water at 25°C results in a clear, colorless isotropic solution (11). Macroscopically this mixture does not change appearance until a 36% SDS solution is obtained. Molecularly, however, dramatic changes are occurring. The first change occurs at the critical micellization concentration (CMC). Before the CMC, the SDS molecules in the bulk water phase can be considered as individually dispersed and as acting as simple electrolytes. Above the CMC, many of the solution's physical properties change. These correspond to the formation of normal micelles (Fig. 1) in which approximately 60 amphiphiles form roughly spherical micelles with a hydrated radius of 25 A. Between the CMC and 25% SDS the micelles are approximately constant in size and maintain a relatively constant number of bound counterions (80%). Above 25% SDS, however, a transition from spherical micelles to rodlike (prolate ellipsoid) shapes rapidly occurs. This effect, sometimes known as the third CMC, is temperature-sensitive (12), occurring at 15% SDS when the temperature is raised to 70°C.

The addition of electrolyte also causes a transition from spheres to rods to occur at lower SDS concentrations (13). At 25°C, a 6.9×10^{-10} M SDS in 0.15 M NaCl solution contains rods with a semiminor axis equal to the radius of spherical micelles (25 A) and a semimajor axis slightly larger, with a length of 33 A. This is dramatically contrasted with a 6.9×10^{-10} M SDS solution in 0.6 M NaCl in which the semimajor axis increases to a length of 208 A, whereas the semiminor axis remains unchanged. When NaCl is present in the SDS—water system, temperature has the opposite effect. Here, decreasing temperature causes micelles to elongate with the greatest distortion occurring at the highest NaCl concentrations (13).

The next phase encountered with further addition of SDS follows directly from the formation of the rodlike micelles. Before the addition of 36% SDS, the rod-shaped micelles are disordered and, therefore, isotropic. After the addition of 36% SDS, the disordered rodlike micelles come into equilibrium with the similar, ordered hexagonal liquid crystal phase (see Fig. 1). From 39% to 50% SDS, all of the SDS amphiphiles become ordered to produce the one-phase hexagonal liquid crystal region. At soap concentrations above 50% SDS, there is no longer enough water to act as a solvent, and the crystalline soap is in equilibrium with the hexagonal liquid crystal. Thus, the baseline of ternary-phase diagrams for crystalline ionic surfactants frequently show this progression of micelles, to hexagonal liquid crystals, to crystalline surfactant. For nonionic surfactants of the polyoxyethyleneglycol type the baseline phase progression is from normal micelle, to lamellar liquid crystal, to inverse micelle or surfactant-rich solution (3).

Upon addition of a third component to an anionic surfactant system, a different characteristic phase progression results. The