SANS BASICS

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  - B- Structure of SDS Micelles
  - C- Polymer Co-solvation and Co-nonsolvation
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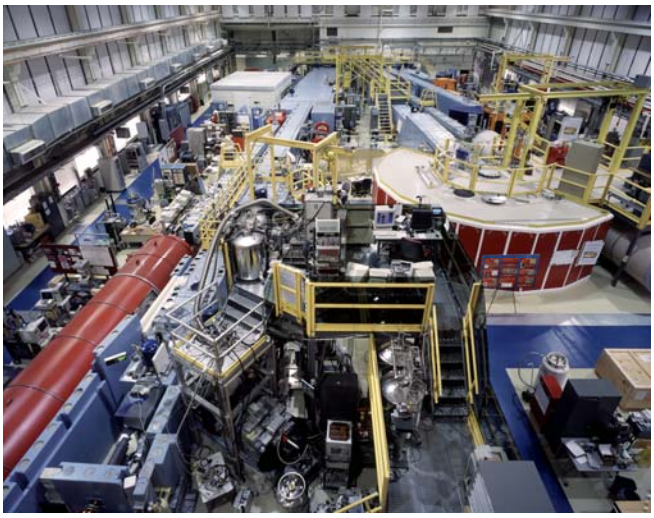
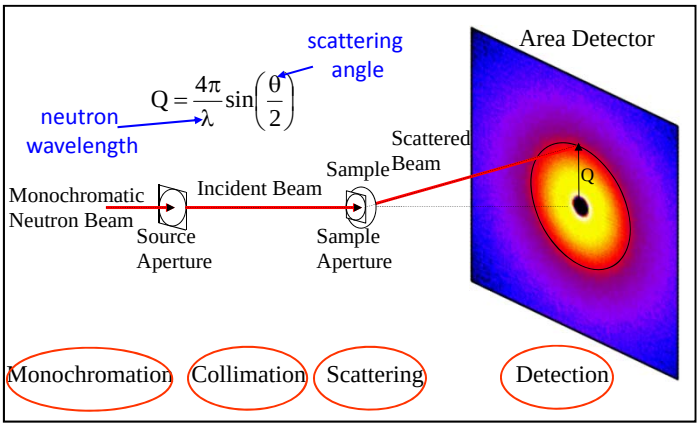
1 – The SANS Technique

