PHASE TRANSITIONS IN POLYMERIC AND MICELLAR SYSTEMS

The most active Small-Angle Neutron Scattering (SANS) research areas are in "Polymers" and "Complex Fluids" which includes micellar systems. Understanding the thermodynamics of mixing of polymers and/or complex fluids is important. This involves insight into the major phase transitions and the various structures that are formed.

Polymer mixtures consist of polymer solutions, polymer blends, copolymers as well as their mixtures. Micelles are comprised of a surfactant mixed with water and oil. These systems form structures in the nanometer length scale covered by the SANS technique.
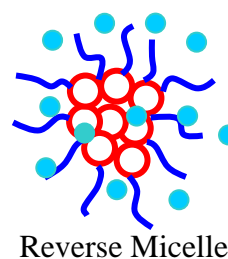
Polymer Solution

Binary Micelle

Polymer Blend
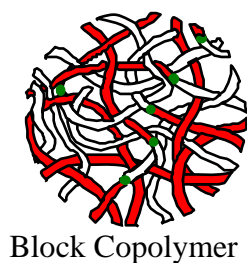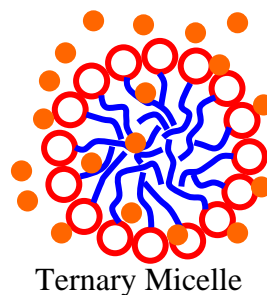
Ternary Micelle

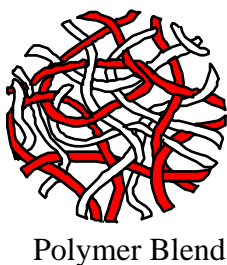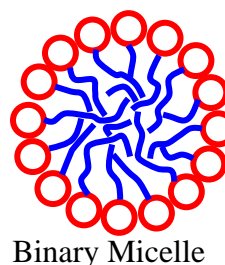Block Copolymer

Reverse Micelle

Figure 1: Various polymeric and micellar systems. The small dots represent solvent molecules.

1. PHASE TRANSITION BASICS

Polymer mixtures phase separate either through cooling and are characterized by an Upper Critical Spinodal Temperature (UCST) or upon heating and are characterized by a Lower Critical Spinodal Temperature (LCST). Combinations of LCST and UCST are also possible.
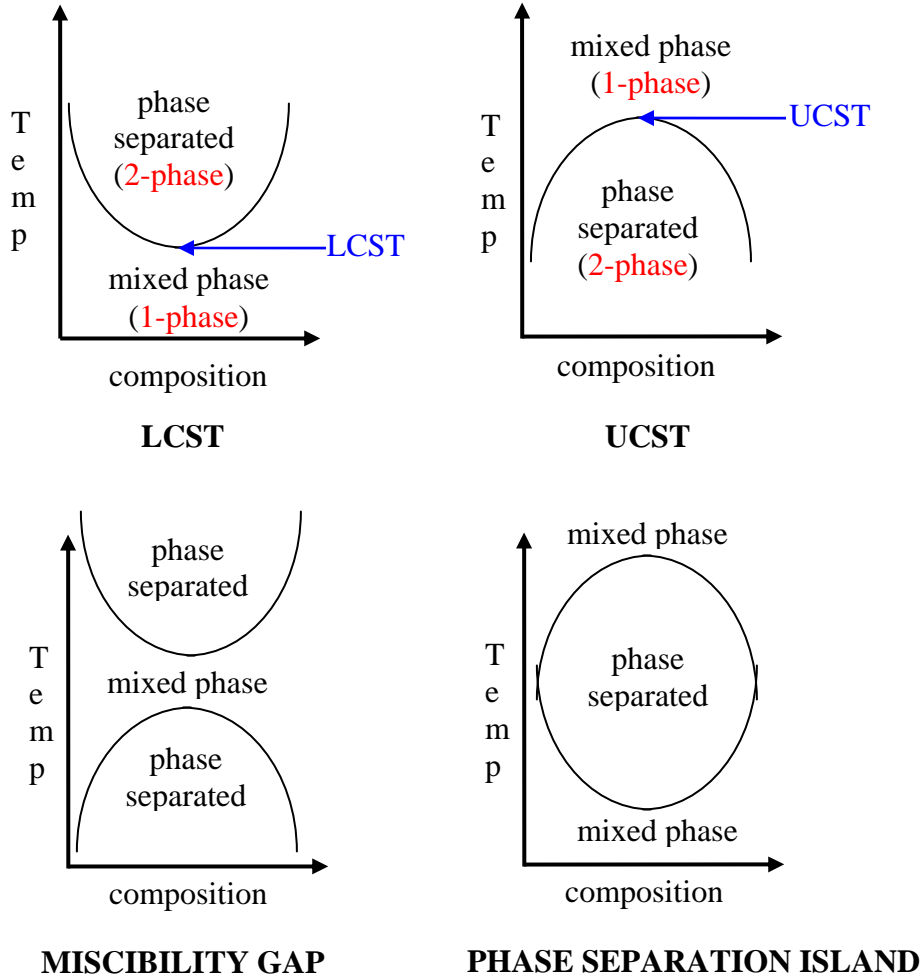
Figure 2: Various possible phase diagrams.

