SANS BASICS

Boualem Hammouda

National Institute of Standards and Technology
Center for Neutron Research

hammouda@nist.gov

OUTLINE

- 1. The SANS Technique

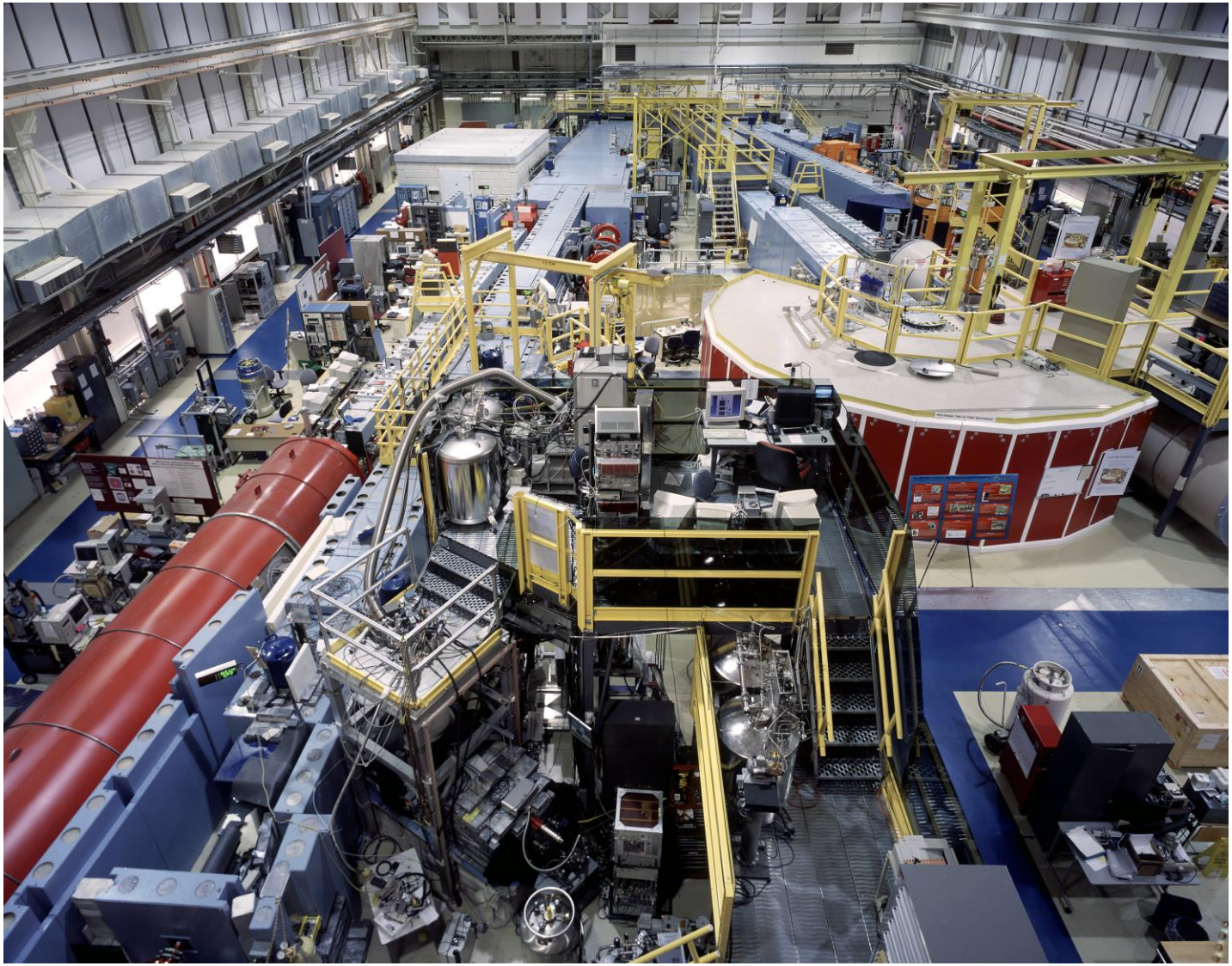
- 2. SANS Data Analysis
  - Standard Plots (Guinier, Porod)
  - SANS Models
  - Inverse Fourier Transform
  - Shape Reconstruction Method

- 3. SANS Research Topics
  - A- Phase Transitions in Pluronic P85 Solutions
  - B- Polymer Co-solvation and Co-nonsolvation
  - C- SDS Micelles with Ethanol Co-surfactant

- 4. Final Points
  - USANS and VSANS
  - Final Words

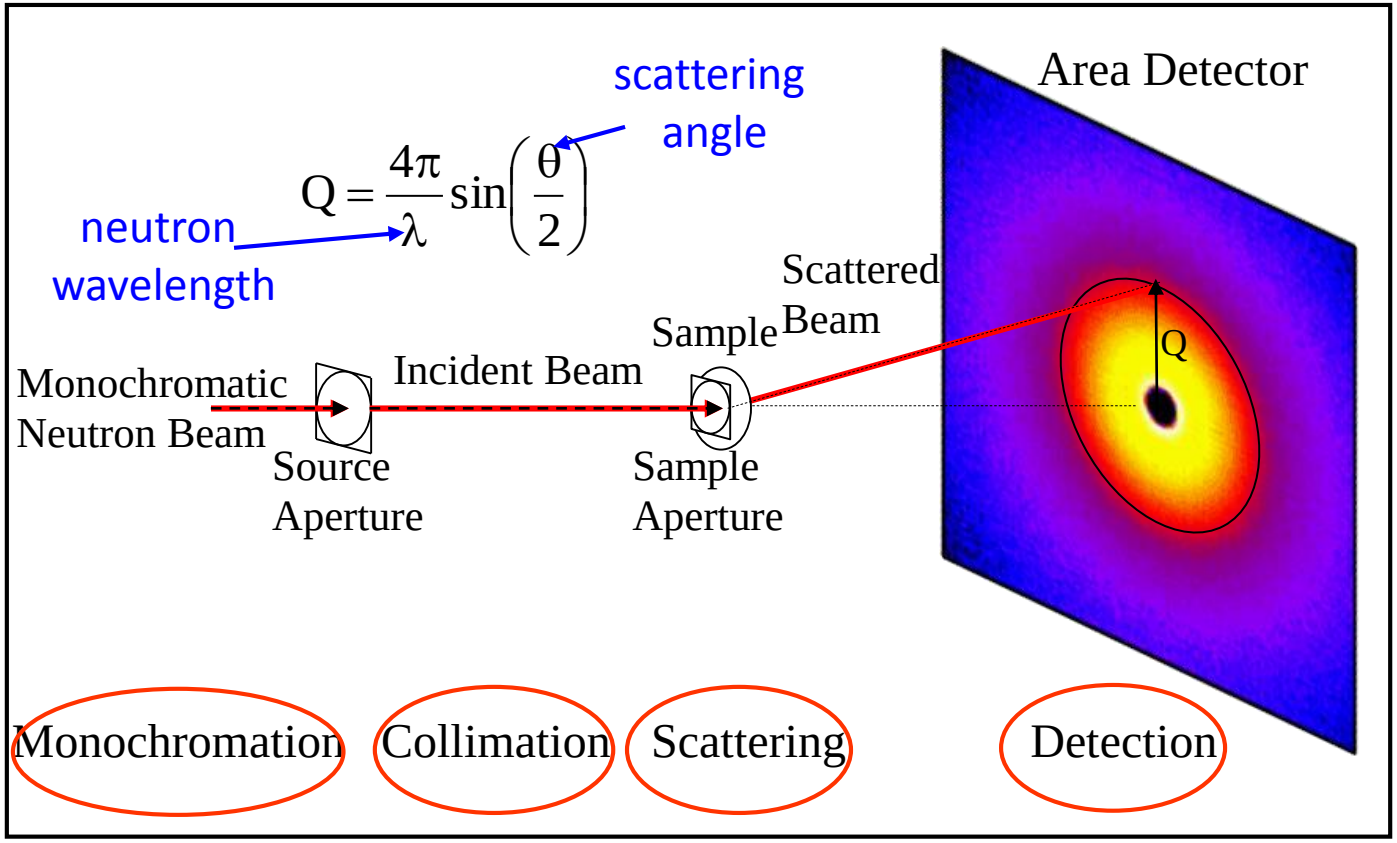
1 – The SANS Technique

The NIST Old Guide Hall

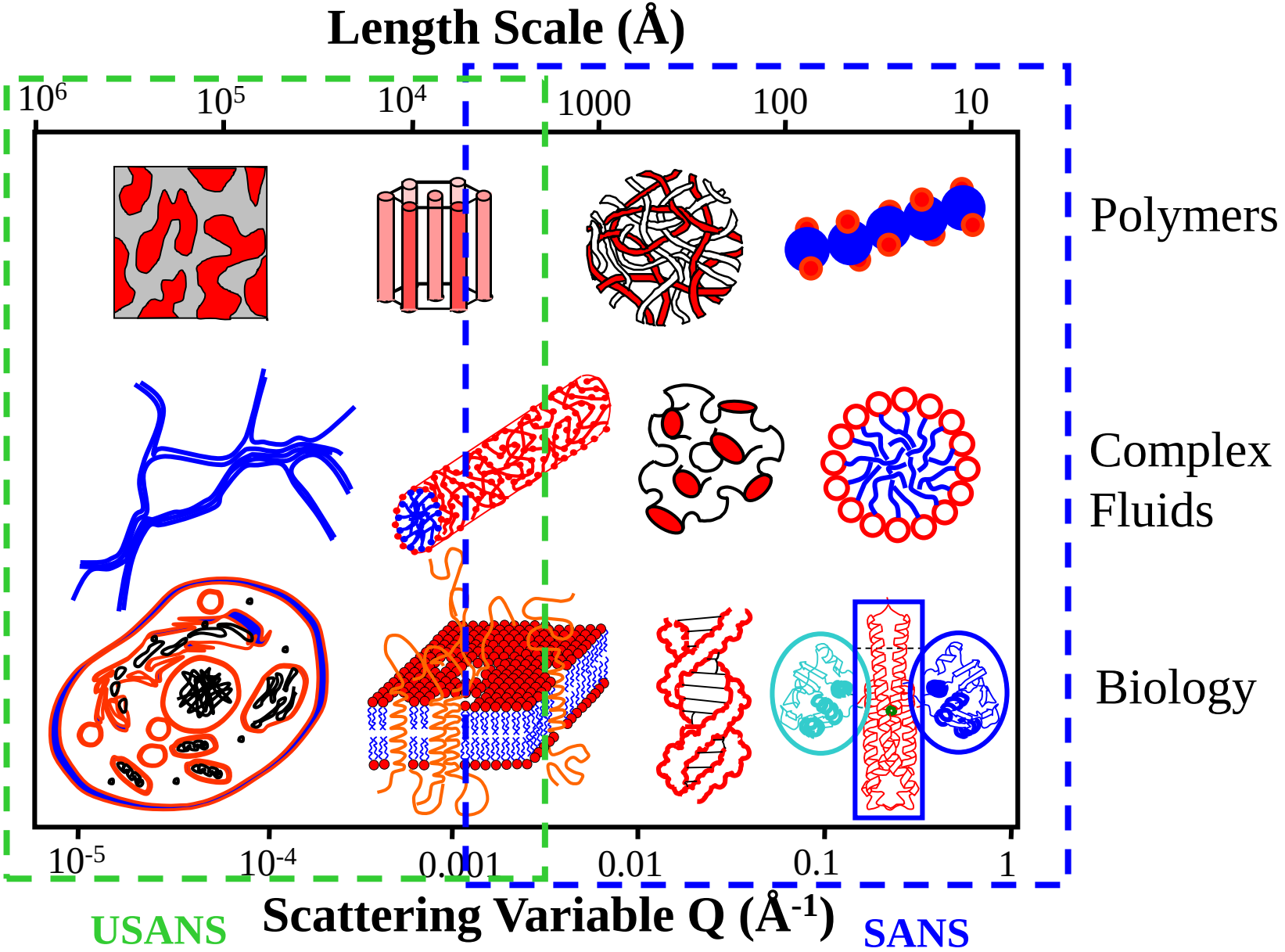


The NIST New Guide Hall

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

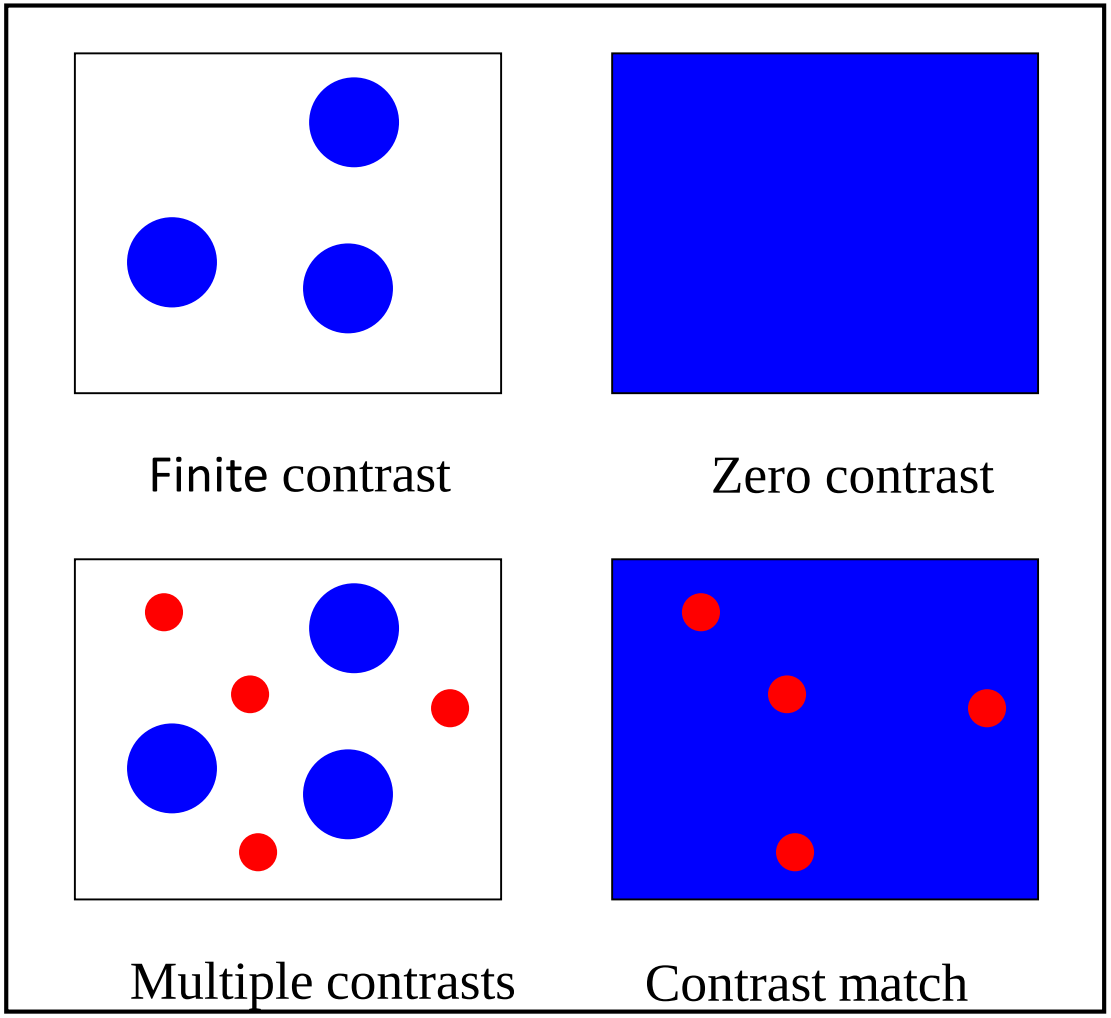
~ Contrast factor = $(\rho_A - \rho_B)^2$
- Info. about structure

