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ORIGINAL CONTRIBUTION

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Emulsion stability in sucrose monoalkanoate system with addition of cosurfactants

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Abstract The hydrophile-lipophile property of the sucrose monododecanoate changes from hydrophilic to lipophilic by adding an alcohol as a cosurfactant. With the addition of a short-alkyl-chain alcohol (pentanol, hexanol), the surfactant forms the middle-phase microemulsion whereas a lamellar liquid crystal (L_α) appears with a medium- or long-chain alcohol (heptanol, octanol, decanol) at the balanced state in water/ SE/ cosurfactant/ decane system. The effect of changing oil was also studied in the presence of a middle-chain cosurfactant (heptanol). A short-chain aromatic oil (*m*-xylene) forms middle-phase microemulsion whereas a longer aliphatic one (hexadecane) forms lamellar liquid crystalline phase in a dilute region when the HLB of surfactant is balanced in a given system. O/W emulsions become stable on the hydrophilic-surfactant-rich side whereas W/O emulsions are stable on the cosurfactant-rich side. Emulsions are very unstable in the three-phase regions. However, when the lamellar phase is produced, emulsions become stable at the balanced state because water and oil are incorporated in L_α phase in the longer cosurfactant systems such as water/ SE/ octanol/ decane and water/ SE/ decanol/ decane.

Keywords Sucrose monododecanoate · Middle-phase microemulsion · LC-present region · Cosurfactant · HLB

Introduction

It is well-known that poly(oxyethylene)-type nonionic surfactants change from water-soluble to oil-soluble with increasing temperature due to the conformational change in the poly(oxyethylene) chain [1]. The emulsion also changes from O/W to W/O type at a certain transition temperature, called HLB temperature or PIT which is also referred to as a balanced state [2, 3, 4]. Usually, surfactant-phase or middle-phase microemulsion coexists with excess water and oil, and the three-phase body appears at the PIT. Emulsion stability is lowest at PIT because the spontaneous curvature of surfactant layer is zero and the surfactant has no ability to determine the emulsion type [3, 5, 6]. On the other hand, O/W emulsion becomes stable at considerably lower temperature than the PIT, whereas W/O becomes stable at higher temperature. Similar trends of phase behavior or emulsion stability are observed by changing the mixing fraction of lipophilic surfactant (or cosurfactant) in a surfactant mixture.

In ionic surfactant systems, a middle-chain alcohol is used as cosurfactant, and a phase behavior similar to the nonionic surfactant is observed at constant temperature by changing the cosurfactant/surfactant ratio. However, in a long-chain amphiphile (surfactant and/ or cosurfactant) system or in surfactant systems for practical applications, a three-phase body is not always observed and, instead, a lamellar liquid crystal is present even in a dilute region at PIT or in a balanced state [7, 8]. Hence, emulsion stability would be different when the liquid crystal is formed in a dilute region.

Sucrose monoalkanoate (abbreviated as SE) is a biocompatible nonionic surfactant since it is synthesized from sugar and natural fatty acids. It is noteworthy that the property of SE-type surfactants is not strongly influenced by the temperature like other nonionic surfactants [9, 10]. Due to the highly hydrophilic nature, sucrose monoalkanoate easily forms O/W emulsion (low CMC), which is a major category of consumer goods.

In order to compensate for its hydrophilicity, it is necessary to add a cosurfactant to tune the surfactant layer curvature. In this present work, we used different sized alkyl-chain alcohols (pentanol, hexanol, heptanol, octanol, decanol). While mixing water, surfactant, cosurfactant, and oil, the water dissolves in the SE + cosurfactant phase infinitely at the lower composition of cosurfactant and an aqueous micellar solution (Wm) is formed. However, the hydrocarbon will dissolve infinitely at high concentration of cosurfactant and the reversed micellar solution (Om) is formed.

Our earlier study [9] showed that the middle-phase microemulsion is formed upon addition of short-alkyl-chain alcohol (hexanol) as a cosurfactant in water/ SE/ hexanol/ decane when the HLB of the surfactant mixture is optimum. However, the combination of sucrose mono- and multi- dodecanoates gives a lamellar liquid crystal instead of three-phase microemulsion in a dilute region at the balanced state [11]. Hence, it is considered that three-phase microemulsion would be changed to lamellar liquid crystal at the balanced state with increasing the chain length of alcohol in SE/ cosurfactant systems. In this context, the present study is focused on the phase behavior and emulsion stability in a sucrose monododecanoate (SE) system with addition of both short- and long-chain alcohol as cosurfactant. We also investigated the effect of changing oils (*m*-xylene, hexadecane) on the formation of emulsions in the water/ SE/ heptanol/ oil systems.