Composition fluctuations are enhanced when phase transition lines are approached from the 1-phase region. This increases the SANS intensity thereby making this technique an adequate probe for thermodynamic (phase transition) studies.

The "binodal" condition is the phase transition line between the homogeneously mixed 1-phase region and the phase separated (i.e., demixed) 2-phase region in the temperature-composition phase diagram. The spinodal line is the deeper part of the demixed 2-phase region. The region between the binodal and the spinodal lines is the nucleation-and-growth region while the region under the spinodal line is the spinodal region. Most water-soluble systems phase separate upon heating due to the softening of hydrogen-bonding at elevated temperatures.
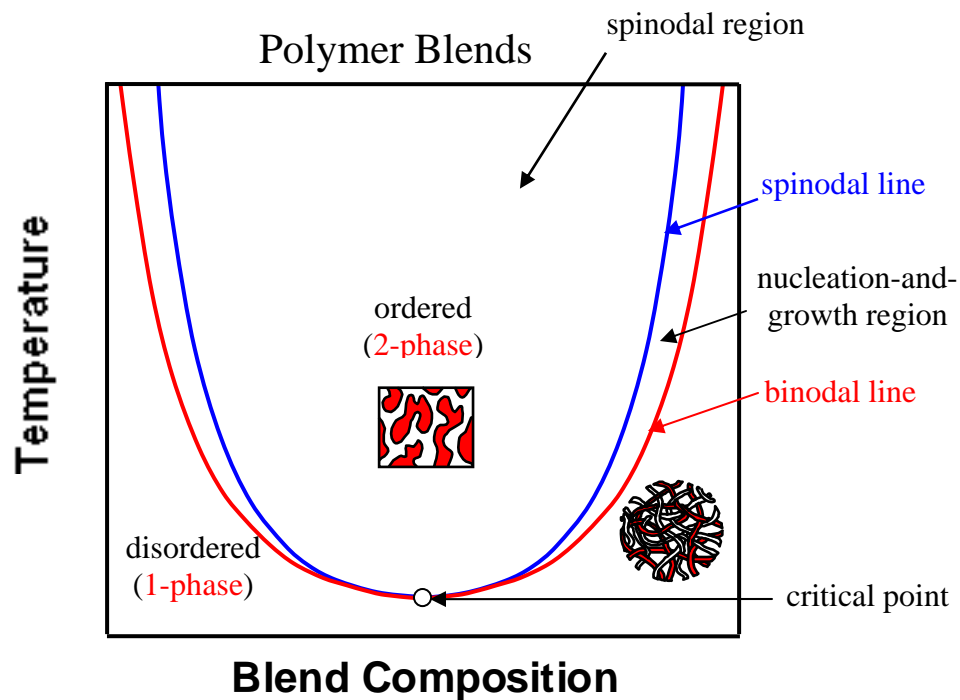
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Figure 3: Schematic representation of the phase diagram for polymer blends.

For block copolymers, the spinodal line is referred to as the Order-Disorder-Temperature (ODT). The ODT defines a region which comprises three main forms of microphase separation; these correspond to spherical, cylindrical and lamellar morphologies. The LCST line is referred to as the Lower Critical Ordering Temperature (LCOT) for copolymers. The copolymer composition is varied by increasing the length of one of blocks in the copolymer.
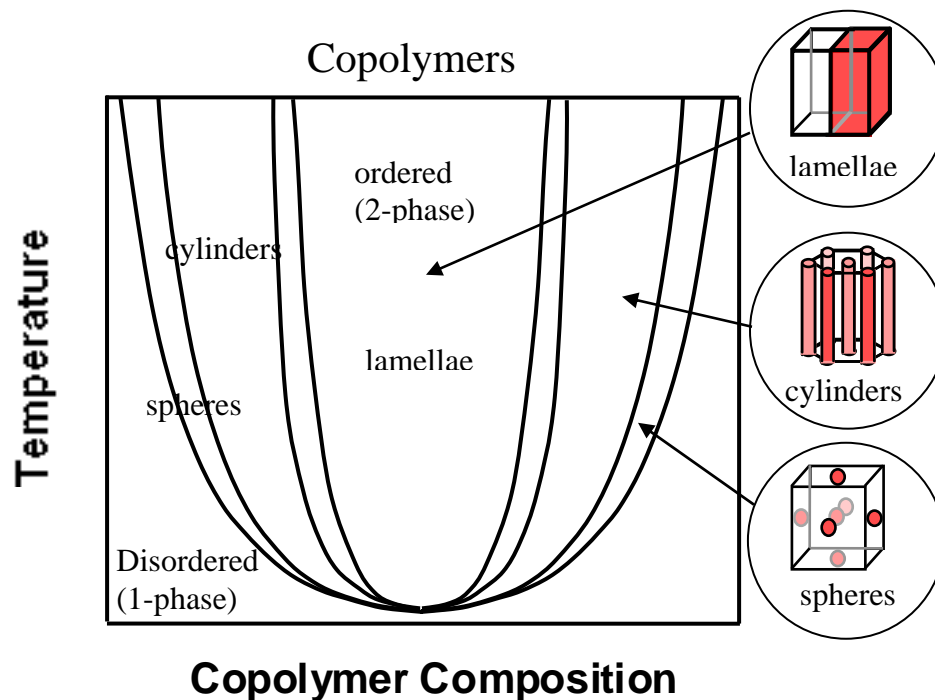
Figure 4: Representation of the various copolymer microphases for a Lower Critical Ordering Temperature (LCOT) system.

