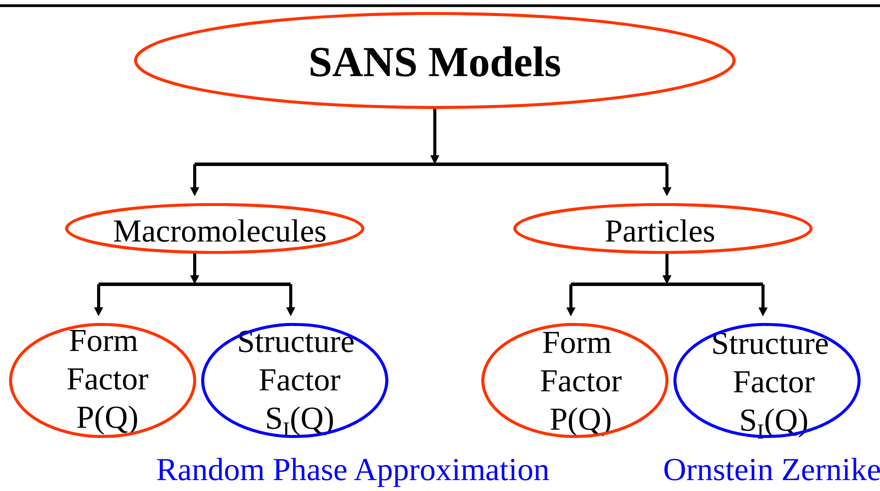
2 –SANS Data Analysis

SANS Data Analysis

- Standard Plots (Guinier Plot, Porod Plot)
- SANS Models
- Inverse Fourier Transform
- Shape Reconstruction Method

Guinier-Porod Regions

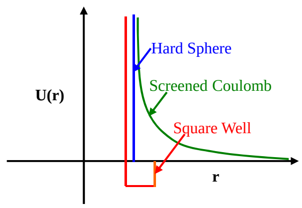




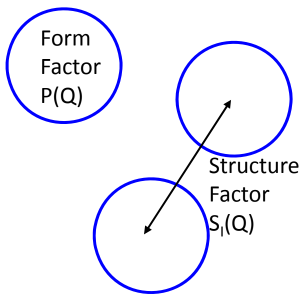
$$\frac{d\Sigma(Q)}{d\Omega} = \phi_A (\rho_A - \rho_B)^2 V_A P(Q) S_I(Q)$$

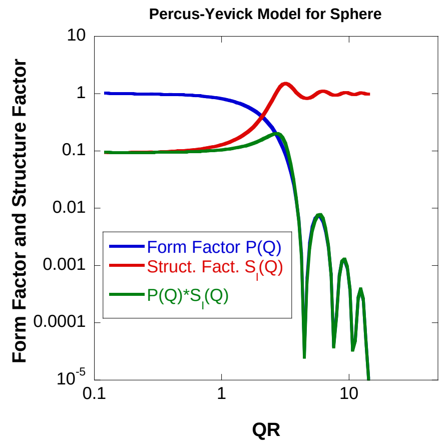
cross section, volume fraction, contrast factor, particle volume, form factor, structure factor

Particle Structure Factor – The Ornstein-Zernike Equation



$$\frac{d\Sigma(Q)}{d\Omega} = \phi_A \left(\rho_A - \rho_B\right)^2 V_A P(Q)\, S_I(Q)$$

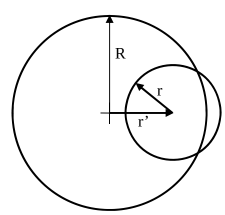




Fourier Transform

Density-density correlation function:

$$P(Q) = \frac{< n(-Q) n(Q) >}{n^2} = \int d\vec{r} \int d\vec{r}\,' \frac{< n(r) n(r') >}{n^2} \exp[i\vec{Q}.(\vec{r}\,'-\vec{r})]$$

