SANS RESEARCH TOPICS

Boualem Hammouda

National Institute of Standards and Technology
Center for Neutron Research

1- Phase Transitions in Pluronic P85 Solutions

2- Structure of SDS Micelles

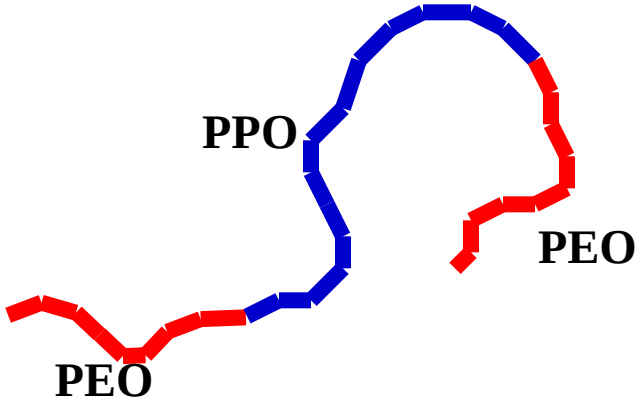
3- Polymer Co-solvation and Co-nonsolvation

4- Final Points

1 - Phase Transitions in Pluronic P85 Solutions

Pluronics

Dissolved Unimer (low temperature)

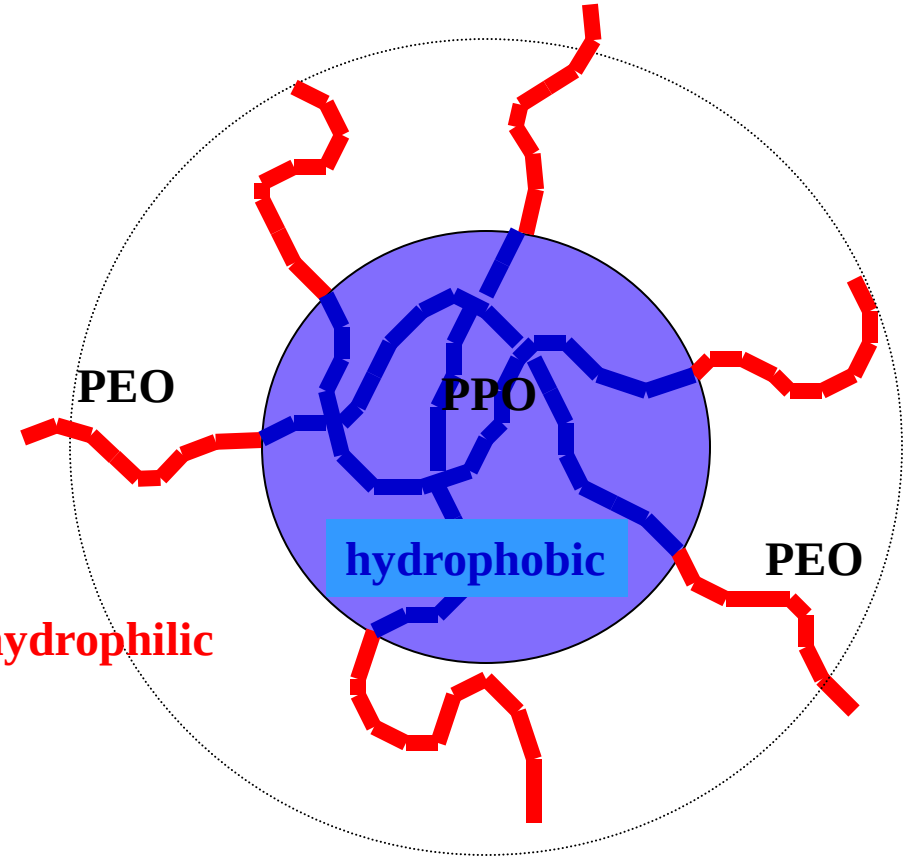


EO:$-CH_2CH_2-O-$

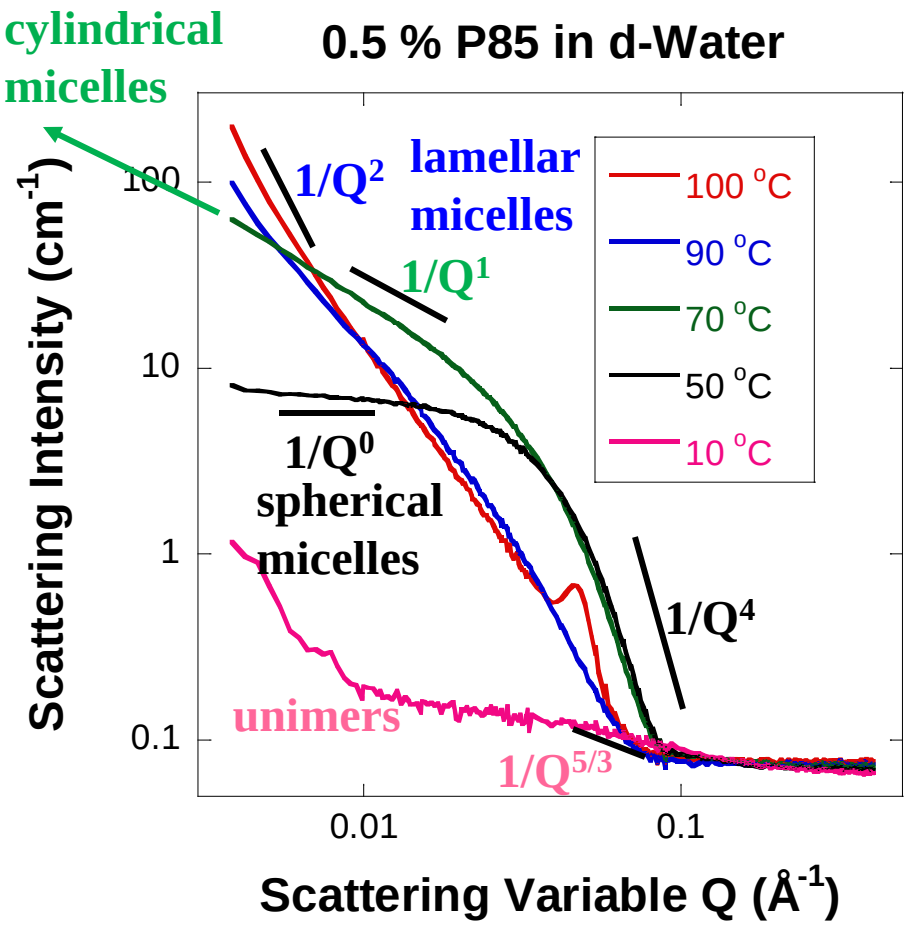
PO:$-CH(CH_3)CH_2-O-$

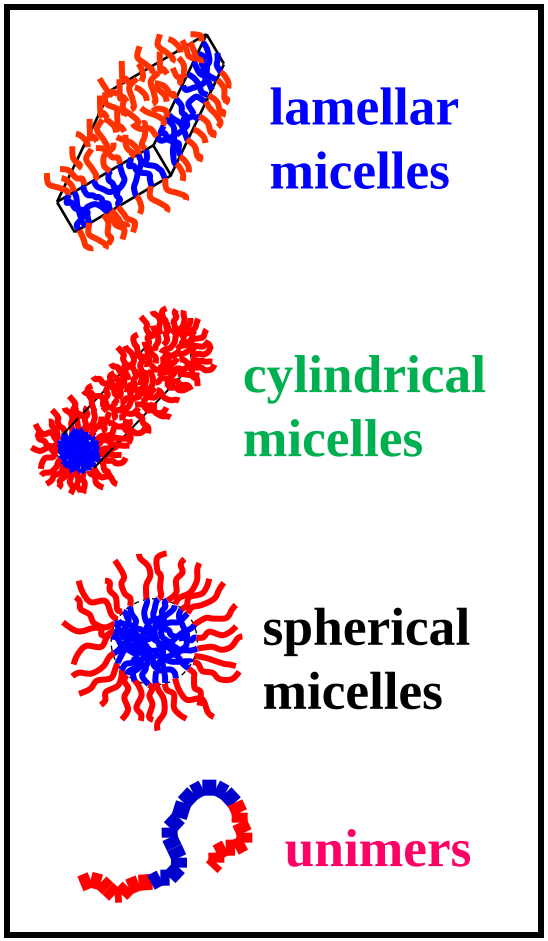
P85: $EO_{26}PO_{40}EO_{26}$

Formed Micelle (high temperature)