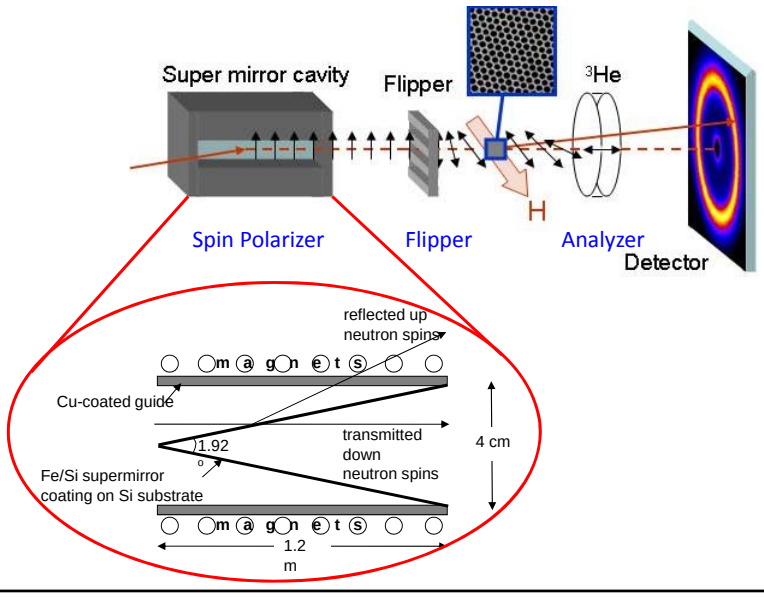
The NIST Center For Neutron Research



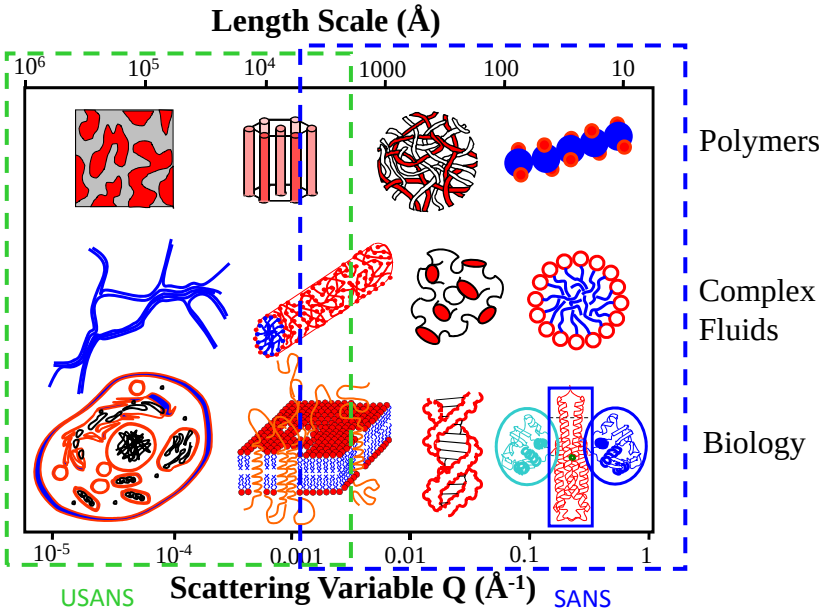
Small-Angle Neutron Scattering



Spin Polarization



Nanoscale Structures



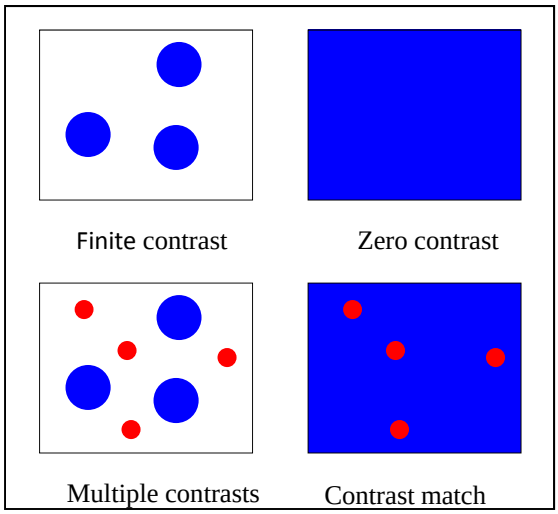
SANS Cross Sections

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

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

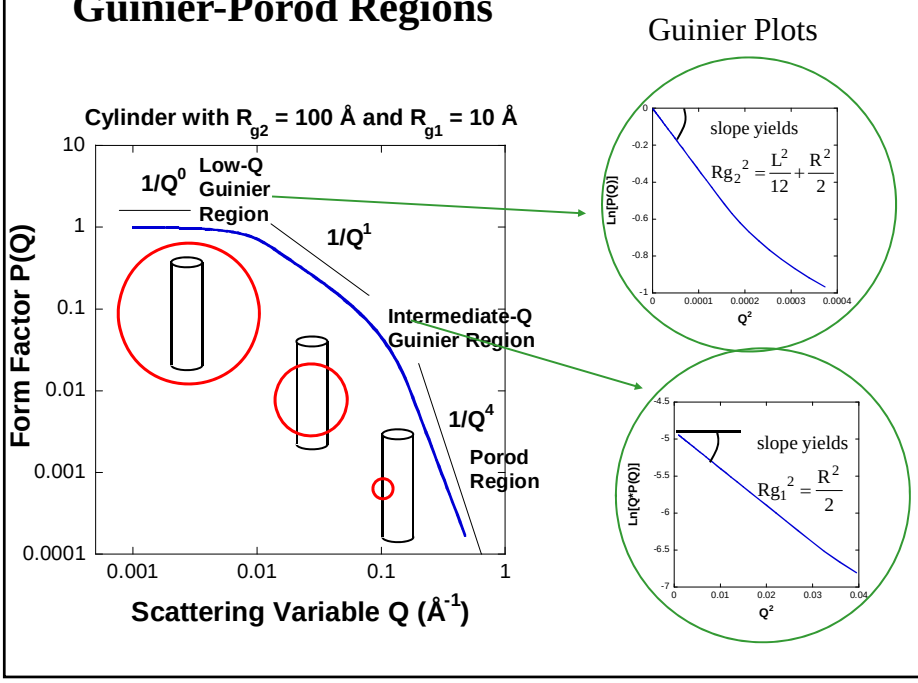


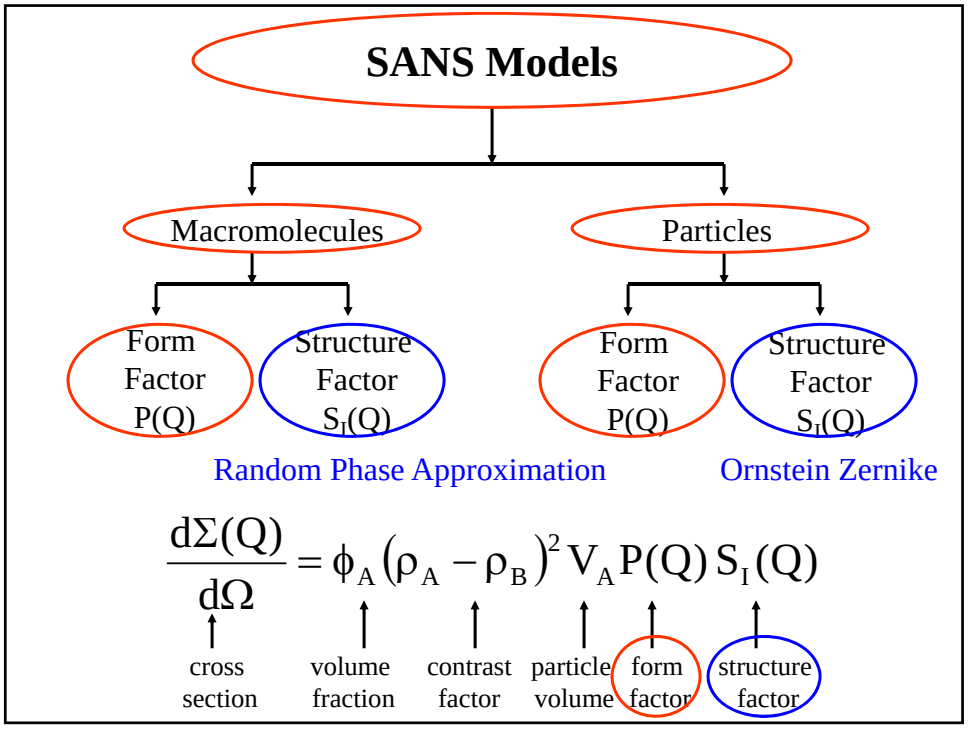
2 –SANS Data Analysis

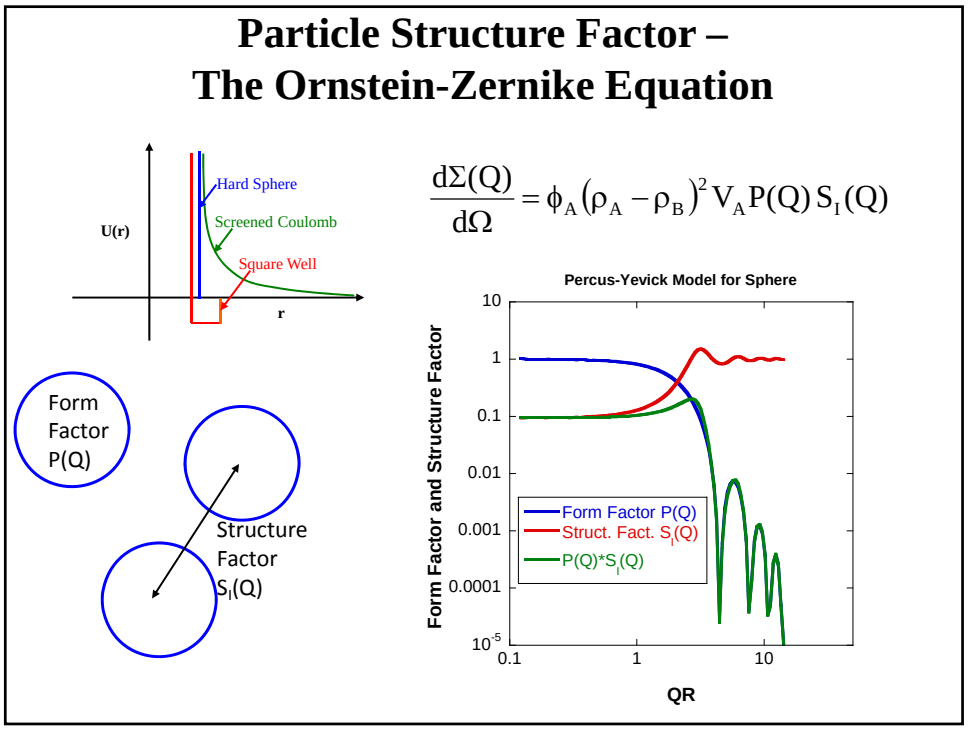
SANS Data Analysis

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

Guinier-Porod Regions



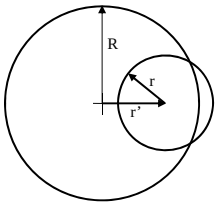

SANS Models
Macromolecules
Particles
Form Factor P(Q)
Structure Factor $S_I(Q)$
Form Factor P(Q)
Structure Factor $S_I(Q)$
Random Phase Approximation