Micelles form when surfactants are mixed with water and oil. They form above a Critical Micelle Concentration (CMC) and Critical Micelle Temperature (CMT). Surfactant molecules can be ionic (i.e., are charged) or anionic (i.e., are neutral). Anionic surfactants are amphiphile molecules with a hydrophilic part and a hydrophobic part. One such example is the pluronics copolymer described next.

2. WHAT ARE PLURONICS?

Poly(ethylene oxide) (referred to as PEO) is the simplest water soluble polymer and has the structure $-CH_2CH_2O-$. Its neighbor in the homologous series poly(propylene oxide) (or PPO) does not dissolve in water at ambient temperature. Pluronics are triblock copolymers composed of one PPO block connected to two PEO blocks. The PEO block dissolves well in aqueous media because it is mostly hydrophilic while the PPO block does not dissolve because it is mostly hydrophobic at ambient temperature. This amphiphilic nature of pluronics molecules makes them form micelles at ambient temperature. At low temperatures, this balance does not hold and both PEO and PPO blocks dissolve in water thereby breaking down the micellar structure. The CMT and CMC vary depending on the block composition of the various pluronics.

Pluronics are commercially available materials used in the cosmetics and pharmaceutical industries. The P85 pluronic considered here consists of 26 EO monomers in each of the outside blocks and 40 PO monomers in the middle block. P85 is referred to as $EO_{26}PO_{40}EO_{26}$. The molecular weight of P85 is around 4,600 g/mol. The P85 Pluronic is ideally suited to investigate phase transitions by SANS since it is a copolymer that forms micelles.

3. SANS FROM P85 PLURONIC

The interest here is in micelle-formation as well as in the investigation of phase transitions that form various microstructures. A series of P85 samples of different weight fractions in d-water were prepared and measured by SANS.

In order to investigate micelle formation, SANS data were taken from 10 % P85 in deuterated water (d-water) at various temperatures (from 20 ^{o}C to 60 ^{o}C). D-water was used in order to enhance the neutron contrast. Micelles are well formed by 30 ^{o}C. When micelles are formed, the scattering is characterized by two features: a peak characteristic of inter-micelles interactions, and decay at high Q characterizing the tail of the single-particle form factor. In-between these two features, the hint of a second peak (shoulder around $Q = 0.15$ Å^{-1}) can be observed. This shoulder is also characteristic of the single particle form factor (oscillation of the spherical Bessel function) and is affected by polydispersity effects.
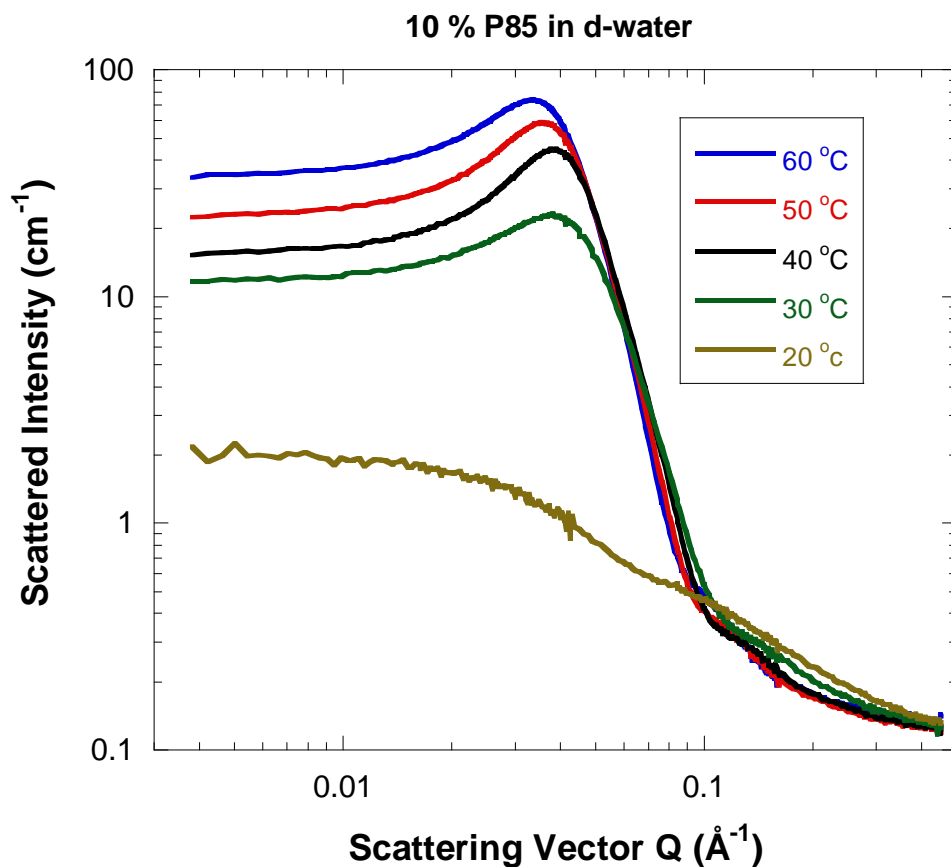
10 % P85 in d-water

Figure 5: SANS data from the 10 % P85 in D_2O at various temperatures. Data statistics are different for the two instrument configurations. The overlap region for the two SANS configurations used is between 0.03 Å^{-1} and 0.04 Å^{-1}.