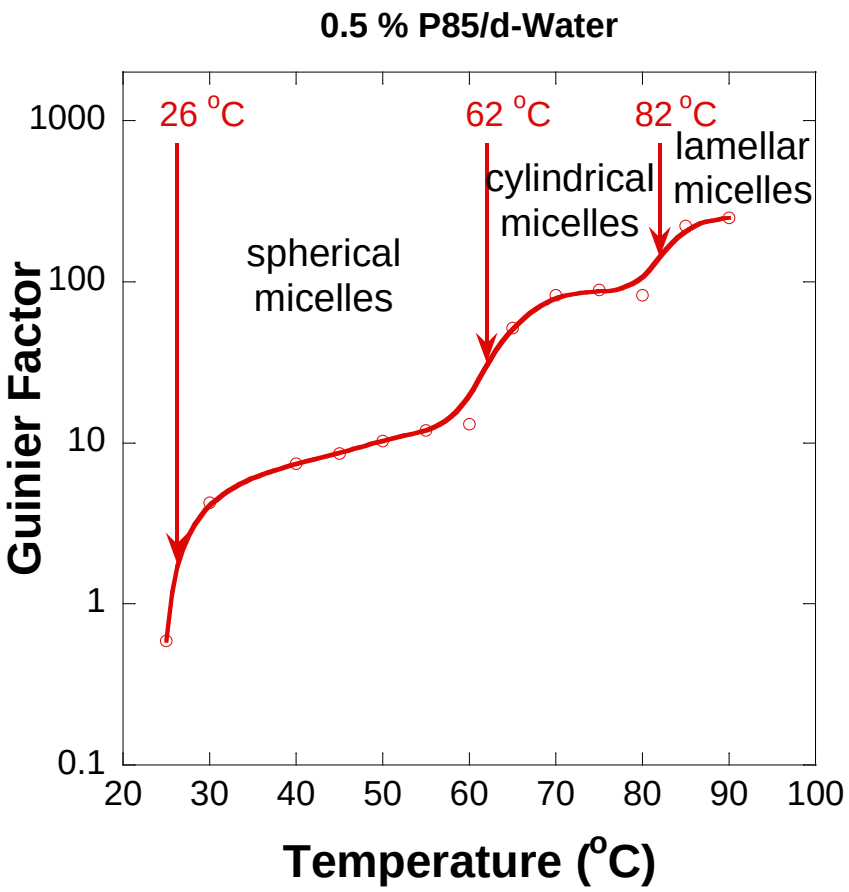


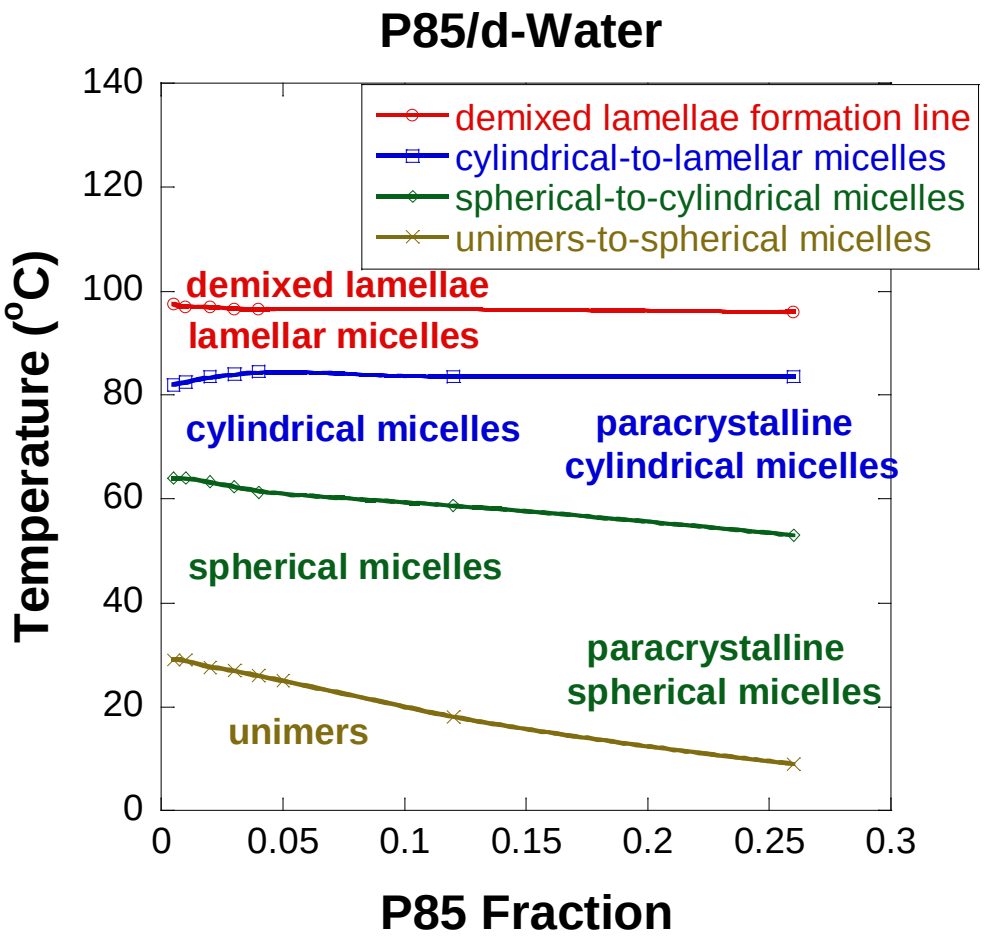
Pluronic Micelles





Phase Diagram

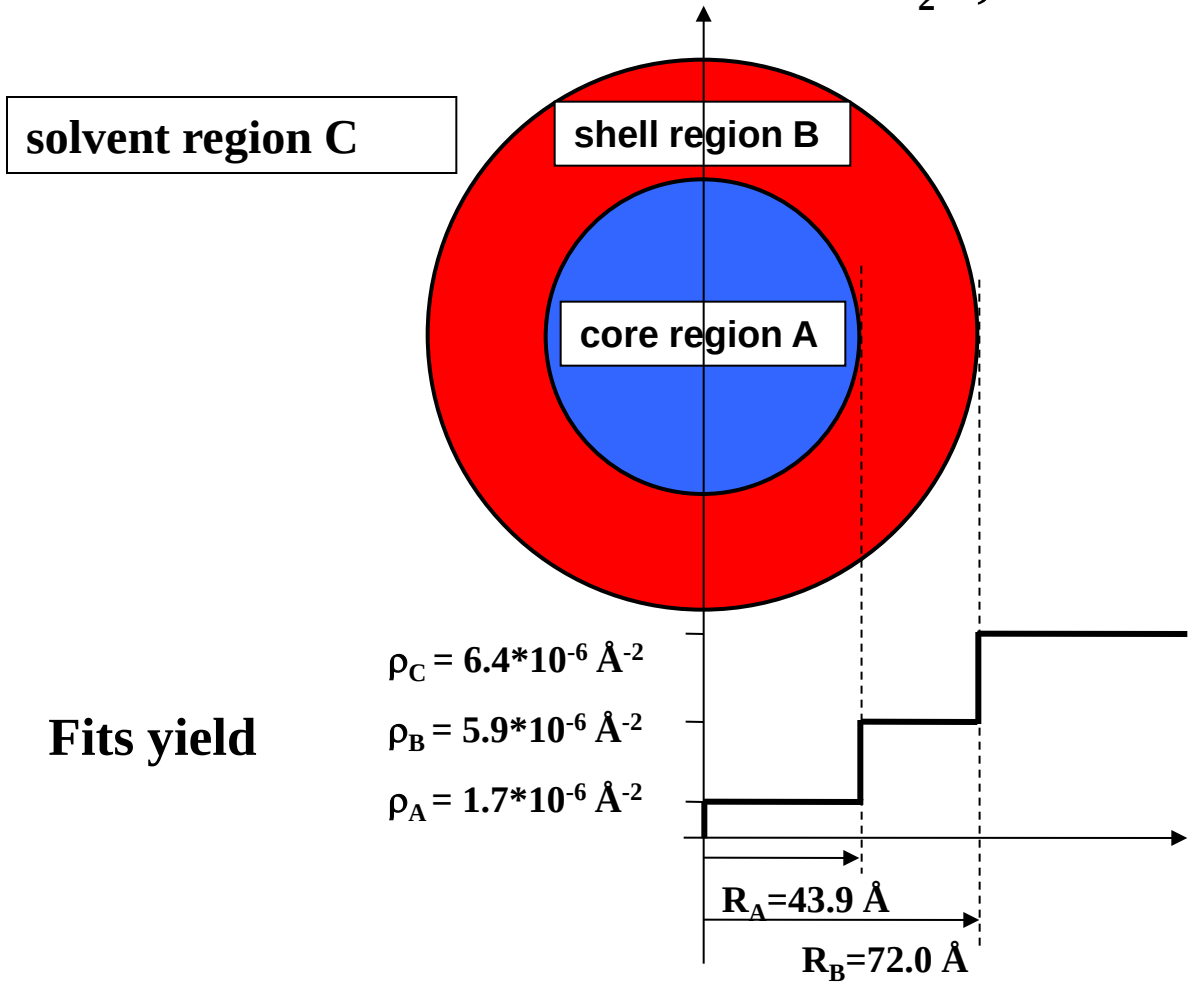




Core-Shell Spherical Particles Model

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

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

2- Structure of SDS Micelles

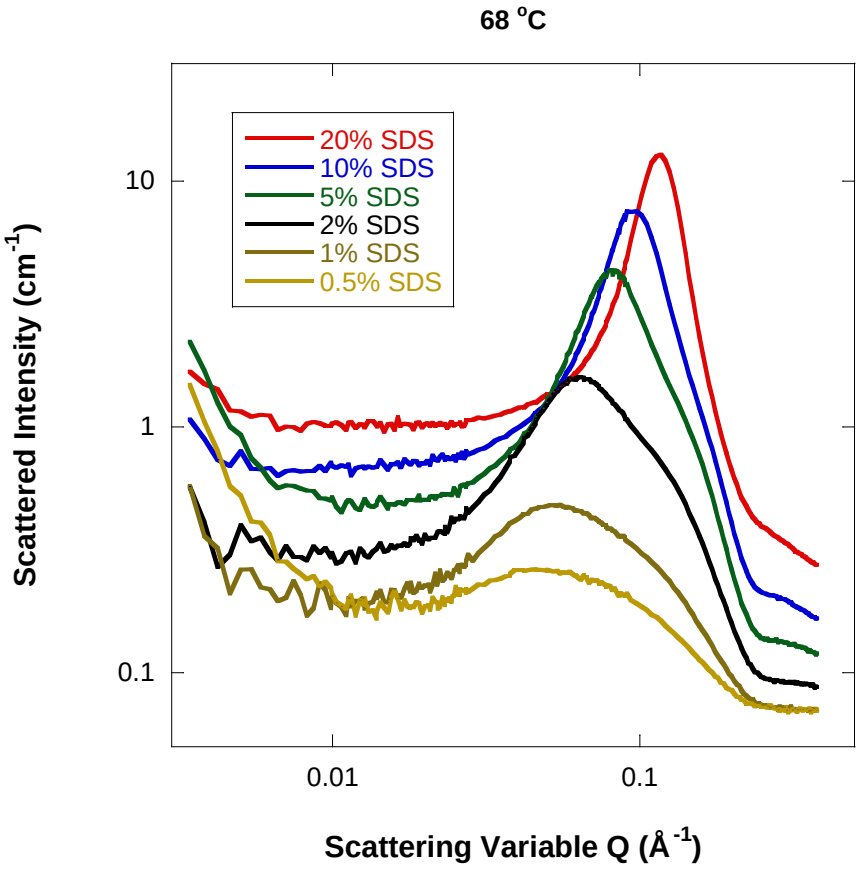
Micelle Formation

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

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

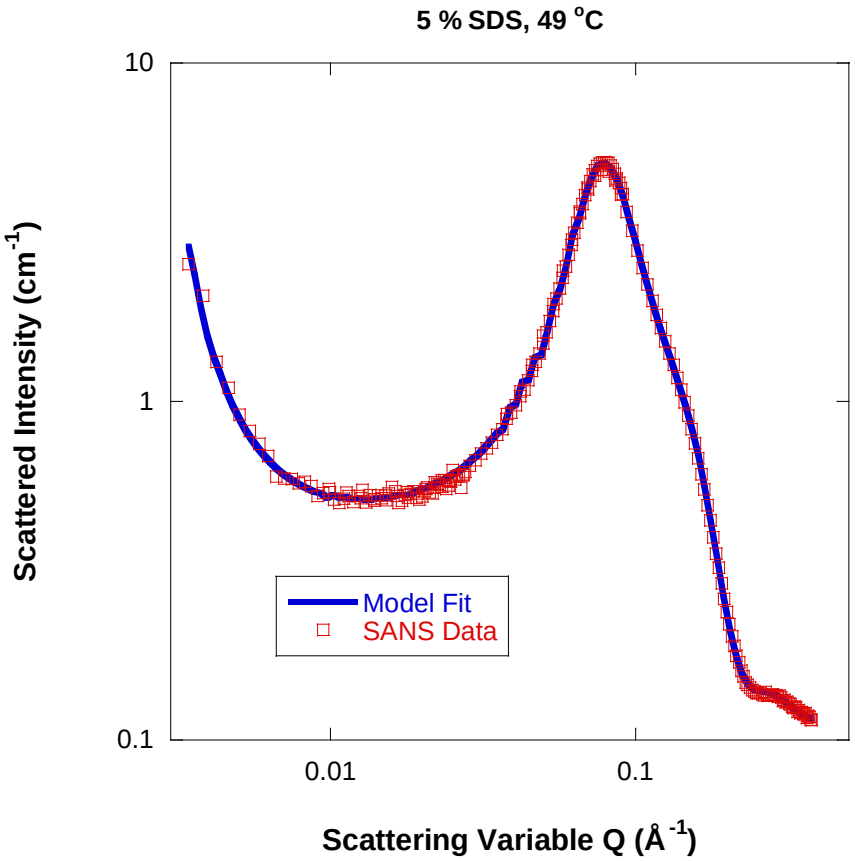
