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A pressure-induced structural phase transition of dense droplet microemulsions

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Introduction

A ternary mixture of water, decane, and AOT (sodium bis(2-ethylhexyl) sulfosuccinate) has been especially popular in the studies of a self-organization of soft-matter systems because it has a large one-phase region without any other additives. The structure of this system at ambient temperature and pressure is known to be a water-in-oil droplet. When the molar ratio of water to AOT was fixed at 40.8, the radius of droplets is kept at about 50 Å, and only the droplet volume fraction, ϕ, increases with decreasing oil volume fraction.

In this study, the structure of mixtures of $0.40 \le \phi \le 0.70$ was investigated by means of small-angle x-ray scattering (SAXS). It is concluded that the radius decreased a little with increasing ϕ. Pressure variation of these systems were also investigated. The droplet structure transformed to the lamellar structure as the case of increasing temperature. These results can be explained by the concept that the increasing inter-droplet attractive force with increasing pressure controls the pressure variation of the structure.

Experiment

The SAXS experiments were performed at BL-15A beam port at Photon Factory. The incident x-ray beam was monochromatized to be 1.504 Å, and a one dimensional position sensitive proportional counter was set 1890 mm apart from the sample position with a vacuum path in between. As a result, covered momentum transfer Q range was from 0.0155 Å^{-1} to 0.181 Å^{-1}. All the samples were contained in a high-pressure cell made of stainless steel with diamond windows. [1]

Results

Droplet volume fraction dependence

The SAXS spectra of $0.4 \le \phi \le 0.65$ are characterized by a broad single peak which corresponds to an inter-droplet correlation. We tried to explain them by a sum of two terms as follows:

$$I(Q) = cP(Q)S(Q) + c_0L_0(Q) ,$$

where $P(Q)$ and $S(Q)$ are a droplet form factor and an inter-particle structure factor, respectively, and $L_0(Q)$ indicates surfactant density fluctuation. Following Ref. 2, the scattering function from the polydisperse droplet for $P(Q)$, the structure factor of a system with hard-sphere and adhesive inter-particle potential for $S(Q)$, and a single Lorentzian for $L_0(Q)$ were used. [2]

The results of the fitting showed that the droplet radius, R, at a distance from the center of a droplet to the hydrocarbon tails of surfactant molecules, decreased with increasing ϕ. The water core radius, R_0 also decreased with increasing ϕ. These results can naturally be explained if one allows deformation of droplets from the spherical shape. When the droplet density is low enough, the free energy condition of a droplet requires the spherical shape. However, with increasing droplet volume fraction, a droplet-droplet distance decreases and the effect of the attractive force of hydrocarbon tails of surfactant molecules becomes more significant; two layers of neighboring droplets will adhere each other and thus the droplets may deform. When a droplet volume is kept constant, the mean radius of deformed droplets is smaller than that of the sphere. Therefore, the mean value of droplet size decreases with increasing droplet volume fraction. This was supported by the evidence that the width parameter, Z, decreases with increasing droplet density, because it decreases with increasing polydispersity.

Pressure dependence

For all the ϕ measured, a broad single peak at ambient pressure shifted to lower-Q with increasing pressure, decreased in height, and finally vanished above a transition finish pressure, P_f. A new sharp peak appeared at higher-Q at a transition start pressure P_s ($P_s < P_f$).This tendency was the same as that for $\phi = 0.6$ in our previous article. [2] Thus we could conclude that the droplet structure at ambient pressure transforms to the lamellar structure with increasing pressure at $0.40 \le \phi \le 0.65$, through the transient state with the droplet and the lamellar structures.

From the data analysis, the followings were concluded: The percolated droplet structure remained up to about 30 MPa, independent of ϕ, and will be destroyed with increasing pressure. Characteristic features of the pressure dependence of the structure were almost the same excluding the pressure dependence of the water core radius. These pressure dependencies may be expressed by the change of solubility of tails of AOT molecules to surrounding oil and tails themselves. [3]

References

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