Ornstein Zernike
$\frac{d\Sigma(Q)}{d\Omega} = \phi_A(\rho_A - \rho_B)^2 V_A P(Q) S_I(Q)$
cross section
volume fraction
contrast factor
particle volume
form factor
structure factor


Particle Structure Factor –
The Ornstein-Zernike Equation
U(r)
r
Hard Sphere
Screened Coulomb
Square Well
Form Factor P(Q)
Structure Factor $S_I(Q)$
$\frac{d\Sigma(Q)}{d\Omega} = \phi_A(\rho_A - \rho_B)^2 V_A P(Q) S_I(Q)$
Percus-Yevick Model for Sphere
Form Factor and Structure Factor
QR
Form Factor P(Q)
Struct. Fact. $S_I(Q)$
P(Q)*S_I(Q)

Fourier Transform

Density-density correlation function:

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

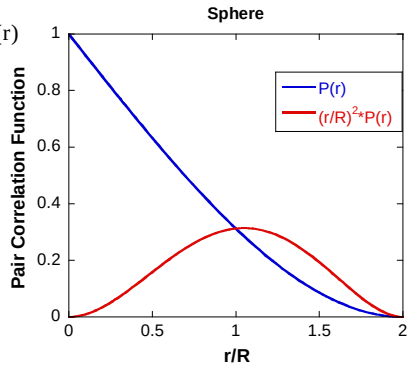


Fourier transform:

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

Radial pair correlation function:

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



3. SANS Research Topics

A- Phase Transitions in Pluronic P85 Solutions

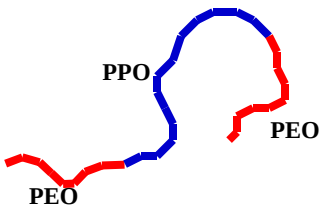
B- Structure of SDS Micelles

C- Polymer Co-solvation and Co-nonsolvation

A - Phase Transitions in Pluronic P85 Solutions

Pluronics

Dissolved Unimer
(low temperature)

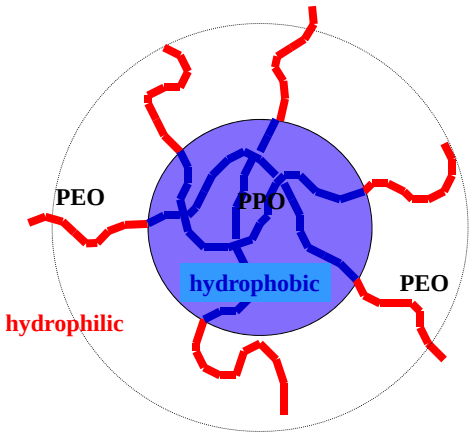


EO:$-CH_2CH_2-O-$

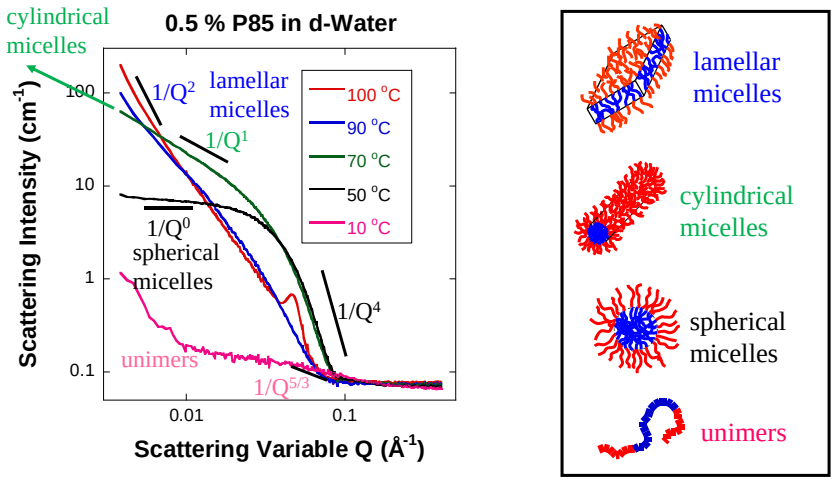
PO:$-CH(CH_3)CH_2-O-$

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

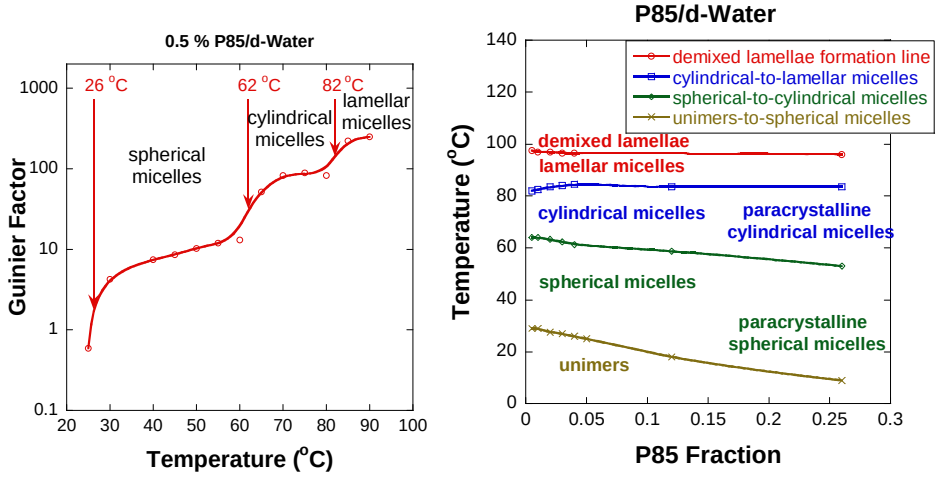
Formed Micelle
(high temperature)



Pluronic Micelles



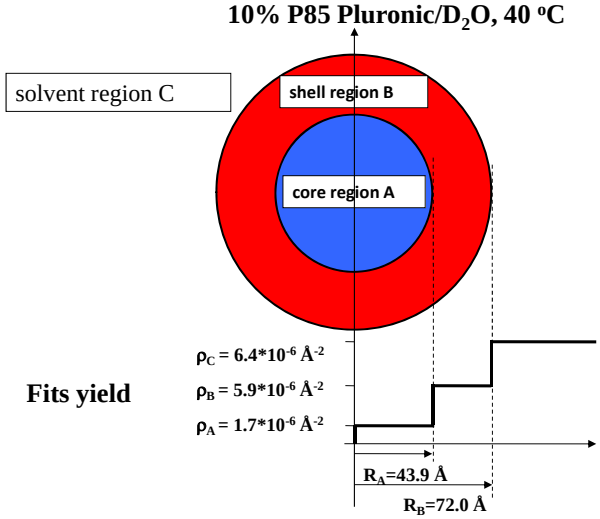
Phase Diagram



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



Fits yield

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 °C:

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

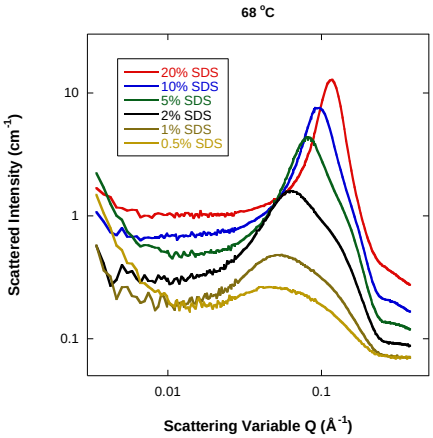
In the shell:
2,943 PEO monomers
34,167 D_2O molecules

B- Structure of SDS Micelles

Micelle Formation

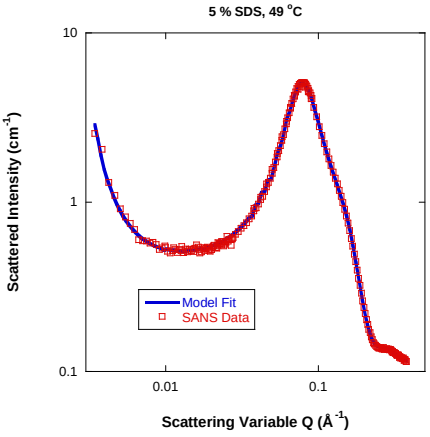
- Surfactants are formed of a hydrophilic head and a hydrophobic tail
- Micelles form when enough surfactants aggregate (above the critical micelle concentration or CMC)
- SDS surfactants form micelles in water (or deuterated water)

SANS from SDS Micelles



- Ellipsoidal micelles form

Ellipsoid Micelles Model Fit

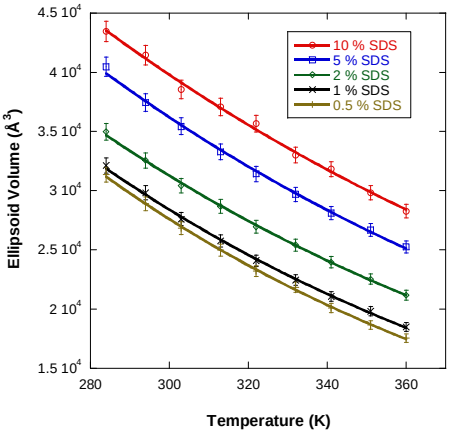


$$I(Q) = \frac{A}{Q^n} + \left[\frac{d\Sigma(Q)}{d\Omega}\right]_{ellipsoids} + B$$

$$\left[\frac{d\Sigma(Q)}{d\Omega}\right]_{ellipsoids} = \phi\Delta\rho^2 V_P P(Q) S_1(Q)$$

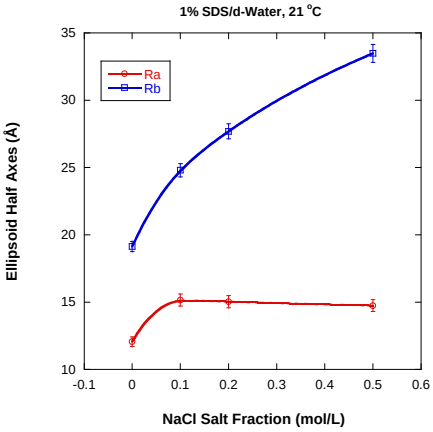
- Power law (low-Q) + ellipsoidal micelles (high-Q) model fits well

Some Fit Results



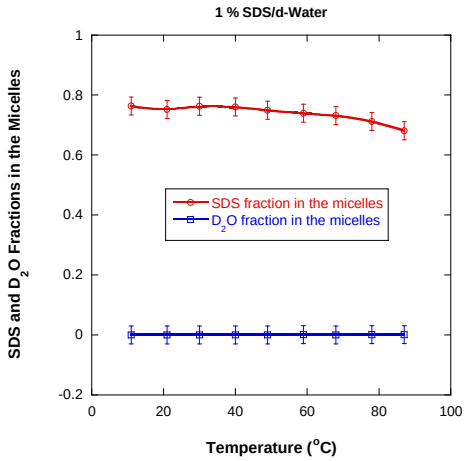
- Micelles become smaller at higher temperatures and lower volume fraction

More Fit Results



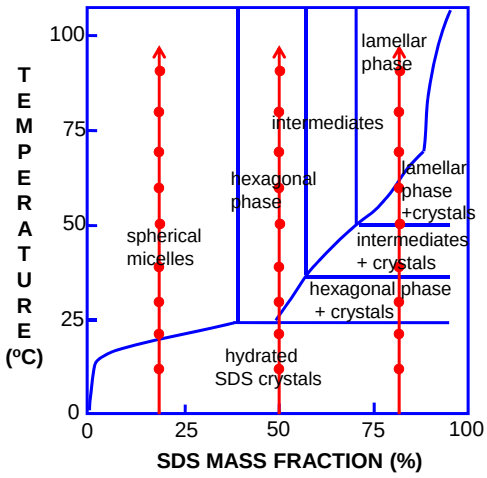
- Salt addition affects lateral growth only