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

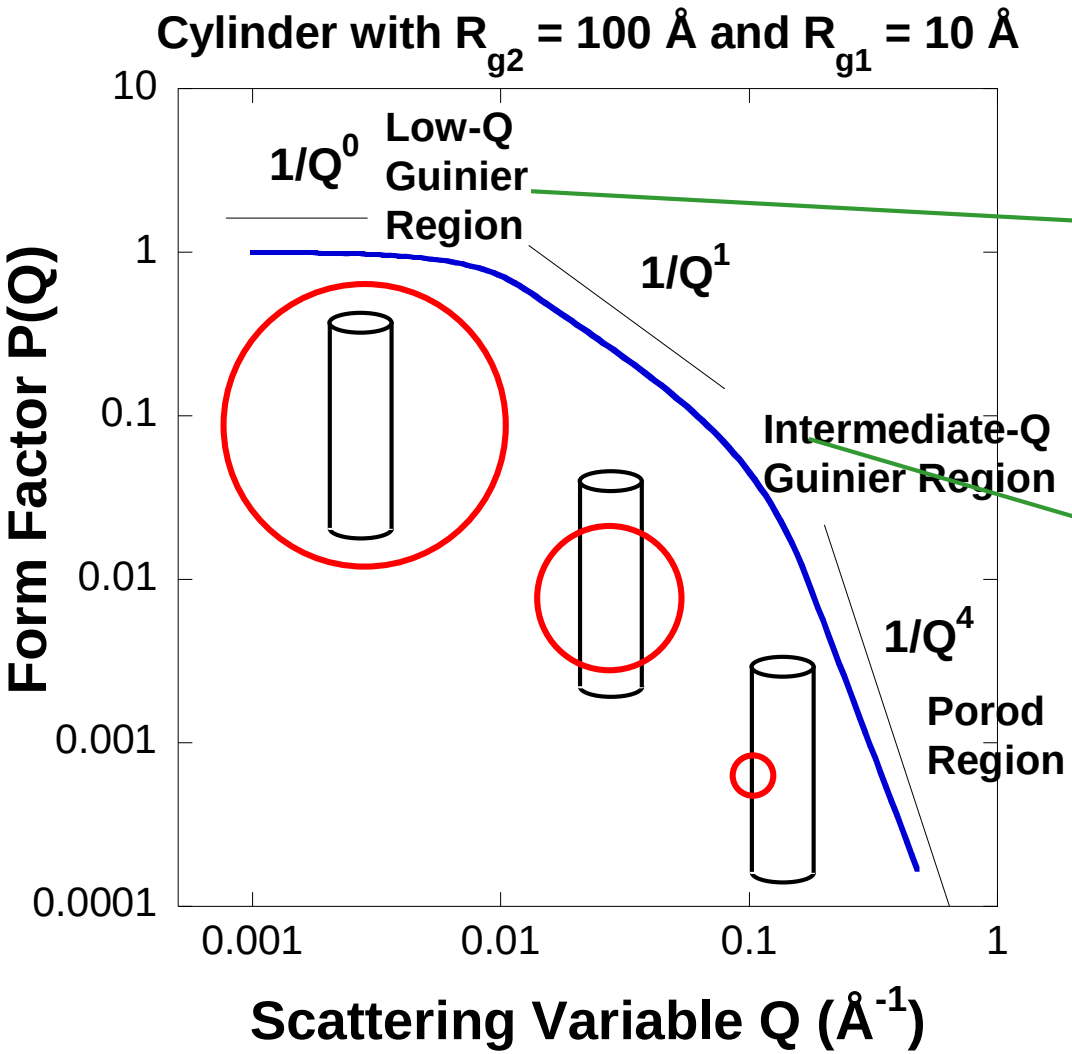


2 –SANS Data Analysis

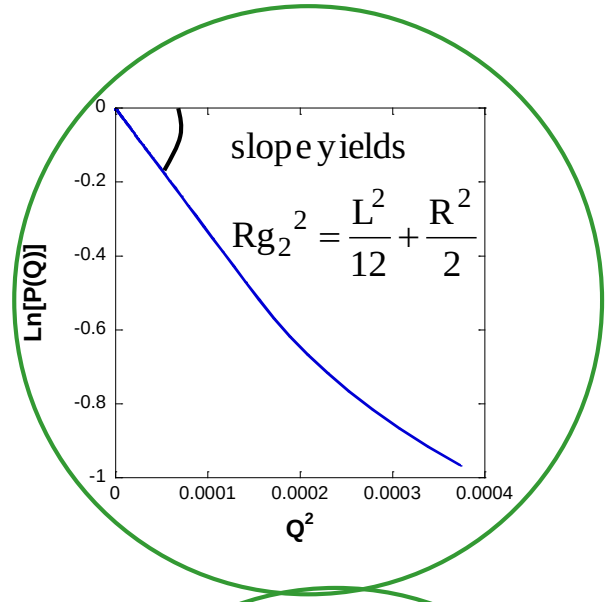
SANS Data Analysis

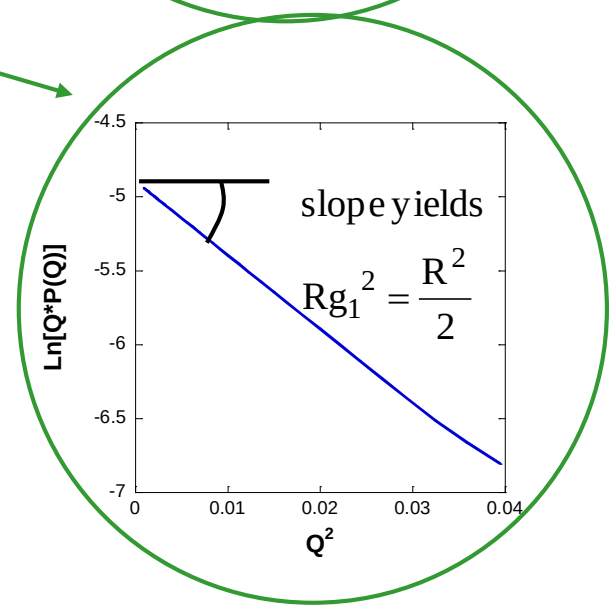
- Standard Plots (Guinier Plot, Porod Plot)
- SANS Models
- Inverse Fourier Transform
- Shape Reconstruction Method

Guinier-Porod Regions



Guinier Plots





SANS Models

- Macromolecules
  - Form Factor P(Q)
  - Structure Factor $S_I(Q)$
- Particles
  - Form Factor P(Q)
  - Structure Factor $S_I(Q)$

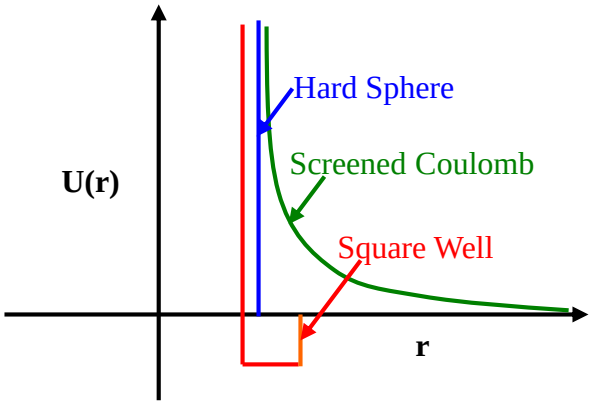
Random Phase Approximation

Ornstein Zernike

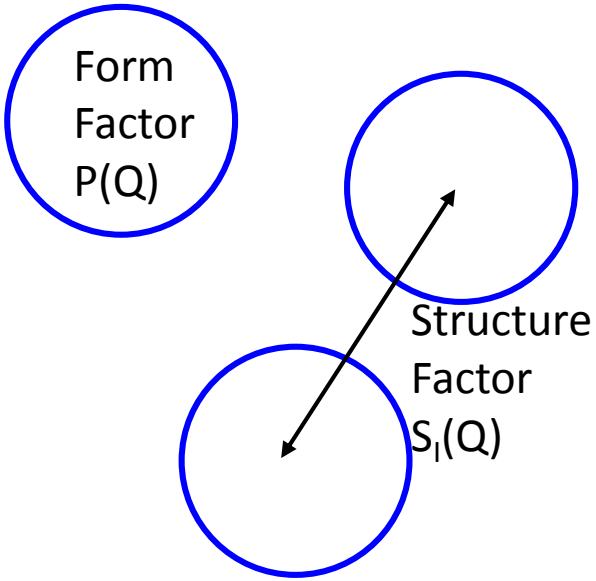
$$\frac{d\Sigma(Q)}{d\Omega} = \phi_A \left(\rho_A - \rho_B\right)^2 V_A P(Q)\, S_I(Q)$$

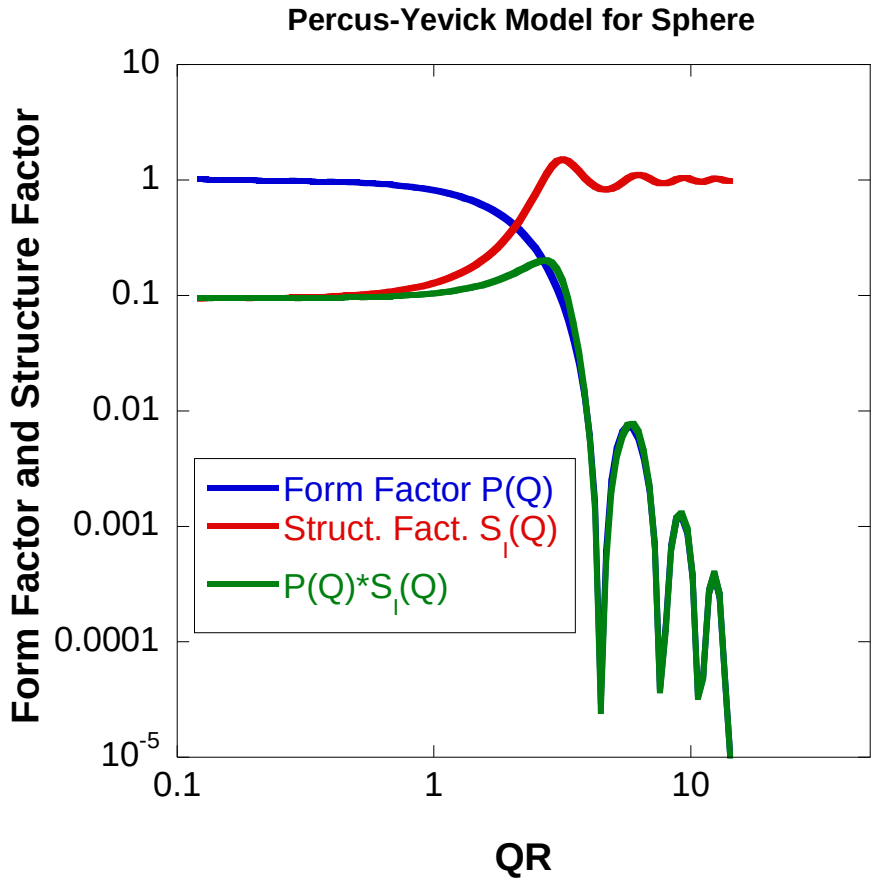
- $\frac{d\Sigma(Q)}{d\Omega}$: cross section
- ϕ_A: volume fraction
- $(\rho_A - \rho_B)^2$: contrast factor
- V_A: particle volume
- $P(Q)$: form factor
- $S_I(Q)$: structure factor

Particle Structure Factor – The Ornstein-Zernike Equation



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

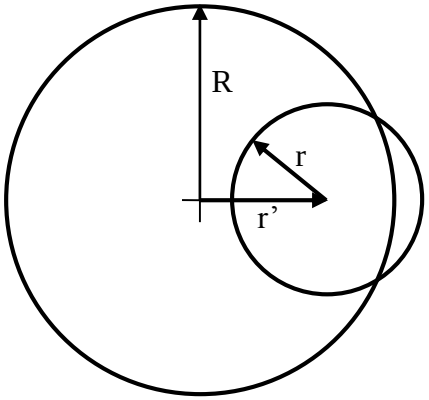




Fourier Transform

Density-density correlation function:

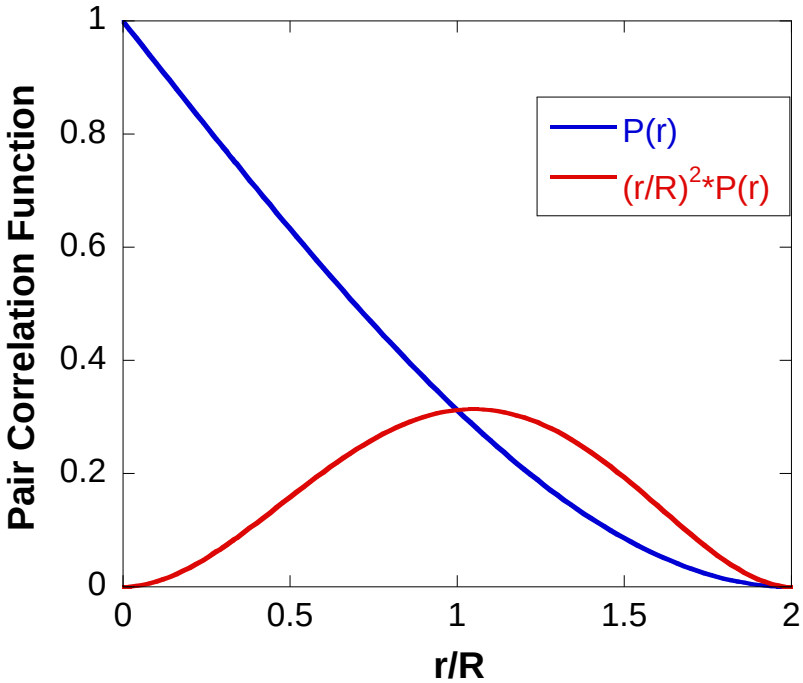
$$P(Q) = \frac{< n(-Q)n(Q) >}{n^2} = \int d\vec{r} \int d\vec{r}' \frac{< n(r)n(r') >}{n^2} \exp[i\vec{Q}.(\vec{r}'-\vec{r})]$$



Sphere

Fourier transform:

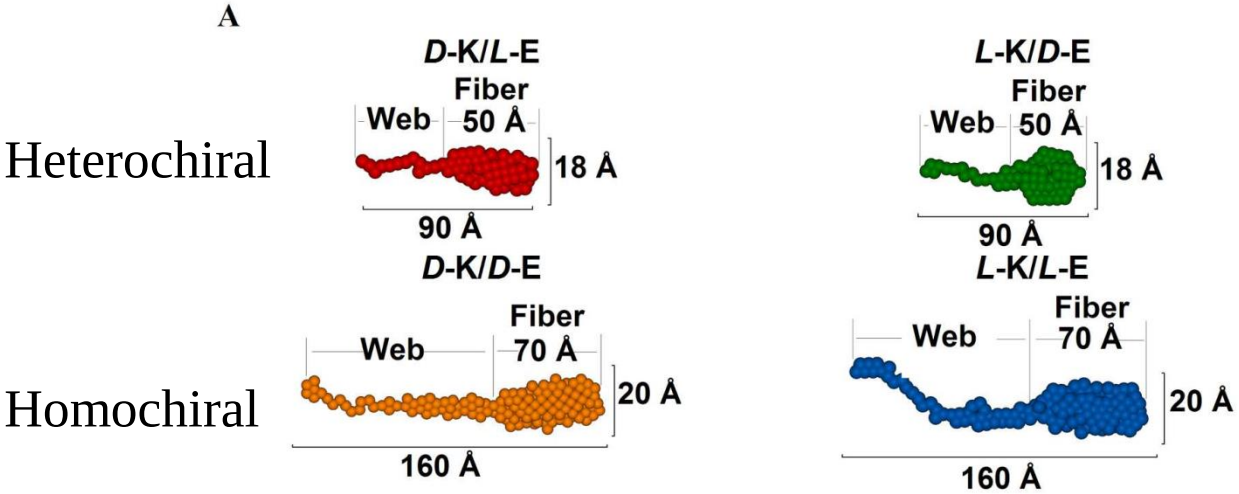
$$P(Q) = \int d^3r \exp[-i\vec{Q}.\vec{r}]\, P(\vec{r}) = \frac{1}{V_P} \int_0^\infty dr 4\pi r^2 \frac{\sin(Qr)}{Qr} P(r)$$