In order to determine the Critical Micelle Temperature, the SANS intensity at a low Q value (Q = 0.02 A^{-1} was chosen) was plotted with increasing temperature. The CMT is seen to be around 22 $^{\circ}$C for the 10 % P85/d-water sample. This characteristic temperature is observed as a jump in the low-Q intensity.
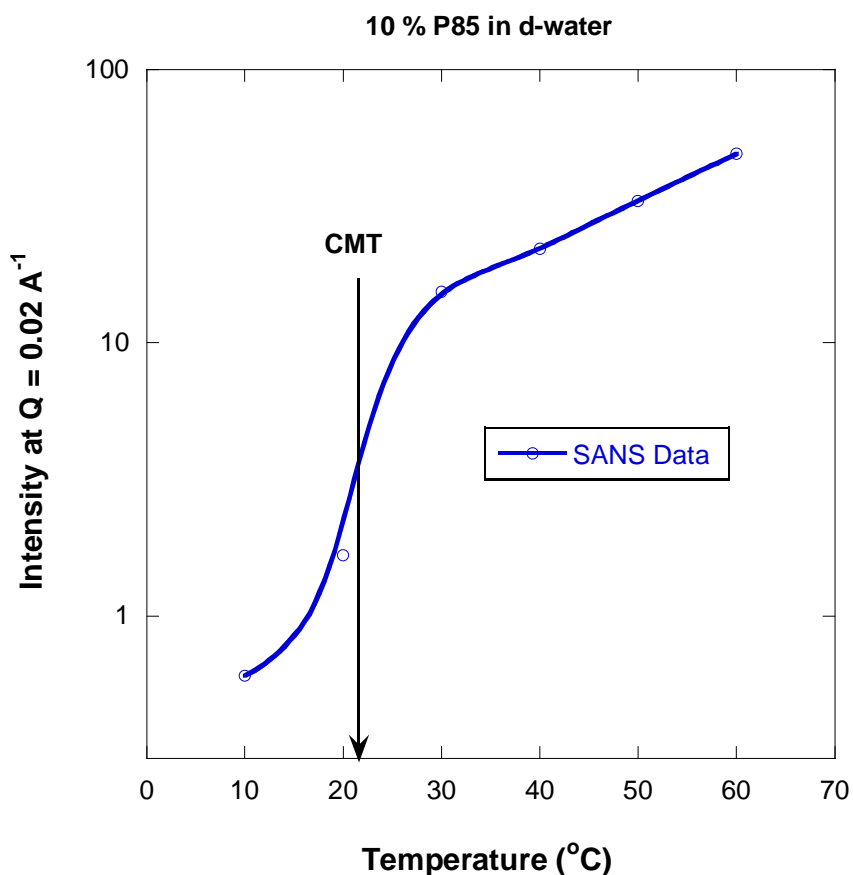
10 % P85 in d-water

Figure 6: Sigmoid shape variation of the low-Q SANS intensity with temperature for the 10 % P85/d-water sample.

SANS data are shown also for a 1 % P85/d-water sample for a wider temperature range (10 ^{o}C to 80 ^{o}C). The low P85 weight fraction allows the observation of the single-particle form factor without interference from the inter-particle interaction peak. The intensity is seen to increase with increasing temperature but the shape of the form factor changes from a phase containing dissolved unimers (below the CMT), to the spherical micelles phase, then to the cylindrical micelles phase.
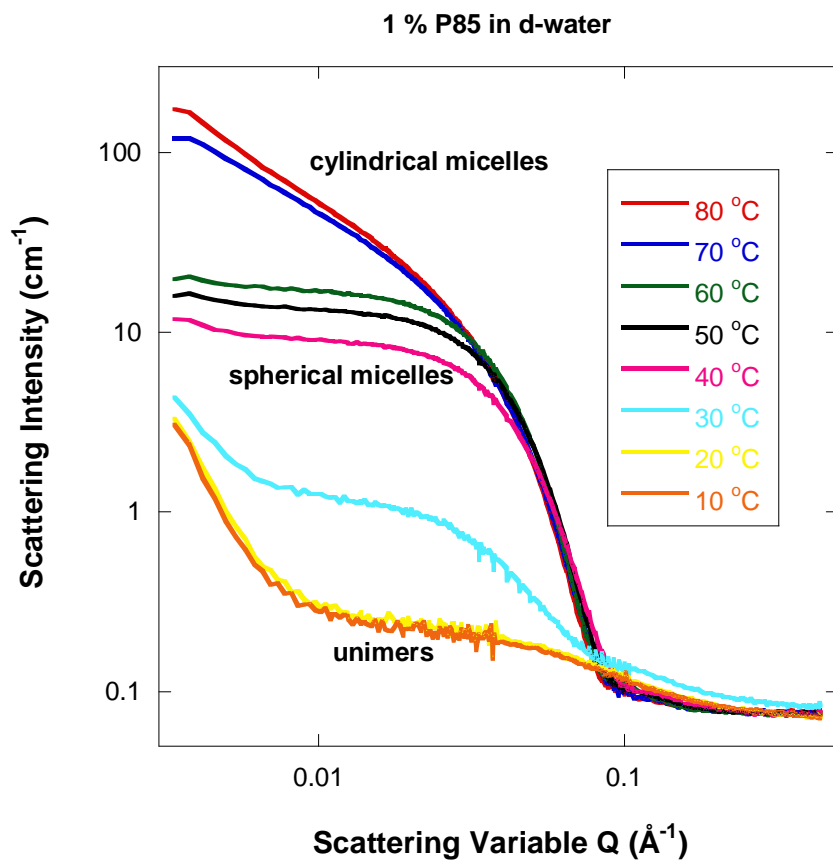
1 % P85 in d-water

Figure 7: SANS intensity increase pointing to the three observed phases (unimers, spherical micelles and cylindrical micelles).