Experimental section

Materials

Pure sucrose monododecanoate (SM-1200, abbreviated as SE) was supplied from Mitsubishi Chemical Co. The monoester content is much higher than 95% and the impurities are mainly unreacted sucrose as well as a small amount of water. The ash content is ~0.3% (K_2SO_4), decane (99%), *m*-xylene (99%), hexadecane (98%). Extra pure grade pentanol, hexanol, heptanol and octanol were obtained from Tokyo Kasei Kogyo, Tokyo. Decanol (99%) was obtained from Aldrich Chemical Company, Inc, USA. All chemicals were used without further purification.

Determination of phase boundaries

Various amounts of water, oil, surfactant, and cosurfactant were weighed and sealed in glass ampoules. Then the ampoules were well shaken using a vortex mixer and kept at 25 °C in a thermostat for several hours to equilibrate. The phase change was detected by direct visual observation with polarizers. Characteristic textures of the liquid crystals were detected by polarized microscope.

Determination of emulsion stability

Sufficient number of samples was made at constant surfactant concentration (7%) in the region of middle-phase microemulsion and LC-region at an increasing order of the weight fraction of cosurfactant in SE + cosurfactant (W_1). Then the samples were well-mixed using a vortex mixer. A high stress was applied to each of the samples (by hand shaking) for 1 min, keeping inside the thermostat to break up any preformed floc structure. The samples were kept for 1 h to measure the phase volumes of the cream, drained, or coalesced phases. The volumes of separated phases were plotted against W_1. The stability of emulsion was also investigated by changing the surfactant concentration in the LC-region in water/ SE/ octanol/ decane and water/ SE/ decanol/ decane systems.

Determination of droplet type in LC-region

Droplet type is determined by the so-called Becke line effect [12, 13] using an optical microscope. Following this method, the focus is adjusted sharply on the droplets and then the microscope tube is racked upwardly while observing the fringe of light around the object. If the fringe is contracted as the tube is racked up, the droplets are considered to be dispersed-oil having a refractive index higher than the continuous phase. On the contrary, if the fringe appears to expand, the droplets are dispersed-water with a refractive index lower than the continuous phase.

Results and discussion

Effect of cosurfactants on the phase behavior

The phase diagram of water/ SE/ pentanol/ decane is shown in Fig. 1a. The surfactant molecules form normal micelles (Wm) in water at low W_1; this aqueous micellar solution phase coexists with excess oil phase. On the other hand, the mixed surfactant forms the reverse micellar solution phase (Om) with excess water being dispersed as droplets at higher W_1. A three-phase region consisting of excess water (W), excess oil (O), and a microemulsion phase (D) exists between the biphasic regions. Since large aggregates are formed at a balanced state, the solubilization capability of surfactant reaches its maximum and ultra-low interfacial tensions are attained in the three-phase region. This is related to the critical solution phenomena among microemulsions, water, and oil phases. [14, 15]. In this stage, the relative HLB of the mixed surfactant is just optimum in the midst of three-phase region and the surfactant (cosurfactant) molecules are distributed among micro-water and oil domains as well as water-oil interfaces inside the middle-phase microemulsion (D). Although there are micro-domains inside the D phase, the microemulsion looks transparent and it is a single phase like a micellar solution. At high total surfactant concentration (20%,

