Chapter 42 – **PHASE DIAGRAMS FOR MICELLAR SYSTEMS**

A substantial fraction of SANS research is performed on "complex fluids". These include micelles, colloids, gels, networks, etc, and could be referred to as "micellar systems". Phase diagrams for micellar systems are discussed in this chapter (Kahlweit-Strey, 1985). This topic is treated at a descriptive level.

1. BASICS OF MICELLAR SYSTEMS

Micellar systems consist of mixtures of water/oil and an amphiphile surfactant that increases their miscibility. The amphiphile surfactant is either not charged (i.e., is nonionic) or consists of an ionic (charged) headgroup. The focus here will be on nonionic micellar systems, their mixing ability and their demixing phase diagram.

The phase diagram of the ternary micellar system 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.
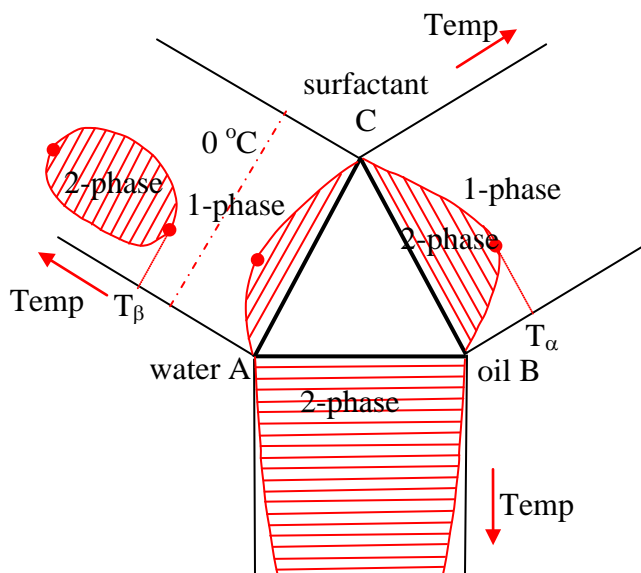
Figure 1: Phase diagram for the three binary mixtures (B-C, A-B, and A-C). The phase separation lines and temperatures are shown. The 0 ^{o}C water-freezing line has also been marked.

Phase separation occurs upon jumping from the mixed phase (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.
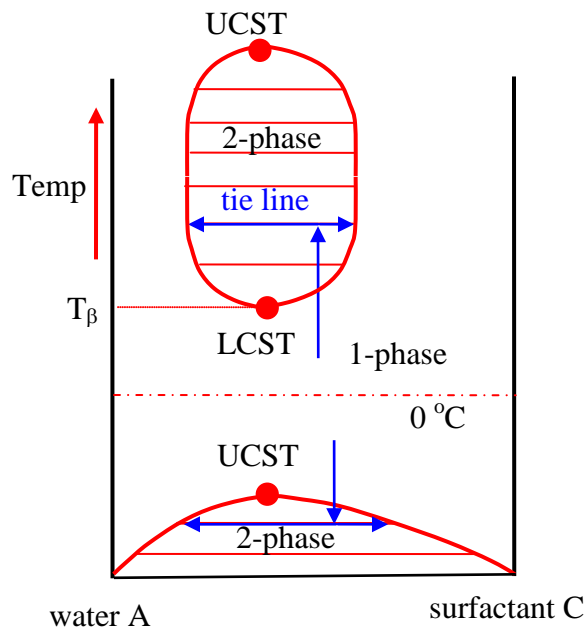

Figure 2: The water/surfactant (A-C) binary phase diagram.

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

2. PHASE DIAGRAM FOR THE TERNARY MIXTURE

The ABC triangle is obtained by combining the three binary mixtures phase diagrams. It contains a micelle-formation phase (m-phase also referred to as "1-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.

Now consider the temperature axis (vertical variable out of the page). A jump from the m-phase region to the 2-phase region prompts phase separation that proceeds along tie lines (that are no longer horizontal). The critical condition for the ternary mixture is referred to as the "plait" point (equivalent to 'critical' point for binary mixtures).

surfactant C

m-phase

plait point

2-phase

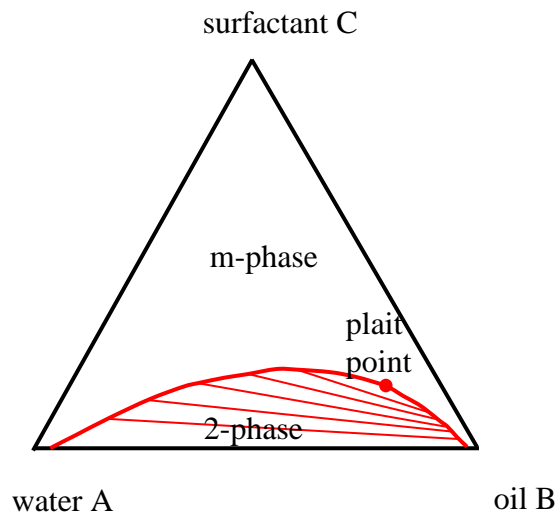water A   oil B

Figure 3: Schematic representation of a generic ternary mixture phase diagram. The m-phase is the micelle-formation phase.

