

## PHASE DIAGRAM FOR TERNARY MIXTURES

The phase diagram for a ternary micellar system (Kahlweit and 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; it is characterized by a UCST behavior at low temperatures and possibly a closed loop immiscibility island at high temperatures; i.e., it phase separates both upon cooling and upon heating and is usually only observed for nonionic surfactants.

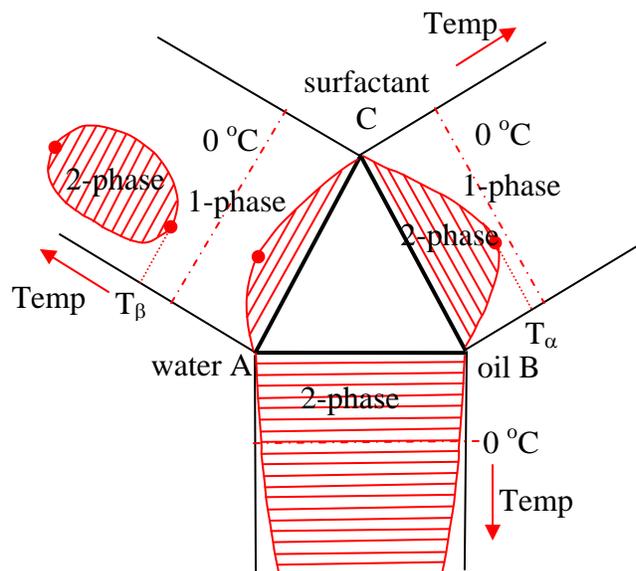


Figure 1: Phase diagram for the three binary mixtures (B/C, A/B, and A/C). The phase separation lines and temperatures are shown. The 0 °C water-freezing line has also been marked.

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.

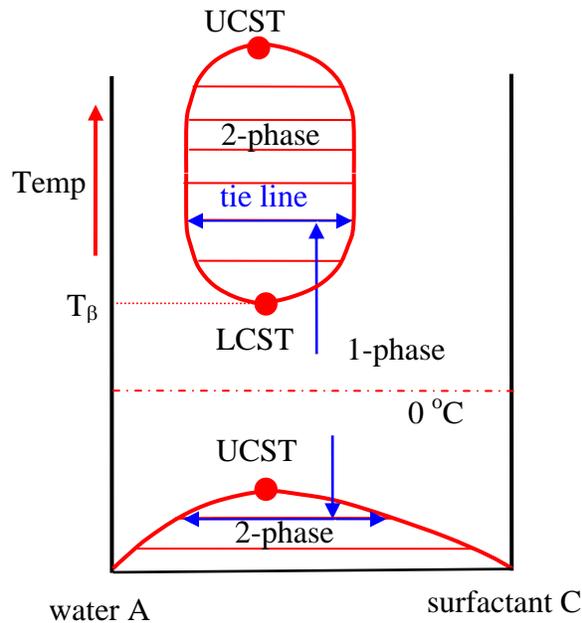


Figure 2: The water/surfactant (A/C) binary phase diagram.

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

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 structures in the nanometer size scale (oil-in-water and water-in-oil micelles). The 2-phase region contains a phase rich in surfactant/water in equilibrium with an oil-rich phase at low temperatures. At higher temperatures, the surfactant is more soluble in oil and the 2-phase equilibrium contains a phase rich in surfactant/oil in equilibrium with a water-rich phase. Note that micelles can form in the 2-phase region as well 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.

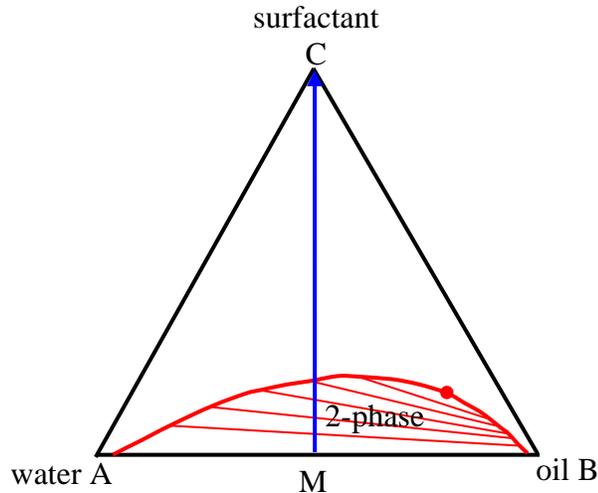


Figure 3: Schematic phase diagram of a generic ternary mixture. The m-phase is the micelle-formation phase.

Note that the case of P85 in d-water described previously corresponds to the left side (AC) 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 in the A/C phase diagram. When the closed loop region is reached, 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 ratio of water to 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.

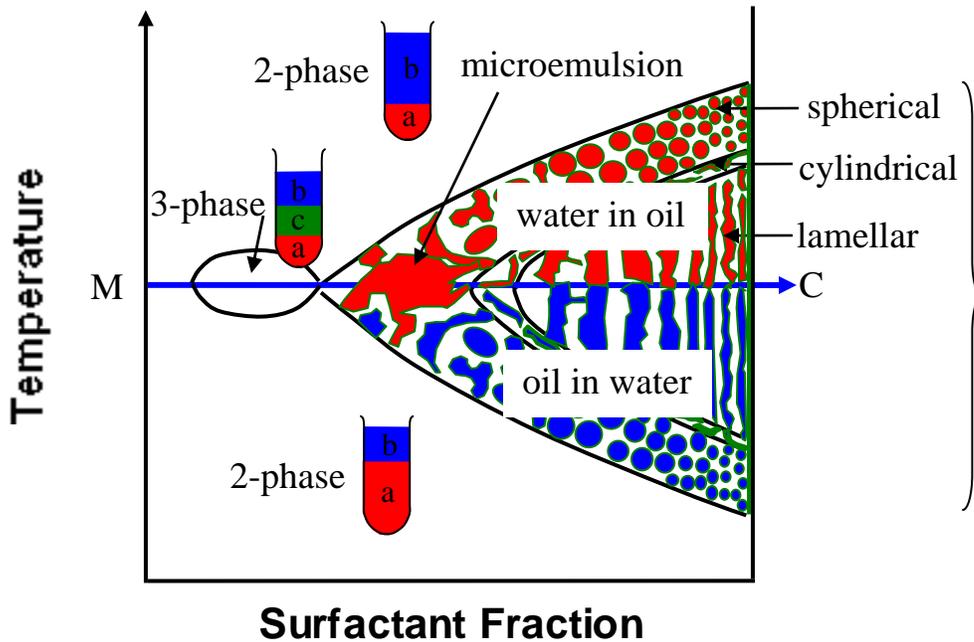


Figure 4: The “fish” phase diagram.

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.

This description was based on studies with common oils and water, using “typical” surfactants of low molecular weight. It is interesting to note that much higher molecular weight copolymers can also play the role of surfactants. When A-C block copolymers are mixed with A and B homopolymers (taking the place of “oil” and “water”), the same “fish” phase behavior is obtained.

## REFERENCES

M. Kahlweit and R. Strey, “Phase Behavior of Ternary Systems of the Type H<sub>2</sub>O-Oil-Nonionic Amphiphile (Microemulsions)”, *Angewandte Chemie International Edition in English* 24, 654–668 (1985).

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