Here also, a plot of the low-Q SANS intensity shows clearly the transition temperatures between the observed phases. Heating and cooling cycles show that these phase transitions are reversible.
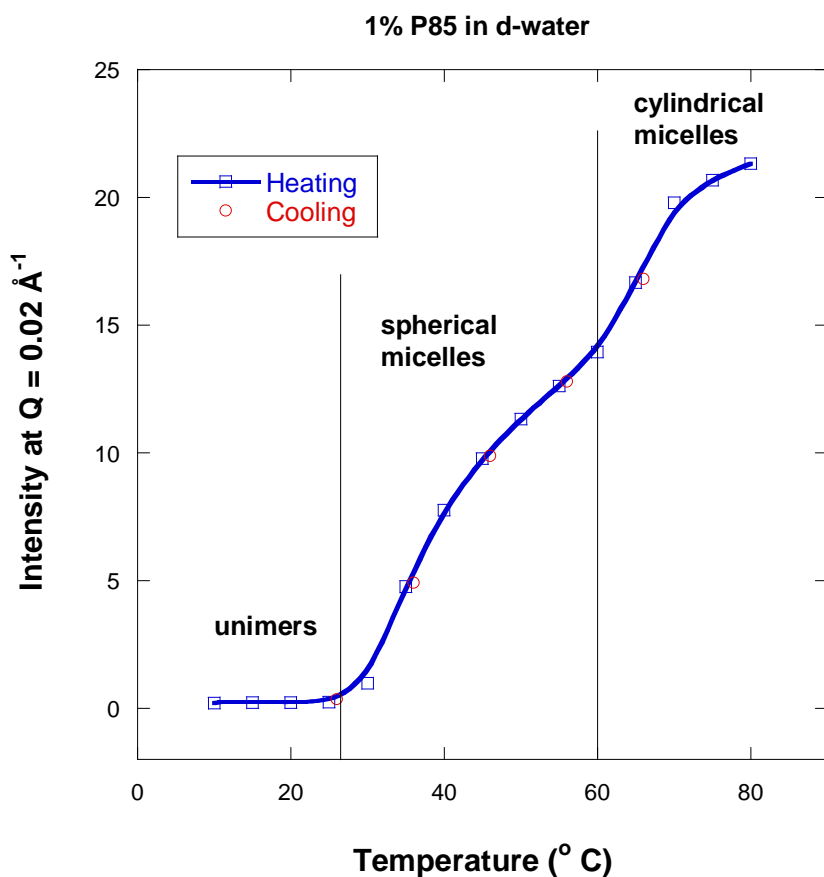
Figure 8: Variation of the low-Q SANS intensity for increasing temperature for the 1 % P85/d-water sample.