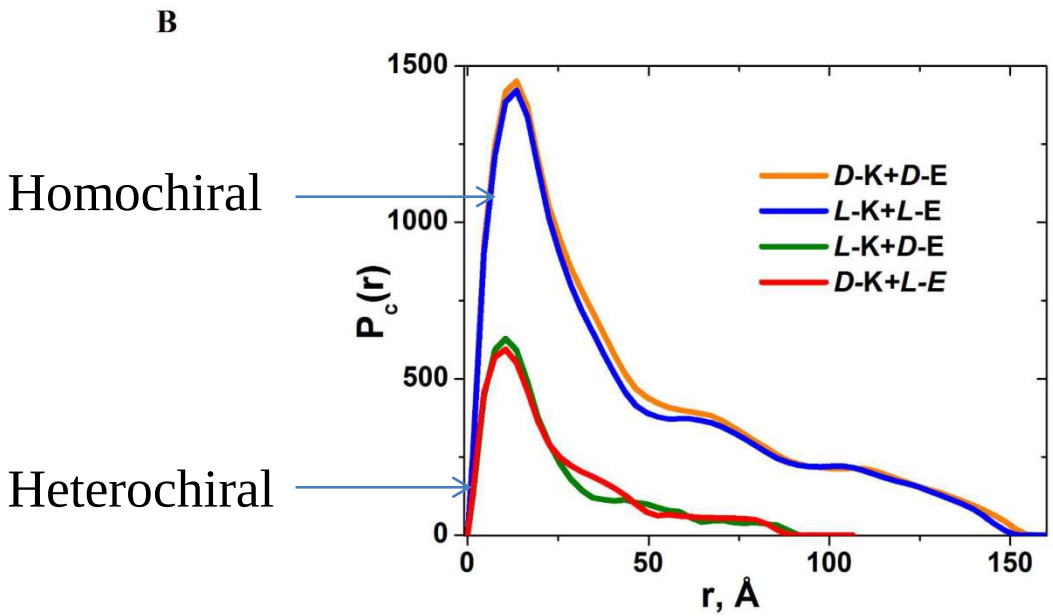
Radial pair correlation function:

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

Shape Reconstruction and Inverse Fourier Transform



Shape Reconstruction
Fiber cross sections



Inverse Fourier Transform

3. SANS Research Topics

A- Phase Transitions in Pluronic P85 Solutions

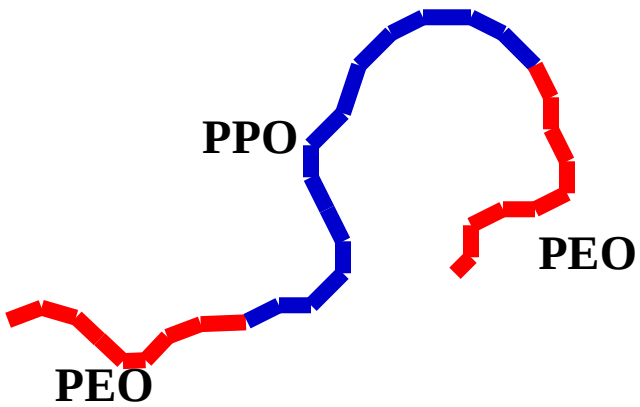
B- Polymer Co-solvation and Co-nonsolvation

C- SDS Micelles with Ethanol Co-surfactant

A - Phase Transitions in Pluronic P85 Solutions

Pluronics

Dissolved Unimer
(low temperature)

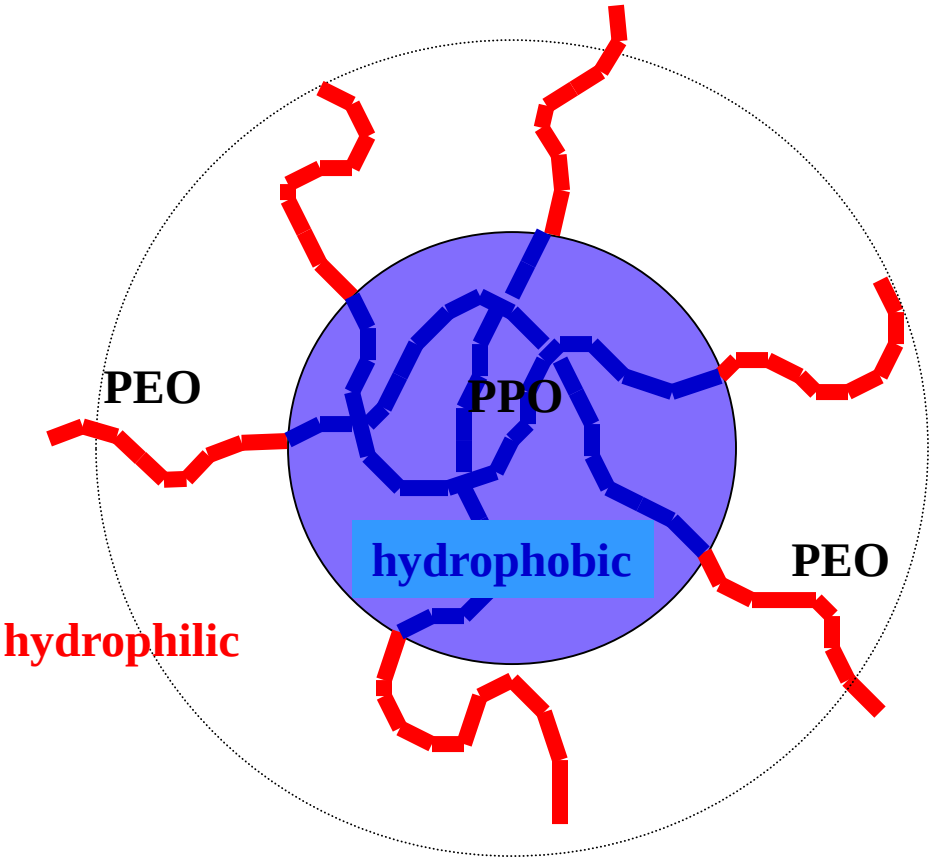


EO:$-CH_2CH_2-O-$

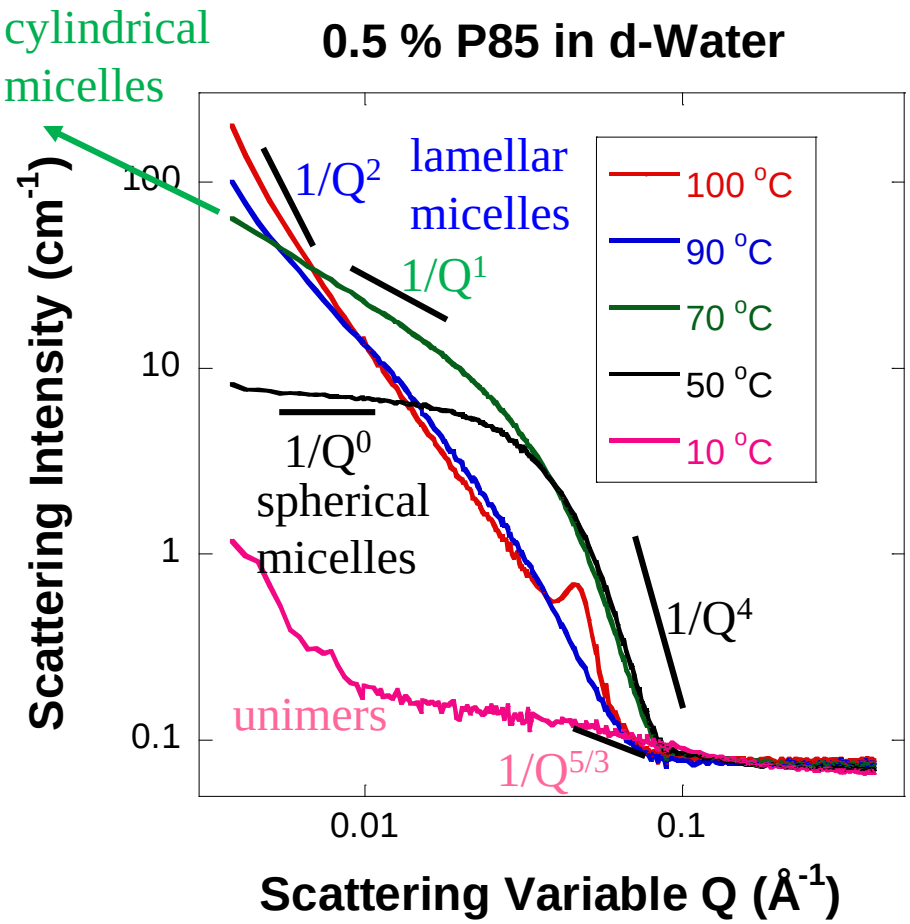
PO:$-CH(CH_3)CH_2-O-$

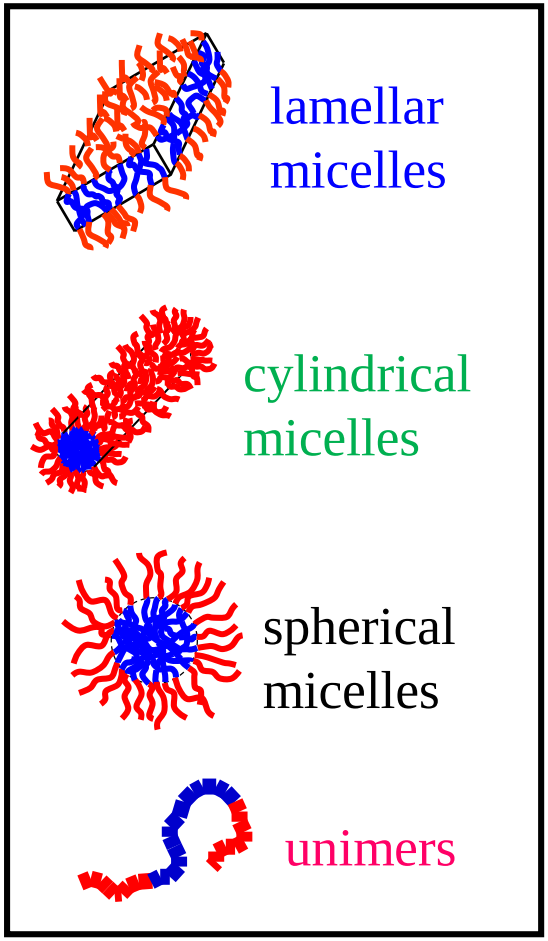
P85: $EO_{26}PO_{40}EO_{26}$

Formed Micelle
(high temperature)

