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Dynamic Processes in W/O Type Microemulsions Studied by a Dynamic Light Scattering Technique

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Dynamic processes in W/O type microemulsions have been studied by using a submicron particle analyzer. When large particles of microemulsion, which include water, are in quiet contact with the smaller particles without any stirring, the size of the microemulsion droplets will change due to solubilizate exchange between W/O type microemulsion droplets.

In recent years, the utilization of W/O type microemulsions have been helpful for the preparation of ultra-micro particles. Our attention has been focused only on the microemulsion as a reaction field.[1-8] The studies have yet made clear the reaction mechanism in microemulsion droplets, especially the solubilizate exchange between them. The middle-phase microemulsion is known to play an important role in enhanced oil recovery. The middle-phase microemulsion structure has been studied by many scientists[9-12] and that is presently a matter of controversy. Understanding of how the solubilizate exchange takes place between microemulsion droplets is of importance to clarify the structure and characteristic of a microemulsion.

In this paper, we have studied the hydrodynamic size and the size distribution of W/O type microemulsions formed by the three-component systems, Aerosol OT (AOT), water, and cyclohexane with a light scattering technique. We report changes of particle size due to coalescence and dispersion of W/O type microemulsions.

Aerosol OT (Sodium di(2-ethylhexyl) sulfosuccinate ; AOT) of reagent grade was purified according to the procedure of Park et al.[13] The purity was ascertained by a solubilization curve of water. The W/O type microemulsion was prepared by adding various amounts of water into 5 wt.% of AOT in cyclohexane.

The hydrodynamic particle size and the size distribution of the microemulsion were measured by a dynamic light scattering apparatus (MALVERN 4700-type Submicron Particle Analyzer). The light source was a Helium-Neon laser (632.8 nm, Spectra Physics Model-124B) and the scattering angle was 90°. The data analysis was performed by the combined use of the cumulant method[14] and the model free algorithm.[14] The most striking characteristic of this apparatus is that it is able to separate clearly two peaks with near particle sizes. We have confirmed it with two standard polystylene latex samples having different particle sizes, as shown in Fig. 1. Before measurement, the microemulsion as a sample was passed through the membrane filter (PTFE ; 200 nm) for optical purification. All these experiments have been carried out at 25 °C.

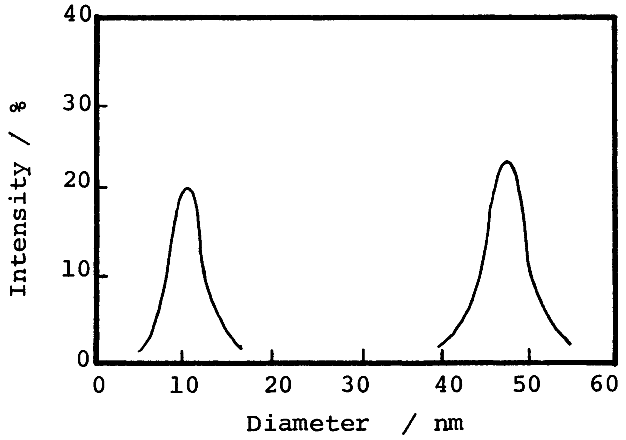

Fig. 1. The particle size distribution curve of two standard polystylene latex samples (109 nm, 482 nm) after mixing. The mixed ratio (109 nm/482 nm) is 1/1.

We obtained co-surfactant free microemulsions at every temperature, as shown in Fig. 2. In the figure, the term "clear" represents the W/O type microemulsion region and the term "turbid" the W/O type macroemulsion region. We tried to measure the microemulsion droplet size between A and B points at 25 °C.

Figure 3 depicts the change of droplet size with amounts of water. The hydrodynamic diameters (z-average and number-average) of W/O type microemulsion droplets increase proportionally with the amounts of water added into the cyclohexane. Moreover, the difference between z-average and number-average diameters increases with an increase in the amount of water. In other words, the distribution of droplet diameters is broadened.

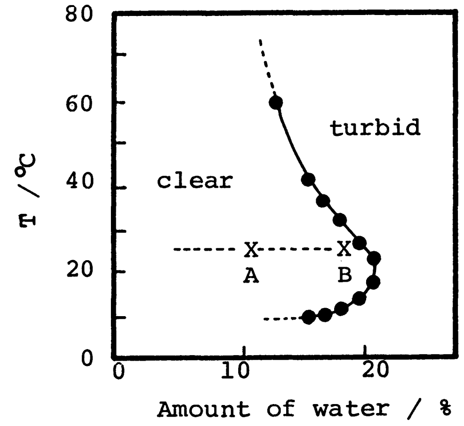

Fig. 2. The solubilization curve of water in cyclohexane solution containing 5 wt.% of AOT.

