Highly Concentrated Cubic-Phase Emulsions: Basic Study on D-Phase Emulsification using Isotropic Gels

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Abstract: In a hydrophilic octaethylene glycol dodecyl ether (C₁₂EO₈)-water system, a micellar cubic phase is formed below 20°C. Upon addition of decane, the maximum temperature of micellar cubic phase (I₁) is increased, and, moreover, the hexagonal liquid crystal region changes to the I₁ phase. Beyond the solubilization limit of decane in the I₁ phase, highly viscous and gel-like O/I₁-emulsions are formed in the two-phase region of I₁+O. In the case of a surfactant mixture (C₁₂EO₈₄) containing C₁₂EO₈+C₁₈EO₈, a single I₁ phase region is not present in a pseudo ternary phase diagram of water/C₁₂EO₈/decane system, but an I₁+O region appears in the oil-rich region. C₁₂EO₈₄ forms lamellar liquid crystal in the aqueous system but C₁₈EO₈ in the mixture is dissolved in oil and the mixing fraction of C₁₂EO₈ in the surfactant aggregate increases as oil is added. Finally, a two-phase region of I₁+O appears.

It is considered that the O/I₁-emulsion or gel based on the cubic phase corresponds to the gel appeared in the so-called D-phase emulsification process. Upon addition of alkyl polyol such as glycerol or 1,3-butandiol, the transparency of the emulsion in the I₁+O region increases because the difference in refractive index between the cubic phase and excess oil is decreased. The maximum temperature of the I₁ phase decreases with increasing polyol content. Consequently, the addition of alkyl polyols is not crucial to form O/I₁ gels in an oil-rich region.


Key words: highly concentrated cubic-phase emulsion, discontinuous cubic phase, D-phase emulsification, polyol

1 Introduction

Since emulsions are in a non-equilibrium state, the emulsion stability or droplet size depends on the emulsification method. Sagitani (1,2) established a so-called D-phase (detergent phase) emulsification method to form fine oil droplets. In the first step of this method, a surfactant aqueous solution containing alkyl polyol such as glycerol, 1,3-butandiol, etc., is mixed with a large amount of oil to produce a translucent or transparent gel. Then, the gel is diluted by excess water to form fine oil droplets dispersed in aqueous medium. This kind of gel appears in the process of other emulsification procedures (3).

Although the gel is considered to be a high-internal-phase-volume-ratio or highly concentrated emulsion, the detailed structure has not been completely understood. Upon addition of alkyl polyol to water, anisotropic liquid crystals formed in an aqueous surfactant system tend to disappear (4). Hence, the addition of alkyl polyols has been considered to be crucial for the formation of isotropic gels.

In our previous studies on highly concentrated emulsions (5,6), it was found that O/W-type highly concentrated emulsions are formed in an oil-rich region and they consist of isotropic oil and aqueous micellar phases, and the volume fraction of continuous micellar phase is very low. They often also look translucent and show gel-like appearance. However, the ratio of water to surfactant in our emulsions consisting of two isotropic fluid phases is much higher
than that in Sagitani’s gel.

Ordinary emulsions are dispersed systems in which one liquid phase is dispersed as droplets in another immiscible liquid phase. In practical applications, liquid crystalline phases are often used to stabilize the emulsions. It is known that a lamellar liquid crystal prevents coalescence of an O/W emulsion (7). It was also found that a reverse hexagonal phase stabilizes a W/O type emulsion (3). Recently, we found that oil droplets are stabilized in a micellar cubic phase formed in a hydrophilic surfactant-water system, and a cubic-phase based O/W emulsion can be produced. These emulsions often look transparent because the refractive index of cubic phase is close to that of the dispersed oil phase (8).

A micellar cubic phase is a kind of lyotropic liquid crystal in which aqueous micelles are packed in a three-dimensional cubic array. This phase is highly viscous and optically isotropic. It seems that the cubic-phase emulsion is related to the gel in the D-phase emulsification, but no experimental evidence has been found yet. In the previous studies on D-phase emulsification, a mixture of surfactants or commercial-grade surfactants with a large distribution in the hydrophilic chains were used. Hence, the surfactant phase behavior is too complicated to know the relation between a micellar cubic phase and Sagitani’s gel due to the difference in distribution of each surfactant in the commercial surfactant between surfactant aggregates and oil.