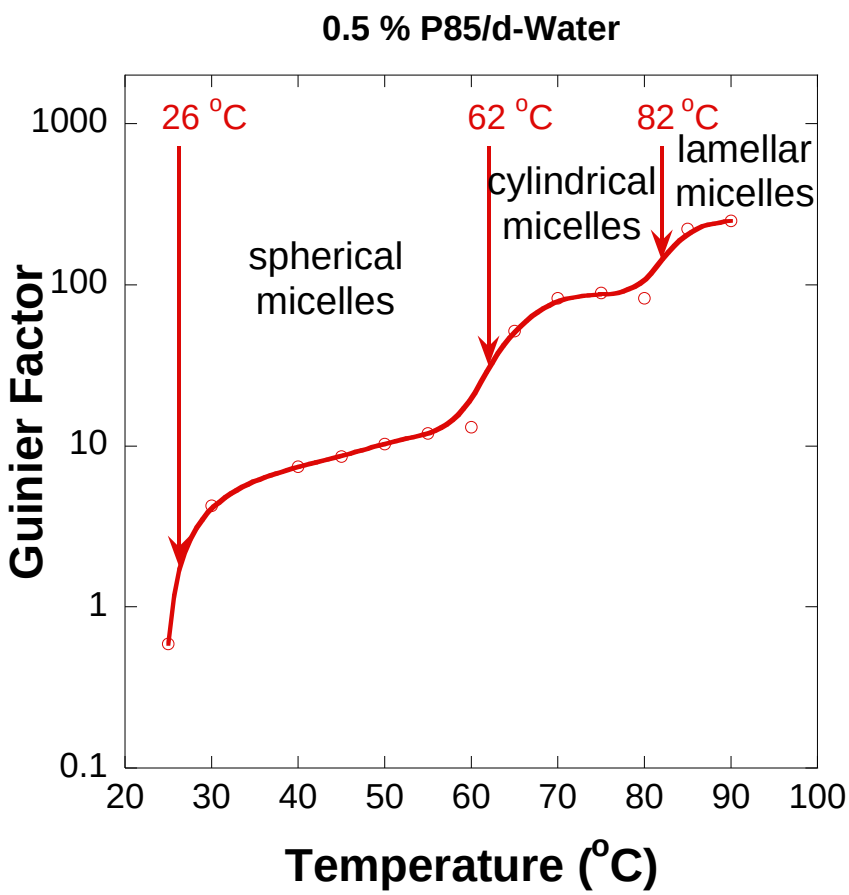


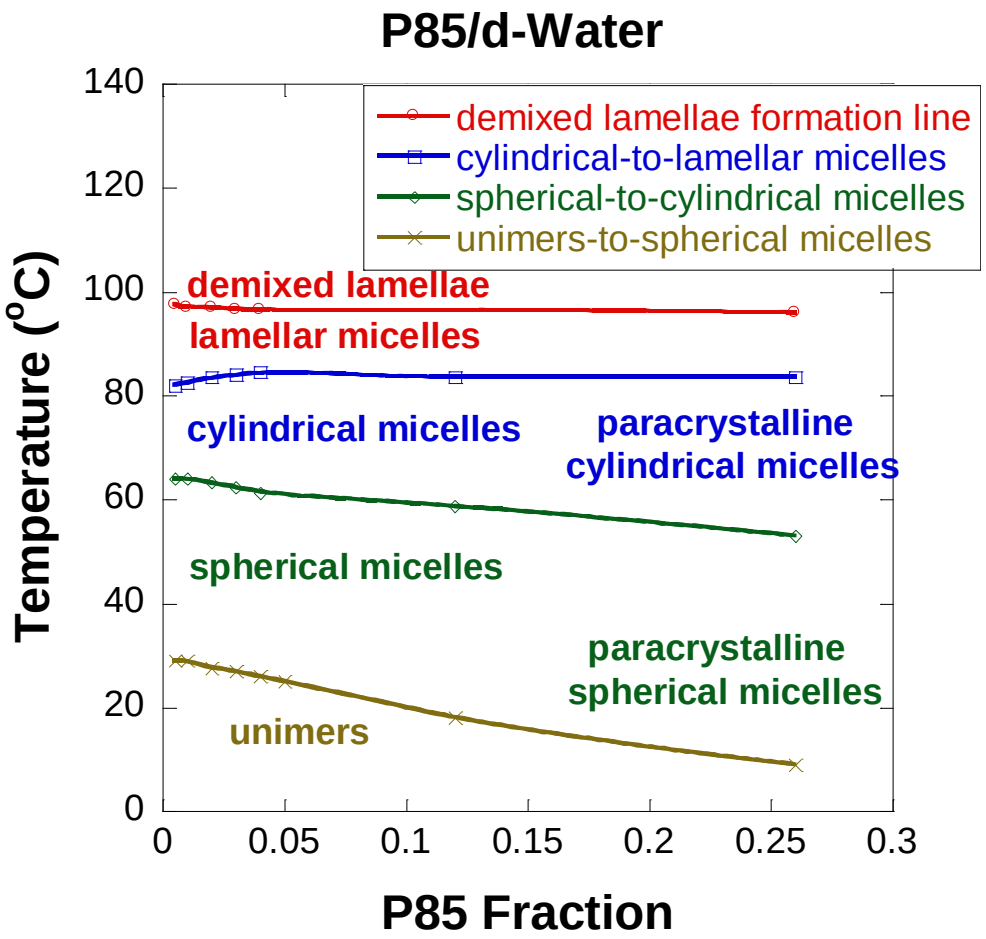
Pluronic Micelles





Phase Diagram

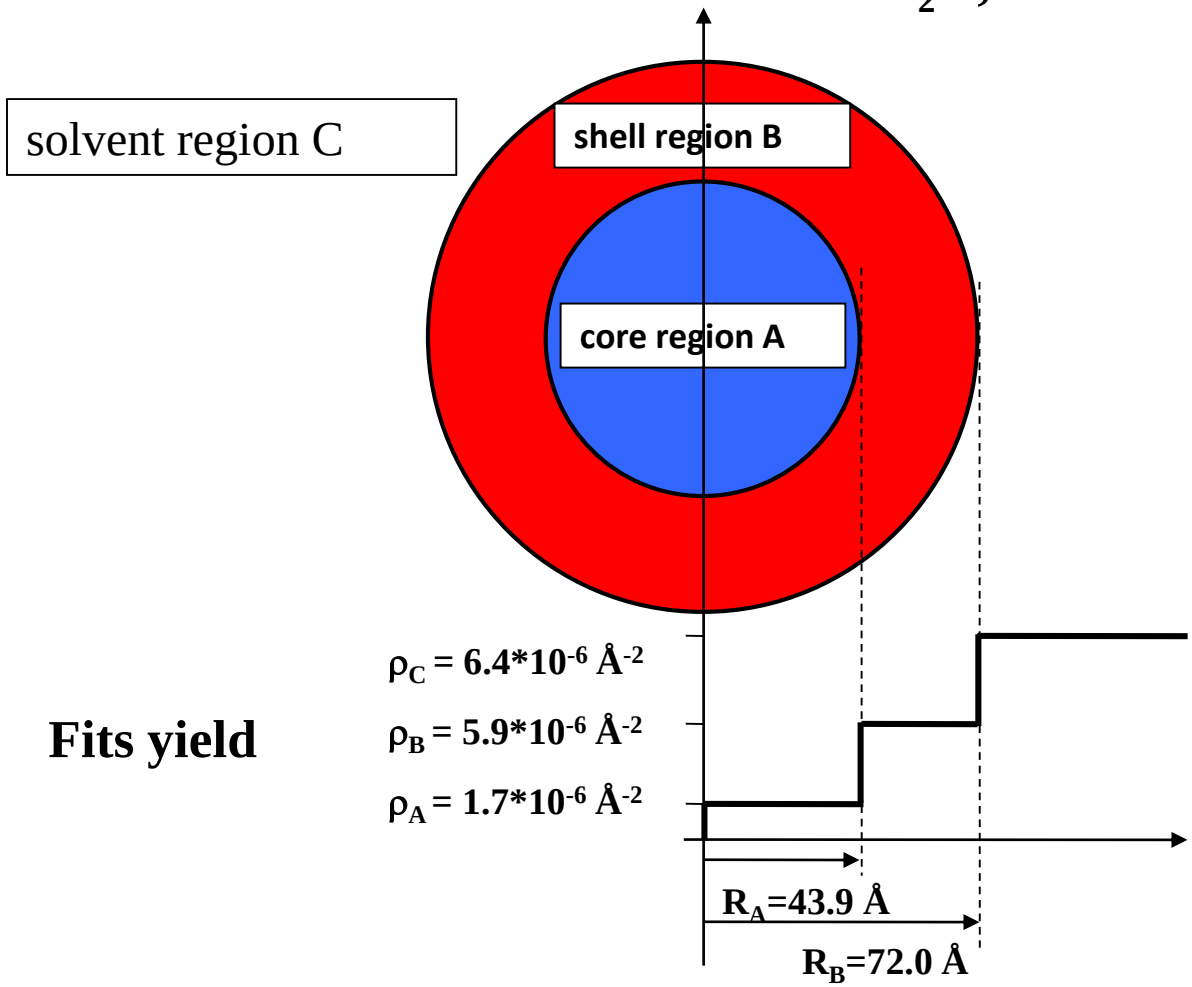




The Core-Shell Particles Model

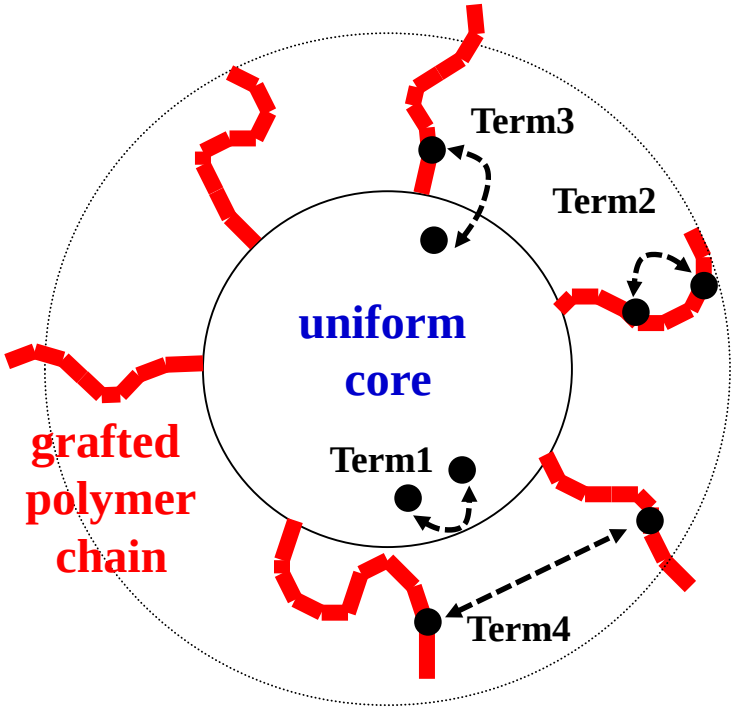
$$\frac{d\Sigma(Q)}{d\Omega} = \frac{N}{V}\left[(\rho_A - \rho_B)V_A \frac{3j_1(QR_A)}{QR_A} + (\rho_B - \rho_C)V_{A+B}\left(\frac{3j_1(QR_B)}{QR_B}\right)\right]^2 S_I(Q)$$

10% P85 Pluronic/D_2O, 40 °C

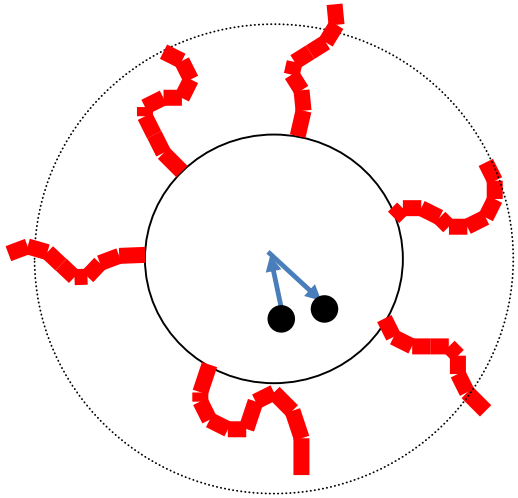


Fits yield

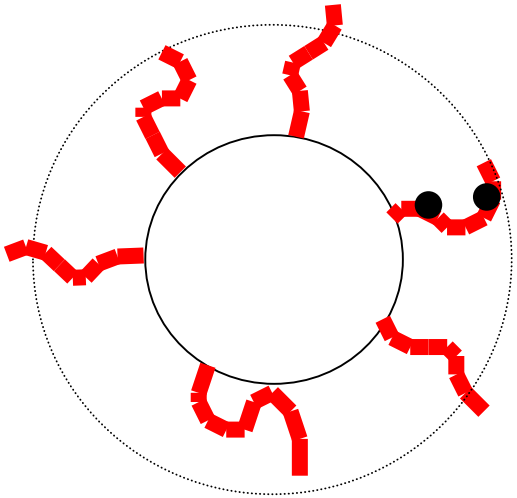
The Core-Chain Model



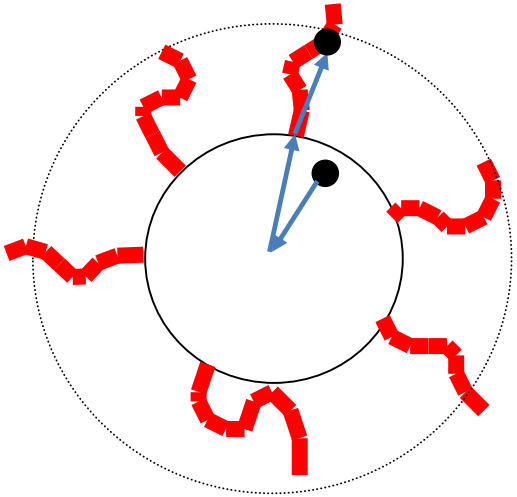
The Core-Chain Form Factors



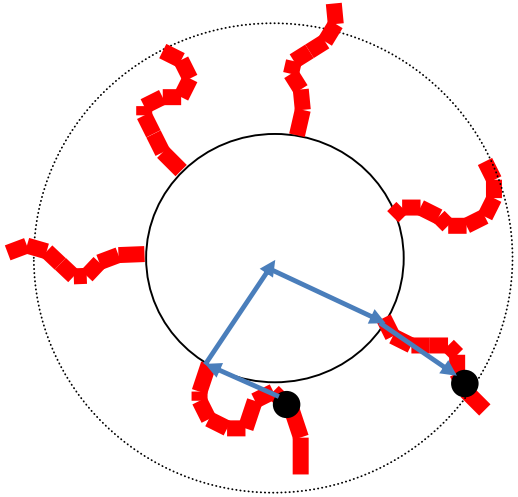
Term1=$P_c(QR)=F_c^2(QR)$



Term2= $P_p(QR_g)$



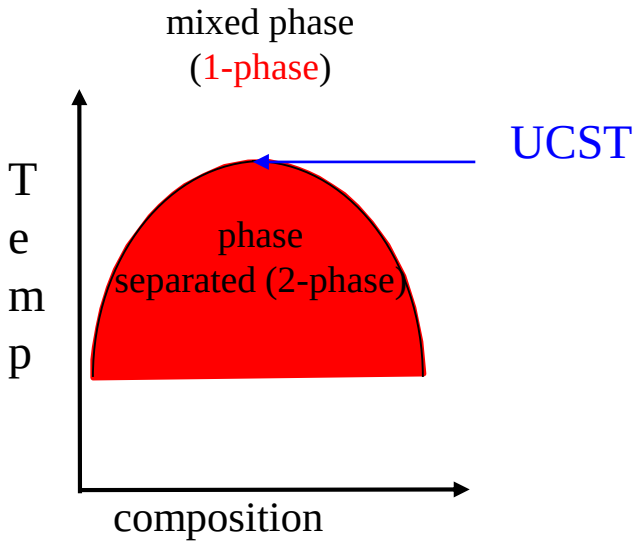
Term3= $F_c(QR)\ E_c(QR)F_p(QR_g)$

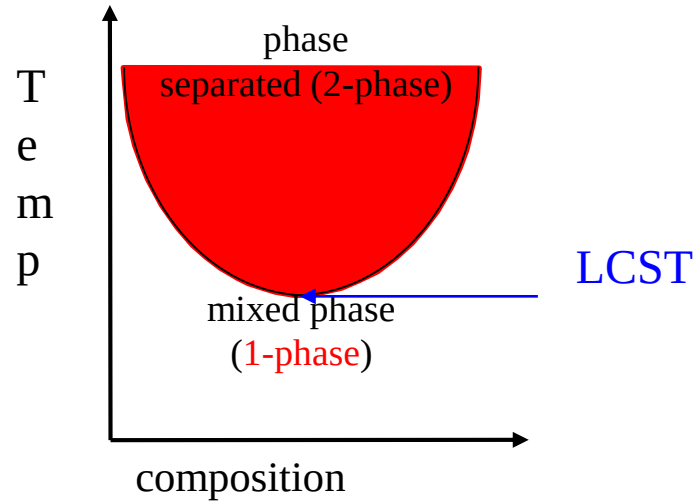


Term4= $F_p(QR_g)\ E_c^2(QR)F_p(QR_g)$

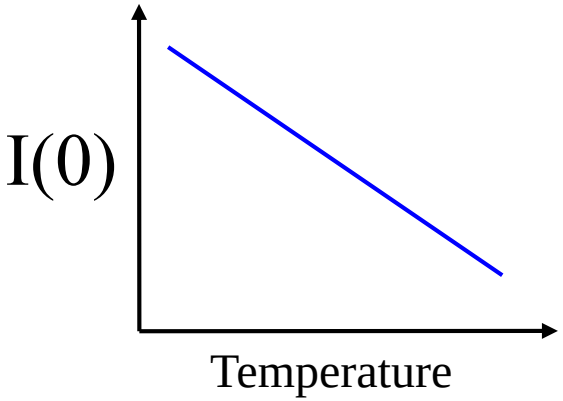
C- Polymer Co-solvation and Co-nonsolvation

Polymer Demixing Phase Transitions

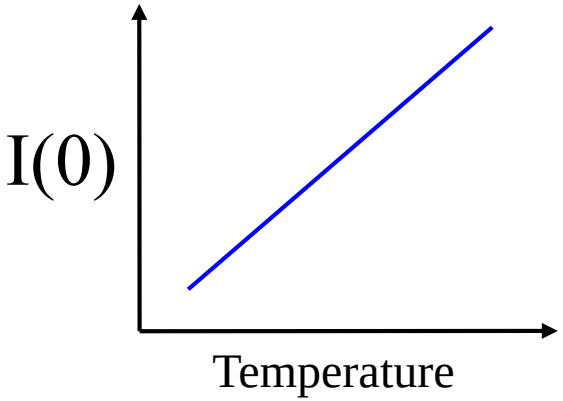




UCST



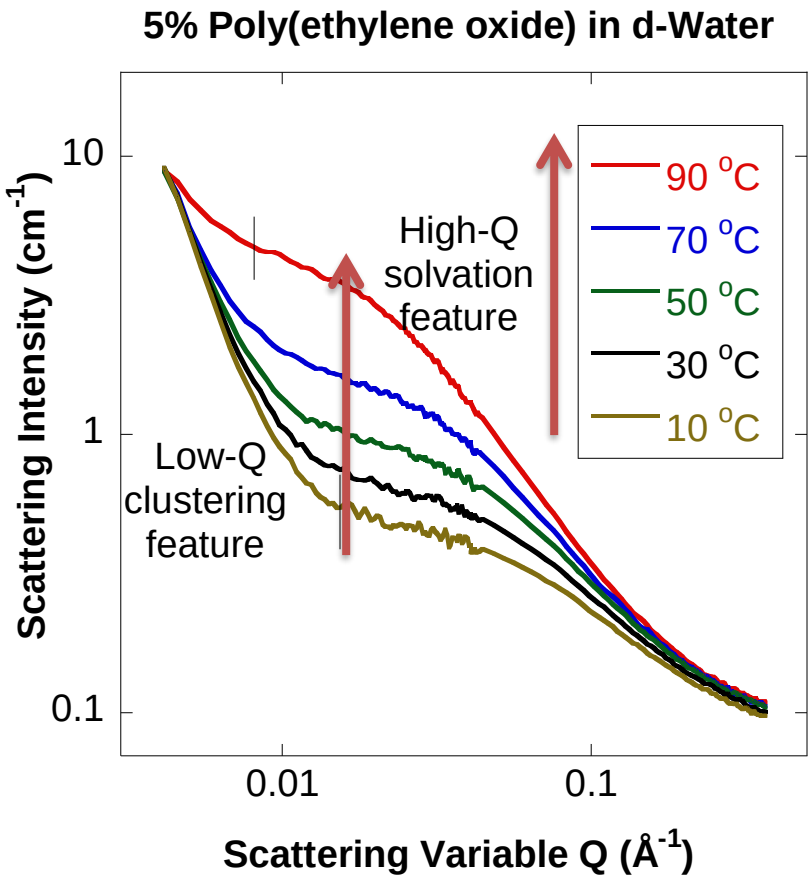
LCST



Upper Critical Solution Temp.