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) and two plait points. The slopes of the tie lines are different. This type of phase diagram is characterized by a 3-phase region inside the triangle that cuts through both 2-phase regions.
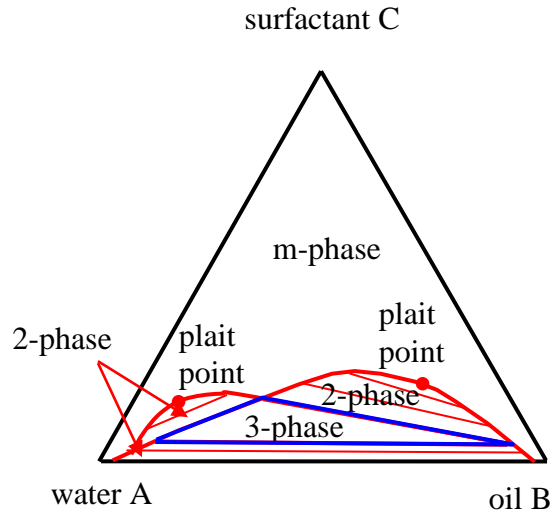
Figure 4: Ternary phase diagram that shows the 3-phase region.

There are three types of "Windsor" phase diagrams: type I corresponding to a 2-phase region where the surfactant is dissolved mainly in the water phase, type II corresponding to a 2-phase region where the surfactant is dissolved mainly in the oil phase and type III corresponding to a 3-phase region where the surfactant forms a phase of its own between the (bottom) water phase and (top) oil phase.

In order to appreciate the cause of the formation of the 3-phase, the temperature variable is added to the phase diagram and explored in more detail.

3. THE CRITICAL POINTS LINE

Consider first the simple case without a closed loop for the water-surfactant binary mixture phase diagram. The 3D phase diagram (referred to as the "prism") is shown here. The plait points form a line that ascends from the oil-rich region.
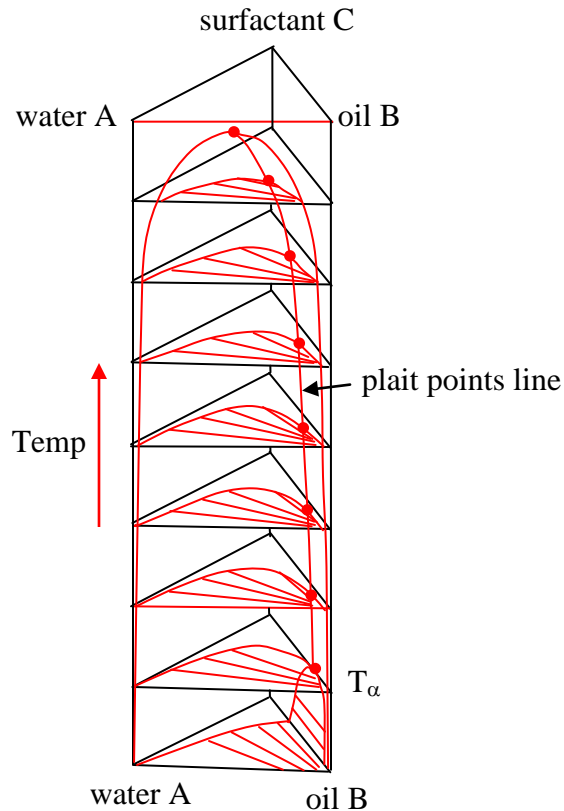
4

Figure 5: The prism phase diagram for a simple ternary mixture.

When the surfactant becomes more amphiphilic, a closed loop appears. This modifies the prism phase diagram to show plait point lines both on the oil-rich (right) side and on the water-rich (left) side. Up to now, there are still the m-phase and the 2-phase regions only; the 3-phase region has not shown up yet. Note that the slopes of the tie lines change with temperature for this case.