- **SDS surfactants form micelles in water (or deuterated water)**

SANS from SDS Micelles



- **Ellipsoidal micelles form**

Ellipsoid Micelles Model Fit

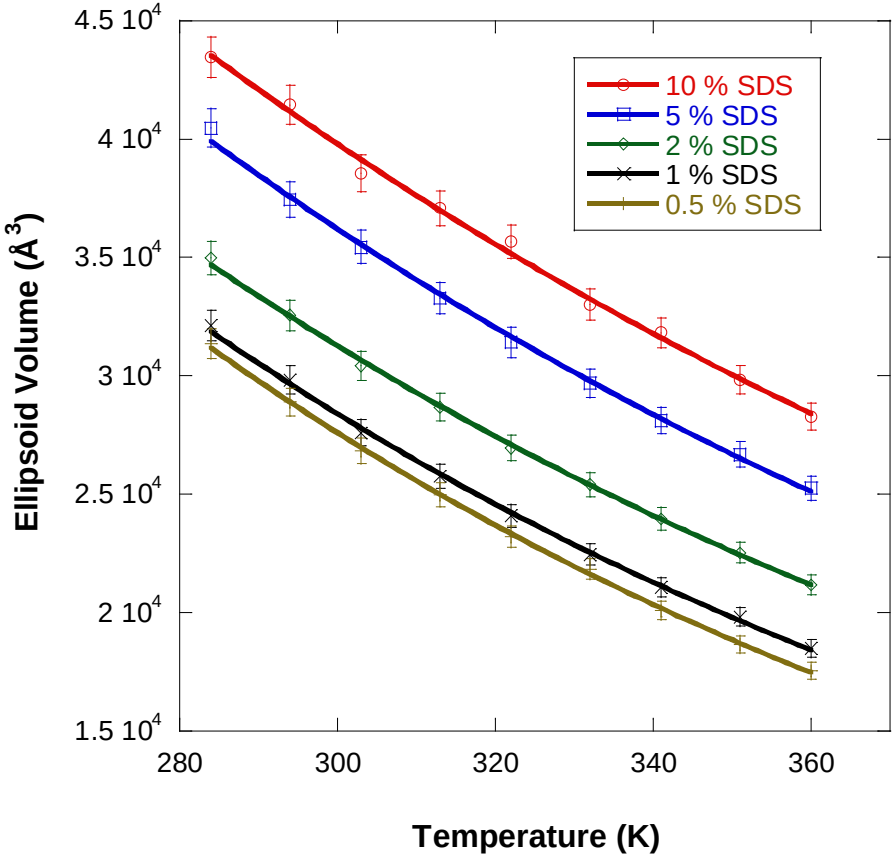


$$I(Q) = \frac{A}{Q^n} + \left[\frac{d\Sigma(Q)}{d\Omega}\right]_{ellipsoids} + B$$

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

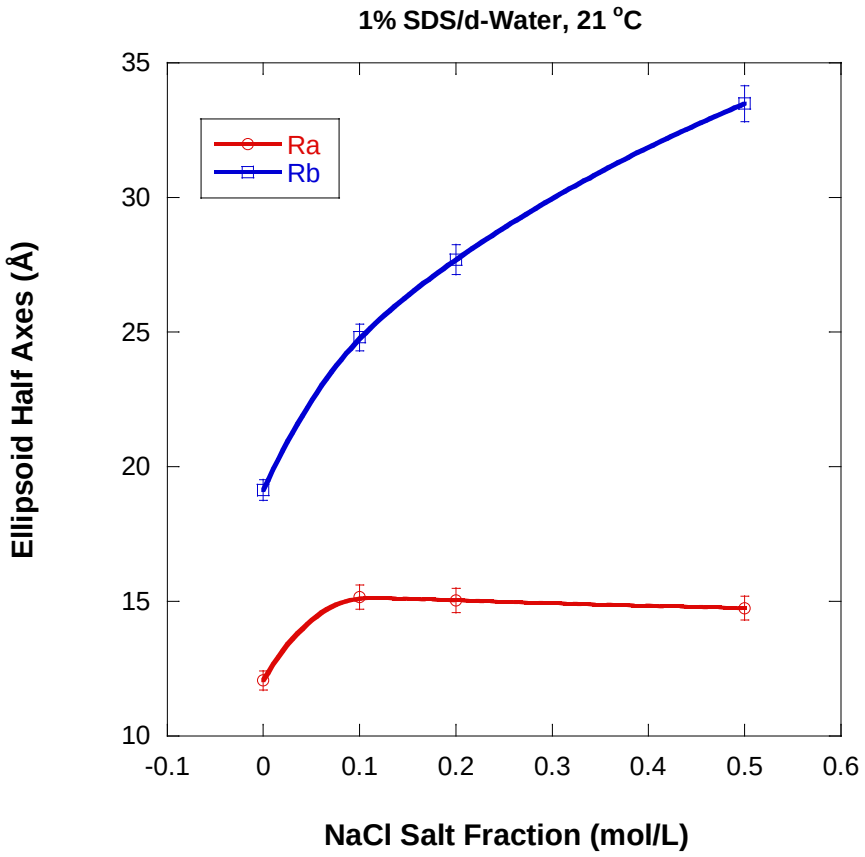
- **Power law (low-Q) + ellipsoidal micelles (high-Q) model fits well**

Some Fit Results



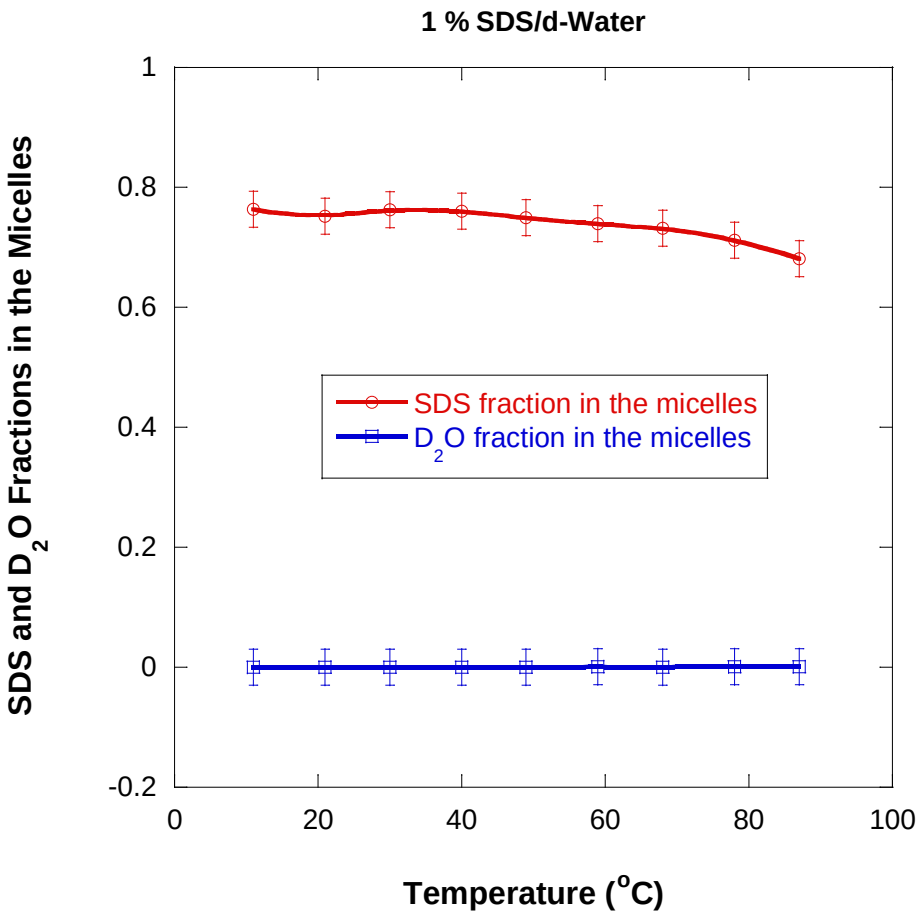
- **Micelles become smaller at higher temperatures and lower volume fraction**

