

Pressure effect on semi-microscopic structures and dynamics in a nonionic microemulsion

H. Seto, M. Nagao¹, Y. Kawabata², M. Shibayama¹, and T. Takeda³

Department of Physics, Kyoto University, Kyoto 606-8502, Japan

¹Institute for Solid State Physics, The University of Tokyo, Tokai 319-1106, Japan

²Department of Chemistry, Tokyo Metropolitan University, Hachioji 192-0397, Japan

³Faculty of Integrated Arts and Sciences, Hiroshima University, Higashihiroshima 739-8521, Japan

Recently, the authors investigated the pressure effects on a structure formation of a ternary microemulsion system consisting of a nonionic surfactant (pentaethylene glycol dodecyl ether; $C_{12}E_5$), water, and octane with a volume fraction of oil and surfactant being 1.37 and a volume fraction of water $\phi_w = 0.37$, by small-angle neutron scattering (SANS). [1] They showed a lamellar structure (L_α) at ambient temperature and pressure transforms to a hexagonal (H_1) phase at $P = 40\text{MPa}$. They estimated the isothermal compressibility of the surfactant molecule as $2.1 \times 10^{-6} \text{ kPa}^{-1}$. The order of this value is the same as that of dodecane ($0.99 \times 10^{-6} \text{ kPa}^{-1}$), [2] whose chemical structure is identical with a hydrocarbon tail of the surfactant molecule. This result suggested that a microscopic origin of the pressure-induced phase transition of the nonionic surfactant microemulsion is the compression of surfactant tails and a change of a spontaneous curvature of surfactant monolayers.

However, the structure parameters in the hexagonal phase, a radius of cylinders and a surfactant layer thickness, can not be defined uniquely by SANS even when the contrast variation method is utilized, because some assumptions were necessary in the data analysis. Thus, we have done further SANS experiment on the same system at different water concentration ($\phi_w = 0.62$) to confirm the previous result.

Figure 1 shows a schematic phase diagram of the ternary microemulsion. At smaller water concentration ($\phi_w = 0.37$), the system transforms to the hexagonal phase with increasing pressure as well as decreasing temperature. [1] In the present concentration, phase transitions from an oil-in-water (L_1) to the lamellar (L_α) and to a bicontinuous (L_3) structures are known to be observed with increasing temperature from 293 K to 306 K.

From the SANS experiment, a high pressure phase above 70 MPa is confirmed to be the L_1 structure by applying a "relative from factor method" [3] in the data analysis. The obtained structure parameters of droplets are as follows; the radius of a droplet core, $r = 65.6 \text{ \AA}$, and the surfactant layer thickness, $t = 11.7 \text{ \AA}$. From these values, the isothermal compressibility of hydrocarbon tails of the surfactants is

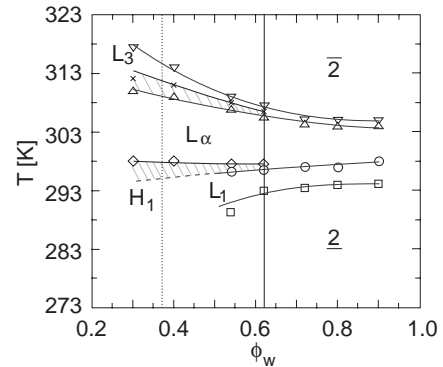


Figure 1: Phase diagram on the T - ϕ_w plane with the volume ratio of oil to surfactant being 1.37.

estimated as follows,

$$\kappa_T = -\frac{1}{V} \left(\frac{dV}{dP} \right)_T \sim 1.5 \times 10^{-6} \text{ kPa}^{-1}. \quad (1)$$

This value is closer to the compressibility of dodecane than that estimated in the previous experiment. [1] We could confirm that the volume change of surfactant tails plays a dominant role in the pressure-induced phase transition in the non-ionic surfactant microemulsion. [4]

A dynamical behavior of surfactant membranes was investigated by neutron spin echo, and it is shown that a bending modulus of membranes increases with increasing pressure. This result also confirmed the origin of the pressure-induced phase transition.

References

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