The water/oil phase volume (relative amount) varies with increasing temperature. At low temperature, the 2-phase consists of a water-surfactant phase (called a) and an oil phase (called b). As temperature is increased, surfactant is distributed equally between a water phase (a) and an oil phase (b). This temperature corresponds to the inflection point in the variation of the plait points' line (also called critical points line). As temperature is increased further, the 2-phase mixture becomes an oil-surfactant phase (b) and a water phase (a).
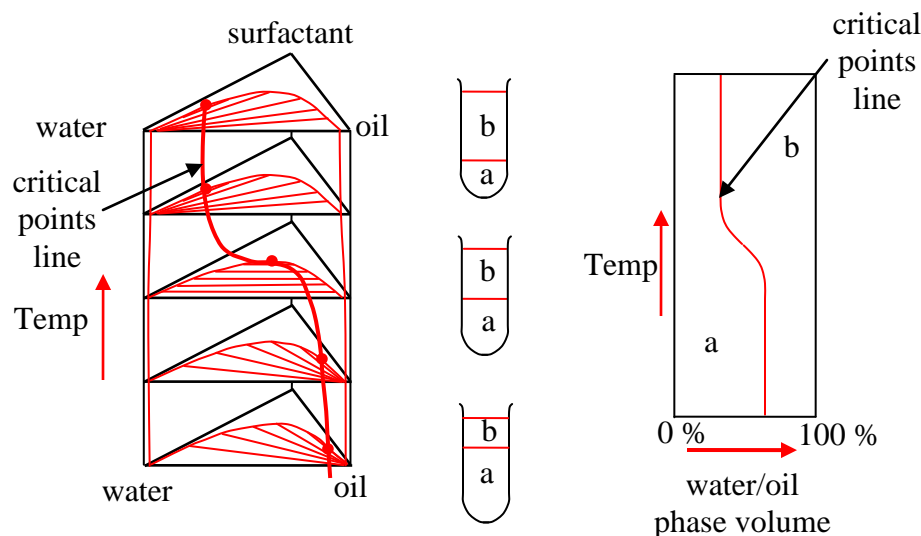
Figure 6: The prism phase diagram when a closed loop is present. The composition of the 2-phase mixtures is represented for increasing temperature.

4. THE THREE-PHASE REGION

Depending on the chemical nature of the amphiphile surfactant and oil used, one could obtain a 3-phase region. In order to understand its origin, consider the variation of the critical points line when the surfactant becomes more amphiphile or when the oil becomes more hydrophobic. The slope at the inflection point becomes steeper till it becomes horizontal. This corresponds to a so-called "tricritical" condition. Beyond that, the critical points line breaks which leads to the formation of a 3-phase region.
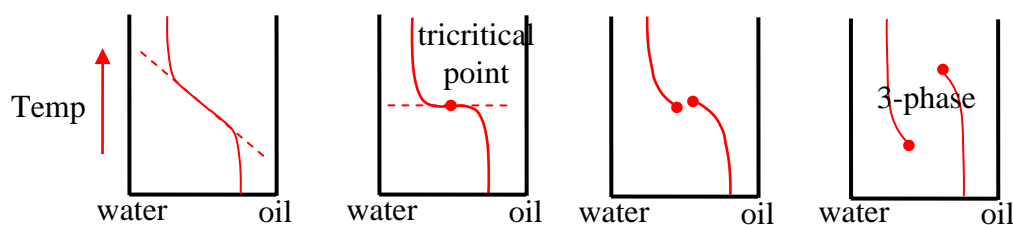

Figure 7: Variation of the critical points line with increasing amphiphile character of the surfactant and/or increasing the hydrophobic nature of the oil.

The critical points line changes drastically when a 3-phase region is present. That line "breaks"and a "sigmoid" (i.e., s-shaped) behavior appears. The 2-phase regions at low temperature and high temperature are almost unchanged but a 3-phase region appears at intermediate temperatures.
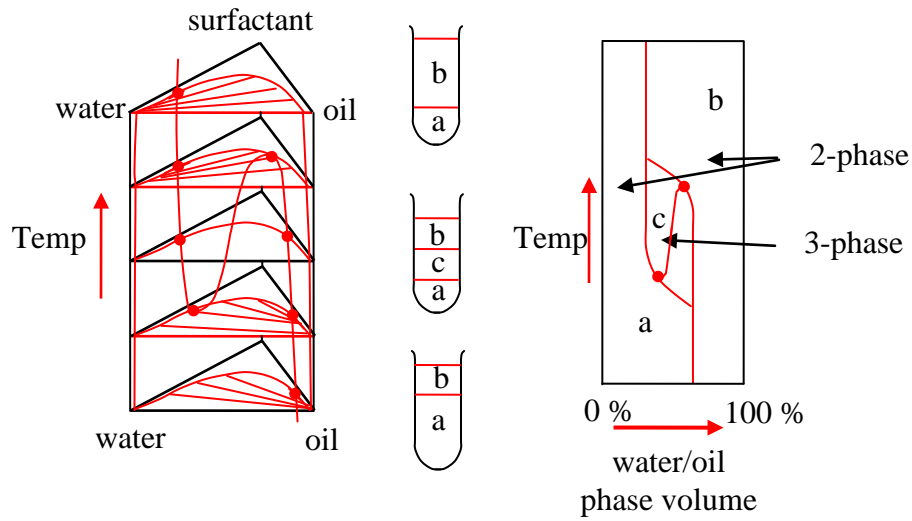
Figure 8: Representation of the ==prism phase diagram== when a 3-phase region is present.