4. THE P85/D-WATER PHASE DIAGRAM

The P85/d-water phase diagram has been worked out (Mortensen, 1996) using the SANS technique (among others). The main phases (unimers, spherical micelles and cylindrical micelles) can be observed at low P85 weight fraction. Other phases (lamellar micelles and disordered phase) are not discussed here.
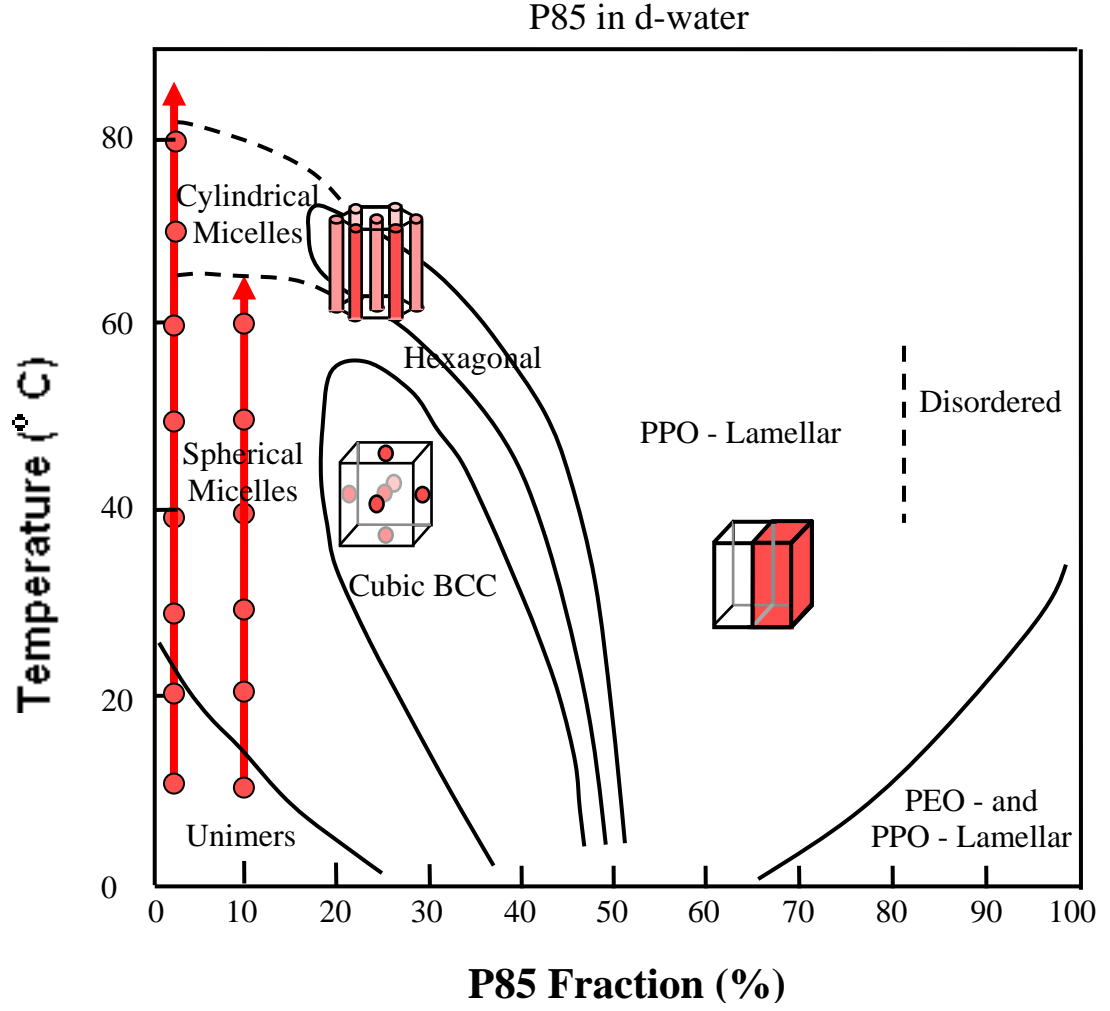
Figure 9: The P85/d-water phase diagram.

5. MICELLAR STRUCTURES

At low P85 weight fraction, spherical micelles then cylindrical micelles form for increasing temperature. Characteristic sizes of these structures are described here. The SANS cross section (scattering intensity) is given as follows:

$$\frac{d\Sigma(Q)}{d\Omega} = \left(\frac{N}{V}\right)\Delta\rho^2 V_P P(Q) S_I(Q) . \qquad (1)$$

Here N/V is the micelle number density, $\Delta\rho^2$ is the contrast factor, V_P is the micellar volume, $P(Q)$ is the single micelle form factor and $S_I(Q)$ is the inter-micelles structure factor. For our condition of low P85 weight fraction (1 %), contribution from the structure factor is small ($S_I(Q) \approx 1$).

Using the 1 % P85 SANS data, fits were performed to a polydisperse spheres model with a hard-sphere inter-particle interaction potential for temperatures between 30 $^{\circ}$C and 55

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^{o}C. Fits were also performed to a cylinders model with polydisperse radius and a hard sphere inter-particle interaction potential for temperatures between 65 ^{o}C and 80 ^{o}C. The form factors for a sphere of radius R and for a randomly oriented cylinder or radius R and length L are given by:

$$P(Q) = \left[\frac{3j_1(QR)}{QR}\right]^2 = \left[\frac{3}{QR}\left(\frac{\sin(QR)}{(QR)^2} - \frac{\cos(QR)}{QR}\right)\right]^2 \qquad (2)$$

$$P(Q) = \frac{1}{2}\int_{-1}^{1}d\mu\left[\frac{\sin(Q\mu L/2)}{Q\mu L/2}\right]^2\left[\frac{2J_1(Q\sqrt{1-\mu^2}R)}{Q\sqrt{1-\mu^2}R}\right]^2.$$

Here $j_1(x)$ is the spherical Bessel function and $J_1(x)$ is the cylindrical Bessel function of first order. Fit results are included in two tables.

Table 1: Results of the fits to a polydisperse spheres model with a hard sphere inter-particle interaction potential.

Temperature (^{o}C)	Radius (Å)	Polydispersity Factor	Length Density Density (Å^{-2})	sld for d-water (Å^{-2})
30	41.9	0.2	$4.14*10^{-6}$	$6.4*10^{-6}$
35	42.3	0.28	$3.51*10^{-6}$	$6.4*10^{-6}$
40	47.9	0.18	$10.71*10^{-6}$	$6.4*10^{-6}$
45	50.4	0.15	$6.73*10^{-7}$	$6.4*10^{-6}$
50	52.6	0.14	$-1.74*10^{-6}$	$6.4*10^{-6}$
55	54.3	0.13	$-8.91*10^{-8}$	$6.4*10^{-6}$

Table 2: Results of the fits to a cylinders model with polydisperse radius and a hard sphere inter-particle interaction potential.