More Fit Results



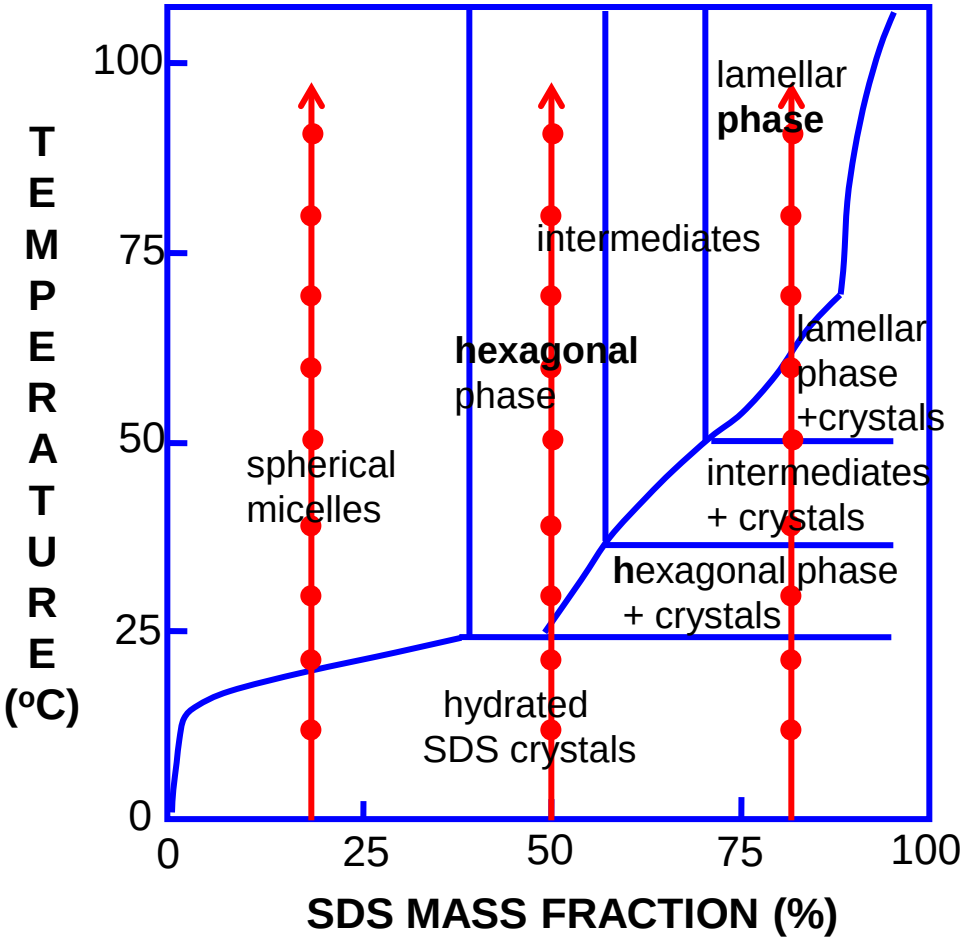
- **Salt addition affects lateral growth only**

Material Balance Equations



- **SDS surfactant fraction remains constant above the CMC**

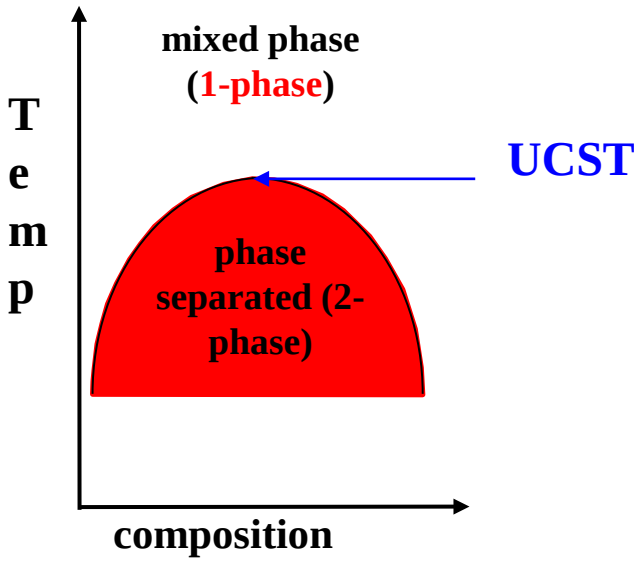
Phase Diagram



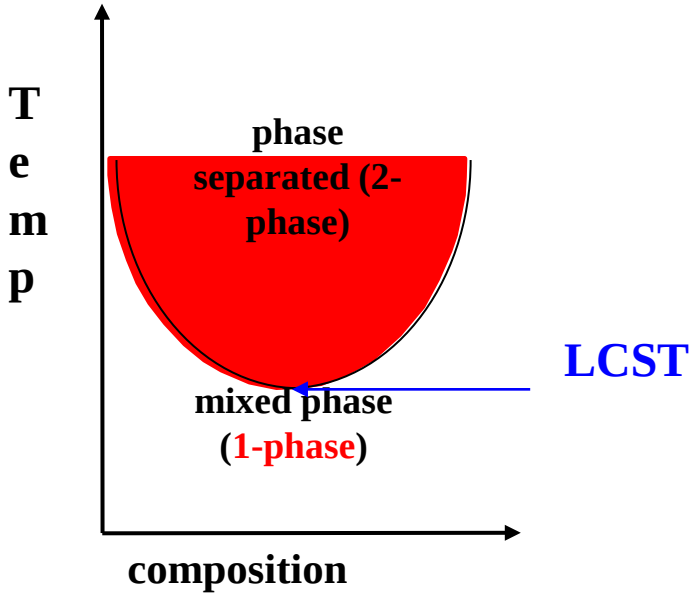
- SDS/water phase diagram from calorimetry

3- Polymer Co-solvation and Co-nonsolvation

Polymer Demixing Phase Transitions



UCST

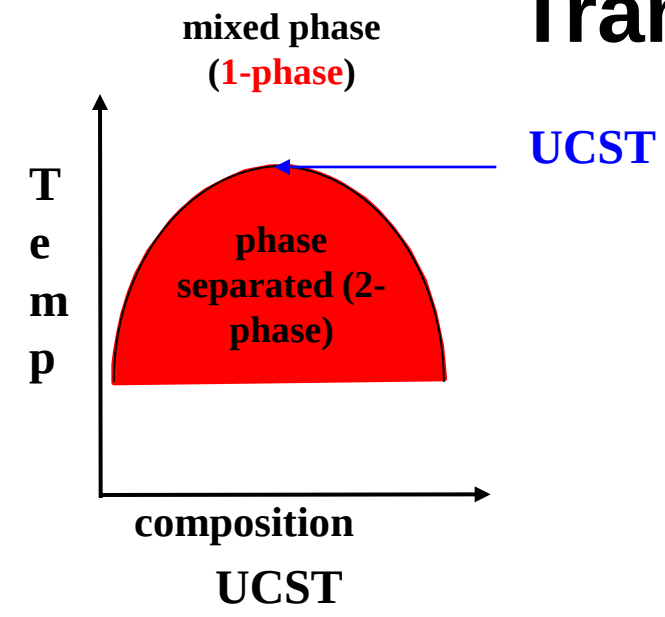


LCST

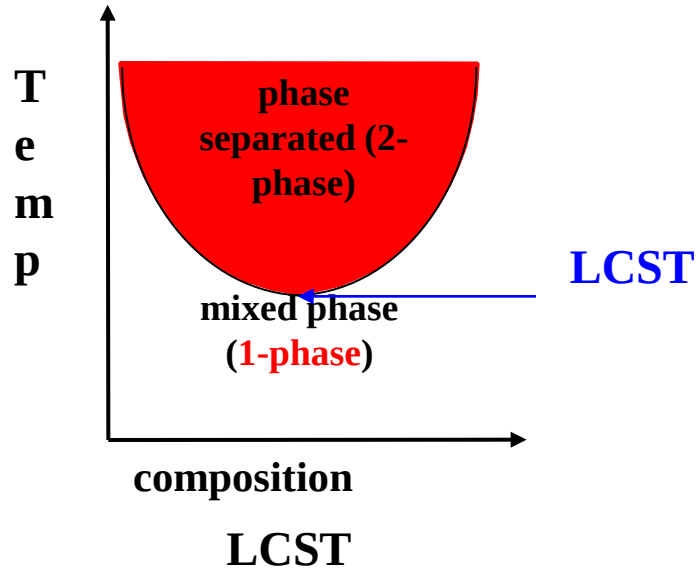
Upper Critical Solution Temp.

Lower Critical Solution Temp.