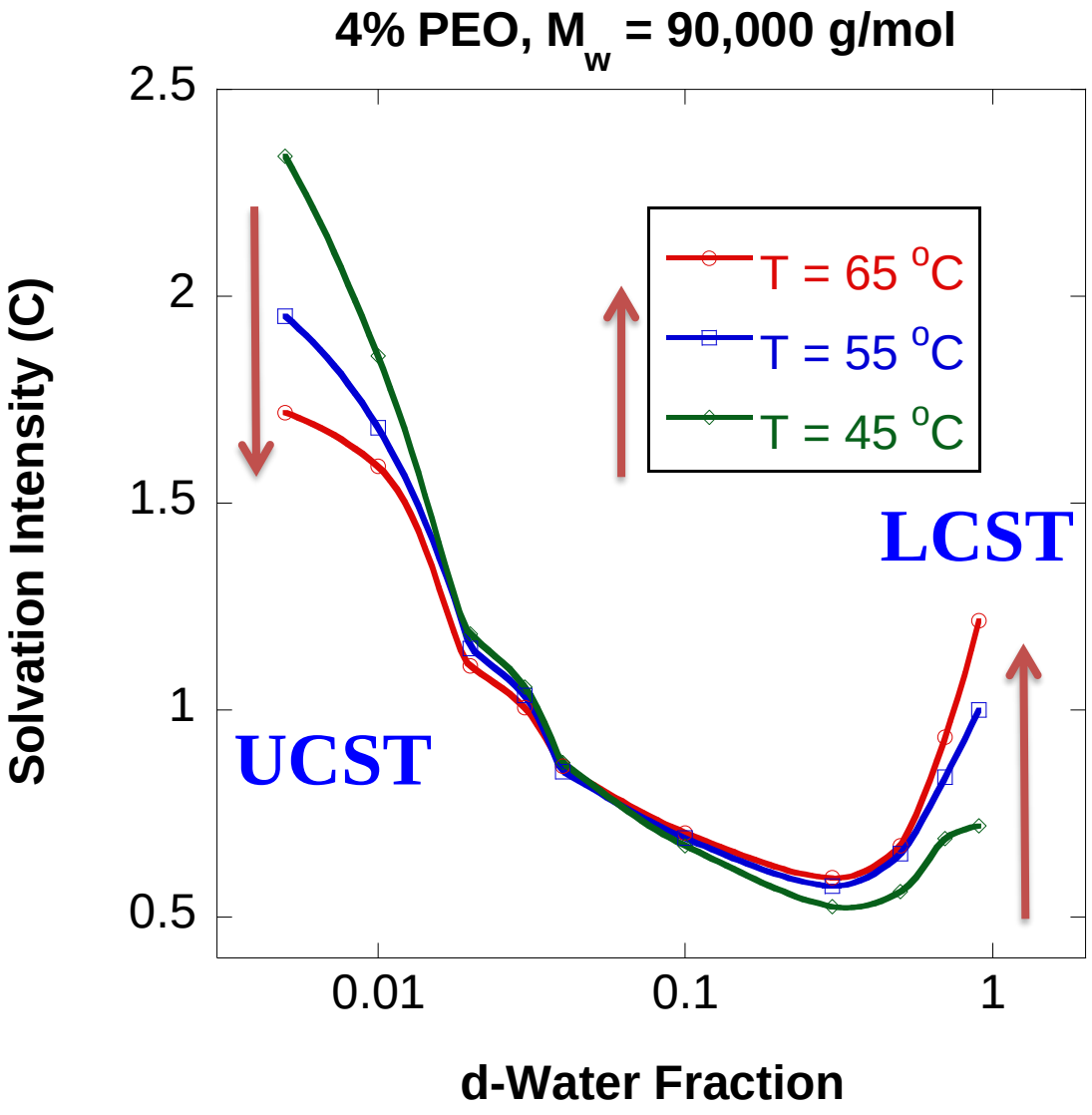
Lower Critical Solution Temp.