Temperature (^{o}C)	Radius (Å)	Length (Å)	Polydispersity Factor	Length Density Density (Å^{-2})	Length Density Density (Å^{-2})
65	45.9	212	0.09	$4.63*10^{-6}$	$6.4*10^{-6}$
70	44.7	1523	0.16	$4.81*10^{-6}$	$6.4*10^{-6}$
75	45.4	3618	0.17	$4.83*10^{-6}$	$6.4*10^{-6}$
80	46.1	4086	0.18	$4.82*10^{-6}$	$6.4*10^{-6}$

Micelles are seen to consistently grow with increasing temperature. Fits are some temperatures are better than others.

6. THE TERNARY PHASE DIAGRAM

The phase diagram of a ternary micellar system (Kahlweit-Strey, 1985) is represented by a triangle (A: water, B: oil and C: surfactant). The three binary systems A/B, A/C and B/C are represented by their characteristic mixed phase (1-phase) and phase separated (2-

phase) regions. The oil-surfactant (B/C) binary mixture is characterized by an upper critical solution temperature (UCST); i.e., it phase separates upon cooling. The water-oil (A/B) binary mixture is also characterized by a UCST behavior but is mostly phase separated (water and oil do not mix). The phase diagram for the water-surfactant (A/C) binary solution is more complex and is characterized by a UCST behavior at low temperatures and a closed loop immiscibility island at high temperatures; i.e., it phase separates both upon cooling and upon heating. The closed loop is due to the breaking of hydrogen bonds upon heating and shows up for strong amphiphile surfactants.
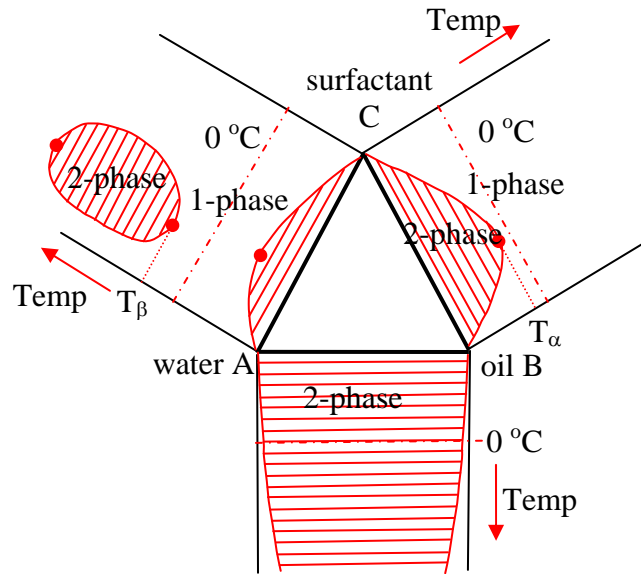

Figure 10: Phase diagram for the three binary mixtures (B/C, A/B, and A/C). The phase separation lines and temperatures are shown. The 0 ^{o}C water-freezing line has also been marked.

Phase separation occurs upon jumping from the phase mixed (1-phase) region to the phase separated (2-phase) region. Phase separation proceeds along tie lines and produces a phase rich in the A component (left side) and a phase rich in the C component (right side). The points at which the phase separation lines have a horizontal slope are the critical points. The A/C binary phase diagram shows three critical points. Note that the lower UCST may lie below the freezing point of the mixture.
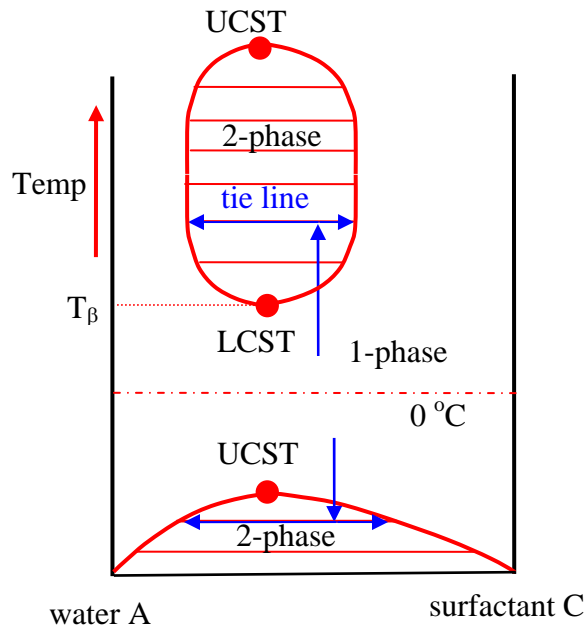
Figure 11: The water/surfactant (A/C) binary phase diagram.

Given the three generic binary mixtures phase diagrams, the phase diagram for the ternary A/B/C mixture is discussed next.