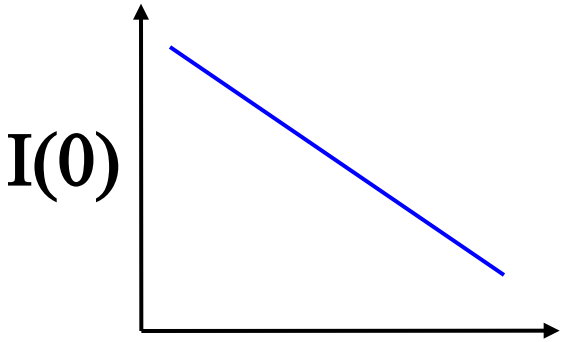
Polymer Demixing Phase Transitions



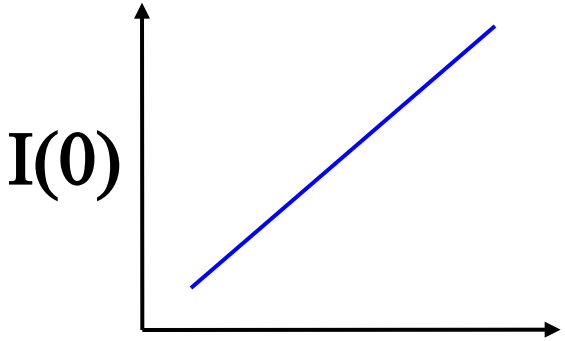
UCST



LCST

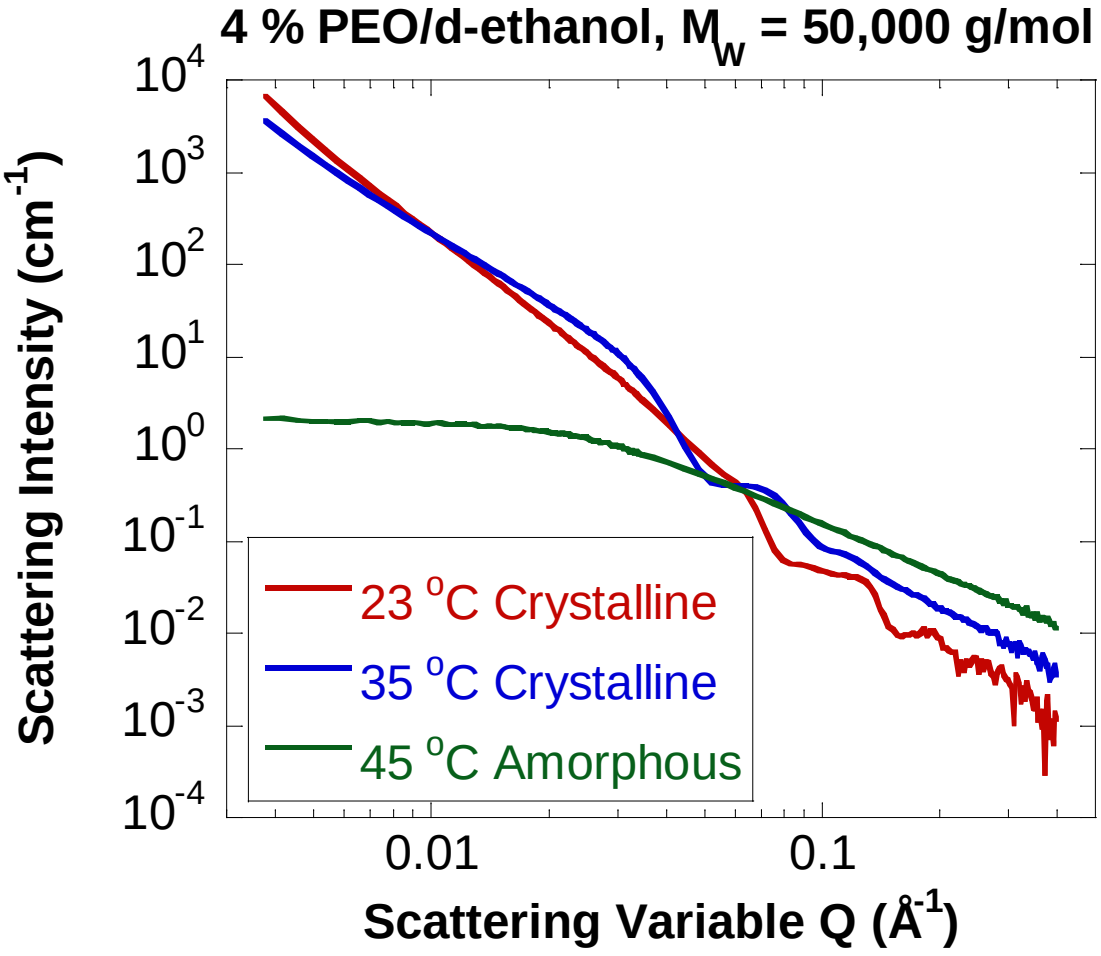


UCST

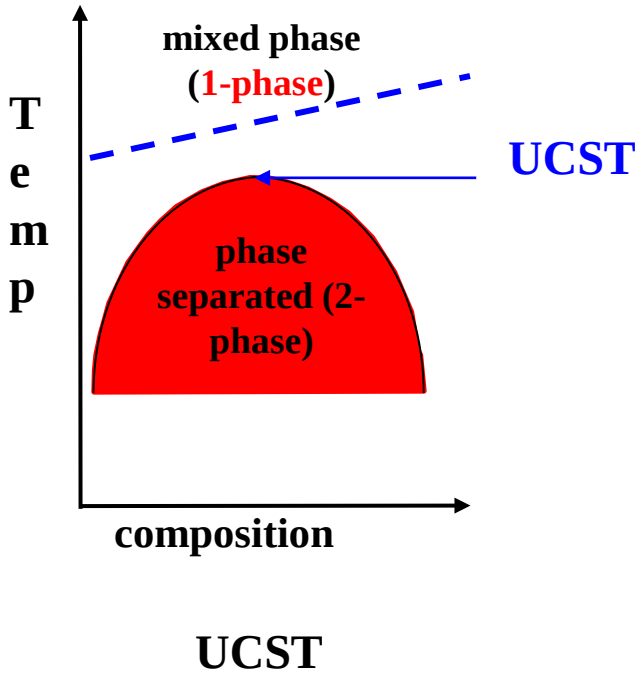


LCST

Poly(ethylene oxide) in d-ethanol



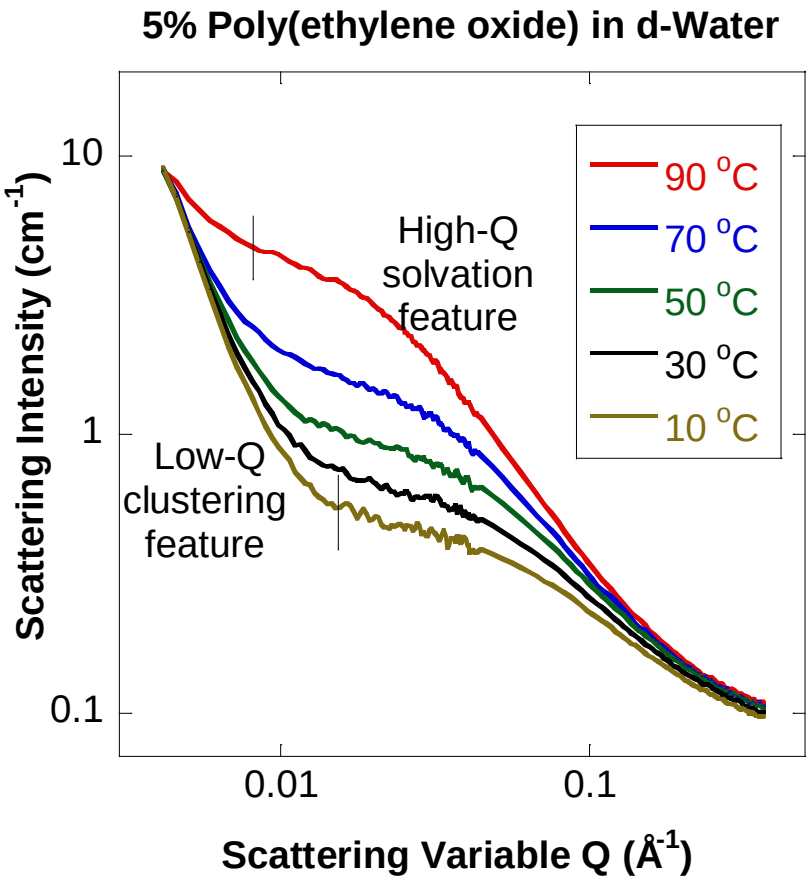
-CH_2CH_2-O-



UCST