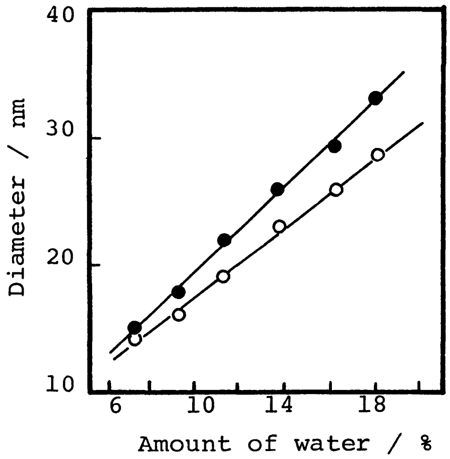

Fig. 3. Relationship between droplet size of microemulsion and various amount of water added.

● : Number-average diameter.

○ : Z-average diameter.

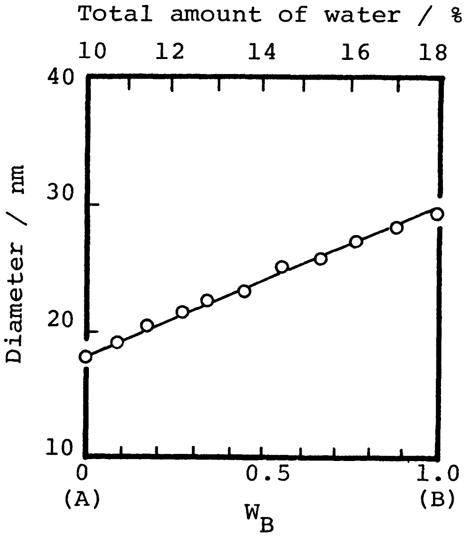

Fig. 4. Z-Average hydrodynamic diameters of microemulsion droplets against the weight fraction of B in the microemulsions after contact.
A : 10% of water contained.
B : 18% of water contained.

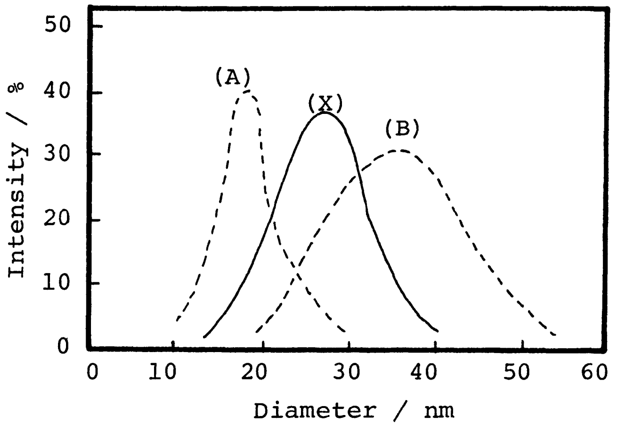

Fig. 5. The distribution curve of the hydrodynamic diameters before and after contact of two microemulsions (A and B) at the weight fraction of 0.5.
A : 10% of water contained.
B : 18% of water contained.
X : after contact (A/B = 1/1).

Figure 4 exhibits the hydrodynamic diameters (z-average) of the microemulsion droplets when two kinds of microemulsions (A and B in Fig. 2) having different sizes and distributions have been in contact with each other for 1 hour without stirring for various weight fractions. The reproducibility of the measurement within 1 hour was invariably poor. As can be seen in Fig. 4, the hydrodynamic diameter (z-average) after contact increases with increasing the weight fraction of microemulsion B (W_B) and is in fair agreement with the solid line which indicates an ideal mixing.

Figure 5 demonstrates the distribution curves of the hydrodynamic diameters before and after two microemulsions are in quiet contact with each other (weight fraction is 0.5). One should note that the particle size distribution, after two different microemulsions are in contact with each other, shows not two peaks, but only a single peak. Namely, the particle size and distribution of microemulsion droplets after the contact are averaged and they become exactly the same as those of the microemulsion prepared by mixing. This means that the solubilizate (water) exchanges between microemulsion droplets, because of coalescence and dispersion of microemulsion droplets. That is to say, coalescence will result from collisions between droplets according to Brownian motion. As for the dispersion, on the other hand, Cook et al.[15)] have suggested that the coalesced droplet has negative surface energy and that its interface is split up until the surface energy goes up to zero. In addition, because of the decreasing of the surface area with the coalescence of droplets, the orientation number of surfactants per unit surface area of the droplet will increase and so the interfacial tension will be smaller.

We consider that the solubilizate exchange between W/O type microemulsions takes place spontaneously without any mechanical mixing, and that its mechanism is due to the coalescence and dispersion of microemulsion droplets.

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