In this context, the effect of added oil on the formation of a micellar cubic phase was investigated in a water/octaethleneglycol dodecyl ether/oil system. Effects of mixing surfactant or added glycerol and 1,3-butanediol on the phase behavior were also studied.

2 Experimental

2·1 Materials

Homogenuous octa- or tri-oxyethylene dodecyl ethers \( \text{C}_{12} \text{H}_{25}(\text{OCH}_{2}\text{CH}_{2})_{n}\text{OH} \) with \( n = 3, 8 \), which are designated by \( \text{C}_{12} \text{EO}_{2} \) and \( \text{C}_{12} \text{EO}_{8} \), were supplied by Nikko Chemicals Co. Distilled water was used in the preparation of the samples.

2·2 Determination of Phase Diagram

Various amounts of water and surfactant were weighed and the mixtures were sealed in ampoules. The phase state was determined by direct visual inspection and by crossed polarizers. The types of liquid crystals were determined from optical microscopy and small-angle x-ray scattering.

2·3 Small-angle x-ray Scattering Measurement

Interlayer spacing of liquid crystal was measured by small-angle x-ray scattering (SAXS), performed on a small-angle scattering goniometer with an 18 kV Rigaku Denki rotating anode generator (Rint 2500) at 25°C. The samples were placed in a metal slit with plastic film (Mylar seal method). The types of liquid crystals were distinguished from the interlayer spacing ratio of first, second, and third scattering peaks.

3 Results and Discussion

3·1 Effect of Added Oil on the Formation of a Micellar Cubic Phase in Aqueous \( \text{C}_{12} \text{EO}_{8} \) System

In a hydrophilic water/\( \text{C}_{12} \text{EO}_{8} \) system, micellar solution (Wm), micellar cubic (I₃), hexagonal liquid crystal (H₃), and lamellar liquid crystal (L₄) phases are successively formed (9,10). The melting temperature of I₃ phase is low (around 18°C). However, with increasing the EO-chain length of surfactant, the melting temperature increases and the I₃ phase is dominant in a phase diagram of binary water-polyoxyethylene-type nonionic surfactant system (11). A ternary phase diagram of water/\( \text{C}_{12} \text{EO}_{8} \)/decane system was constructed at 25°C and is shown in Fig. 1. There are neither cubic phase nor lamellar liquid crystal on the water-surfactant axis because their melting temperatures are below 25°C. When decane is added to the aqueous system, the I₃ and L₄ phases appear as is shown in Fig. 1. In other words, rod micelles in the H₃ phase are changed to spherical micelles in the I₃ phase upon addition of oil at constant temperature. The oil-induced H₃-I₃ transition is observed in many surfactant systems (12-16). In the case of dilute aqueous micellar solution phase, the shape of micelles is also changed from rod-like to spherical upon addition of oil, especially, long chain hydrocarbons (17). Since the I₃ phase is present between the Wm phase and the H₃ phase, it is considered to be the I₃ phase consisting of spherical micelles stacked in a cubic array.

The I₃ phase has a face-centered cubic structure (Fm3m), judging from the SAXS peak ratios, 1 : \( \sqrt{3}/4 \) : \( \sqrt{3}/8 \) (18). The interlayer spacing in the I₃ phase increases with increasing oil content as is shown in Fig. 2. Beyond each solubilization limit of Wm, H₃,
Fig. 1 Phase Diagram of Water/C_{12}E_{8}/Decane System at 25°C. W_{m} is an aqueous micellar solution phase. I_{1}, H_{1}, V_{1}, and L_{w} indicate discontinuous micellar cubic phase, normal hexagonal phase, normal bicontinuous cubic phase and lamellar phase, respectively. O_{m} is a surfactant liquid or reverse micellar solution phase. O is an excess oil phase. S is a solid present phase.