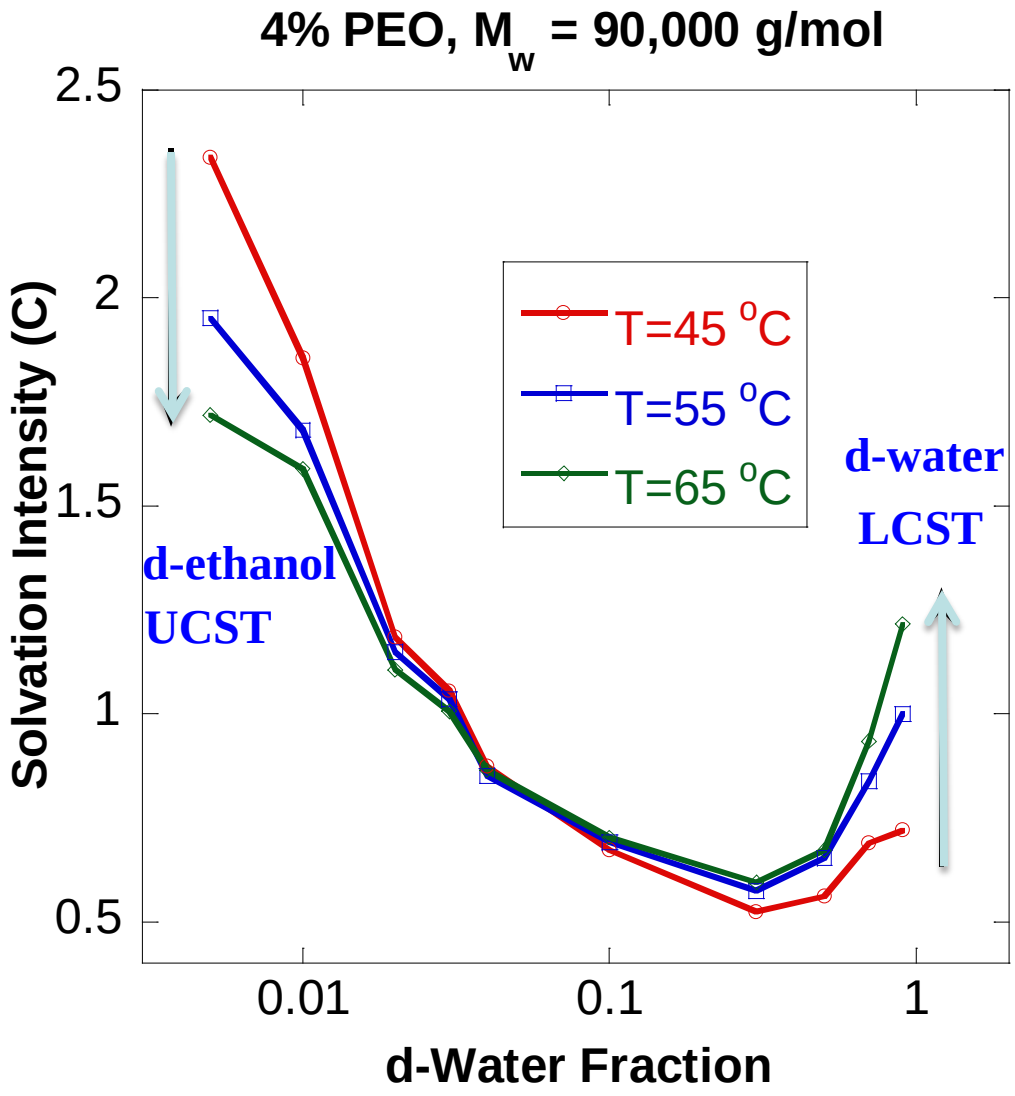
Upper Critical Spinodal Temperature

Poly(ethylene oxide) in d-water

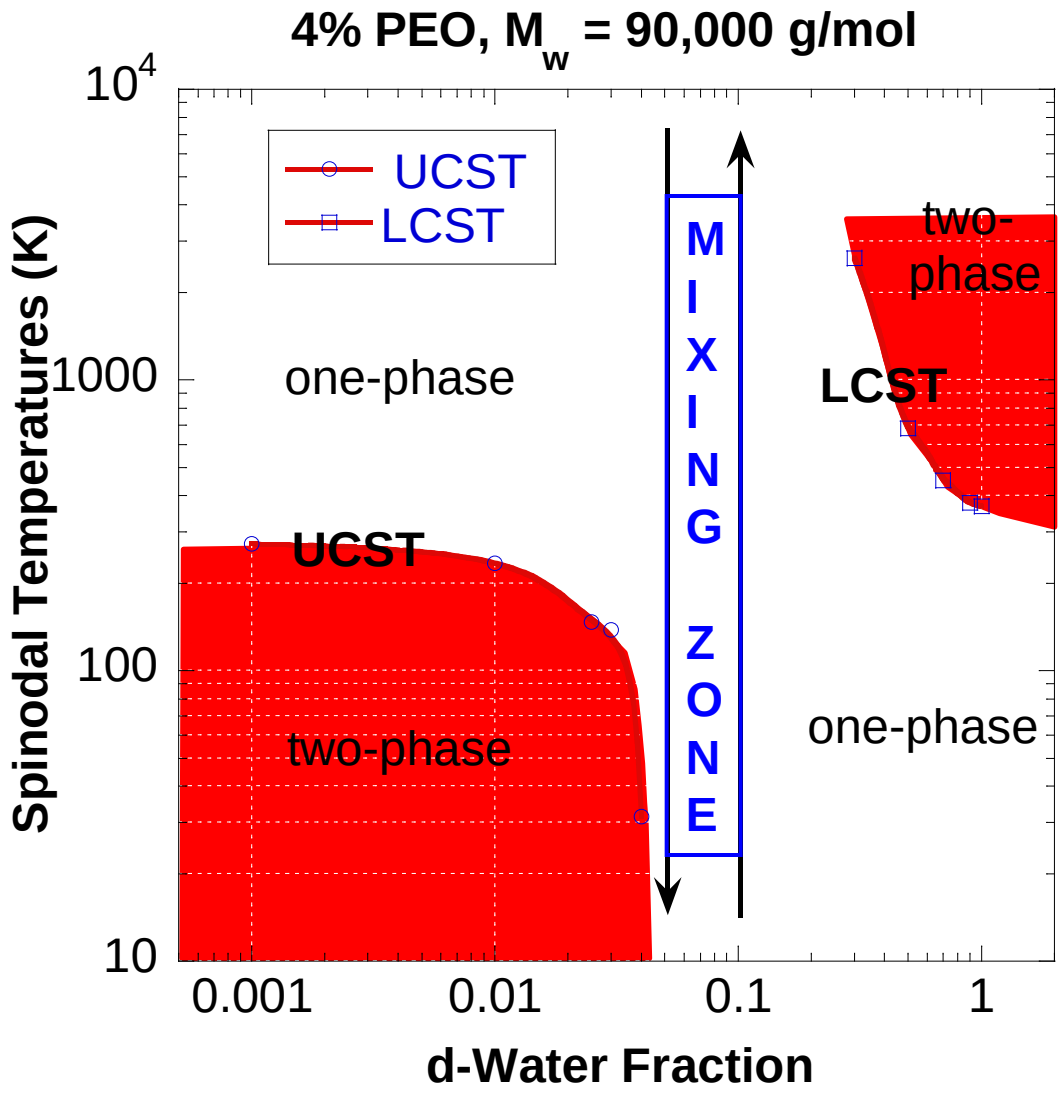


Lower Critical Spinodal Temperature

PEO in d-ethanol/d-water Mixtures

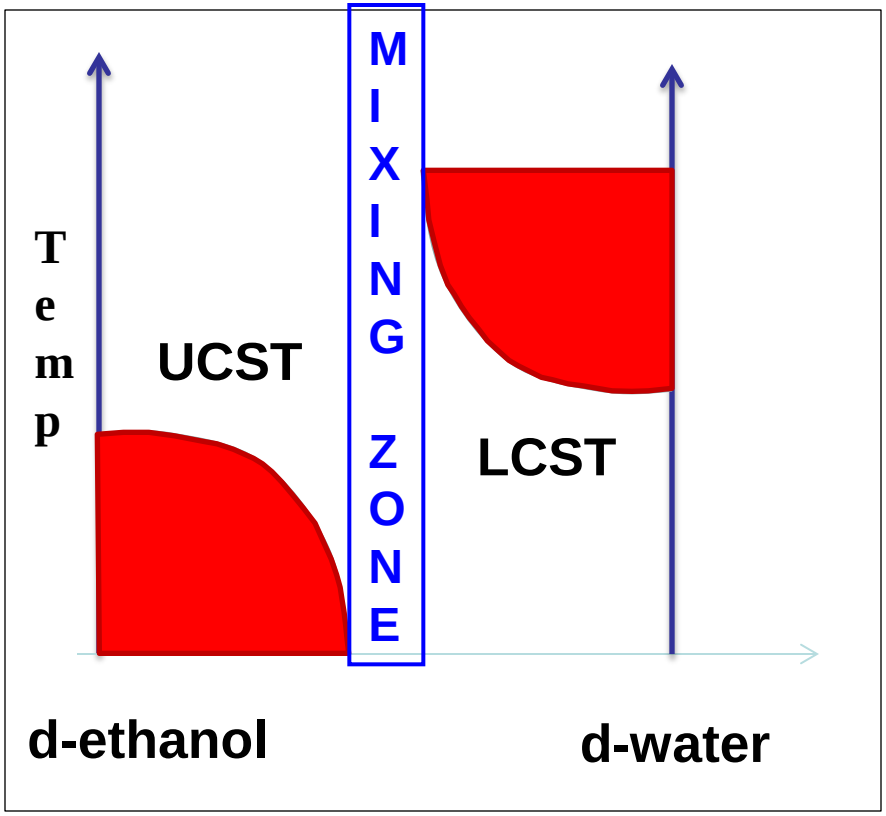


PEO in d-ethanol/d-water Mixtures

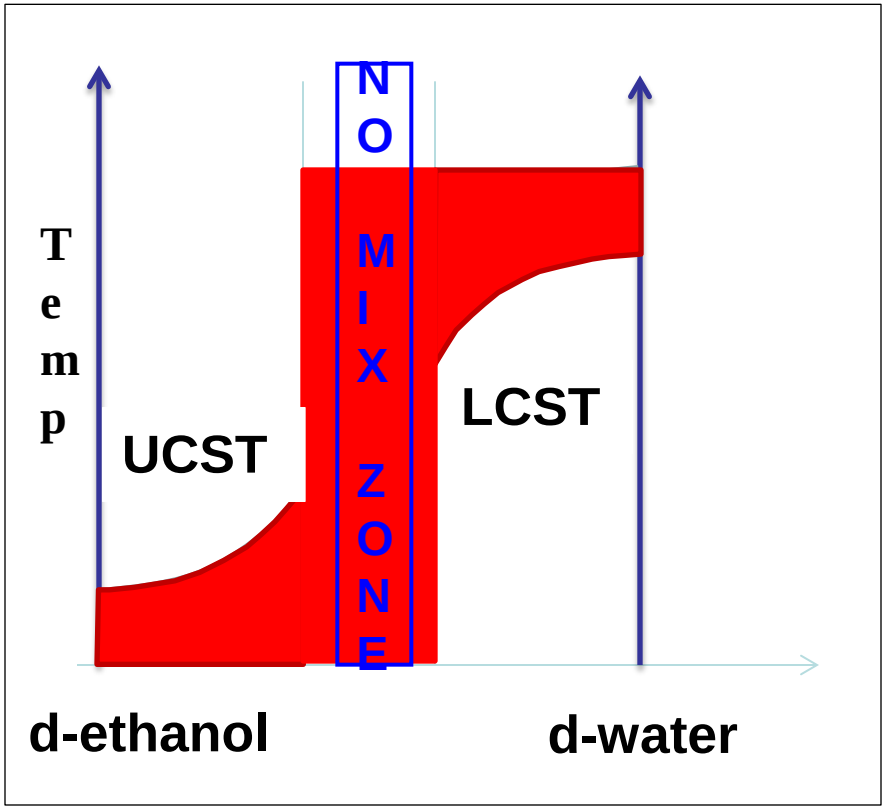