==The surfactant is transferred continuously from the water-rich phase to the oil-rich phase as temperature is increased.== Consider a triangle phase diagram at a temperature for which a 3-phase region exists. The 1-phase region is close to the surfactant corner. The 2-phase regions are on each of the three sides of the 3-phase region. The 3-phase region itself is a triangle within the triangle. The 3-phase triangle size varies depending on the ternary system used and on the temperature considered.
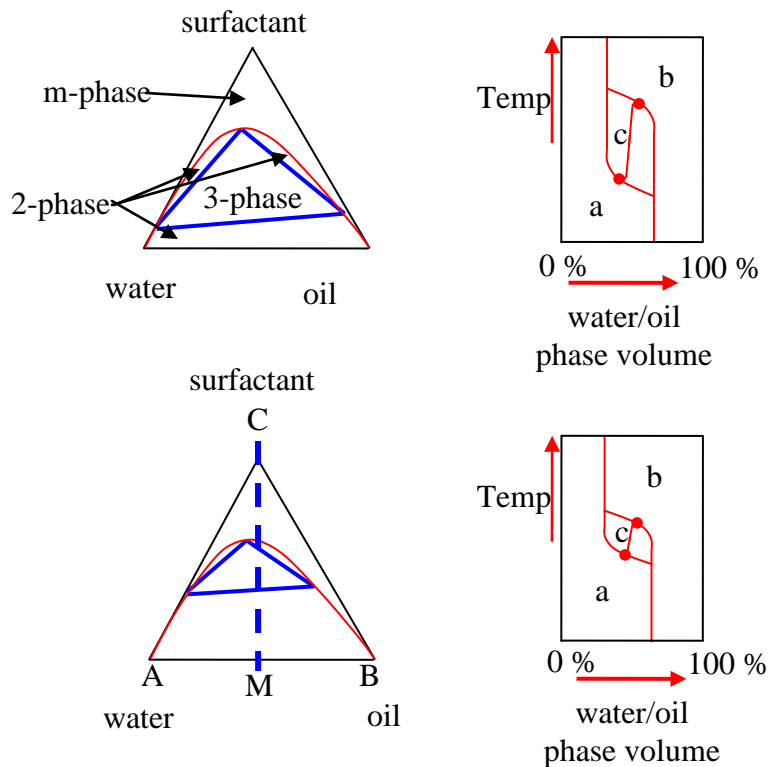
Figure 9: The triangle delimiting the 3-phase region.

Consider a vertical cut MC (referred to as the "isopleth" line) through the ABC triangle. Representing the phase diagram along the MC cut gives the "fish" phase diagram.

5. THE FISH PHASE DIAGRAM

The "fish" phase diagram is obtained when an MC cut is taken across the ABC triangle phase diagram (i.e., along the isopleth line). This cut corresponds to increasing the surfactant concentration but keeping the amount of water and oil constant. Representation of the temperature/ surfactant concentration phase diagram comprises the m-phase region at high surfactant concentration, 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.
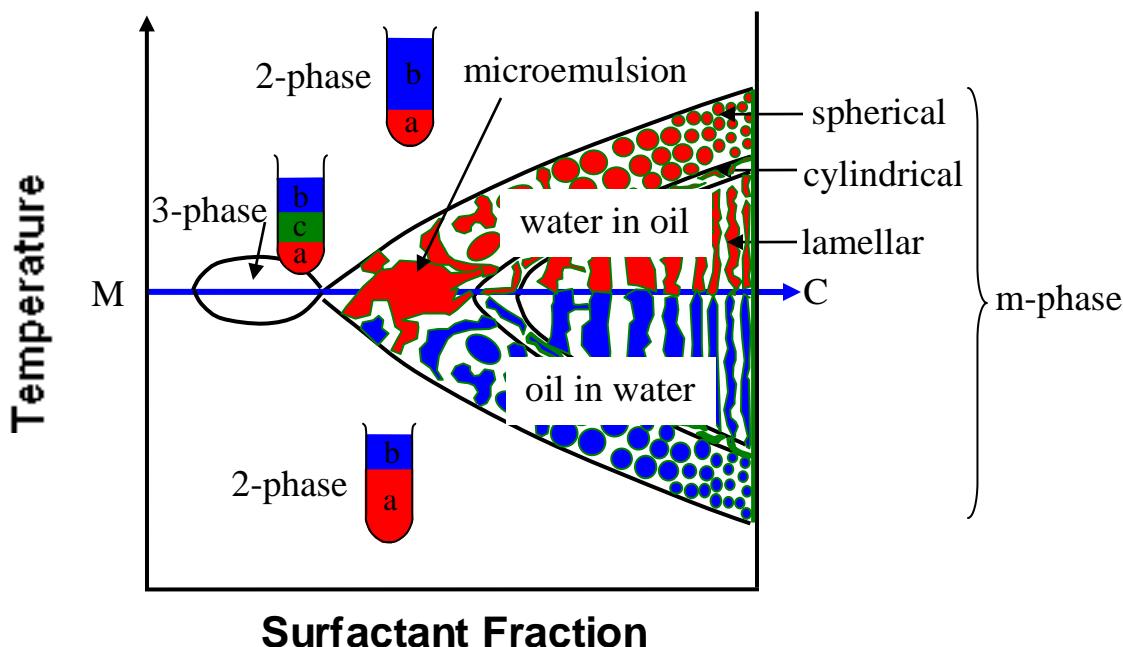
Figure 10: The fish phase diagram.