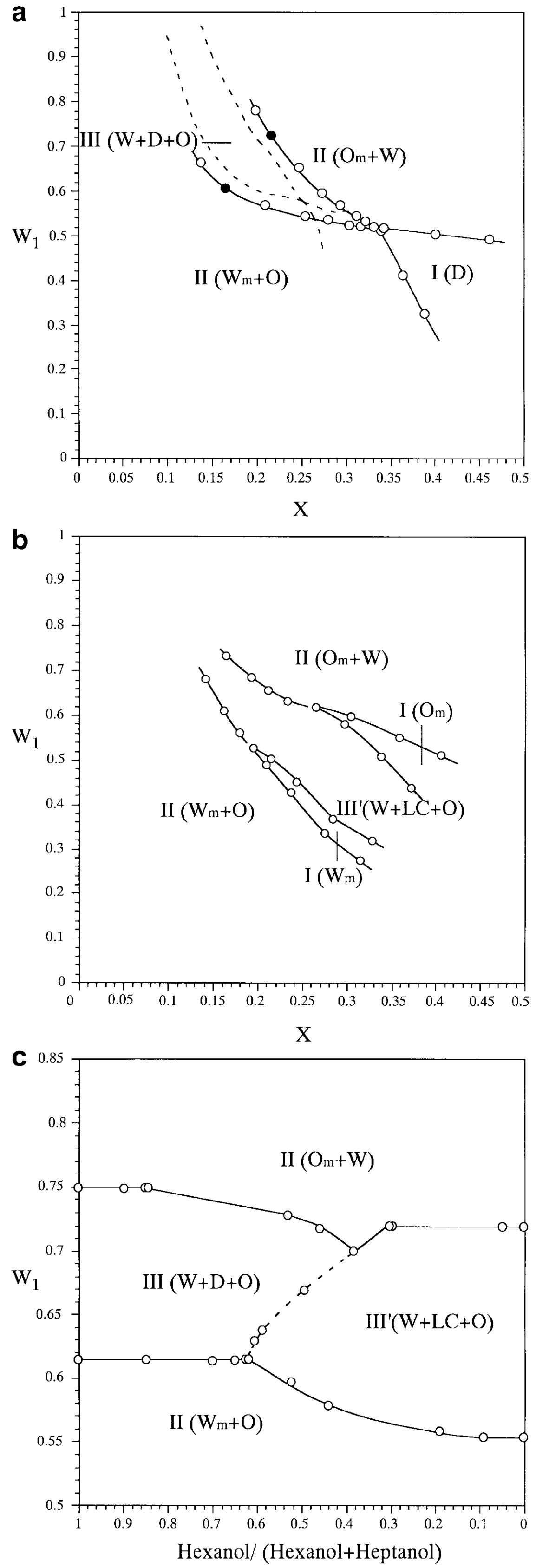

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Fig. 1a–c. Phase diagrams of water/ SE/ cosurfactant/ decane at 25 °C. Cosurfactants are pentanol (**a**) and heptanol (**b**). X is the weight fraction of total surfactant in the system and W_1 is the weight fraction of cosurfactant in the total surfactant mixture. *Filled circles* indicate the composition at 7% SE. *Dotted lined phase boundary* indicates the water/ SE/ hexanol/ decane system [9]. Part (**c**) shows the phase transition from the bluish middle-phase microemulsion (III) to the milky liquid crystal-present region (III') with increasing heptanol content in the water/ SE/ (hexanol + heptanol)/ decane system at constant X = 0.175. The water/oil ratio is 50/50. I, II are the isotropic one- and two-phase regions

$W_1 = 0.51$), all the oil and water molecules are solubilized into a single microemulsion phase, defined as maximum solubilization limit.

In the phase diagram of water/ SE/ heptanol/ decane system (Fig. 1b), an optically anisotropic liquid crystal-present (LC) region appears between two microemulsion phases, and there is no three-phase body. The presence of this phase would enhance the stability of emulsion [16, 17, 18]. As the lateral interactions between surfactant and alcohol increases with increasing the chain length, the cosurfactant tends to solubilize between the lipophilic bi-layer. Thus the surface of the aggregates becomes arranged and rigid, favoring the formation of lamellar liquid crystal when the hydrophile-lipophile property of the surfactant is balanced.

At low W_1, the surfactant molecules form normal micelles and coexist with excess oil. Apparently, this phase looks milky even keeping for several hours but oil separation takes place afterwards. Concerning the pentanol and hexanol system, such phase separation is very abrupt and prominent showing a clear unstable emulsion state for a system with short-chain cosurfactant.