Poly(ethylene oxide) in d-water

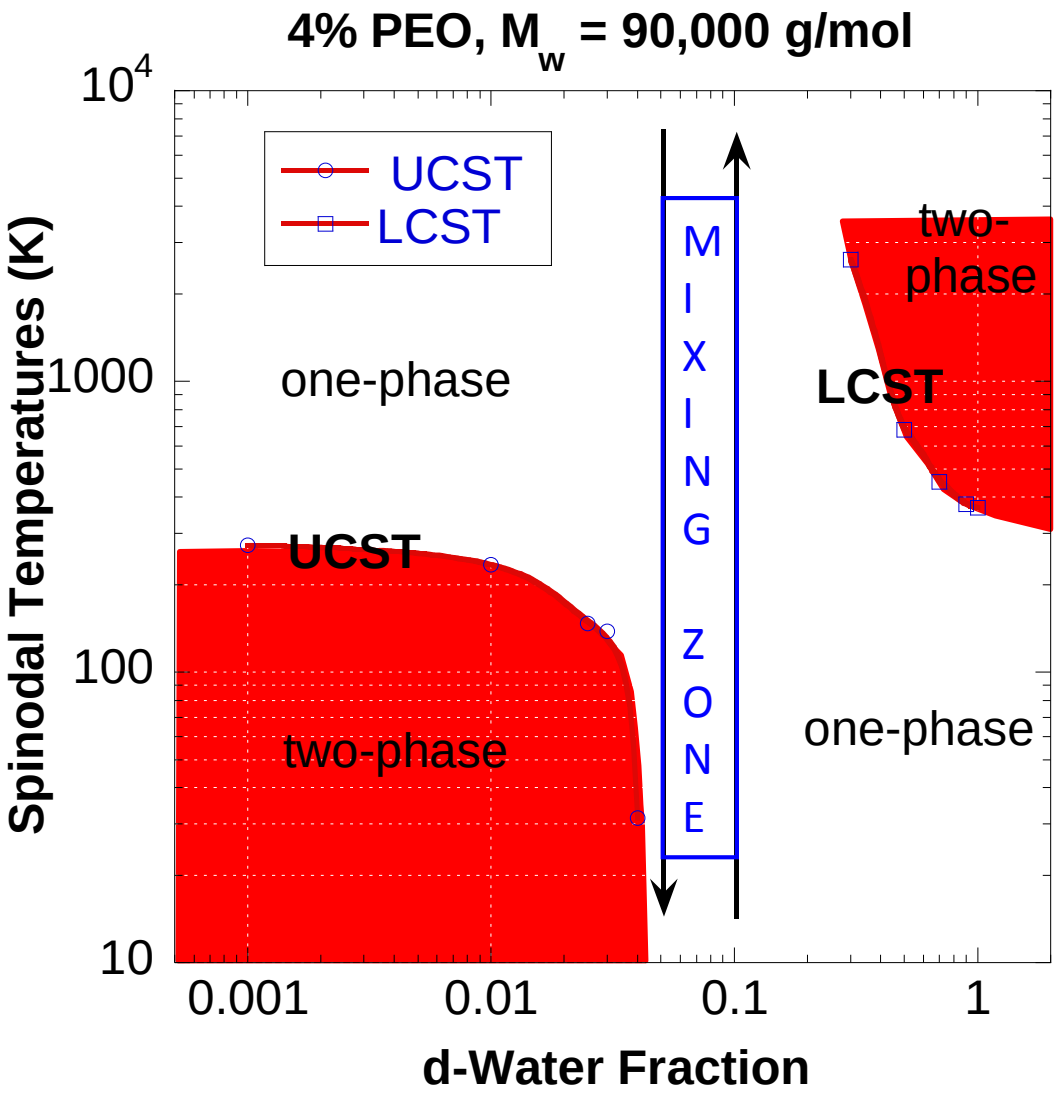


Lower Critical Spinodal Temperature

PEO in d-ethanol/d-water Mixtures

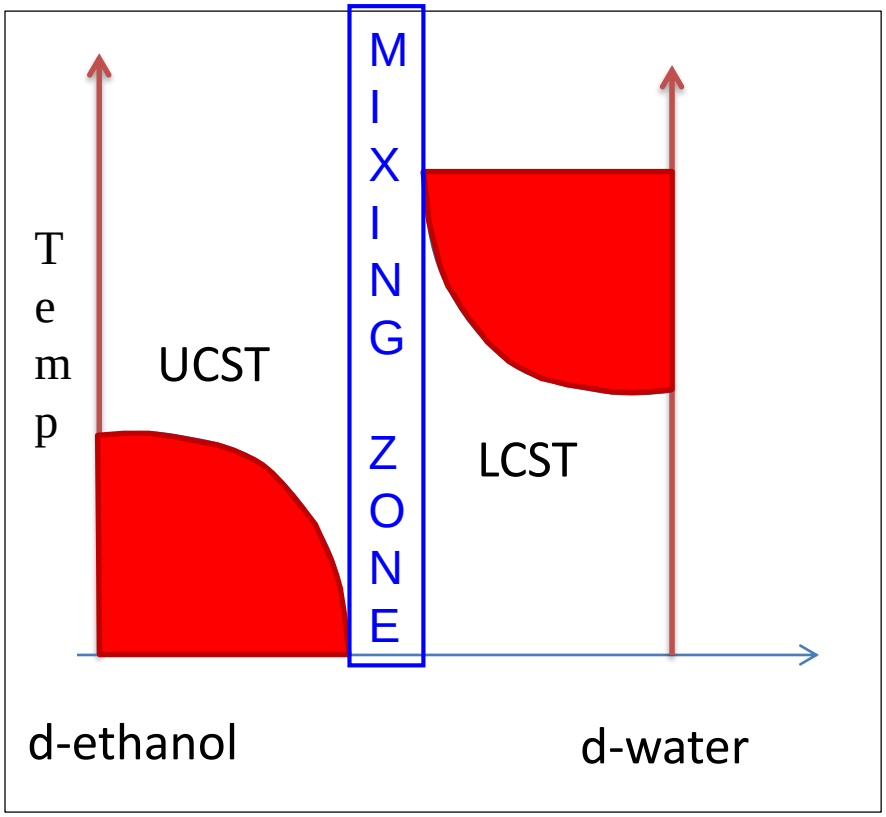


PEO in d-ethanol/d-water Mixtures

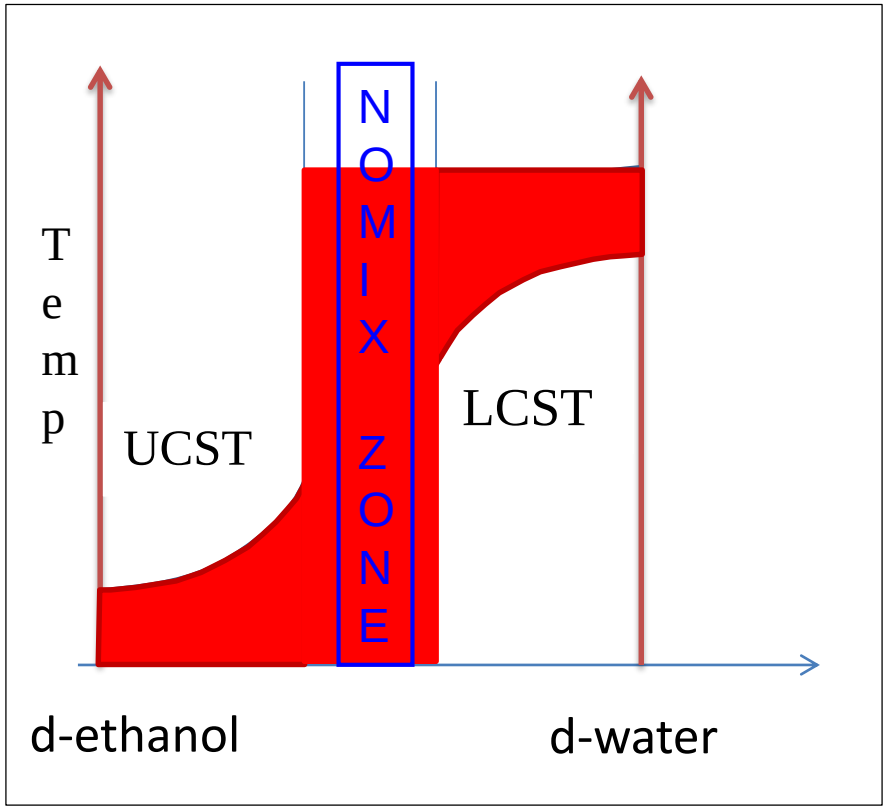


Co-solvation and Co-nonsolvation

PEO



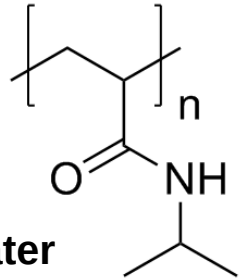
PNIPAM

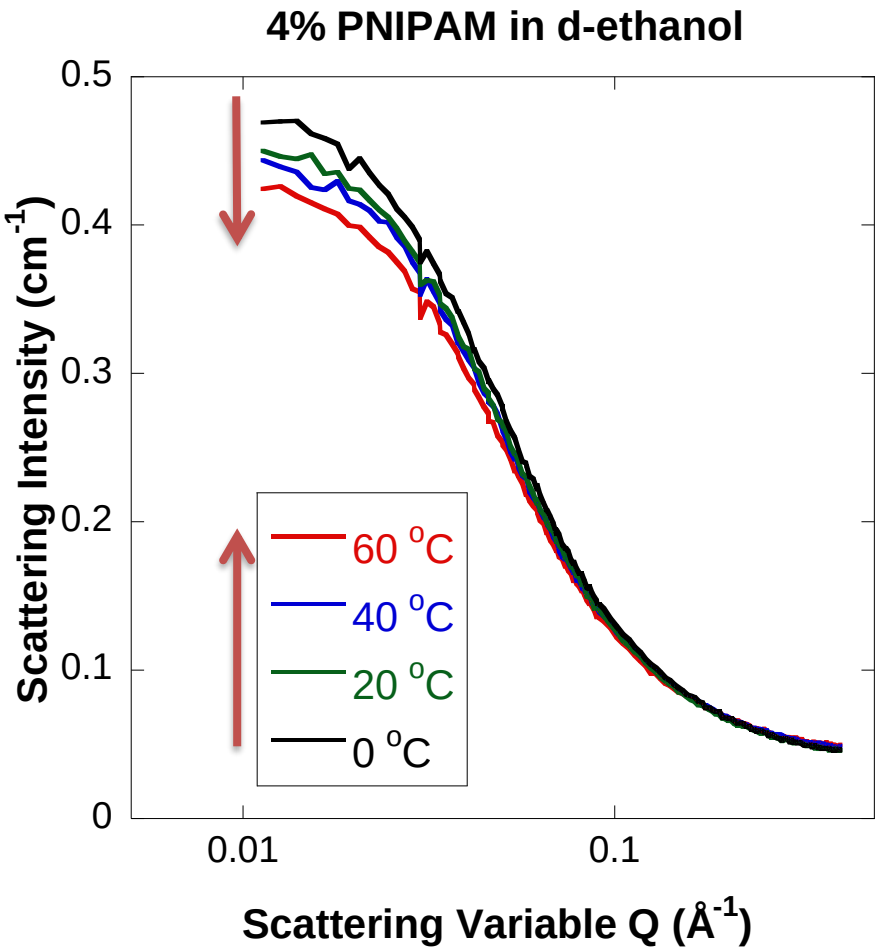


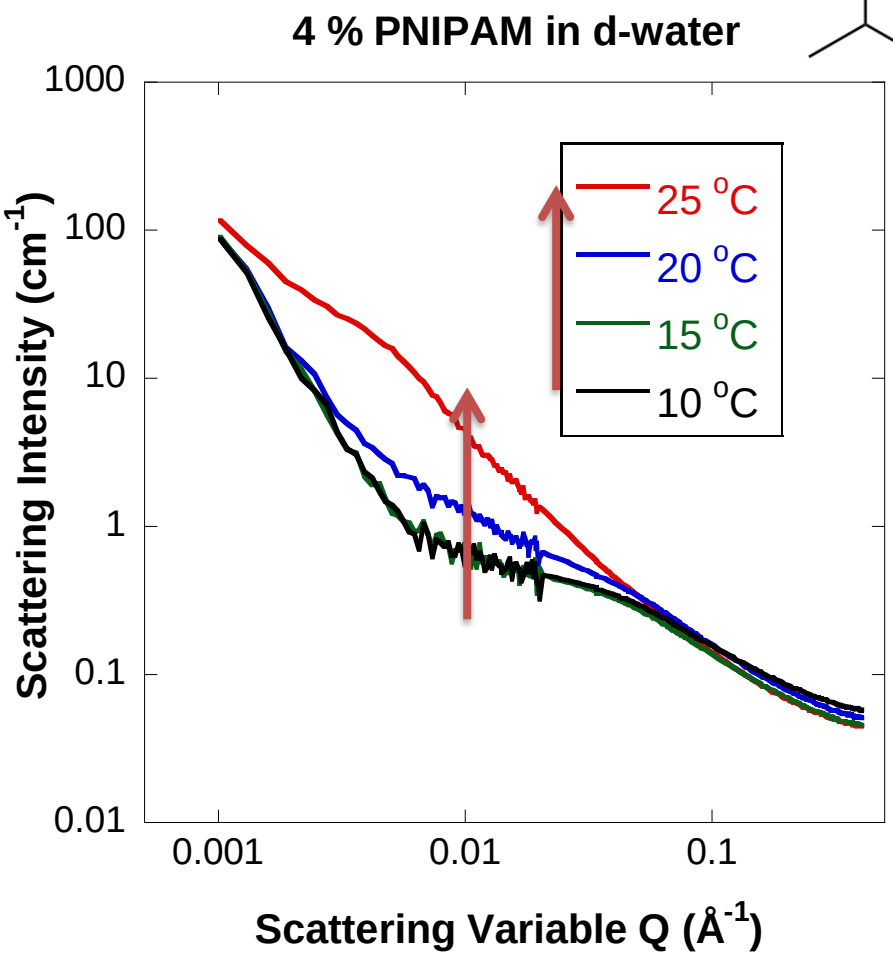
Co-solvation

Co-nonsolvation

PNIPAM in d-ethanol/d-water Mixtures

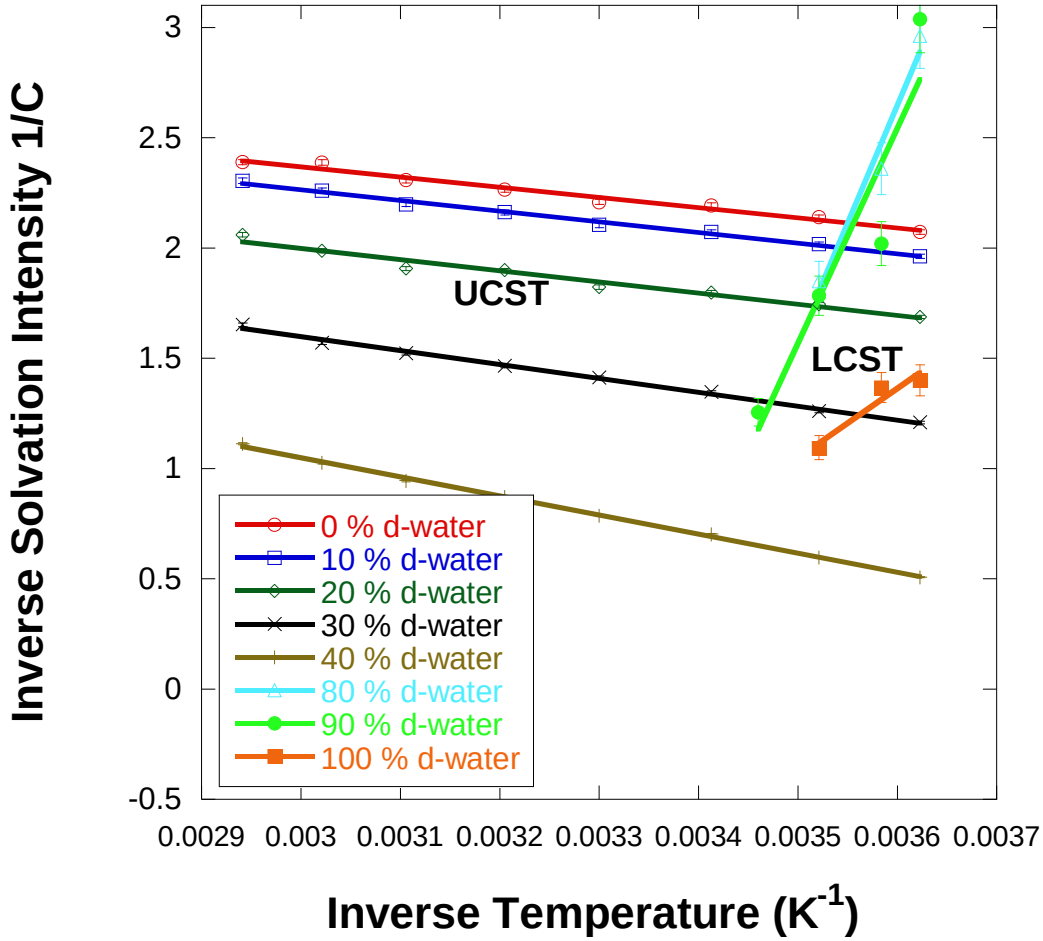




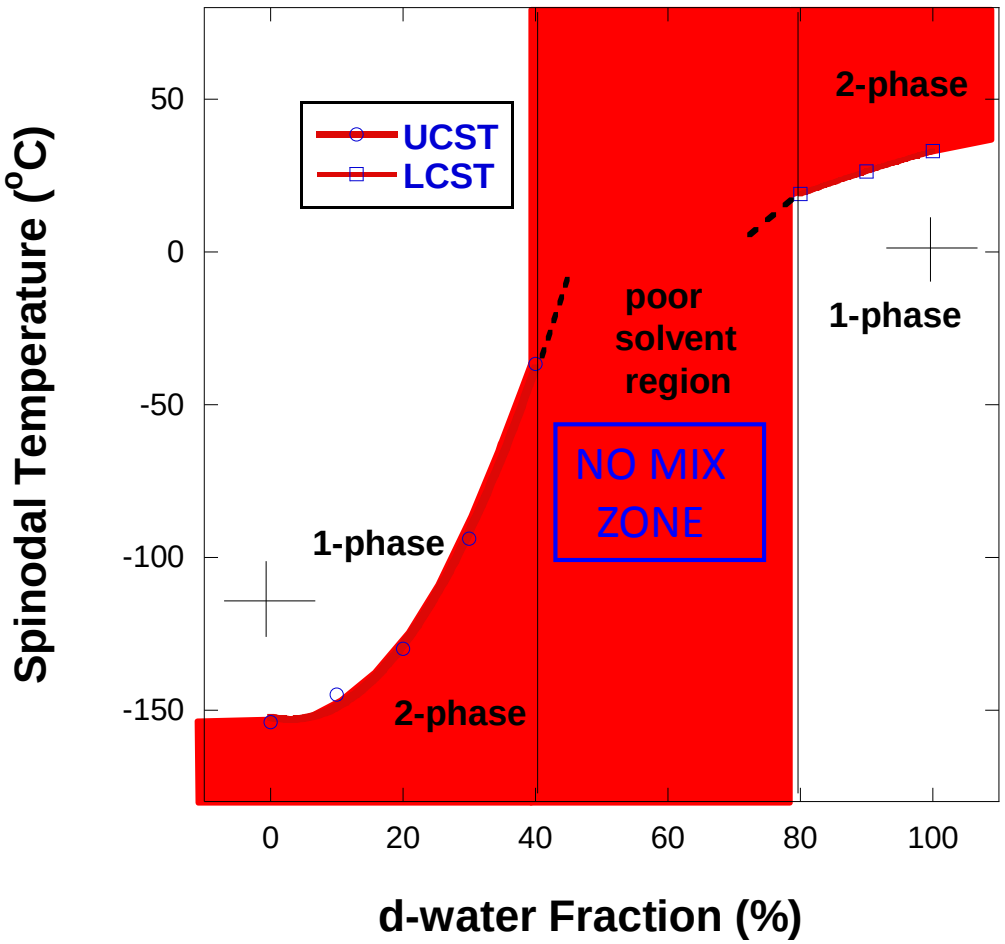


UCST **LCST**

PNIPAM in d-ethanol/d-water Mixtures



PNIPAM in d-ethanol/d-water Mixtures



Results

- Most polymers dissolve better in solvent mixtures (cosolvation)

- PNIPAM obeys a co-nonsolvation rule

- PEO is characterized by a “perfect” solvation window for 10 % d-water.

- PEO dissolves in water while PMO and PPO do not dissolve.

- Water and water-ethanol mixtures form cage-like structures.

- PNIPAM is characterized by a non-solvation window for 60 % d-water.

- SANS is a valuable thermodynamic probe to study phase transitions as well as nanostructures

C- SDS Micelles with Co-surfactant

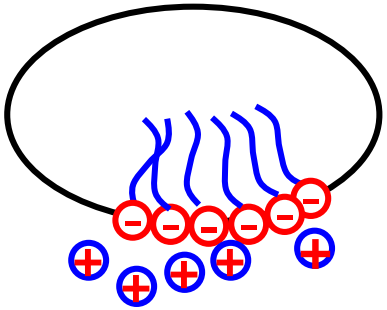
Micelle Formation

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

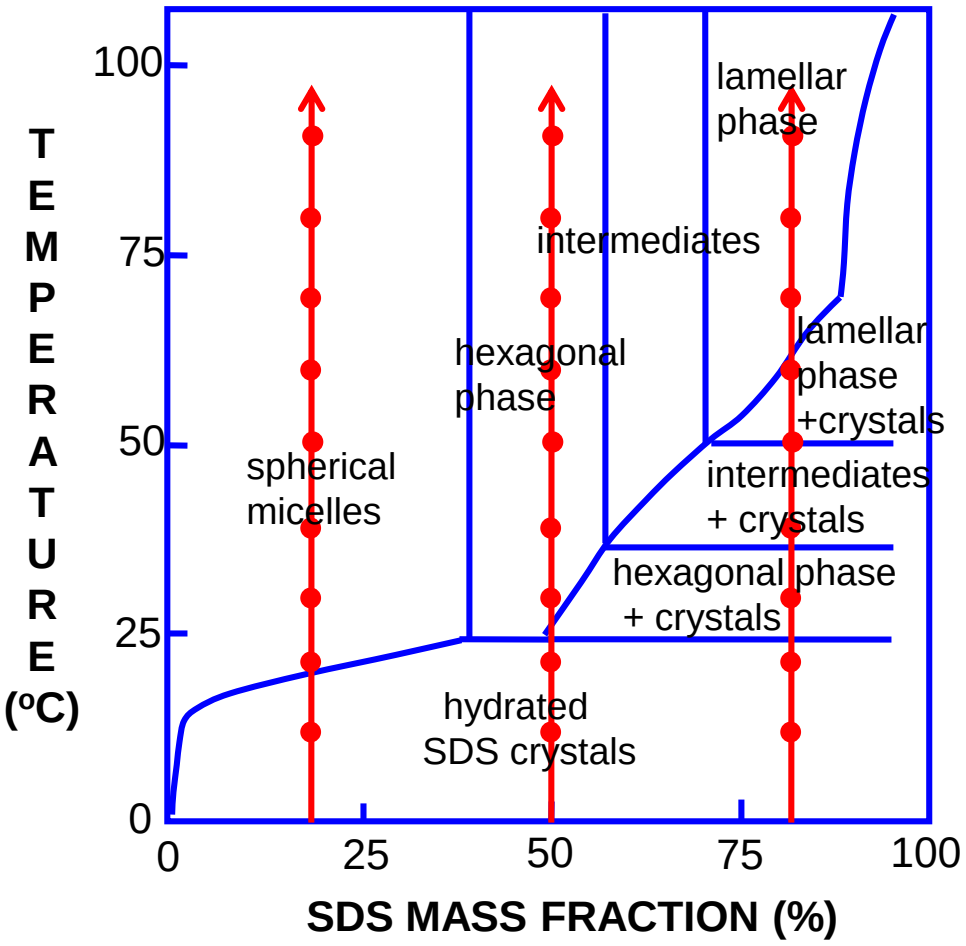
- Micelles form when enough surfactants aggregate (above the critical micelle concentration or CMC)