The m-phase region is the focus of most SANS investigations since it is the region of micelle formation and micelles are of nanometer size. 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 (spherical micelles), hexagonal (cylindrical micelles) and lamellar symmetry respectively. Note also that the "microemulsion" is 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.

Water-in-oil and oil-in-water micelles form in the m-phase region. Micelles can also form in the 2-phase region as well. These micelles are different from those found in the m-phase region and would be formed of surfactant/water (or surfactant/oil) only. Micelles form above a critical micelle temperature (CMT) and/or critical micelle concentration (CMC).

6. THE MICELLE-FORMATION PHASE

SANS data for a nonionic surfactant (Pluronic P85) mixed with d-water are described here. This copolymer solution is equivalent to a surfactant/water mixture. Strictly speaking, this is not a ternary mixture; its phase diagram is different from the surfactant/water/oil mixture but shows some of the same microphases. The Pluronic molecule is a triblock copolymer PEO-PPO-PEO which forms micelles above a critical temperature and concentration. PPO is hydrophobic and PEO is hydrophilic. P85 is

different from a ternary water/oil/surfactant system, but the overall trends remain the same. Unimers (dissolved macromolecules) are obtained at low temperature and micelles form at high temperature. The critical micelle temperature and concentration are referred to as the CMT and CMC. At fixed surfactant concentration, micelles form as shown by an increase in the low-Q SANS intensity.

1 % P85 in d-water
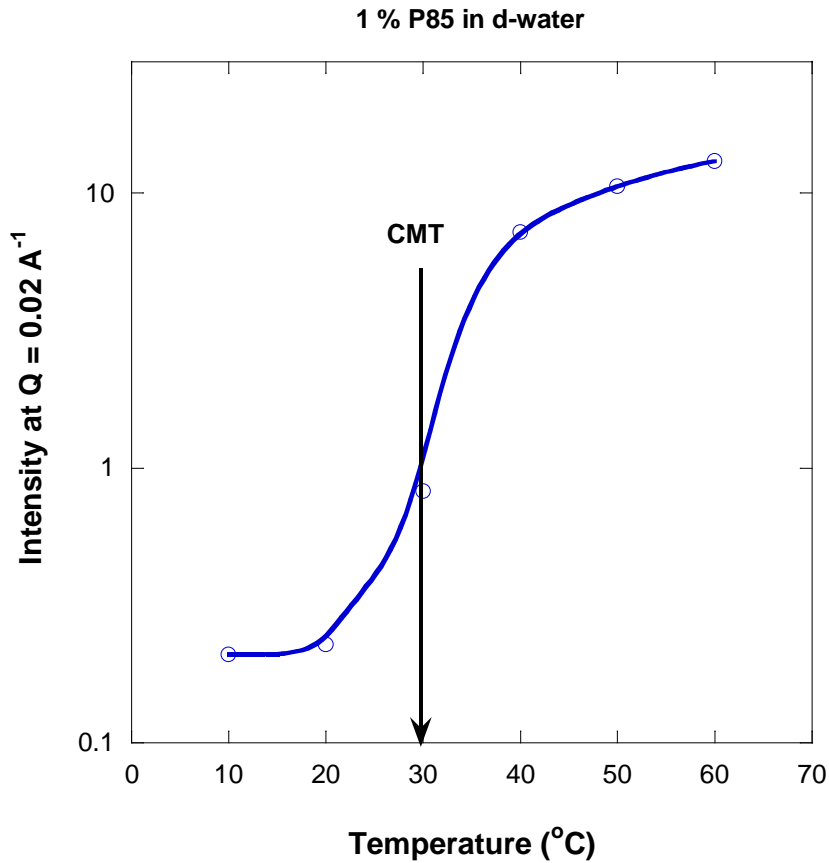

Figure 12: Low-Q SANS data from 1% P85 Pluronic in d-water. The sigmoid shape function characterizes the critical micelle temperature (CMT).