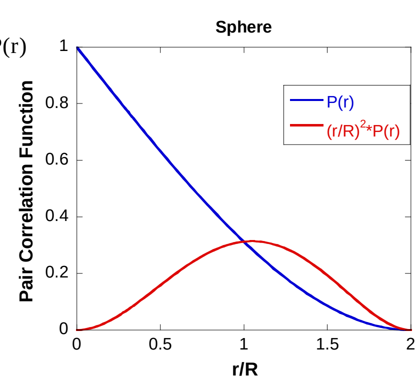


Fourier transform:

$$P(Q) = \int d^3 r \exp[-i\vec{Q}.\vec{r}]\, P(\vec{r}) = \frac{1}{V_P} \int_0^\infty dr 4\pi r^2 \frac{\sin(Qr)}{Qr} P(r)$$

Radial pair correlation function:

$$P(r) = 1 - \frac{3}{4}\left(\frac{r}{R}\right) + \frac{1}{16}\left(\frac{r}{R}\right)^3$$



3. SANS Research Topics

A- Phase Transitions in Pluronic P85 Solutions

B- Role of Chirality in Peptide Biogels

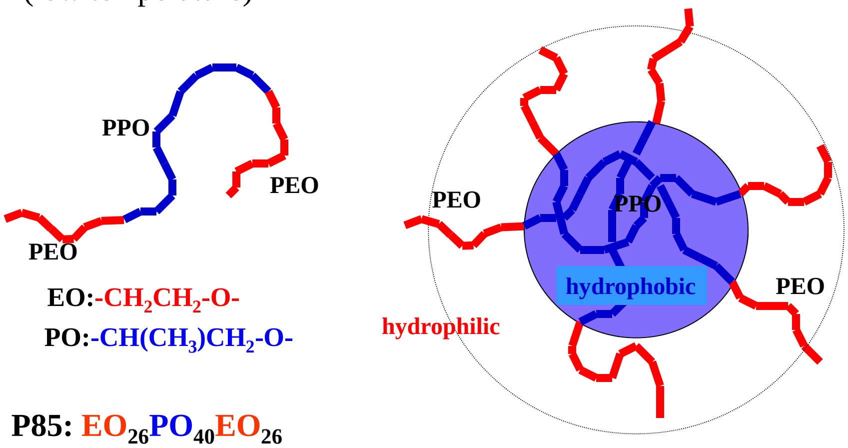
C- Structure of SDS Micelles

A - Phase Transitions in Pluronic P85 Solutions

Pluronics

Dissolved Unimer
(low temperature)

Formed Micelle
(high temperature)