Fig. 2 Change in Interlayer Spacing, d, in the I_{1} Phase as a Function of Decane Content in Water/C_{12}E_{8}/Decane System at 25°C. The water/C_{12}E_{8} weight ratio is fixed at 62/38.

Fig. 3 Microphotograph for O/I_{1} Gel Emulsion. The composition is 12.4% water, 7.6% C_{12}E_{8}, and 80% decane.

and I_{1} phases, an excess oil phase (O) is separated and two-phase regions are formed. Stable, very viscous, and gel-like emulsions of O/I_{1} type were formed in the I_{1}+O region. A microphotograph for the O/I_{1}-emulsion is shown in Fig. 3. It is a highly concentrated emulsion in which the shape of droplets is not spherical but polyhedral. The appearance of this emulsion is similar to that of gel emulsion obtained in the D-phase emulsification (1). Since the refractive index of I_{1} phase is high and is comparable with that of oil, the I_{1}+O region often looks like a transparent or translucent gel (8). In the present system, however, although a highly concentrated O/I_{1} phase emulsion is formed, the difference in refractive indices is rather large and the viscous emulsion looks turbid.

The effect of added oil on the melting temperature of the I_{1} phase was determined at constant water/surfactant ratio and the phase diagram as a function of temperature is shown in Fig. 4. Upon addition of decane, the melting temperature of the I_{1} phase increases abruptly. The melting temperature reaches 58°C and then becomes constant in an oil-rich region. The W_{m} phase is present above the I_{1} phase and the solubilization of oil in the W_{m} phase increases with increasing temperature. The PIT or HLB temperature of this system is around 78°C. At higher temperature, the surfactant becomes lipophilic and a two-phase region of O_{m}+W is formed where O_{m} is a reverse micellar solution phase and W is an excess water phase. It is clear from Fig. 4 that oil enhances the stability of I_{1} phase. As a matter of fact, the I_{1}
phase appears only upon addition of oil in many ternary phase diagrams of water/hydrophilic surfactant/oil systems (12-16).

3.2 Effect of Mixing Surfactant on the Phase Behavior

Most of nonionic surfactants used for practical applications are commercial surfactants, which have a distribution in hydrophilic-chain length and often contains unreacted alcohol. In these systems, a phase diagram like Fig. 1 is not obtained because they are not three-component systems and therefore the phase rule does not hold on the triangular phase diagram. In order to understand the effect of mixing surfactant on the cubic-phase region, we constructed a phase diagram of water/C_{12}EO_{4.8}/decane system at 25°C as is shown in Fig. 5. C_{12}EO_{4.8} is an equal-weight mixture of C_{11}EO_{4} and C_{13}EO_{5}.

Since the average EO-chain length is short, a lamellar liquid crystal is present in a wide range of composition in the vicinity of the surfactant-water axis. There is no single I_{c} phase region in the phase diagram. Instead, there is a two-phase region of I_{c}+O in the oil-rich region. When the oil content in the system is low, i.e. in the vicinity of the water-surfactant axis, all the surfactant molecules are practically incorporated in aggregates because the cmc of surfactant in water is extremely small. With increasing oil content, some fraction of the surfactant is dissolved as monomers in oil. In general, the solubility in oil of a lipophilic or short-EO-chain surfactant is much larger than that of a hydrophilic one. Then, the mixing fraction of hydrophilic surfactant at the interface of aggregates or micelles increases, and structures with high curvature like the cubic phase are favored. Consequently, the L_{a} or H_{c} phases are formed on the water-surfactant axis in the mixed C_{12}EO_{4.8} system, whereas the I_{c}+O two-phase region appears in an oil-rich region as is shown in Fig. 5.