Varying temperature for a fixed P85 mass fraction shows a transition from a spherical to a cylindrical morphology in the micelle-formation region.
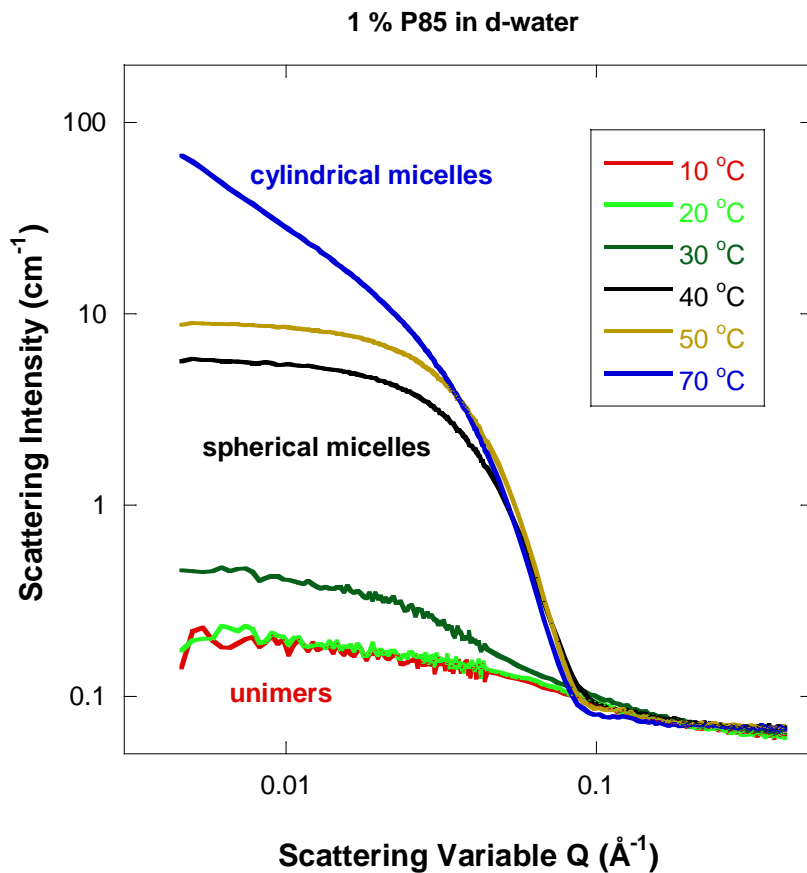
1 % P85 in d-water

Figure 13: Transition from the unimers to the spherical micelles phase to the cylindrical micelles phase regions as temperature is increased for 1 % P85 in d-water.

The transitions from the unimers region to the spherical micelles region, then to the cylindrical micelles region are clearly seen in the next figure as well. The heating/cooling cycle shows no hysteresis.
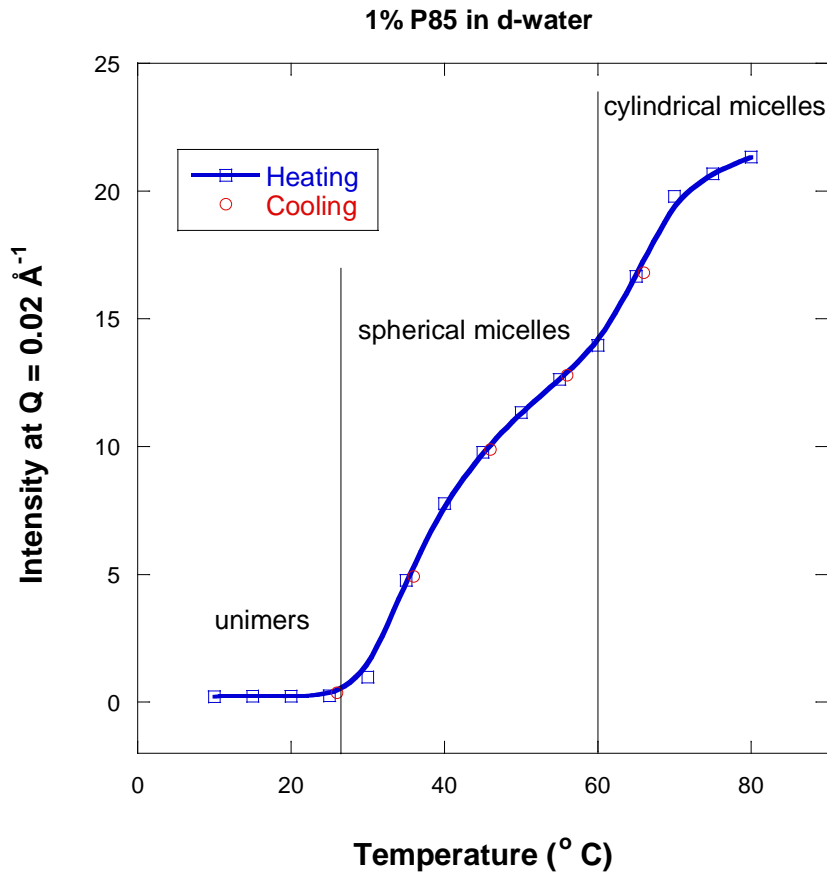
11

1% P85 in d-water

Figure 14: The unimers-to-spherical micelles and then to cylindrical micelles transitions are clearly seen.

Note that the empirical Guinier-Porod model could have been used to obtain a more precise delimitation of the various phase boundaries.