One-phase micellar regions are formed at both sides of the LC-region; they are normal-type and reverse-type due to the hydrophilic and lipophilic nature of the surfactant mixture, respectively. The maximum solubilization limit for the single-phase micellar solution and the reverse micellar solution is reached at a surfactant concentration of 10% ($W_1 = 0.53$) and 12% ($W_1 = 0.62$), respectively. The LC-region and the isotropic single-phase region shift towards higher W_1 with decreasing the total surfactant concentration (X) due to the high solubility of heptanol in the oil phase [19, 20, 21].

The phase transition from the middle-phase microemulsion (W + D + O) to the LC-present region (W + LC + O) at constant X = 0.175, is shown in Fig. 1c in water/ SE/ (hexanol + heptanol)/ decane system with changing the mixing ratio of heptanol in the total cosurfactant (hexanol + heptanol). This kind of phase transition takes place due to the gradual increase of lateral interaction between surfactant and comparatively longer-chain-length alcohol. The transition from one three-phase body to another takes place at a hexanol content of 38% ($W_1 = 0.7$) and 62% ($W_1 = 0.615$) in the upper and the lower end, respectively. There should be a four-phase region between the middle-phase microemulsion and the LC-regions according to the phase rule [22]. However, since it is very narrow, the region was not determined. Therefore, the demarcation line is indicated by a dashed line.

The phase behavior of water/ SE/ octanol/ decane system (Fig. 2a) resembles that of the heptanol system. The maximum solubilization limit for the single-phase micellar solution and the reverse micellar solution is reached at a surfactant concentration of 14% ($W_1 = 0.43$) and 15% ($W_1 = 0.58$), respectively. In this case, the LC-region is slightly wider than that of the heptanol system. In the water/ SE/ decanol/ decane system (Fig. 2b), the maximum solubilization limit of the single micellar phase is attained at 15% surfactant ($W_1 = 0.425$) in the system.

Effect of changing oil on the phase behavior

An alteration in the kind of oil can play an important role in changing the phase behavior. The phase transition takes place from the middle-phase microemulsion to the LC-region in water/ SE/ hexanol/ decane [9] and water/ SE/ heptanol/ decane systems. So the turning point of changing the phase behavior is while adding a cosurfactant from a short to a comparatively long one. Using heptanol as a cosurfactant, the phase behavior was determined by adding a short-chain aromatic oil (*m*-xylene) and a long-chain aliphatic oil (hexadecane).

The phase behavior of water/ SE/ heptanol/ *m*-xylene system is shown in Fig. 3a. The system remains hydrophilic at low W_1 and forms a microemulsion phase region (D) with a maximum solubilization of 14% surfactant ($W_1 = 0.345$). Below and above this boundary, the structure of the micelle is changed from the normal to reverse-type through the bicontinuous-type narrow three-phase body. In this case, the short-chain aromatic hydrocarbon (*m*-xylene) tends to penetrate in the surfactant palisade layers or in the vicinity of the interface. Therefore, it is considered that the palisade layer is very flexible to the change in W_1 and the bicontinuous structure is kept in a narrow range of W_1 followed by the wide region of micellar phase with excess oil (Wm + O). In the water/ SE/ heptanol/ hexadecane system (Fig. 3b), the long-chain hexadecane penetrates less into the surfactant palisade layer and, rather than solubilizing between the lipophilic bi-layer, it makes the surface of the aggregates comparatively rigid. Thus an LC-present region appears when the HLB of the mixture (surfactant + cosurfactant) is optimum. No single micellar phase is formed in this system. For all the systems, LC-present region consists of lamellar liquid crystal and other isotropic phase (water and/ or oil phases), confirmed by its texture through polarized microscopy. However, the phase separation is very slow in the LC-present region and it is of a milky appearance. Figure 4 represents the lamellar liquid crystal at a surfactant concentration of 20% in the water/ SE/ decanol/ decane system.