In order to confirm that the mixed surfactant becomes hydrophilic at a high oil content, the phase diagram of water/C_{12}EO_{4.8}/decane system was constructed as a function of temperature and the result is shown in Fig. 6. The I_{c}+O region appears at high oil content and shifts to higher oil concentration as temperature is increased. Since the nonionic surfactant becomes relatively lipophilic with increasing temperature due to the change in conformation of the EO chain (19), the increasing in the thermal stability
of the $I_1+O$ region with oil content indicates that the mixed surfactant becomes more hydrophilic. It is clear from these results that the $I_1+O$ region or gel region based on the $I_1$ phase appears only in an oil-rich region in a mixed surfactant system, because the lipophilic surfactant, C12EO8, is more soluble in oil than C12EO9. Due to the same reason, it has been reported that the HLB temperature or PFT is also shifted to higher temperature with increasing oil content in mixed nonionic surfactant (20).

3-3 Effect of Added Glycerol or 1,3-butanediol on the Phase Behavior

It is known that the cloud temperature of aqueous nonionic surfactant solutions decreases upon addition of glycerol to water, whereas it increases with 1,3-butanediol (21). Effect of added glycerol and 1,3-butanediol on the melting temperature of the $I_1$ phase was investigated and the results are shown in Fig. 7.

With increasing the alkyl polyol content, the maximum temperature of the $I_1$ phase decreases. Hence, the addition of alkyl polyol induces instability on the cubic phase (8). Other liquid crystals like the $H_3$ phase are also destabilized upon addition of these alkyl polyols (4). Moreover the O/I1 gel emulsion becomes less stiff. Upon further addition of alkyl

Fig. 6  Phase Diagram of Water/C12EO8/Decane System as a Function of Temperature. The water/C12EO8 ratio is fixed at 69/31. I and II indicate one and two-phase region, respectively.

Fig. 7  Effect of Added Glycerol (a) and 1,3-butanediol (b) on the Formation of $I_1$ phase in Water/C12EO8/Decane System. The alkyl polyol concentration in water + alkyl polyol is plotted on the horizontal axis. The (water + polyol)/C12EO8/decane weight ratio is fixed at 40/18/42. LC present indicates the existence of birefringent liquid crystals.
polyl, I₁ + O region changes to a two-liquid phase region, and gel-emulsion cannot be formed. Therefore, the I₁ phase is necessary for the formation of the gel emulsion, but the addition of alkyl polyl is not crucial. However, the reduction of viscosity upon addition of polyl would make the handling of O/I₁ gel emulsion easier.

3.4 Transparency of O/I₁ gel Emulsion

In the polyl-free system, the O/I₁ gel emulsion is turbid because the difference in refractive indices between two phases is large. When alkyl polyl is added, the refractive index of the I₁ phase increases. The change in refractive index of I₁ phase as a function of alkyl polyl content in water is shown in Fig. 8. With increasing the alkyl polyl content, the refractive index approaches to that of decane (= 1.4094). As is shown in Fig. 9, the stable gel emulsion becomes translucent upon addition of glycerol. Hence, addition of alkyl polyl is very effective to increase the refractive index of I₁ phase.

4 Conclusions

A micellar cubic (I₁) phase is formed in water/C₁₂EO₅ system. The maximum temperature of the I₁ phase increases upon addition of hydrocarbon and a O/I₁ gel emulsion is formed in the two-phase region of I₁ + O at high oil content. Even if the I₁ phase does not appear in a binary water-surfactant system, it is formed in the presence of oil. The O/I₁ gel emulsion corresponds to Sagitani’s gel emulsion in the process of D-phase emulsification.

In the case of mixed nonionic surfactant or commercial surfactant, the fraction of surfactant in aggregates becomes hydrophilic at high oil content. For this reason, only I₁ + O region or gel emulsion appears and no single I₁ phase is found in a pseudoternary phase diagram, while other lipophilic liquid crystals appear in the vicinity of water-surfactant axis. Hence, in the previous study on the D-phase emulsification, one could not identify that the cubic phase is involved in the gel emulsion.

The addition of alkyl polyl is not crucial for the formation of O/I₁ gel emulsion. However, it destabilizes the cubic phase and it would be easy to handle it because of the reduction of viscosity. Alkyl glycerol changes the refractive indices of the cubic phase and a turbid concentrated emulsion changes to a translucent gel.
References