両親媒子三元系におけるミクロ構造と相転移*

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Microstructure and Phase Transition in an Amphiphilic Ternary System

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Summary

Amphiphiles, which are often called surfactants, have a hydrophilic polar head and hydrophobic nonpolar tails. It is natural to think that a mixture of water and oil is immiscible; however, it can be mixed in presence of a little amount of suitable amphiphiles. As a consequence of their amphibious structure almost all amphiphiles remain on the water-oil interface in an aqueous-oil-amphiphile ternary system and organize various topologically distinct structures depending upon the temperature and the concentration of the components. In a binary system with water (or oil), amphiphiles form bilayer and remain between two water (or oil) domains. The structures of a binary or ternary amphiphilic system can be classified into isotropic disordered phases such as micelles, vesicles, droplet or bicontinuous microemulsions and lyotropic ordered phases such as hexagonal arrays of cylinders and lamellar structures.

Enormous efforts have been dedicated to examine the self-assembly, microstructures and dynamics of amphiphilic systems using several experimental methods such as small angle scattering, freeze fracture electron microscopy, NMR self-diffusion, static light scattering, electrical conductivity, etc. However, many interesting aspects are still unknown or little known. In the present thesis, we have investigated a ternary amphiphilic system consisting of water, n-octane and $C_{12}E_5$ by means of small angle X-ray scattering (SAXS), small angle neutron scattering (SANS) and electrical conductivity. $C_{12}E_5$ is a non ionic amphiphile and the phase diagram of this system shows a variety of structures as a function of both temperature and amphiphile concentration. For instance, in a dilute concentration of amphiphile if we increase temperature, the system shows a microemulsion phase at lower temperature, a lamellar phase at middle temperature and another microemulsion phase at

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**現在の所属：Venture Business Laboratory, Hiroshima University, 2-313 Kagamiyama, Higashihiroshima 739, Japan higher temperature. These phases are called low temperature microemulsion (LTM) phase, middle temperature lamellar (MTL) phase and high temperature microemulsion (HTM) phase, respectively. Previous studies in this system have revealed many aspects such as self-assembly, microstructure and direct images of local structures.

The aim of this thesis is to elucidate the mechanism of the phase transition and to clarify the structural differences in different phases of water/n-octane/$C_{12}E_5$ system. We have investigated the phase transition mechanism, microscopic structure parameters and interaction parameters by means of SAXS and SANS. To understand the structural evolution we have also investigated the electrical conductivity as a function of temperature in different phases.

SAXS was measured at a mirror-monochromator point focusing camera using CuK_α characteristic line from a rotating anode X-ray generator (Rigaku, RU-200). SANS experiment was performed at SANS-U of JRR-3M at Japan Atomic Energy Research Institute.

SAXS profiles were analyzed by means of phenomenological model, which is well established in amphiphilic systems to represent the scattering profiles. In each one-phase region (LTM, MTL or HTM phase) the scattering data shows a single scattering peak. However, we observed that two scattering peaks exist in a region between LTM and MTL or MTL and HTM phases. It means that two different structures coexist in the transition region between microemulsion and lamellar phase. We argue that in the transition region one peak represent microemulsion structure while the other one represent lamellar structure. From now, this region, where two peaks co-exist, will be named as coexistence region. The two peaks in coexistence region show a very systematic gradual change with respect to the peak positions and the intensity at peak positions. These behavior is in good agreement with the lever rule in phase diagram. In order to explain the experimental results in transition region we have supplemented the bending energy model developed by Andelman et. al. [1]. We have introduced a temperature dependence of the mean curvature of interfacial surfactant film. The phase transitions between microemulsion and lamellar phase have been explained as a result of the changes of curvatures of the interface film as a function of temperature and subsequent changes of bending elastic energy. A boundary of the coexistence region is estimated by the double tangent construction to the free energies of microemulsion and lamellar phases. These results are shown in ref. [2].

Structure parameters are determined by the phenomenological model analysis, while the interaction parameters are determined by microscopic spin lattice model analysis. Results are given in ref. [3].

From the phenomenological model analysis, the structural parameters such as average repeat distance of the structure D, correlation length ξ and $k\xi$ ($= 2\pi\ \xi/D$) are determined. Although the microstructures are different, we observed that the average repeat distance D between two water (or oil) domains are almost equal in LTM and HTM phases. Correlation length ξ has an increasing tendency with increasing surfactant volume fraction (ϕ_s) in LTM and MTL phases, while in HTM phase ξ has a lower value that decreases slowly with ϕ_s. Dimensionless parameter $k\xi$, which characterizes the structure, increases with ϕ_s in both LTM and MTL phases while it remains almost constant in HTM phase. A higher value of $k\xi$ in LTM phase with respect to HTM phase implies that LTM has a better order than HTM. Thermal fluctuations in HTM phase may make the structure less ordered than that in LTM phase. For an ideal lamellar phase $k\xi$ should be infinitely large, which indicates that the MTL phase, we studied, may not be a perfect lamellar phase or it may have lower order. A low ordered MTL phase might be constructed by the randomly oriented domains of lamellar liquid crystal.

Microscopic interaction parameters that were determined in terms of Gompper and Schick's (GS) microscopic spin lattice theory have reasonable order of magnitude for a lattice size d = 15Å in [111] direction. The inequality condition among the interaction parameters $|L| > J/4$, where J is the strength of the segregation between water and oil, L is the amphiphilicity of the amphiphile, suggests strong amphiphilic interaction for all three phases.

In order to investigate the mechanism of self-assembly, partial structure functions and local curvature of the surfactant film were determined by means of SANS [4]. Isotopic substitution of hydrogen atoms by deuterium in water and oil in the sample enabled us to measure partial structure functions from the observed scattering intensity. Results show that cross partial structure functions, which arise from the correlation between water-surfactant (or oil-surfactant), change sign from positive to negative (or vise versa) when the temperature passes through the hydrophile-lipophile balance (HLB) line. It indicates that the interaction parameter C, the preference of oil against water by an amphiphile, of the spin lattice model changes its sign on HLB line.

Mean curvature of amphiphilic film, $\langle c \rangle$ is determined at different temperatures and in different phases. We have considered the idea that the area of amphiphile-water interface is larger than that of oil-amphiphile interface if the amphiphile film is curved towards oil. The interfacial area and film thickness were determined from the fitting of modified Porod's law at higher q region. Experimental results show that the mean curvature increases as the temperature increases at a rate of 1.5×10^{-3} [$Å^{-1}K^{-1}$] . A positive curvature means that surfactant film bends towards water. In this system the behaviors of mean curvature that is $\langle c \rangle < 0$ at lower temperature and $\langle c \rangle > 0$ at higher temperature correspond to those of the imbalance of amphiphilicity towards oil that is $C < 0$ at lower temperature and $C > 0$ at higher temperature. Thus $\langle c \rangle$ and C correlate to each other in the same sense.

Significant differences between the structures of LTM and HTM phases are observed by electrical conductivity measurements. The high electrical conductivity in LTM phase indicates that the brine domain is well connected. Our results of mean curvature and electrical conductivity suggest an oil in water (o/w) droplet structure in the lower temperature region of the LTM phase. From the mean curvature measurement we observe that as the temperature increases the absolute value of mean curvature decreases in LTM phase. It can be explained if the droplets deform. The deformed droplets then stick together and from bicontinuous structure in the higher temperature region of LTM phase. In HTM phase a bicontinuous structure is consistent with our results.

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