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STUDIES OF LYOTROPIC LIQUID CRYSTALLINE PHASE IN SODIUM DODECYLSULFATE - WATER SYSTEM BY DENSITY AND CONDUCTIVITY MEASUREMENTS

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Abstract: Phase transition of isotropic micelle solution (I) to middle(M_1) phase in sodium dodecyl sulfate(SDS) - water system has been studied by density and conductivity measurements. Plots of density and conductivity versus SDS concentration exhibited a discontinuous change near the concentration of the transition (about 37 wt% of SDS). From these results, the mechanism of I-M_1 phase transition was discussed.

INTRODUCTION

The lyotropic mesomorphic state in sodium dodecyl sulfate - water(SDS-H_2O) system has been studied by several workers.[1-4] Luzatti et al.[1,2] have found by X-ray studies that this system exhibits middle(M_1), complex hexagonal and lamellar liquid crystal phases as functions of volume fraction of SDS and temperature, and determined the lattice constant and the

surface area of polar groups in the M_1 phase.

The present study has aimed at clarifying the mechanism of the transition between I and M_1 phase by density and conductivity measurements. The density measurements should be one of distinct methods to clarify a change of molecular packing in the I-M_1 phase transition.

EXPERIMENTAL

SDS was obtained from Nakarai Chemical Ltd., Tokyo (Specially prepared reagent, SDS-4, the purity is 99% in catalog). The sample was purified by recrystallizing several times from absolute ethanol solution. The critical micelle concentration(CMC) of SDS determined by conductivity measurements was 8.3 mM for the first CMC and 64 mM for the second CMC, being consistent with the past work.[5,6] The concentrated solution of SDS was prepared as follows; SDS and water was mixed alternately in a glass tube and after sealing the tube in vacuo, SDS was dissolved in water by stirring the mixtures at about 70°C for less than 24 hrs.

Phase diagrams were determined by a polarized microscope with a hot stage, using a tube slide(macro-micro slide, Vitro Dynamics Inc., U.S.A.). Density measurements were carried out with a Lipkin-Devidson pycnometer. Conductivity was measured by a conductance meter(TOA Electrics Ltd., Type CM-IDB) and a universal bridge(Ando Electrics Co., Type LCR-10).

RESULTS AND DISCUSSION

Phase diagram of SDS-H_2O system is shown in Figure 1. The M_1 phase appears in the higher concentration range above about 37 wt% of SDS. SDS is known to decompose to dodecyl alcohol by a dehydration reaction at higher temperatures.[3,7] The decomposition ratio of SDS was roughly estimated to be less than 5% for about 30 hrs at 70°C and 50-60% for about one

hour at 125°C, respectively, by determining dodecyl alcohol extracted by ether. Therefore, we could not determine phase transition above 100°C, especially since alcohol may affect sensitively the phase transition in SDS-H_2O system.[3]

Figure 2 shows plots of specific volume, v, versus SDS wt% in SDS-H_2O system at various temperatures. The value of v decreases with increasing SDS wt%. The abrupt decrease of v is observed apparently around 37 wt% of SDS. This concentration is consistent with I-M_1 phase transition. Figure 3 shows plots of specific conductivity versus SDS wt% at various temperatures. The conductivity increases linearly with the increase of SDS wt% in I phase below 20 wt% of SDS, and the increase begins to be gradually supressed with SDS concentra-

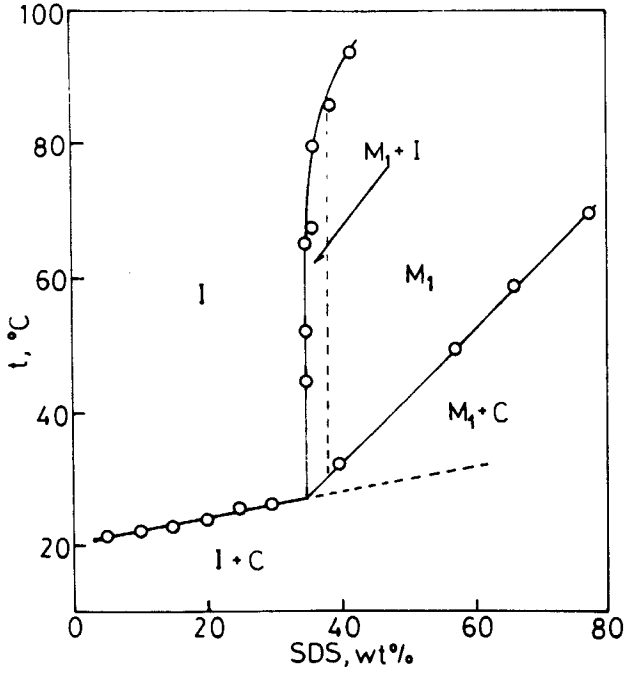

FIGURE 1 Phase diagram of SDS-H_2O system.