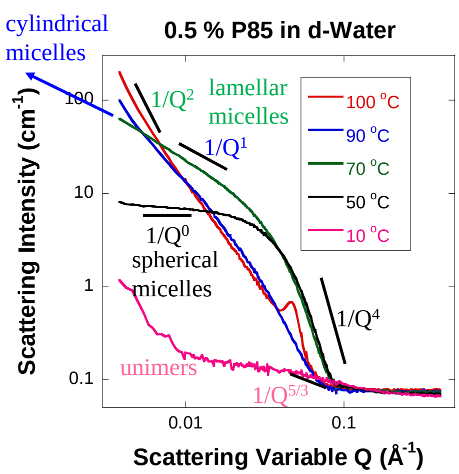


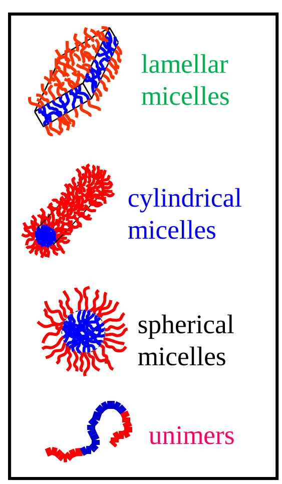
EO:-CH_2CH_2-O-

PO:-$CH(CH_3)CH_2$-O-

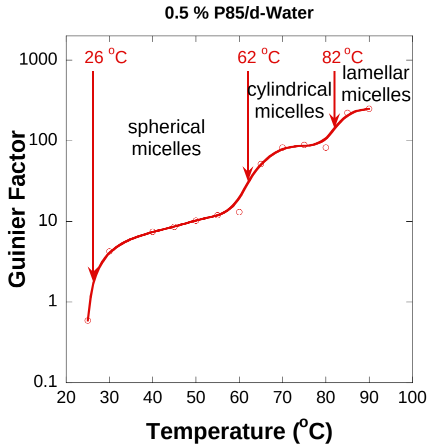
P85: $EO_{26}PO_{40}EO_{26}$

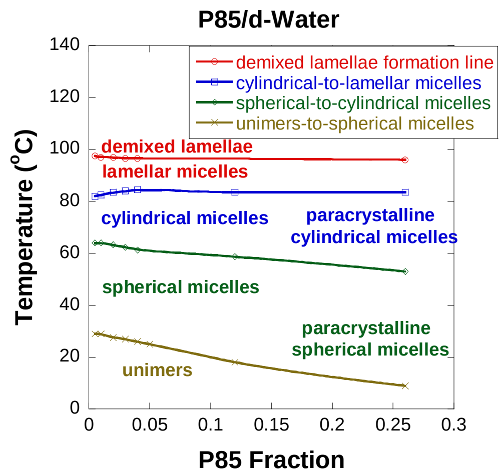
Pluronic Micelles





Phase Diagram

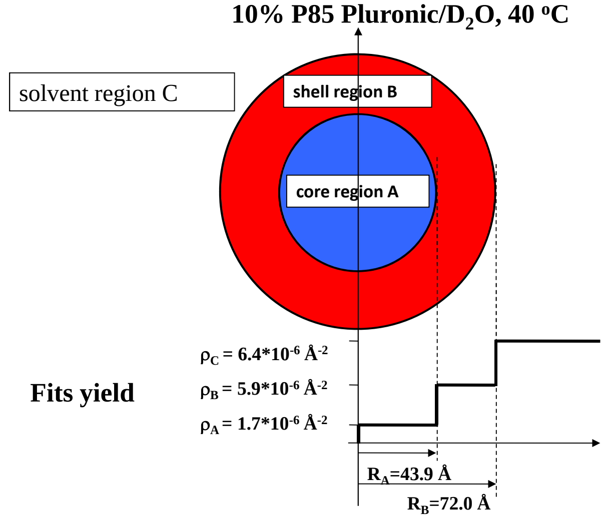




Core-Shell Spherical Particles Model

$$\frac{d\Sigma(Q)}{d\Omega} = \frac{N}{V}\left[(\rho_A - \rho_B)V_A \frac{3j_1(QR_A)}{QR_A} + (\rho_B - \rho_C)V_{A+B}\left(\frac{3j_1(QR_B)}{QR_B}\right)\right]^2 S_I(Q)$$

10% P85 Pluronic/D_2O, 40 °C



Core-Shell Spherical Particles

Material Balance Equations:

$$\frac{4\pi}{3}R_A^{\ 3} = N_{ag}.\left[40.v_{PO} + 52.f.v_{EO} + 52.f.v_{D_2O}.y_A\right]$$

$$\frac{4\pi}{3}(R_B - R_A)^3 = N_{ag}.\left[52.(1-f).v_{EO} + 52.(1-f).v_{D_2O}.y_B\right]$$

$$\rho_A = \frac{N_{ag}[40b_{PO} + 52.b_{EO}.f + 52b_{D_2O}.f.y_A]}{\frac{4\pi}{3}R_A^{\ 3}}$$

$$\rho_B = \frac{N_{ag}[52.b_{EO}.(1-f) + 52.b_{D_2O}.(1-f).y_B]}{\frac{4\pi}{3}\left(R_B^{\ 3} - R_A^{\ 3}\right)}$$

Results for 10% P85 at 40 ºC:

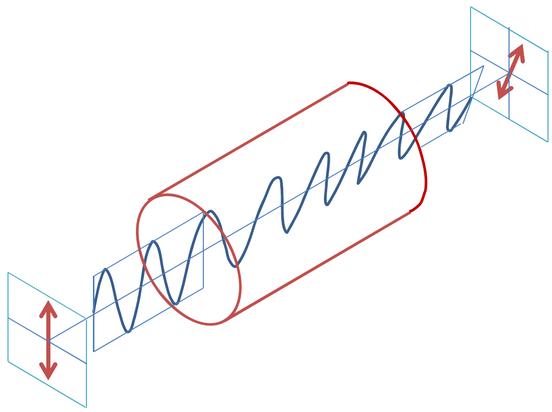
In the core:
2,795 PPO monomers
690 PEO monomers
490 D_2O molecules