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

- What is the effect of ethanol co-surfactant on SDS micellar structure

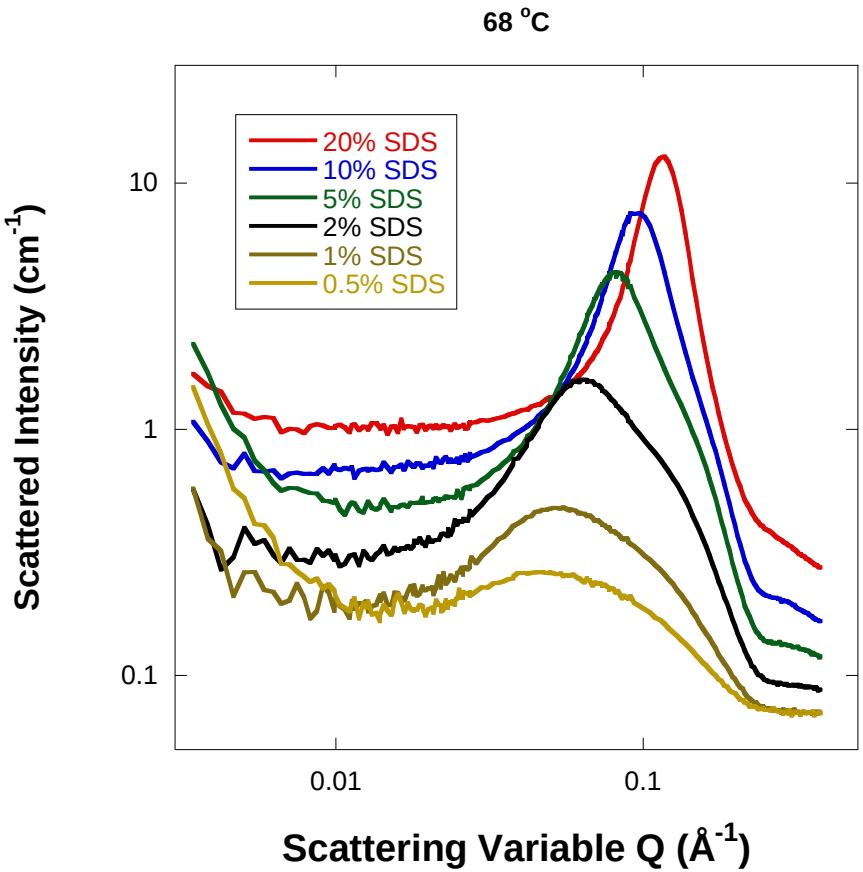


Phase Diagram

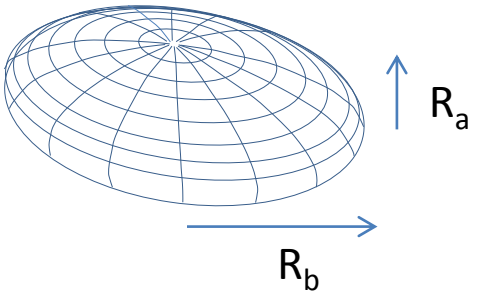


- SDS/water phase diagram from calorimetry

SANS from SDS Micelles

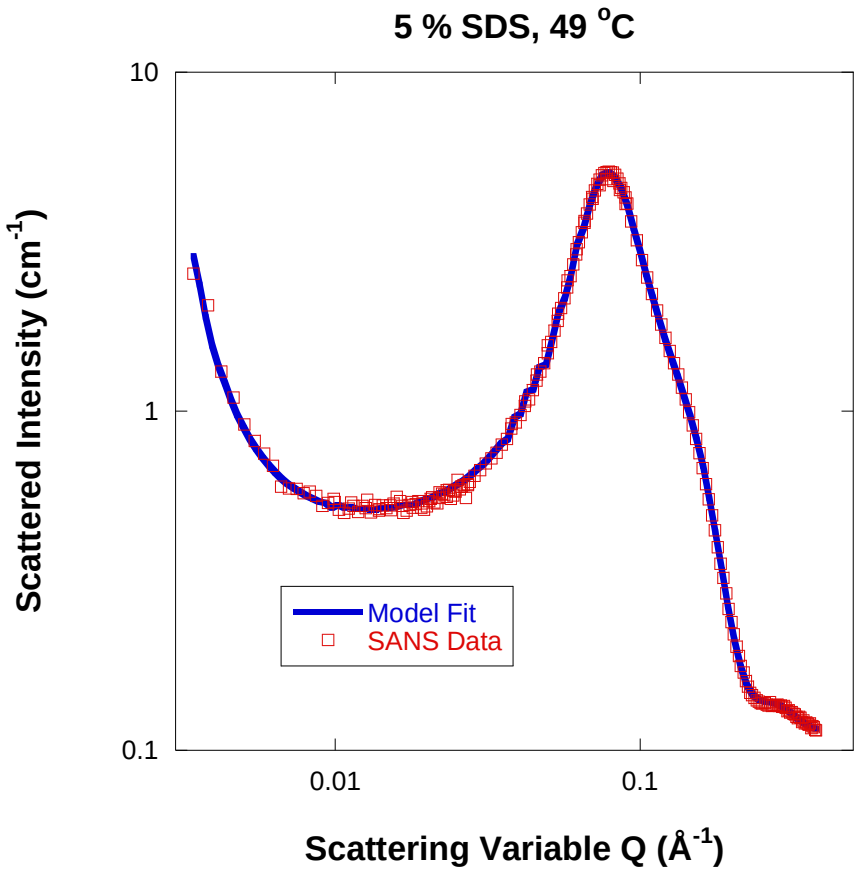


Oblate ellipsoid



- Ellipsoidal micelles form

Ellipsoid Micelles Model Fit

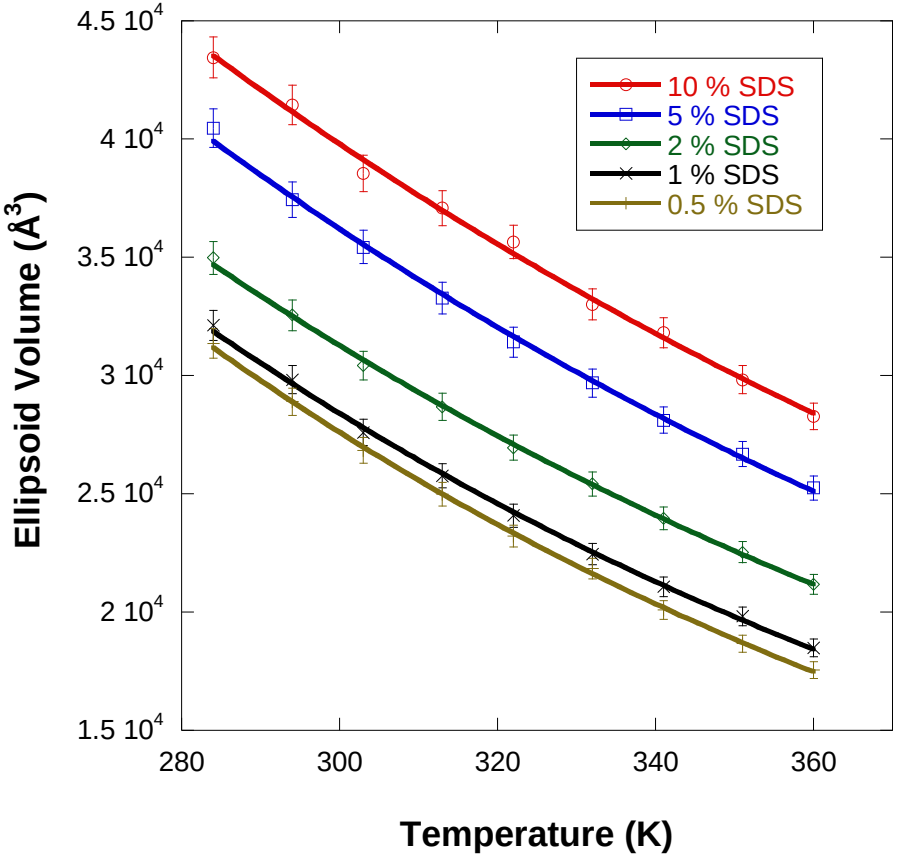


$$I(Q) = \frac{A}{Q^n} + \left[\frac{d\Sigma(Q)}{d\Omega}\right]_{ellipsoids} + B$$

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

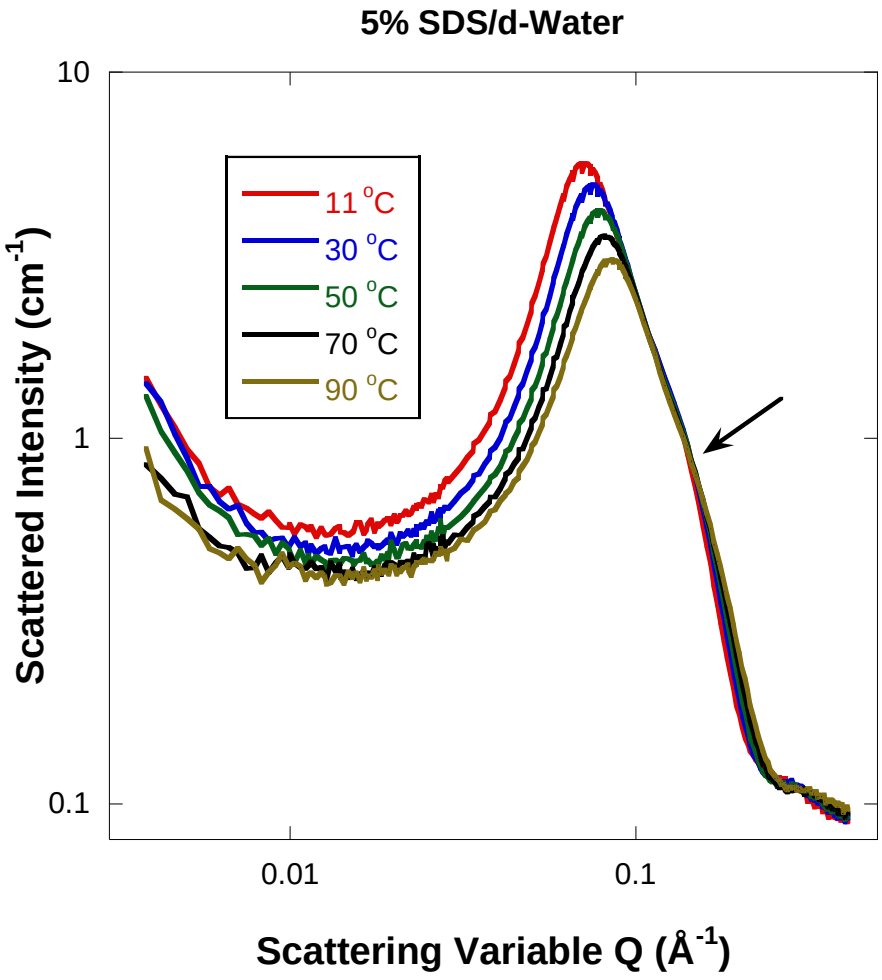
- Power law (low-Q) + ellipsoidal micelles (high-Q) model fits well

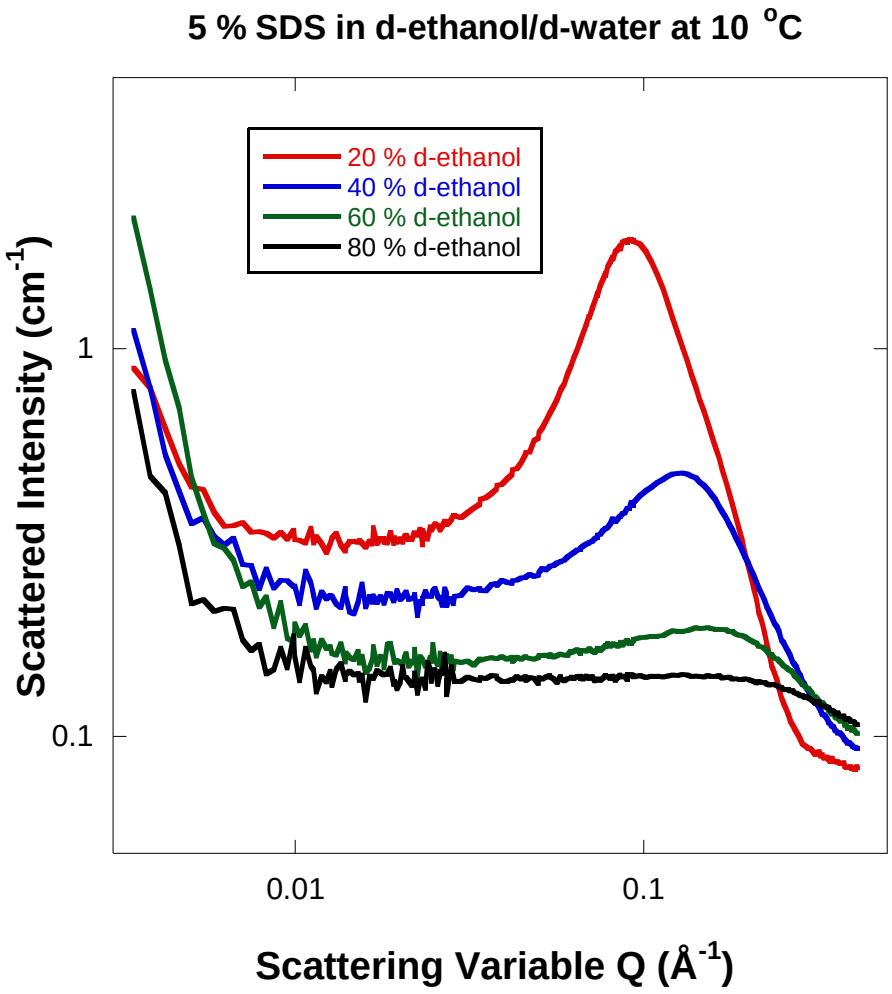
Some Fit Results



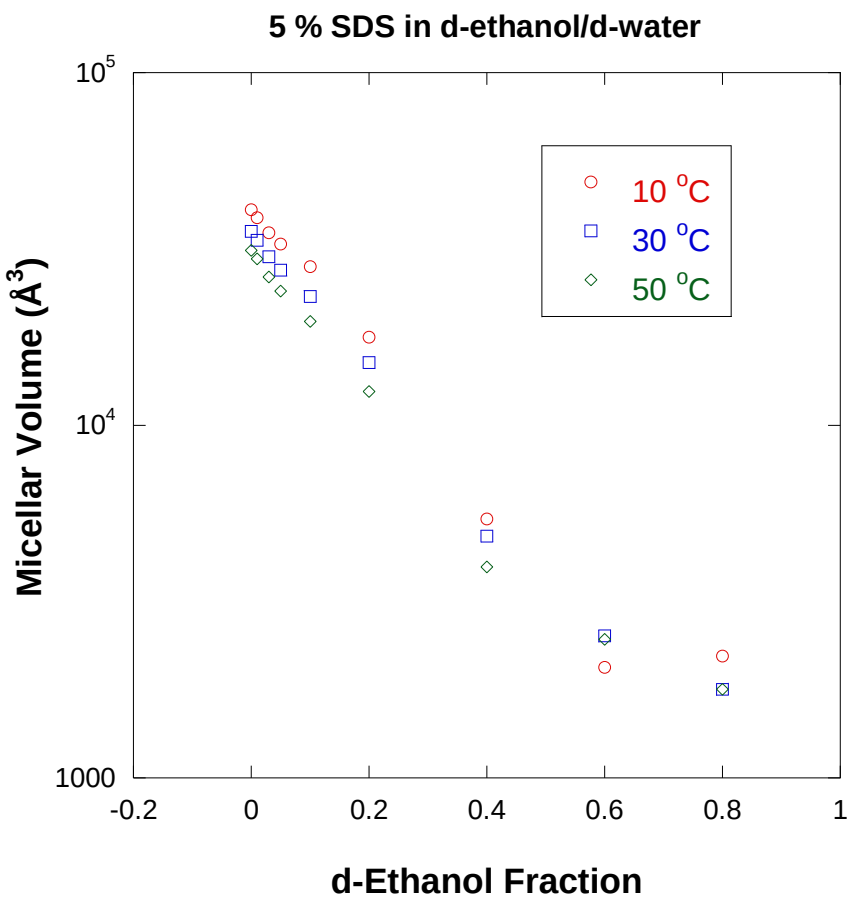
- Micelles become smaller at higher temperatures and lower volume fraction