I: isotropic micelle solution, M_1: middle phase,
C: crystalline phase

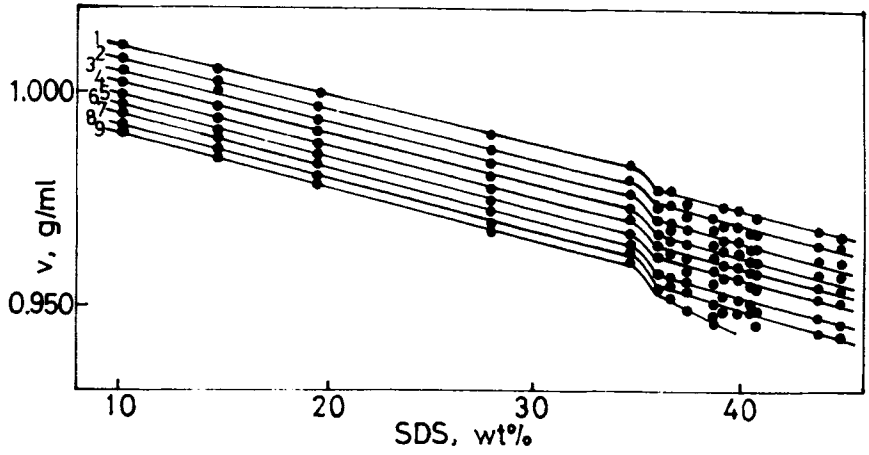

FIGURE 2 Plots of specific volume, v, versus SDS wt% in SDS-H_2O system.
1: 70°C, 2: 65°C, 3: 60°C, 4: 55°C, 5: 50°C,
6: 45°C, 7: 40°C, 8: 35°C, 9: 30°C

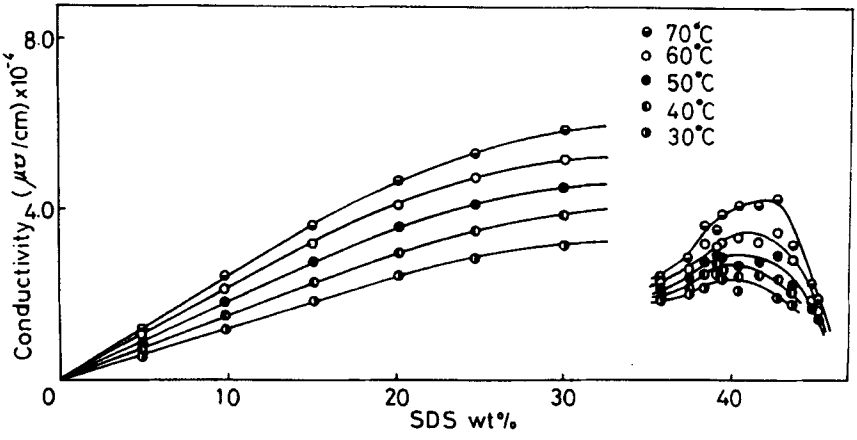

FIGURE 3 Plots of conductivity versus SDS wt% in SDS-H_2O system at several temperatures.

tion above 20 wt%. Then the abrupt decrease is observed near 37 wt% of SDS corresponding with I-M_1 phase transition.

Clunie et al.[8] measured density at a wide concentration range including micelle solution, middle, viscous isotropic and neat phases for N,N,N,-trimethylamino decanoimide - H_2O system. The density - specific volume fraction of surfactant curve had no discontinuous change at every transition concentrations. Furthermore, they observed a bend near the transition temperature from the middle to the isotropic phase in density - temperature plots at a definite concentration. From these results, they concluded that the phase transition in this system is a second order phase change, and for I-M_1 phase transition, proposed a model that the spherical micelles aggregate together to form a rigid string of spheres and this cylindrical string is packed in a hexagonal array to form M_1 phase. Although we could not measure density - temperature plots because of the decomposition of SDS at high temperatures, a discontinuous change was apparently observed near the concentration of I-M_1 phase transition in SDS-H_2O system. This suggests that the transition in SDS-H_2O system obeys a mechanism which is different of that of the transition in N,N,N,-trimethylamino decanoimide - H_2O system. In aqueous solution of surfactant, the formation and structure of micelle has been extensively studied. As well known,[4,5] surfactant molecules aggregate to a spherical micelle at the first CMC, and the state of aggregates changes somewhat at the second CMC. However, the state of aggregates retains a stable state in each phase. The discontinuous change in density and conductivity near SDS concentration of I-M_1 transition means that the spherical micelles change to a cylindrical micelles and that the latter micelles form a hexagonal arrangement to become M_1 phase. This model is, therefore, different from the rigid string model of Clunie et al. for N,N,N,-trimethylamino decanoimide - H_2O system. It is of interest and worthwhile to study a

relation between molecular structure of surfactant and structure of middle phase in various systems of surfactant with water.

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