In the shell:
2,943 PEO monomers
34,167 D_2O molecules

B- Role of Chirality in Peptide Biogels

Faraday Rotation

Substances rotate linearly polarized light
to the left (L-type) or to the right (D-type)



Chirality

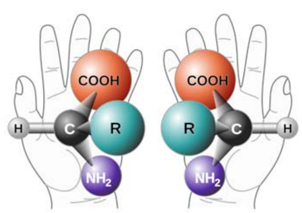
- A molecule is chiral if it is different from its mirror image

- Human hands are chiral

- Non-biological substances are heterochiral . They can be of the L-type or D-type

- Biological substances are homochiral. They are either of the L-type or of the D-type

- Proteins are of the L-type. Sugars are of the D-type. DNA is of the D-type.
The reason is still a mystery



Left handed Right handed

Proteins

- Proteins are responsible for most biological function. They are made out of peptides. Peptides are made out of amino acids. There are 20 amino acids.

- Examples of amino acids include Lysine (K), Glutamate (E), Tryptophan (W) and Alanine (A)

- Most proteins rotate polarized light to the left. They are left handed or L-type

DNA

- DNA is the blueprint for life. It is the template for the synthesis of proteins

- DNA is made out of nucleotides. There are 4 DNA nucleotides: A, C, T and G

- The human genone contains 6 billion nucleotides making up some 23,000 genes

- Most DNA rotate polarized light to the right. They are right handed or D-type

Peptide Biogels

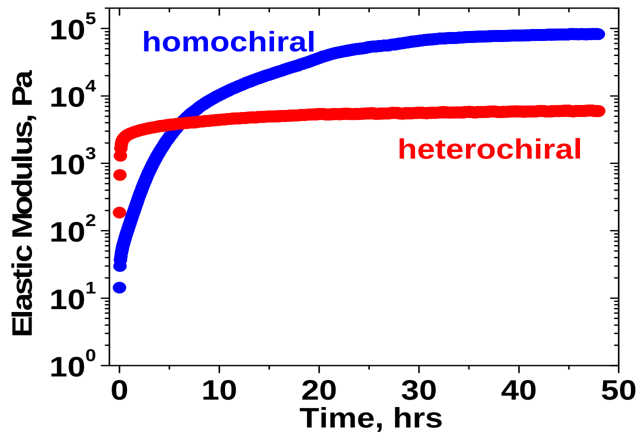
- Peptides can be synthesized to be L-type or D-type

- Series of L-type and D-type short peptide sequences (11 amino acids) were synthesized.

- These were combined to give L-D- or D-L- heterochiral mixtures and L-L- or D-D- homochiral mixtures

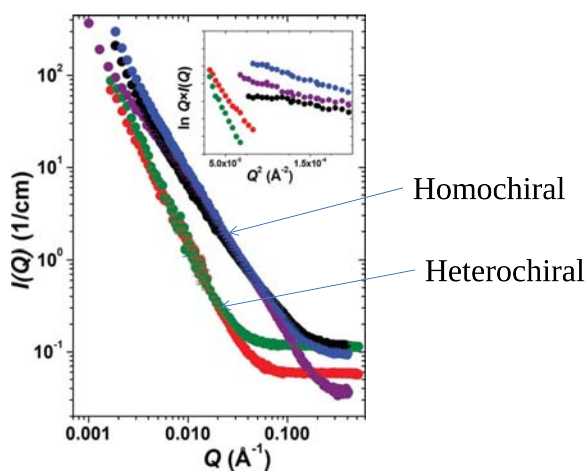
- The resulting gels were investigated using mechanical testing (shear response) and SANS measurements