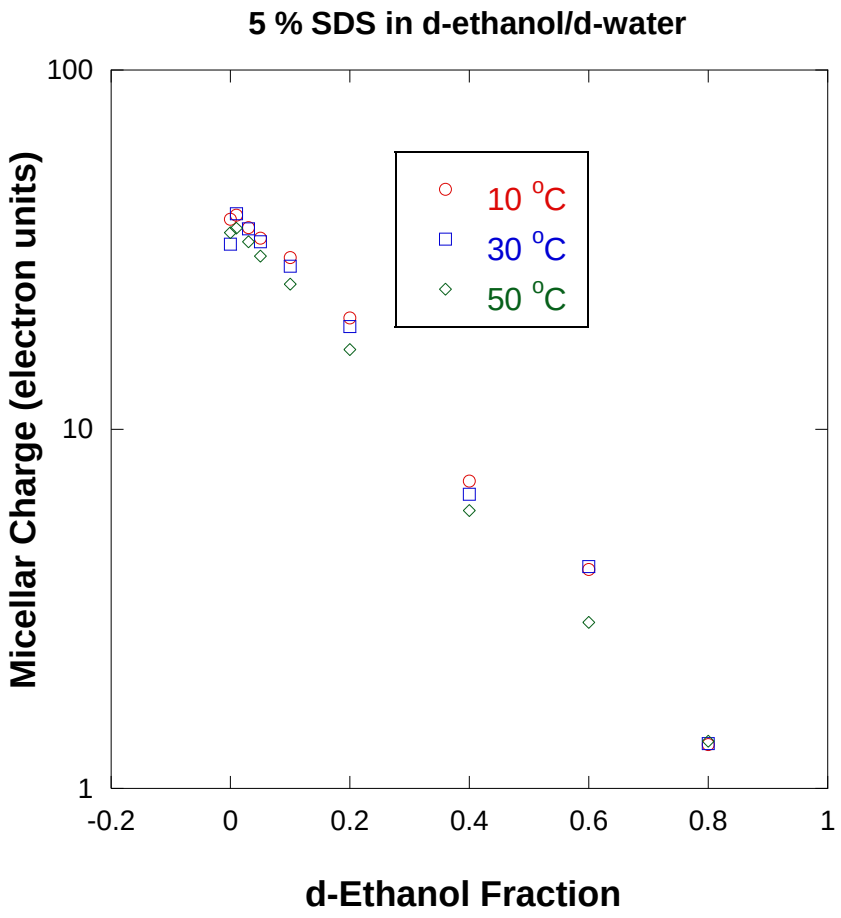
Varying Temperature and SDS Fraction



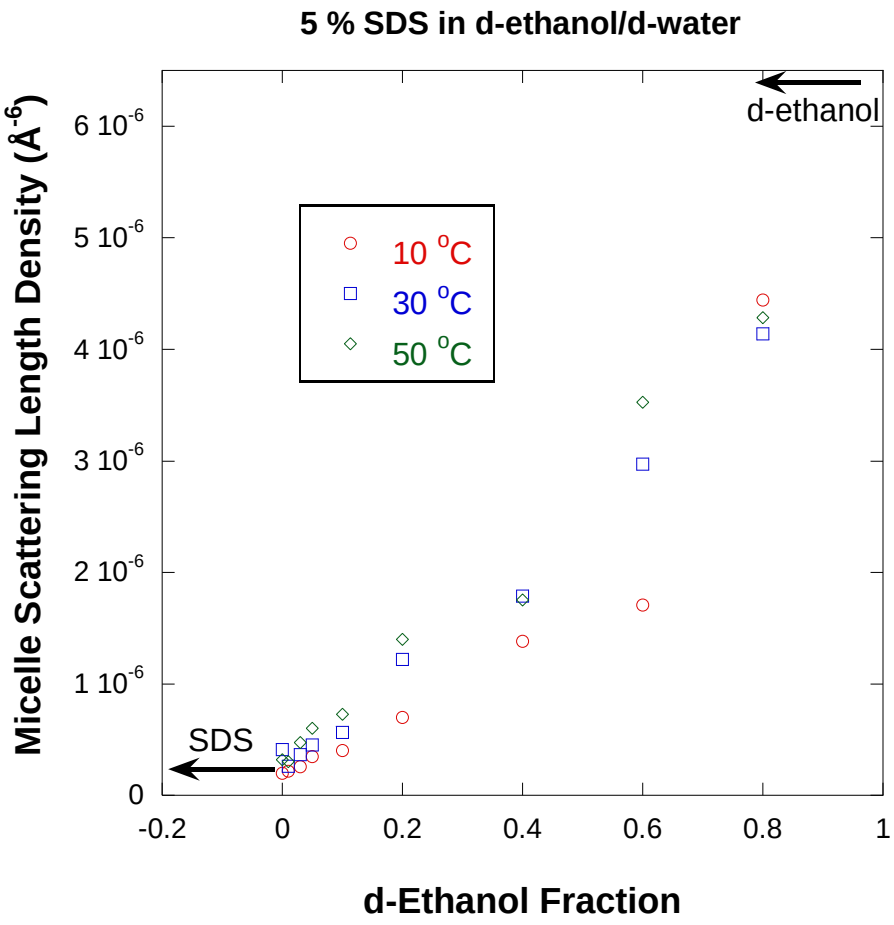


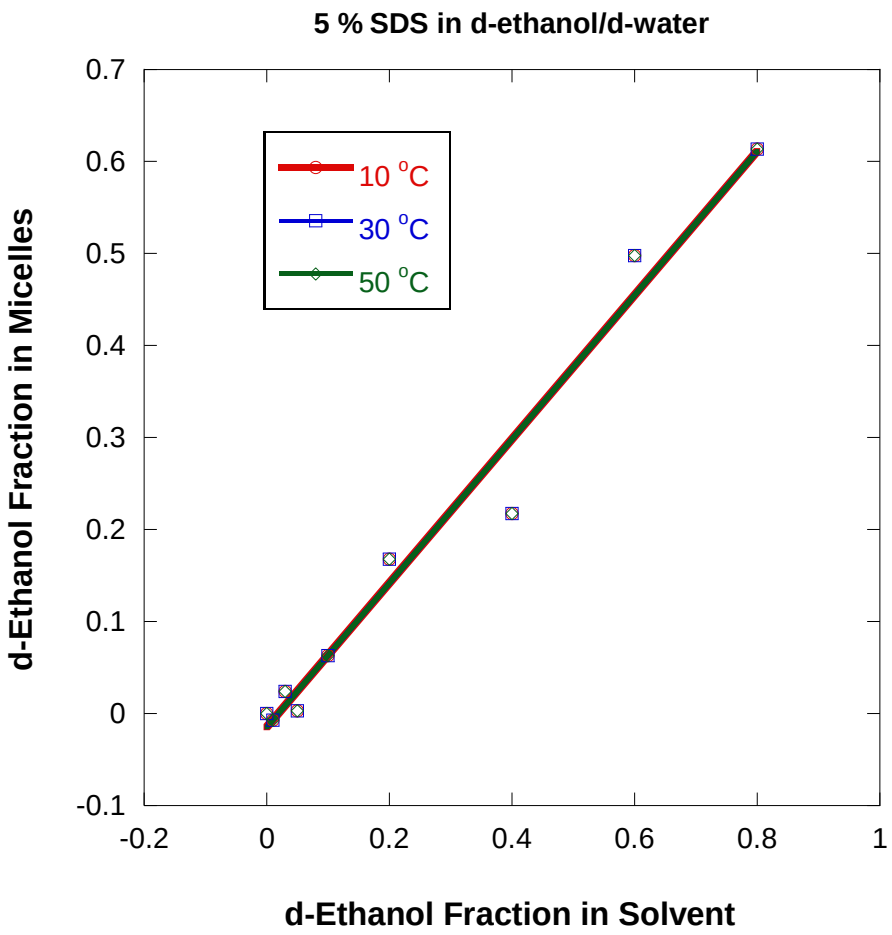
Adding Ethanol Co-surfactant





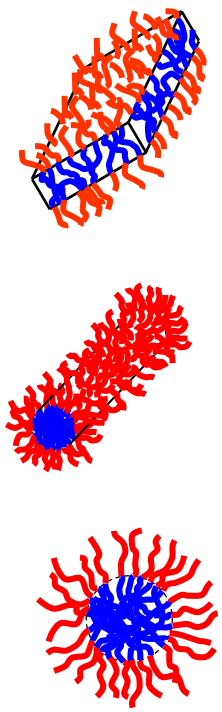
Adding Ethanol Co-surfactant



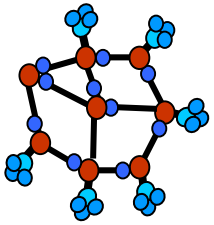


Summary –All Three Projects

P85 Micelles



PEO and PNIPAM Polymers

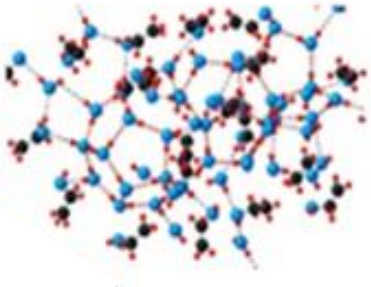


CH_3CH_2-OH H-OH

-CH_2CH_2-O- PEO

-CH_2CH_2-(O)NH-$(CH_3)_2$- PNIPAM

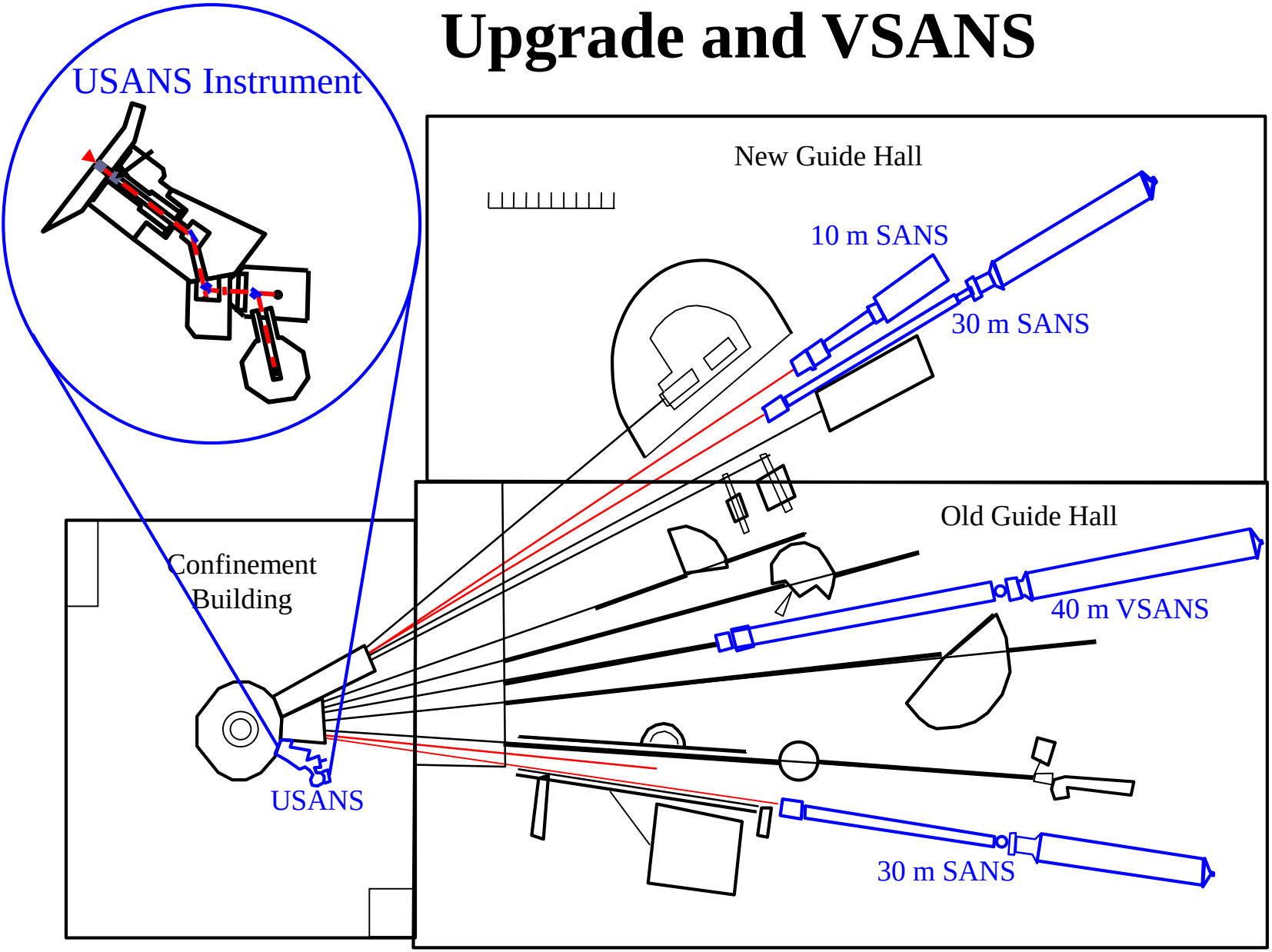
SDS Ionic Micelles



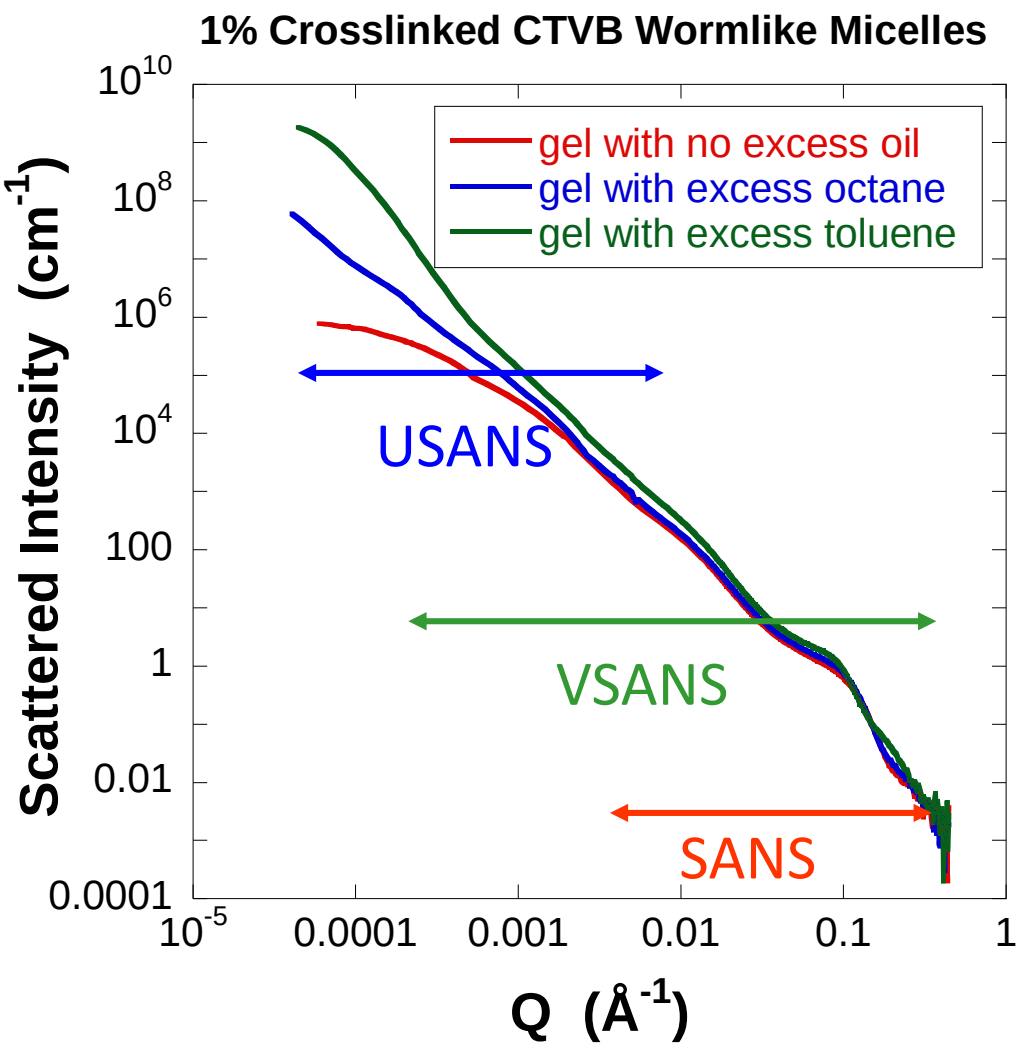
Cage-like Structures

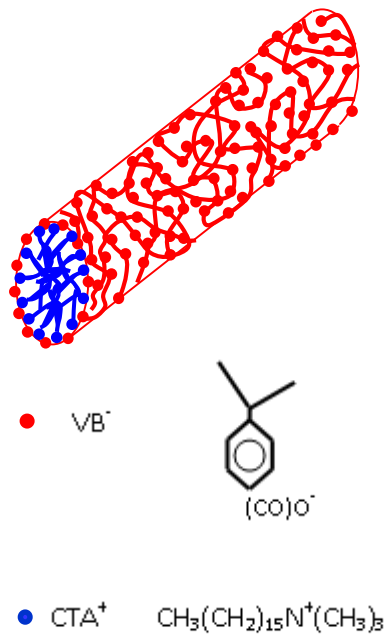
4. Final Points

Upgrade and VSANS



SANS, VSANS and USANS Ranges



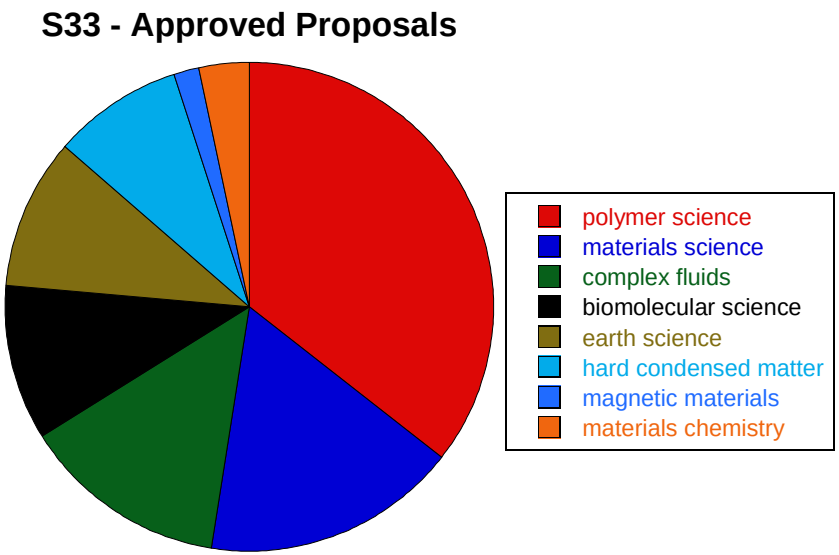


Final Words

THE SANS PROGRAM AT NIST

200 experiments per year

80 publications per year



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