7. THE P85/D-WATER PHASE DIAGRAM

The P85/d-water phase diagram has been mapped out (Mortensen, 1996) using the SANS technique (among other techniques). The main phases (unimers, spherical micelles, cylindrical micelles and lamellar phase) can be observed at low P85 weight fraction. Other phases (ordered spherical micelles, hexagonal phase and a disordered phase) are not discussed here.
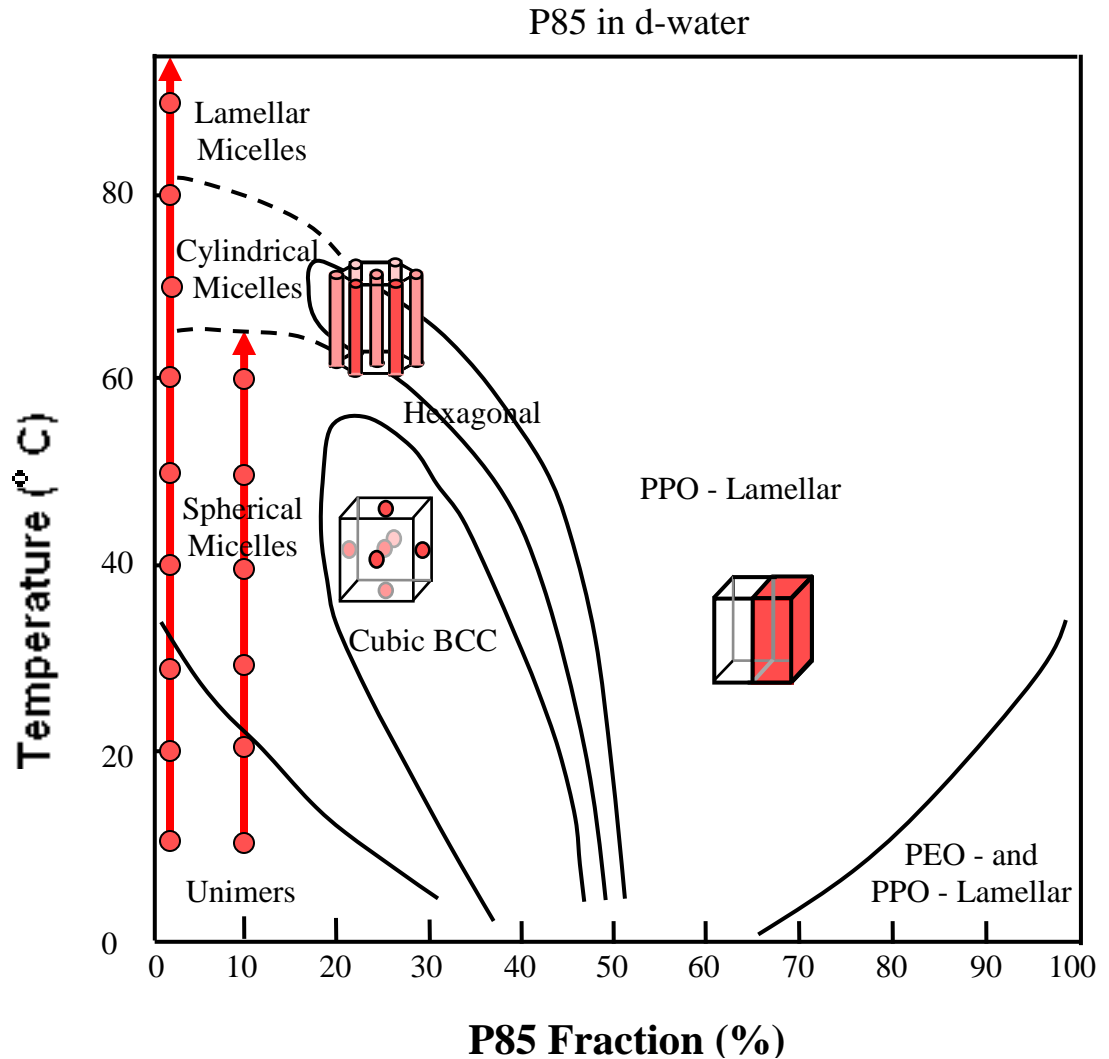
P85 in d-water

Figure 15: The P85/d-water phase diagram.

8. TYPICAL SURFACTANTS

P85 was used as a typical nonionic surfactant. A class of nonionic surfactants is denoted C_iE_j. They are comprised of a hydrophobic alkyl chain containing i carbons $H(CH_2)_i$- and a hydrophilic ethoxy group containing j alkylpolyglycol ethers $-(OCH_2CH_2)_jH$.

Ionic surfactants contain a charged headgroup and a hydrophobic tail. Model ionic surfactants include cetyletrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), bis(2-ethylhexyl) sodium sulfosuccinate (AOT) also called diocyl sulfosuccinate, sodium salt, etc. The phase diagram for the water/oil/ionic surfactant case is similar (but not identical) to the nonionic surfactant case.

A table summarizes the chemical formulas and scattering length densities for some common surfactants. Deuterated water and a typical deuterated oil (d-decane) have also been included. Note that some of the densities have been estimated.