The ABC triangle is obtained by combining the three binary mixtures phase diagrams. It contains a micelle-formation phase (m-phase) region and a 2-phase region. The m-phase region contains oil-in-water and water-in-oil micelles. The 2-phase region contains a phase containing water and surfactant and another phase containing mostly oil at low temperatures. Note that micelles can form in the 2-phase region since binary mixtures (water/surfactant or oil/surfactant) can form micelles. The m-phase region is inhomogeneous (contains micelles) in the nanometer size scale but homogeneous in the micrometer (optical range) size scale. The m-phase region is "clear" for light but "cloudy" for neutrons.
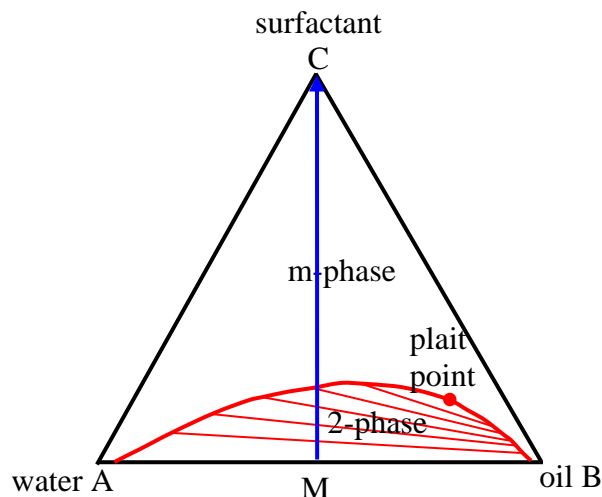
Figure 12: Schematic representation of a generic ternary mixture phase diagram. The m-phase is the micelle-formation phase.

Note that the case of P85 in d-water described previously corresponds to the left side of the ternary phase triangle.

This simple representation of the ternary phase diagram is valid for low temperatures; i.e., before reaching the closed loop region. When the closed loop region is reached and with strong amphiphilic surfactants, there is an interplay of interactions which adds two 2-phase regions (one water-rich and one oil-rich).

The "fish" phase diagram is obtained when an MC cut is taken across the ABC triangle phase diagram. This cut corresponds to increasing the surfactant concentration but keeping the amount or water and oil constant. Representation of the temperature/ surfactant fraction phase diagram comprises the m-phase region at high surfactant fraction, two 2-phase regions (at low and high temperatures) and a 3-phase region at intermediate temperatures. The name "fish" stems from the shape of the phase diagram with the 3-phase as the fish head.
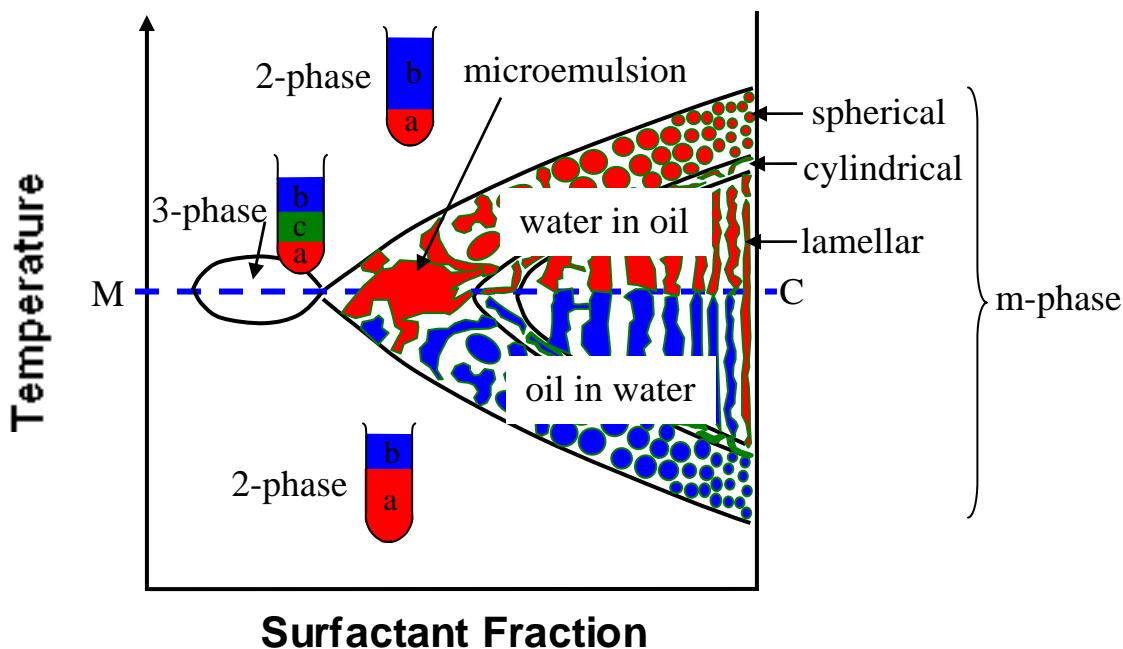
Figure 13: The "fish" phase diagram.

The m-phase region is the focus of most SANS investigations since it is the region of micelle formation. The m-phase region is rich in mesophases (with various morphologies). It contains spherical, cylindrical (also called wormlike) and lamellar micelles depending on the temperature range. Structures for these mesophases correspond to cubic, hexagonal and lamellar symmetry respectively. Note also the "microemulsion" (also called bicontinuous) phase. Moreover, oil-in-water micelles are obtained at low temperature and "reverse" (water-in-oil) micelles are obtained at high temperatures.

Note that copolymers play the role of surfactants. When A-C copolymers are mixed with A and B homopolymers, the same "fish" phase behavior is obtained.

REFERENCES

M. Kahlweit and R. Strey, "Phase Behavior of Ternary Systems of the Type H_2O-Oil-Nonionic Amphiphile (Microemulsions)**,** Angewandte Chemie International Edition in English 24, 654–668 (1985).

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http://www.ncnr.nist.gov/staff/hammouda/the_SANS_toolbox.pdf. Check out chapters 42 and 44.