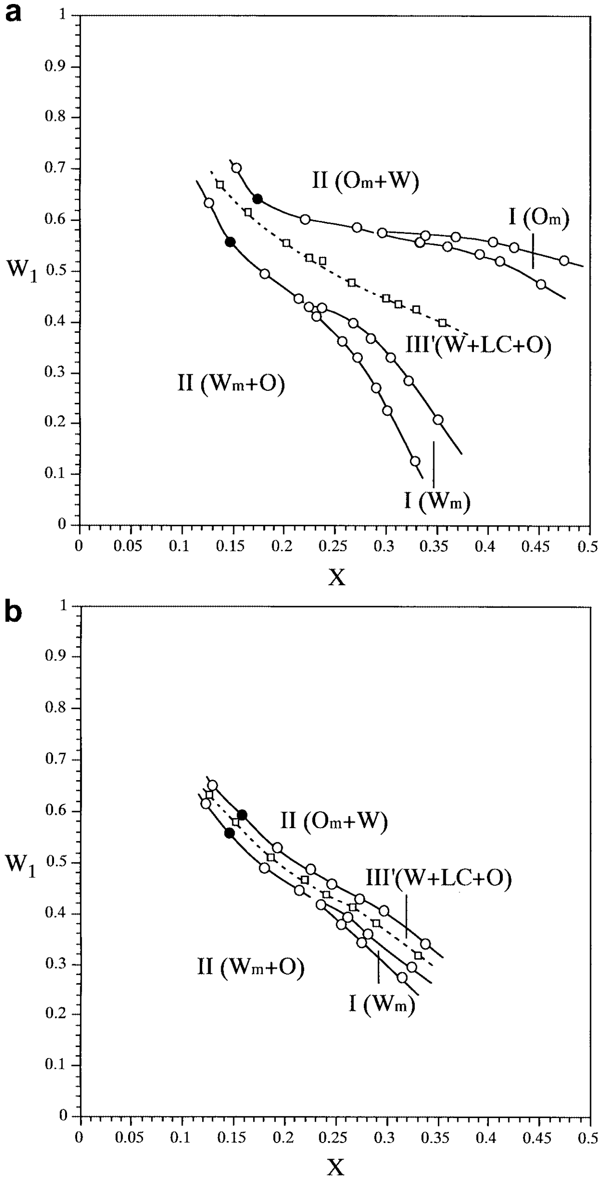

Fig. 2a–b. Phase diagrams of water/ SE/ octanol/ decane **(a)** and water/ SE/ decanol/ decane **(b)** systems at 25 °C. X is the weight fraction of total surfactant in the system and W_1 is the weight fraction of cosurfactant in the total surfactant. *Filled circles* indicate the composition at 7% SE. *Blank squares* are the midpoints at different surfactant concentration in the milky liquid crystal-present region (III'). I, II are the isotropic one- and two-phase regions. The water/oil weight ratio is 50/50