Mechanical Testing



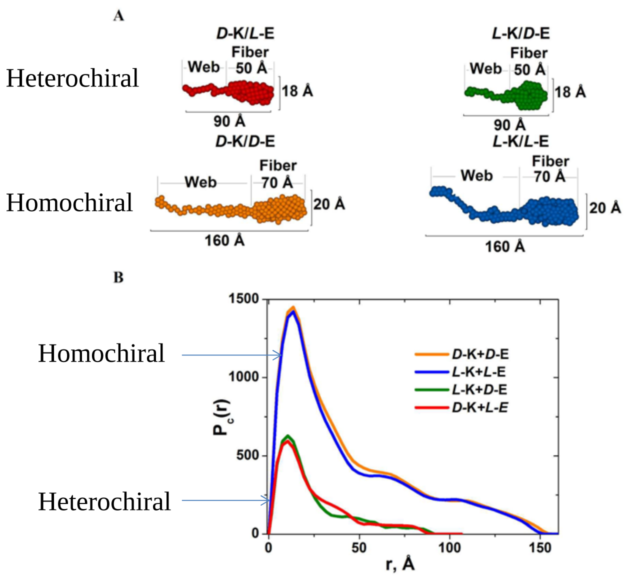
- Heterochiral samples gel faster. Homochiral samples are slow to gel.
- Homochiral gels are initially weaker then become stronger

SANS Data



- Heterochiral gels scatter differently from homochiral ones
- They are all characterized by fibrilar structure

SANS Data Analysis

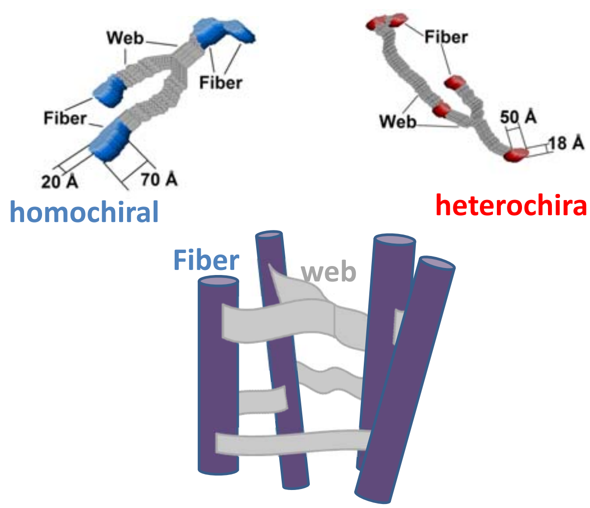


Shape Reconstruction
Fiber cross sections

Inverse Fourier Transform

- Homochiral fibers are thicker and denser than heterochiral ones

Fiber-Web Structure



- Peptide biogel is formed of fibers joined by a web

Results

- Chirality plays a role in the mechanical properties and structure of biogels

- Homochirality confers higher strength (shear modulus) and yield stress value. **Right-right hand-shake is stronger.**

- Heterochirality confers faster gelation kinetics

- Biogel structure consists of main fibers held together by a web of cross fibers

- Fibers for homochiral biogels are thicker and denser

- Advantages conferred to homochirality lead to enhanced stability

C- Structure of SDS Micelles

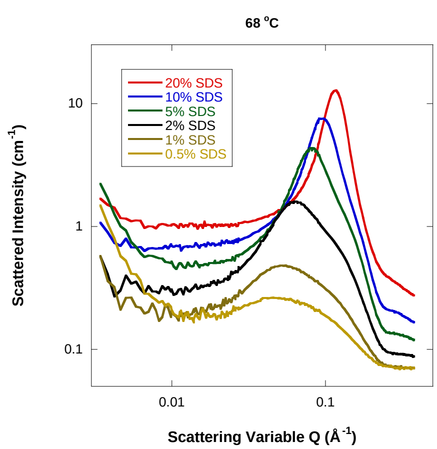
Micelle Formation

- Surfactants are formed of a hydrophilic head and a hydrophobic tail

- Micelles form when enough surfactants aggregate (above the critical micelle concentration or CMC)

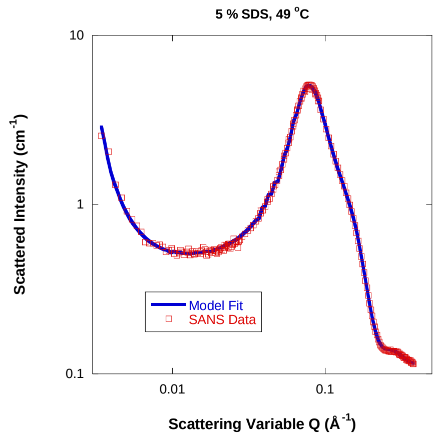
- SDS surfactants form micelles in water (or deuterated water)