Material Balance Equations



- SDS surfactant fraction remains constant above the CMC

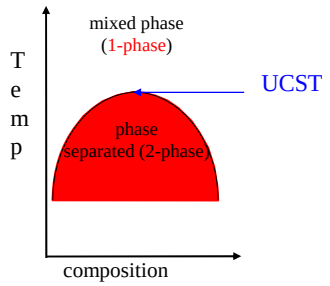
Phase Diagram



- SDS/water phase diagram from calorimetry

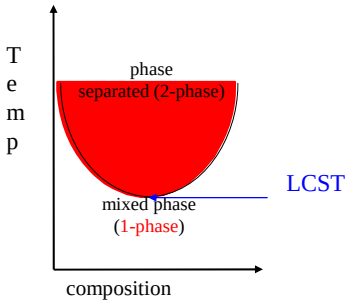
C- Polymer Co-solvation and Co-nonsolvation

Polymer Demixing Phase Transitions



UCST

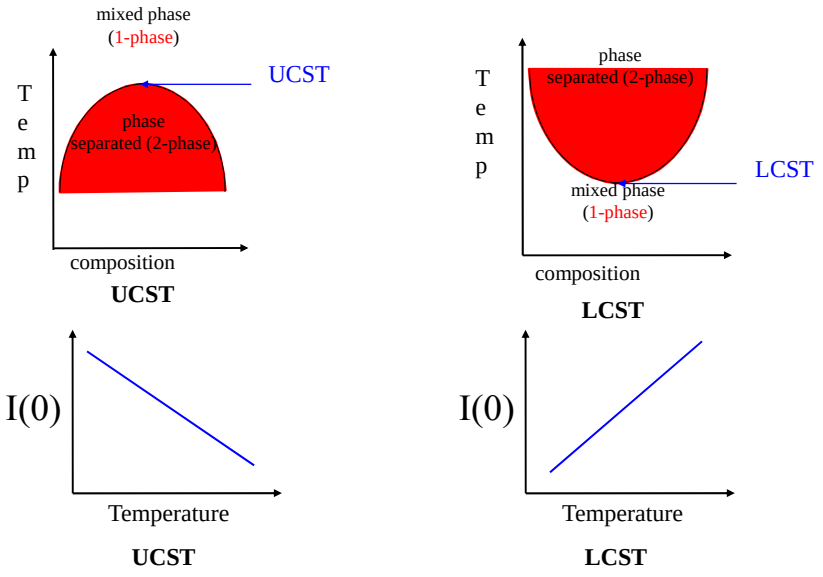
Upper Critical Solution Temp.



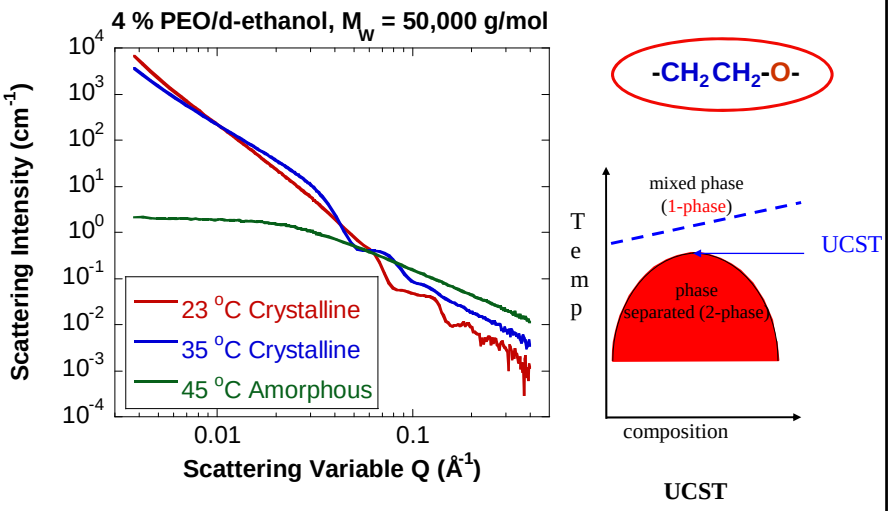
LCST

Lower Critical Solution Temp.