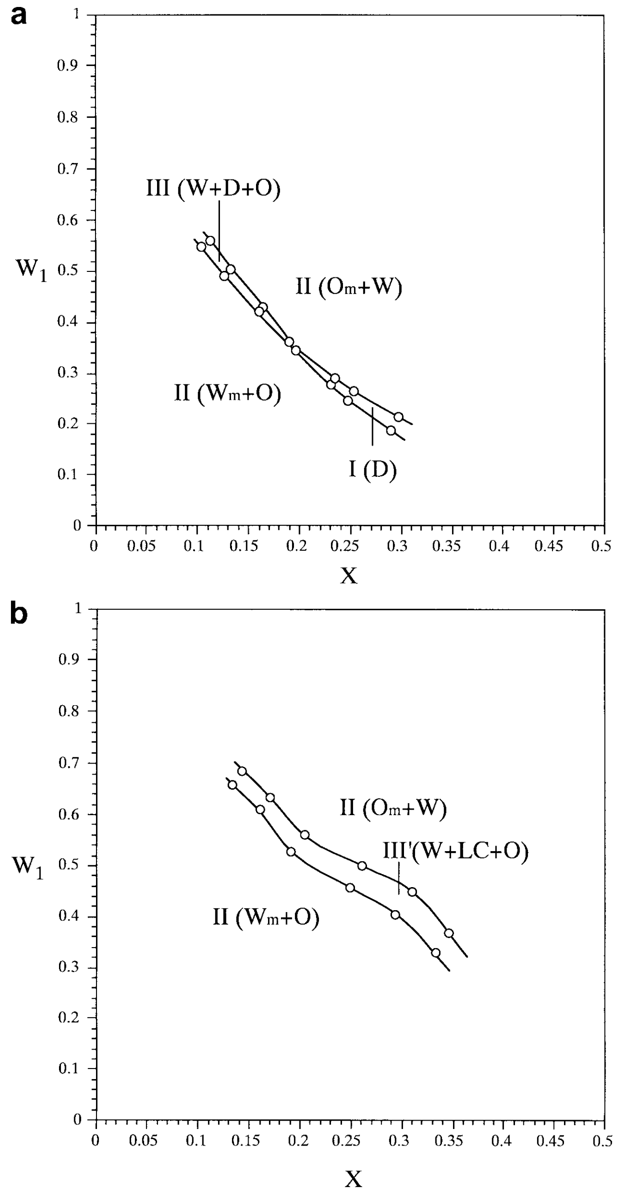

Fig. 3a–b. Phase diagrams of water/ SE/ heptanol/ oil at 25 °C. Oils are *m*-xylene **(a)** and hexadecane **(b)**. X is the weight fraction of total surfactant in the system and W_1 is the weight fraction of cosurfactant in the total surfactant. I, II, III are the isotropic one-, two- and three-phase regions, respectively. III' indicates the milky liquid crystal-present region. The water/oil weight ratio is 50/50

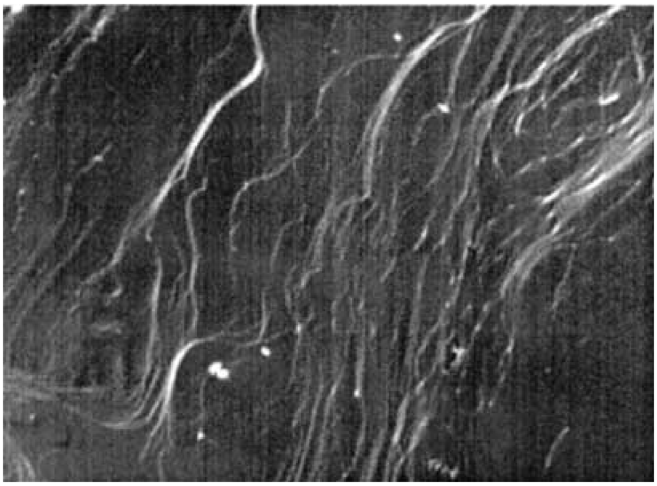

Fig. 4. Photomicrograph of a lamellar liquid crystal in water/ SE/ decanol/ decane at 25 °C. The water/oil weight ratio is 50/50. SE concentration is 20 wt%

Emulsion test for different cosurfactants

From the phase study, it is inferred that the formation of middle-phase microemulsion is induced by short-alkyl-chain cosurfactant (pentanol, hexanol), whereas a lamellar liquid crystalline phase forms by adding the medium or a long one (heptanol, octanol, decanol) at the balanced state. To determine the emulsion stability, time-dependent creaming profiles were determined by keeping the samples in a thermostat at 25 °C for 1 h and the phase volume (vertical axis) was plotted against W_1 (horizontal axis). The result is shown in Fig. 5. In all systems, the surfactant concentration was kept constant at 7%.

In the water/ SE/ pentanol/ decane system (Fig. 5a), phase separation is completed within half an hour and each phase is clear and transparent. The separation of oil as a transparent phase from the normal micellar solution (Wm) proceeds until $W_1 = 0.61$. Reverse micellar solution (Om) starts to separate from water when $W_1 = 0.725$ through the formation of a middle-phase microemulsion in between.

The coexistence of O/W-cream and normal micellar phase is observed until $W_1 = 0.56$ in the water/ SE/ octanol/ decane system (Fig. 5b). Although the coalescence of the water and oil droplets from the liquid crystal is facilitated, this liquid crystalline phase is creamy, looks milky and in non-equilibrium state. Some water and oil molecules are stably dispersed in it. At slightly negative surfactant curvature ($W_1 = 0.645$), the coalesced oil droplets tend to be separated from W/O-cream. Similar type of emulsification is observed in the water/ SE/ decanol/ decane system (Fig. 5c), where the water and oil droplets are separated from liquid crystal in between $W_1 = 0.56$ and $W_1 = 0.595$, which is narrower than that of the octanol system. As the melting point of decanol is higher than room temperature, the solid phase appears easily at $W_1 = 0.685$. We cannot distinguish W with Wm or O with Om phases in Fig. 5b and 5c, because they are continuously connected. On the other hand, although all O/W-, LC- and W/O-cream are white and turbid, we could distinguish each cream by visual observation with the polarizer.