SANS from SDS Micelles



- Ellipsoidal micelles form

Ellipsoid Micelles Model Fit

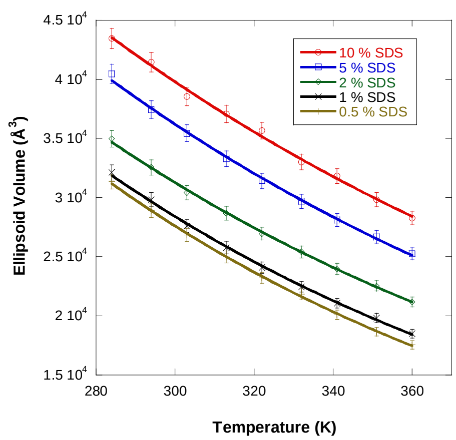


$$I(Q) = \frac{A}{Q^n} + \left[\frac{d\Sigma(Q)}{d\Omega}\right]_{ellipsoids} + B$$

$$\left[\frac{d\Sigma(Q)}{d\Omega}\right]_{ellipsoids} = \phi \Delta\rho^2 V_P P(Q) S_I(Q)$$

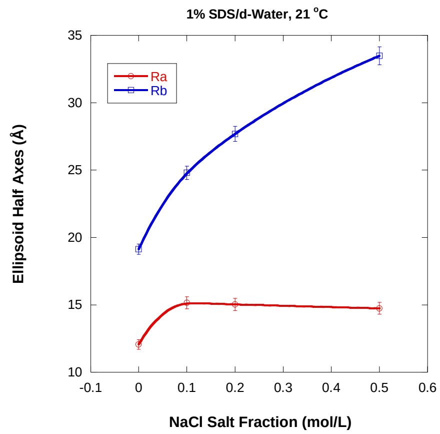
- Power law (low-Q) + ellipsoidal micelles (high-Q) model fits well

Some Fit Results



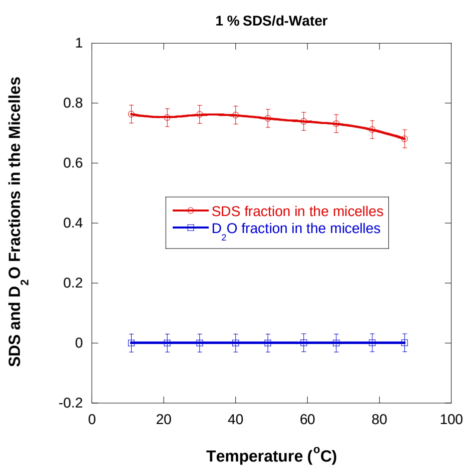
- Micelles become smaller at higher temperatures and lower volume fraction

More Fit Results



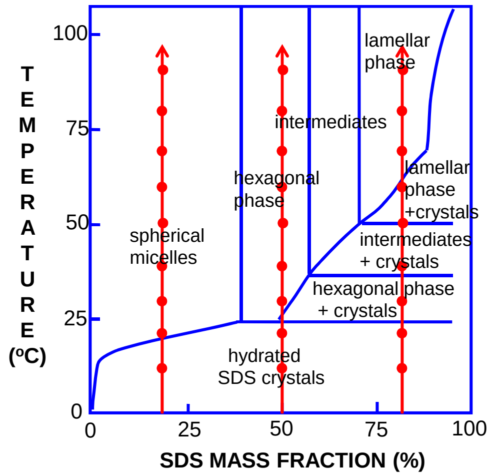
- Salt addition affects lateral growth only