Polymer Demixing Phase Transitions

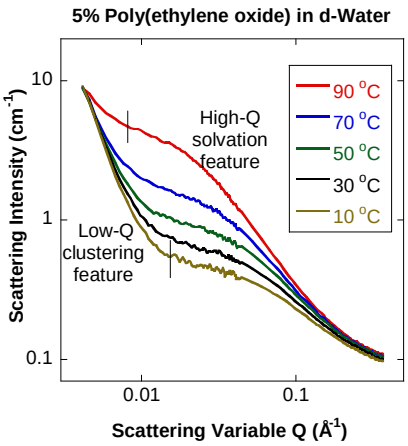


Poly(ethylene oxide) in d-ethanol



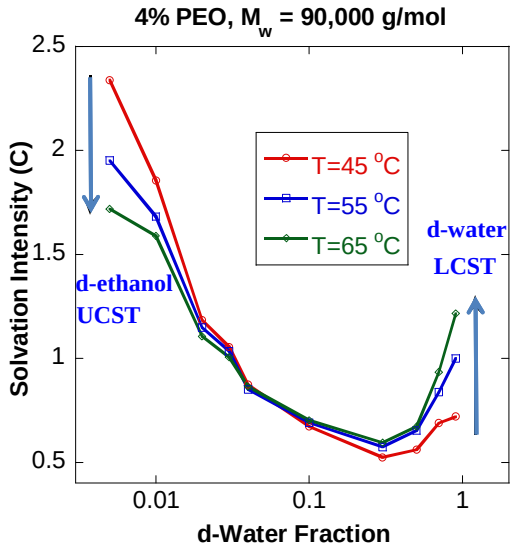
Upper Critical Spinodal Temperature

Poly(ethylene oxide) in d-water

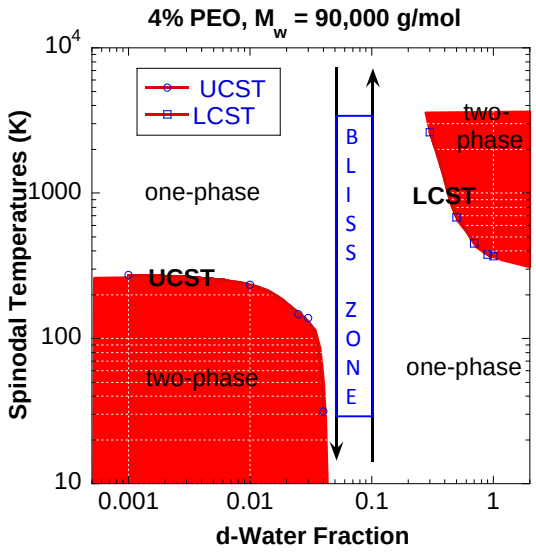


Lower Critical Spinodal Temperature

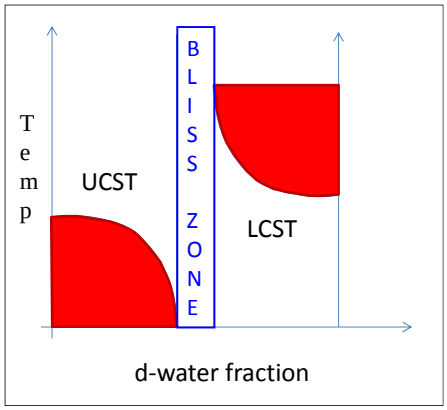
PEO in d-ethanol/d-water Mixtures



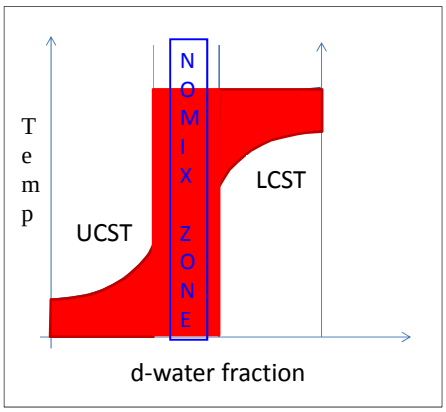
PEO in d-ethanol/d-water Mixtures



Co-solvation and co-nonsolvation

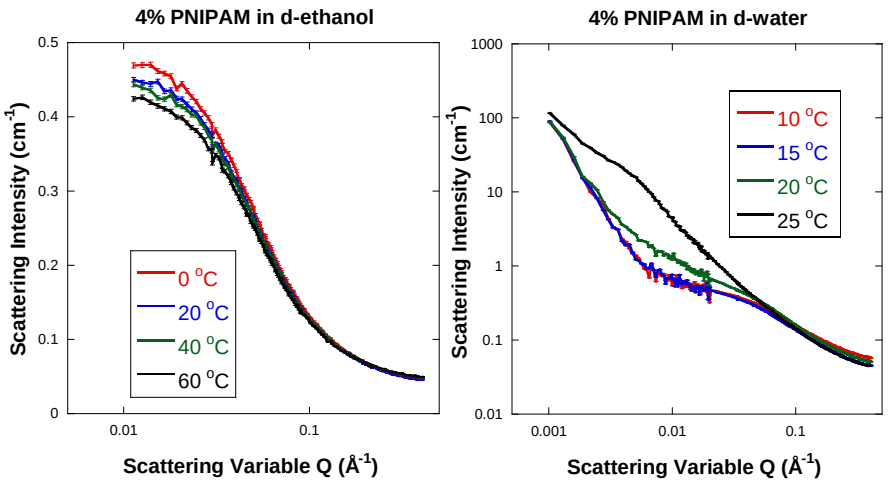


Co-solvation



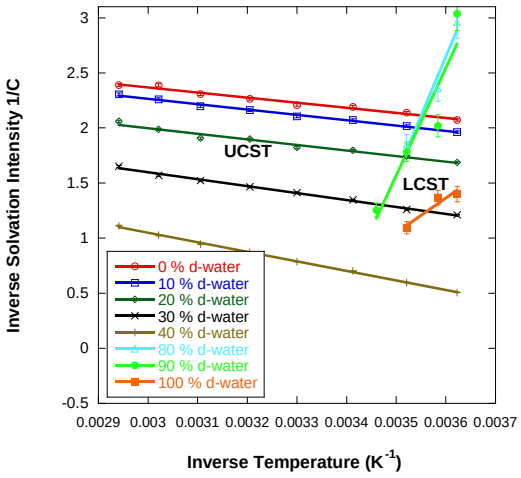
Co-nonsolvation

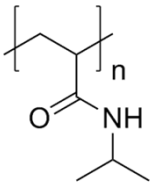
PNIPAM in d-ethanol/d-water Mixtures



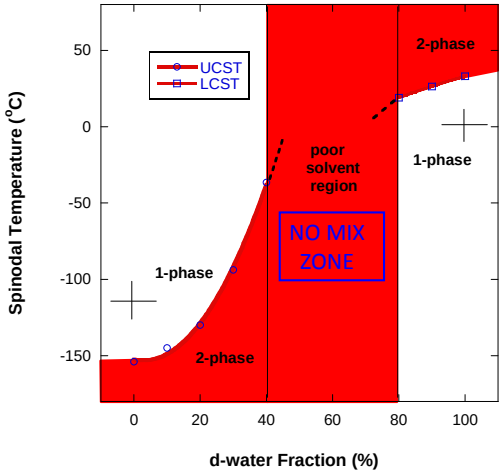
UCST **LCST**

PNIPAM in d-ethanol/d-water Mixtures





PNIPAM in d-ethanol/d-water Mixtures



Results

- Most polymers dissolve better in solvent mixtures (cosolvation)