Table 1: Typical ionic surfactants and their scattering length densities.

Surfactant	Chemical Formula	Density (g/cm^3)	Scattering Length Density $(Å^{-2})$
CTAB	$CH_3(CH_2)_{15}N(CH_3)_3Br^-Na^+$	0.9	$-1.54*10^{-7}$
SDS	$H(CH_2)_{12}OSO_3^-Na^+$	0.9	$3.72*10^{-7}$
AOT	$CH_3(CH_2)_3CH(C_2H_5)CH_2O_2CCH_2CH(SO_3^- Na^+)CO_2CH_2CH(C_2H_5)(CH_2)_3CH_3$	0.9	$5.08*10^{-7}$
d-water	D_2O	1.11	$6.39*10^{-6}$
d-decane	$CD_3(CD_2)_8CD_3$	0.73	$5.7*10^{-6}$

9. SELF-ASSEMBLING SYSTEMS

A slightly more general category than "complex fluids" could be referred to as "self-assembling systems". These include a large class of molecular systems that do not stay dissolved. The following couple of chapters cover "self-assembling" systems. Two nonionic systems will be considered: crystalline lamellae in solution and spherical micelle-forming Pluronic. An ionic system forming wormlike micelles will also be included.

Soft materials include gels and networks that trap solvent and form regular amorphous structures. Strong driving forces such as hydrophobic/hydrophilic or Coulombic interactions and other specific interactions (such as hydrogen bonding or dipolar interactions) form self-assembling systems.

Various salts are added to micellar systems in order to control solubility. For example, lyotropic salts decrease the mutual solubility of water and amphiphiles (they increase the closed loop immiscibility island) whereas hydrotropic salts increase solubility (they shrink the closed loop).

Micellar systems are part of main-stream chemical-engineering. They find applications in detergents and cosmetics formulation, drug design and delivery, pharmaceuticals, oil recovery and treatment and in the food industry.

REFERENCES

M. Kahlweit and R. Strey, "Phase Behavior of Ternary Systems of the Type H$_2$O-Oil-Nonionic Amphiphile (Microemulsions)**",** Angewandte Chemie International Edition in English 24, 654–668 (1985).

K. Mortensen, "Structural Studies of Aqueous Solutions of PEO-PPO-PEO Triblock Copolymers: Their Micellar Aggregates and Mesophases; A SANS Study" J. Phys.; Condensed Matter 8, A13 (1996).

http://www.ncnr.nist.gov/resources/sldcalc.html contains a scattering length density calculator.

QUESTIONS

1. What is the difference between an LCST and a UCST phase separation?
2. What is a miscibility gap? How about an immiscibility island?
3. What is a tie line?
4. Define the critical point for a binary mixture.
5. What name replaces the critical point for a ternary mixture?
6. Define the 2-phase region for a ternary water/oil/surfactant system.
7. Describe the 1-phase for binary and for ternary mixtures. Contrast the main difference.
8. How many types of surfactant are there? Name them.
9. What is referred to as the "fish" phase diagram?
10. What is the "prism" phase diagram?
11. What are the two main criteria for the formation of a 3-phase region?
12. In which part of the phase diagram is the SANS technique most effective for a ternary system? Why?

ANSWERS

1. Phase separation occurs upon cooling for a UCST system and upon heating for an LCST system.
2. A miscibility gap is a miscibility region between a UCST at low temperature and an LCST at high temperature. A closed loop immiscibility island is a phase separation region between an LCST at low temperature and a UCST at high temperature.
3. A tie line is the line in the temperature-concentration phase diagram along which phase separation proceeds. The final product is a 2-phase mixture.

4. The critical point for a binary mixture (say water and surfactant) is the maximum point on the binodal line (also called coexistence curve) in the temperature-concentration phase diagram.

5. The plait point is used to refer to the critical point for a ternary mixture.

6. The 2-phase for a ternary system consists of a mixture of two phases (one rich in water and one rich in oil).

7. The 1-phase region for binary systems consists of a homogeneously mixed phase (i.e., mixed at the molecular level). The micelle-formation phase (m-phase) is sometime referred to as the 1-phase for ternary systems. This m-phase is mixed at the micrometer (so-called optical) scale but shows micellar structure at the nanometer (SANS) scale.

8. There are two types of surfactants: nonionic and ionic (i.e., charged).

9. The "fish" phase diagram maps out the 2-phase, the 3-phase and the m-phase regions in a temperature/surfactant concentration plot.

10. The "prism" phase diagram is the extension of the ABC triangle phase diagram to 3D by adding the temperature variable (out of the page). A prism shape is obtained.

11. A 3-phase region forms when the water-surfactant binary phase diagram contains a closed loop immiscibility island and the surfactant is a strong amphiphile.

12. The SANS technique is most effective in the micelle-formation phase since micelles are of nanometer sizes. The 2-phase and the 3-phase regions are characterized by huge (micrometer scale or larger) droplets.