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Pressure-effects on the structure formation in microemulsion systems

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非イオン性界面活性剤$C_{12}E_5$、水、油からなる三元系マイクロエマルションの構造変化に及ぼす圧力効果を調べた。実験は、小角中性子散乱（SANS）及び中性子スピンエコー（NSE）により行い、静的構造変化と動的構造変化について測定した。圧力上昇に伴う、ラメラからヘキサゴナルへの構造変化が観測され、圧力印加による活性剤の体積変化によって自発曲率変化が誘発されるためであることがわかった。一方、温度下降でも同様の構造変化が観測されるが、温度変化による構造変化の起源は活性剤の体積変化による自発曲率変化では説明できない。また、NSEにより活性剤膜の弾性率を測定したところ、圧力上昇による膜の硬化現象が観測された。この現象は、イオン性界面活性剤膜の場合にも観測されており、マイクロエマルション系では加圧によって活性剤膜が硬化する、という描像が一般的であると考えられる。

0.1 Introduction

Recent studies in AOT (dioctyl sulfosuccinate sodium salt), water, and oil systems indicated that the bending modulus of surfactant layers increased with increasing pressure, while it decreased with increasing temperature. [1, 2] In the case of ionic surfactants, however, Coulomb interaction plays a significant role in self-assembling, and therefore, in order to investigate the effect of pressure on the structural formation a non-ionic surfactant is preferable. In this contribution, we describe a temperature and pressure variation of SANS experiment for a $C_{12}E_5$, water, and octane microemulsion system.

0.2 Experiment

The SANS experiment was conducted on the SANS-U instrument installed at the cold neutron guide hall of JRR-3M in JAERI, Tokai, Japan. The covered momentum transfer, q, ranged over $0.014 \leq q \leq 0.14$ Å^{-1}. Hydrostatic pressure was applied by using a hand pump and the pressure was measured with a HEISE gauge within an accuracy of ±0.1 MPa. The covered temperature and pressure ranges were $292.15 \leq T \leq 309.28$ K and $0.1 \leq P \leq 103.0$ MPa, respectively. The ratio of the volume fraction of octane and $C_{12}E_5$ was fixed to be 1.37 and the volume fraction of water, ϕ_w was $\phi_w = 0.37$ ($\phi_o = 0.36$ and $\phi_s = 0.27$).

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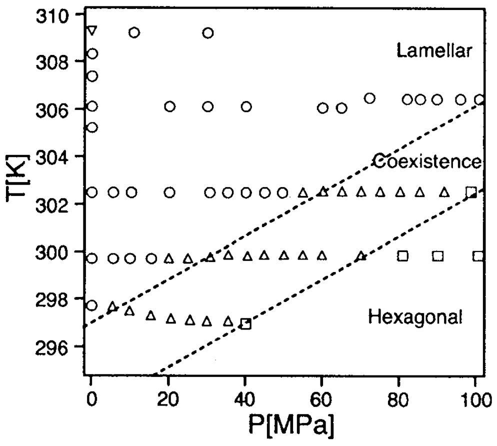

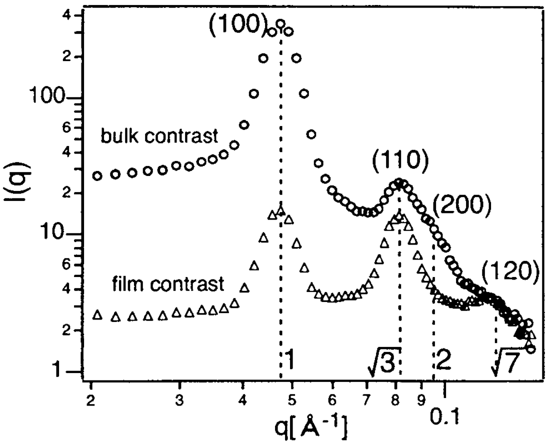

Figure 1: Phase diagram on $T-P$ plane.

Figure 2: SANS profile from the hexagonal structure.

0.3 Results

Figure 1 is the phase diagram on $T-P$ plane of the mixture with $\phi_w = 0.37$ determined by SANS. The symbols indicate the points experimentally accessed. With applying pressure, a phase transition from the lamellar (L_α) to the hexagonal phases (H_1) with a coexistence phase in between was observed at $T \leq 303$ K. The phase boundaries indicated by the dashed lines show the positive slope, which means that the effect of pressure is opposite to that of temperature on the phase behavior.

In Fig. 2, the SANS profile obtained from the bulk contrast sample is compared with that from the film contrast at $T = 299.85$ K and $P = 80$ MPa. Here, the bulk contrast sample means that the neutron scattering contrast is between oil and deuterated water, and the film contrast sample means that it is between surfactant layer and deuterated water or oil, respectively. The ratio of the q values of these peaks was $1 : \sqrt{3} : \sqrt{7}$ for the film contrast sample, which could be indexed as (100), (110), and (120) assuming the hexagonal structure. Therefore, both profiles clearly suggest the existence of cylindrical domain structures. From the detail analyses of the profile, we concluded that the high pressure phase is the oil-in-water cylinders packed hexagonally, which is identical to the low temperature hexagonal phase at ambient pressure. [3]

References

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