- PNIPAM is the only known polymer to obey a co-nonsolvation rule

- PEO is characterized by a "perfect" solvation window for 10 % d-water. This corresponds to 10 d-water, 25 d-ethanol molecules per PEO monomer

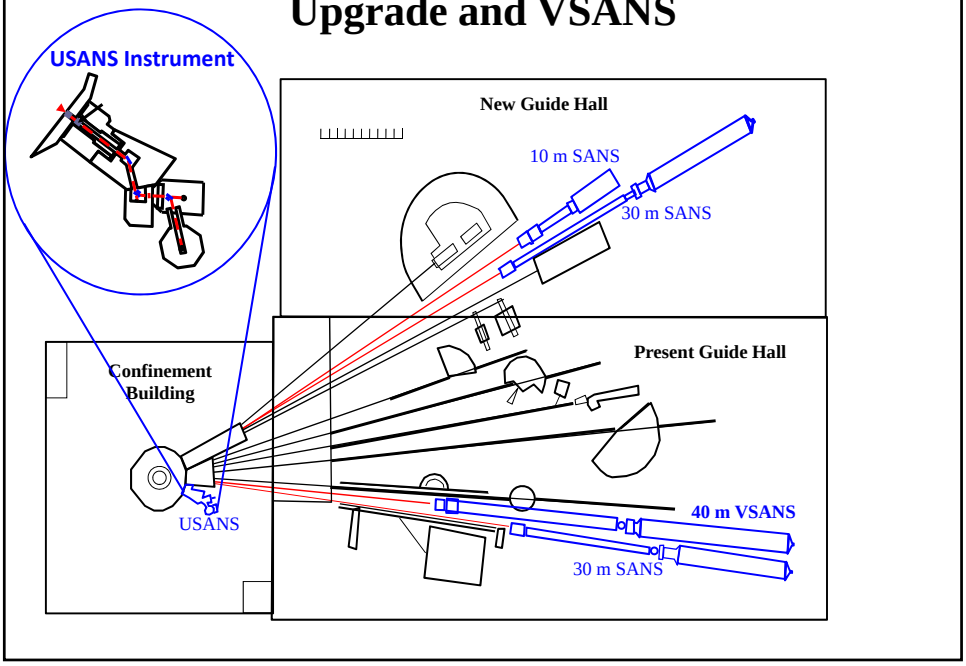
- PNIPAM is characterized by a non-solvation window for 60 % d-water. This corresponds to 2.5 d-water and 4.4 d-ethanol molecules per PNIPAM monomer

- The Random Phase Approximation (RPA) is useful for describing ternary mixtures (polymer/solvent 1/solvent 2)

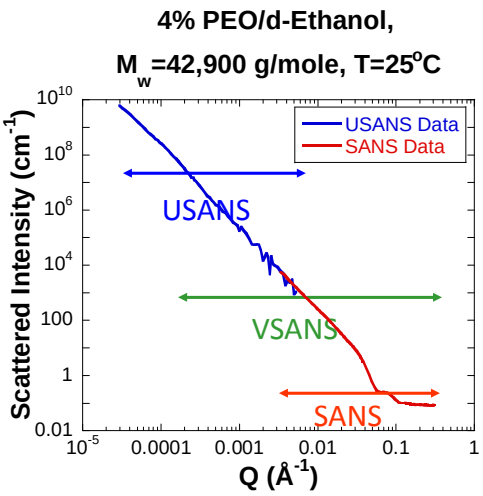
- SANS is a valuable thermodynamic probe to study phase transitions as well as nanostructures

4. Final Points

Upgrade and VSANS



SANS, VSANS and USANS Ranges



Final Words

THE SANS PROGRAM AT NIST

200 experiments per year

15 theses per year

80 publications per year

ACKNOWLEDGMENTS

Steve Kline, Derek Ho, Mike Hore, He Cheng

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