Co-solvation and co-nonsolvation

PEO



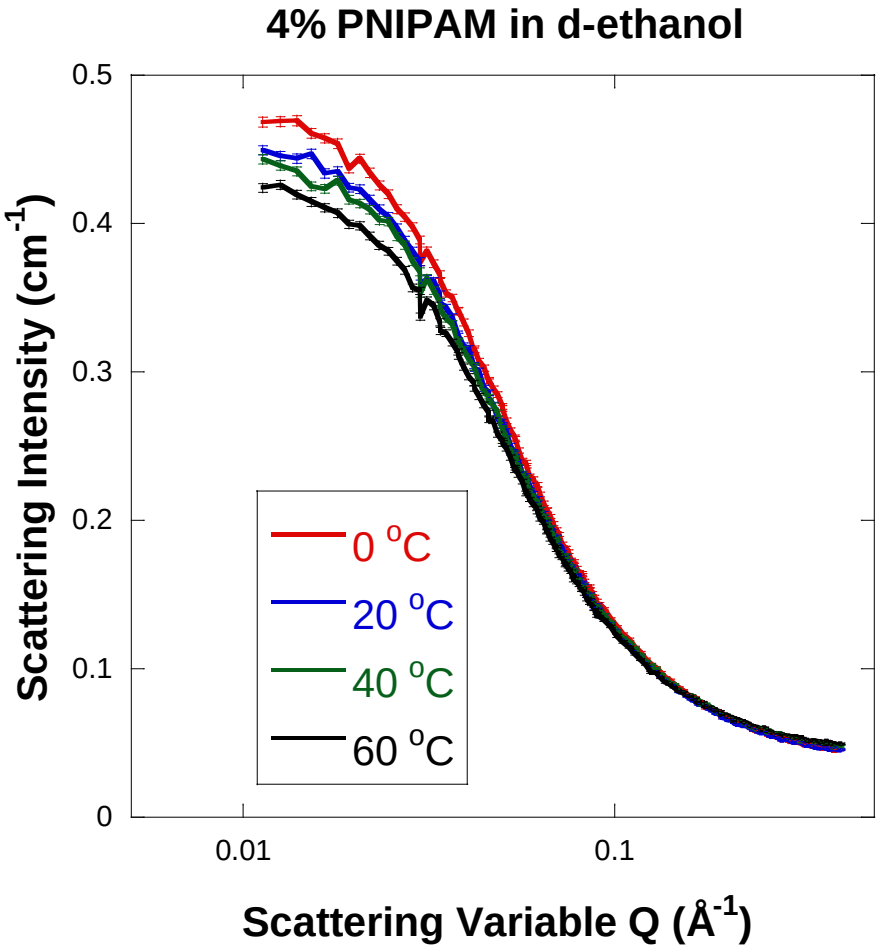
PNIPAM



Co-solvation

Co-nonsolvation

PNIPAM in d-ethanol/d-water Mixtures



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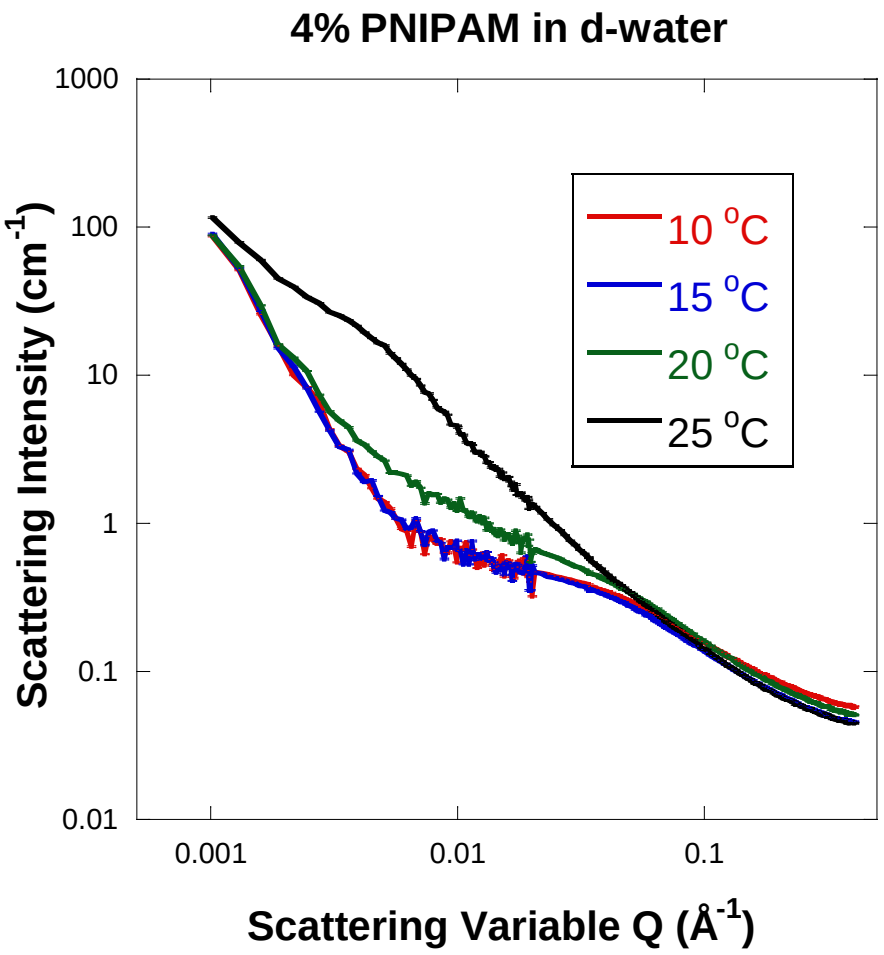
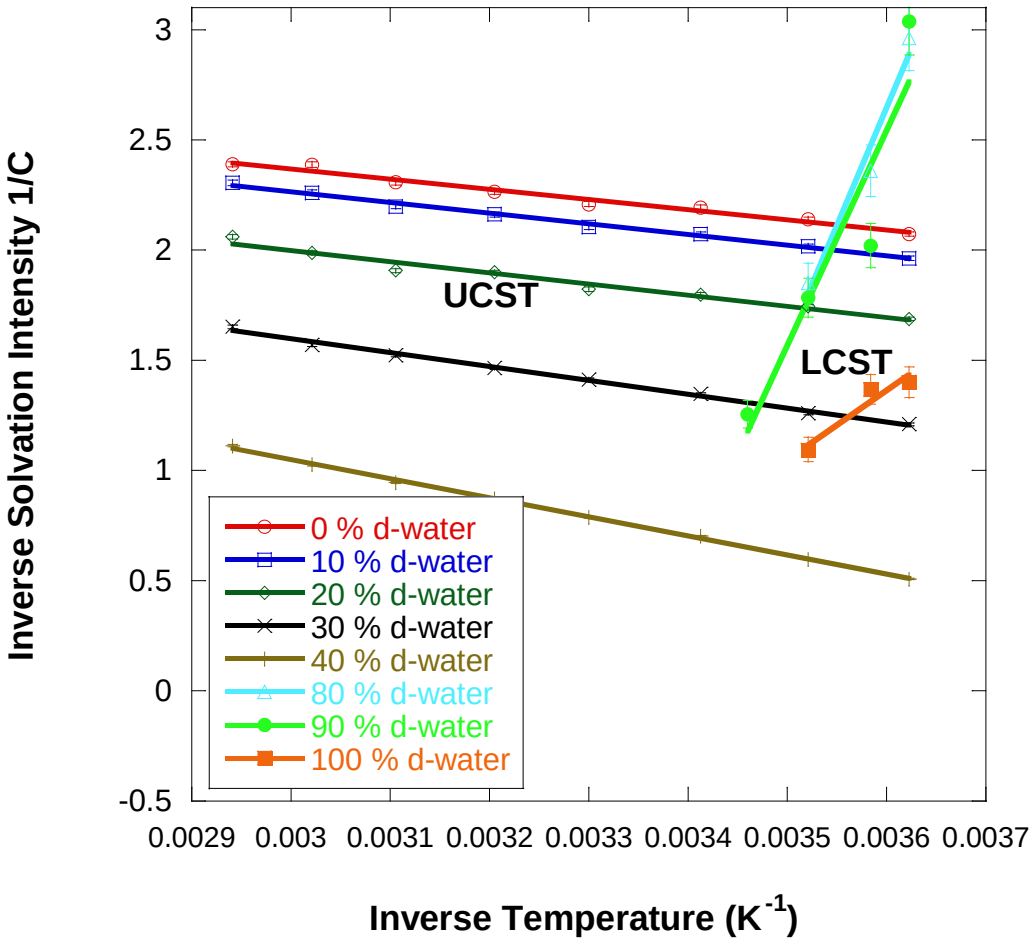
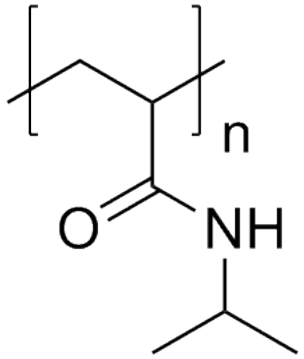