Material Balance Equations



- SDS surfactant fraction remains constant above the CMC

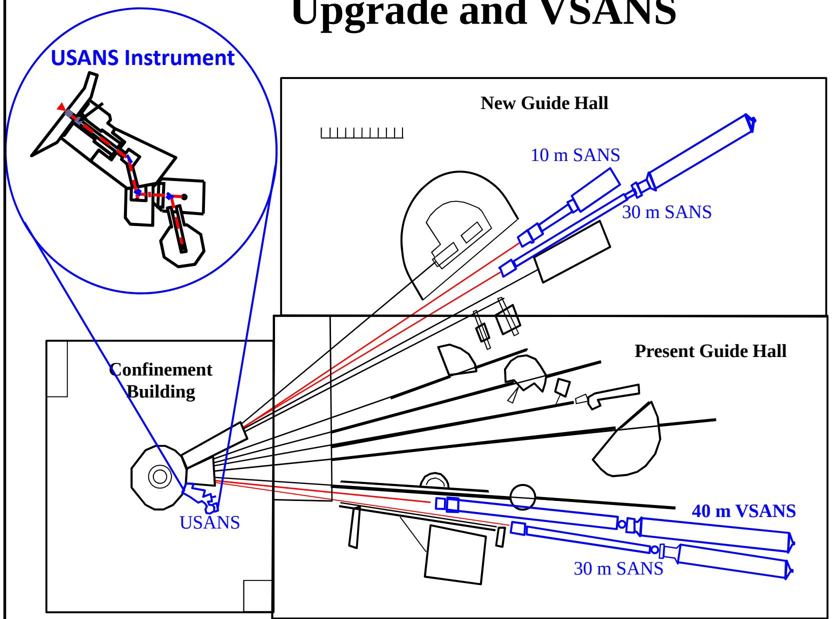
Phase Diagram



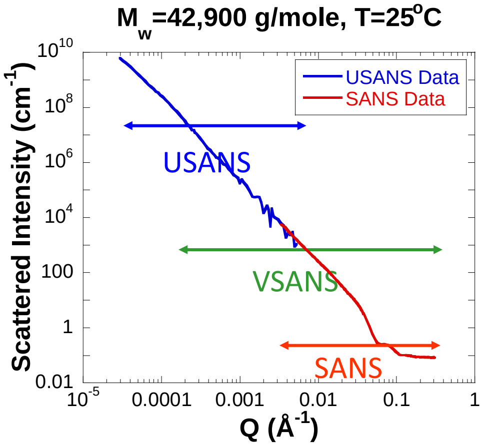
- SDS/water phase diagram from calorimetry

4. Final Points

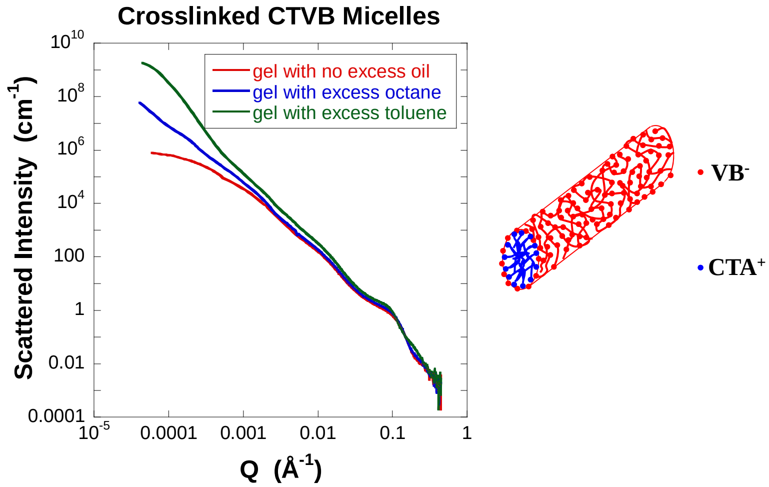
Upgrade and VSANS



SANS, VSANS and USANS Ranges



SANS and USANS Data



Final Words

THE SANS PROGRAM AT NIST

200 experiments per year

15 theses per year

80 publications per year

ACKNOWLEDGMENTS

Steve Kline, Marc Taraban, Bruce Yu

REFERENCES

- B. Hammouda, "Probing Nanoscale Structures – The SANS Toolbox", (2009). Book available online.
- M. Taraban, Y. Feng, B. Hammouda, L. Hyland and B. Yu, "Chirality-Mediated Mechanical and Structural Properties of Oligopeptide Hydrogels", Chemistry of Materials (2012)

http://www.ncnr.nist.gov/staff/hammouda/