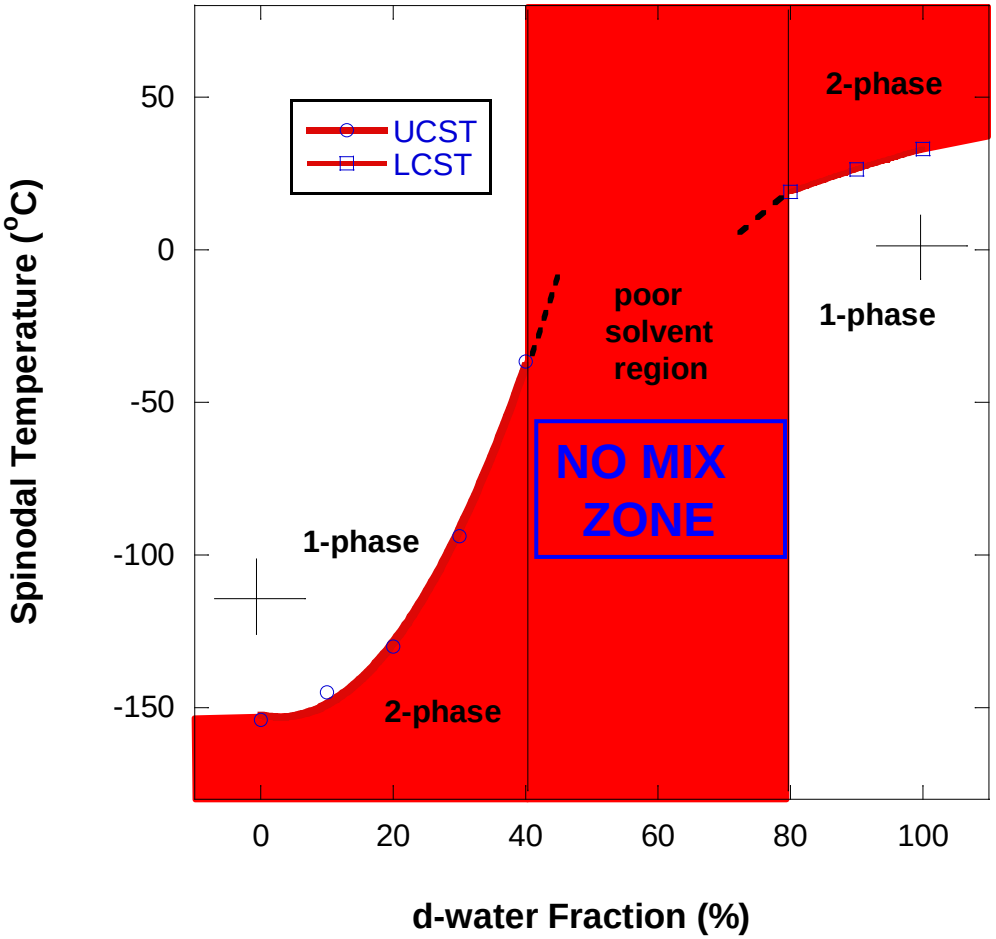
LCST

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

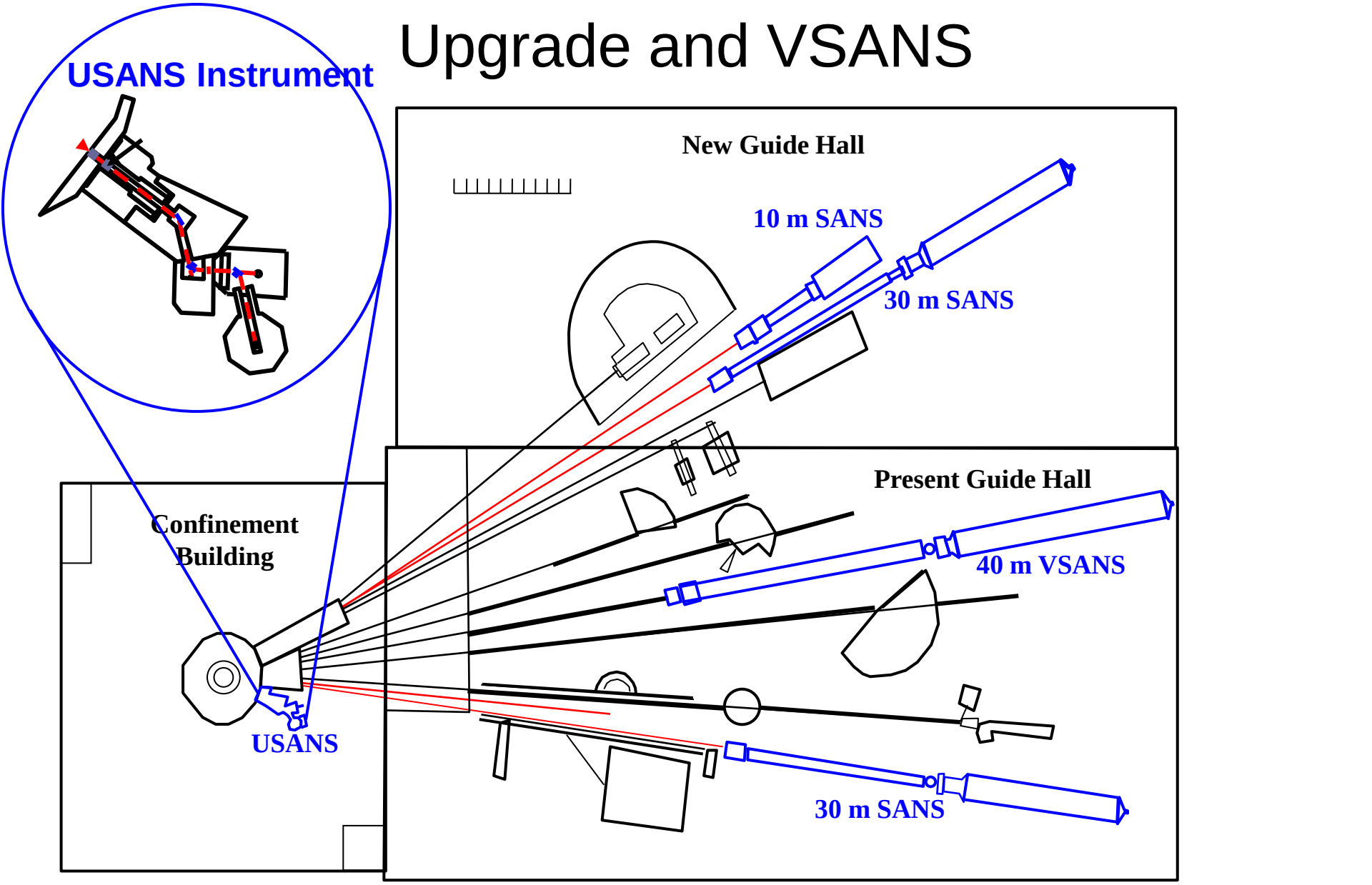
- PEO is characterized by a “perfect” solvation window for 10 % d-water.

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

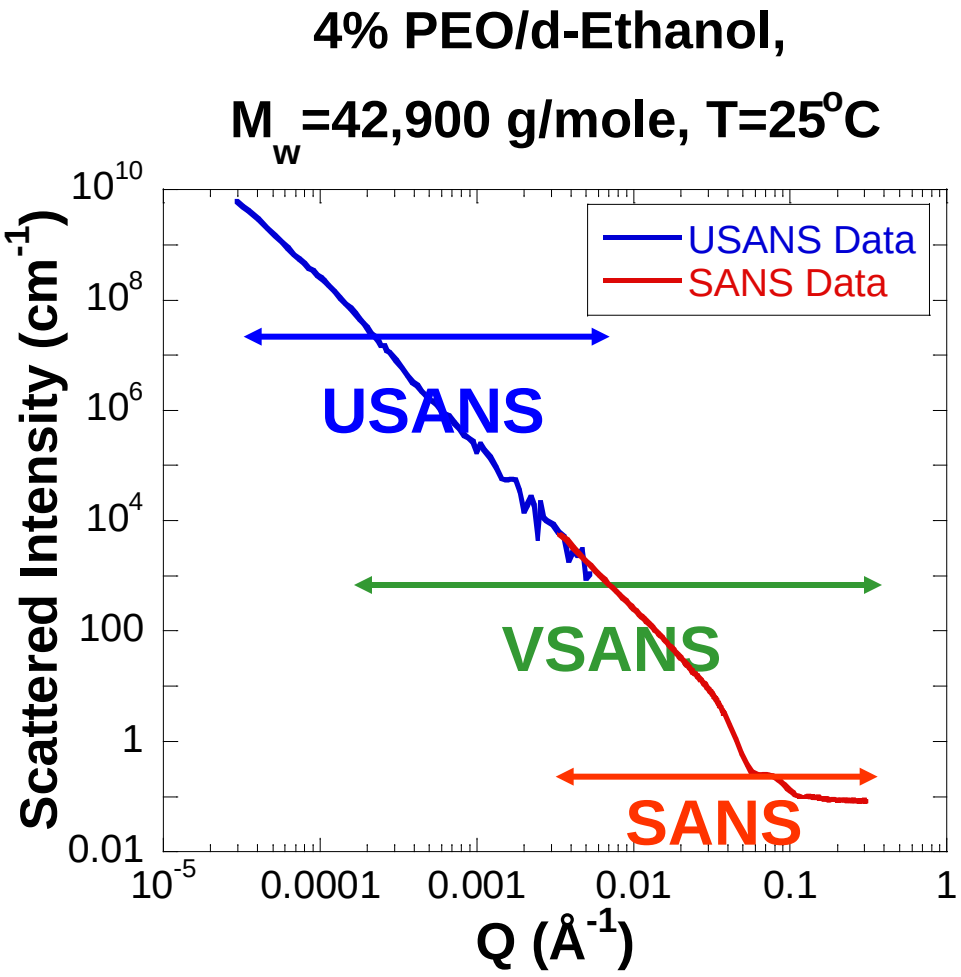
- SANS is a valuable thermodynamic probe to study phase transitions as well as nanostructures

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/