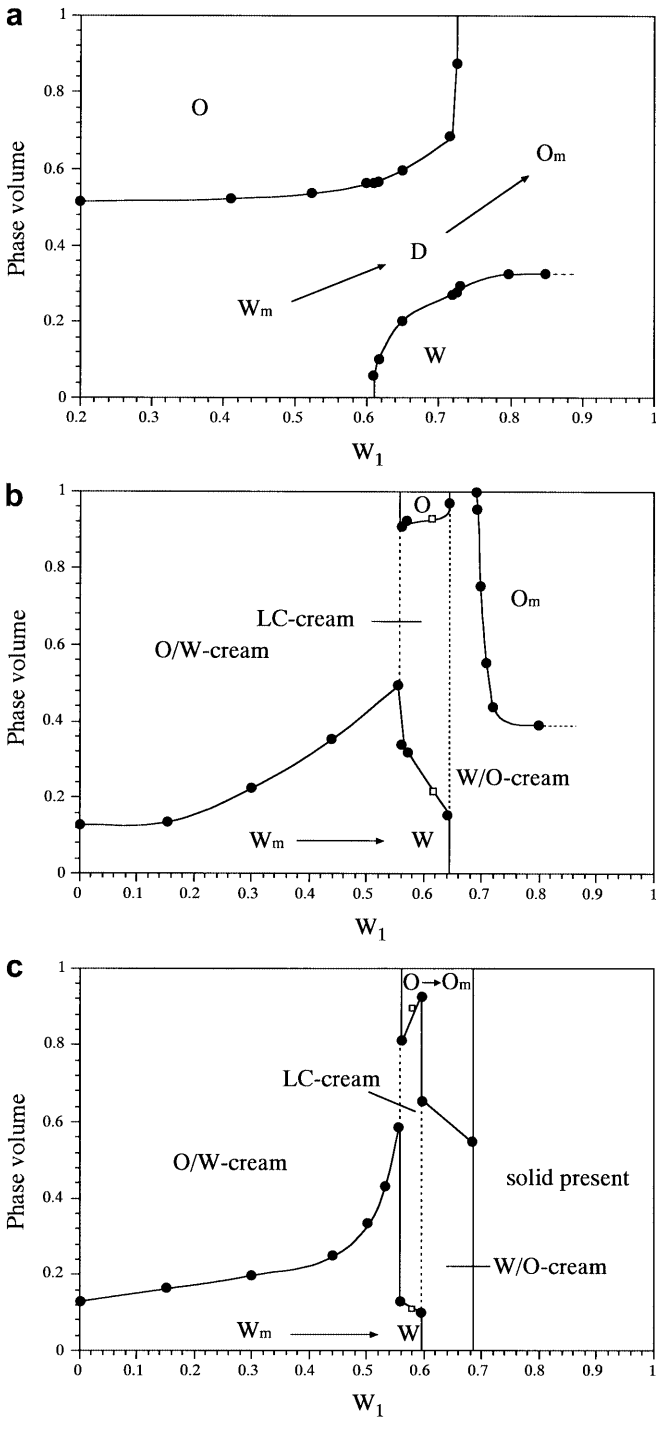

Fig. 5a–c. Phase distribution in water/ SE (7%)/ cosurfactant/ decane systems at 25 °C after keeping in the thermostat for 1 h. Cosurfactants are pentanol **(a)**, octanol **(b)**, and decanol **(c)**. Water/ oil weight ratio is 50/50. W_1, is the weight fraction of cosurfactant in the total surfactant mixture. D denotes the middle-phase microemulsion. *Blank squares* indicate midpoints inside creamy liquid crystal region. W, O are the water and oil phases in the equilibrium state. Wm, Om are the normal and reverse micellar solutions

Stabilized emulsion in LC-region

When a liquid crystalline phase separates instead of the surfactant phase, the emulsion stability is increased [6]. This is due to the fact that the liquid crystal forms a covering skin around the droplets and prevents coalescence or creaming. This also increases the mechanical strength of the oil/water interfacial film and a fixation of the emulsion droplets in the structure [23, 24]. So, it is expected that the emulsion is more stable in the systems forming the liquid crystalline phase (heptanol, octanol, decanol) than in the systems forming middle-phase microemulsion (pentanol, hexanol), when the HLB of the mixture (surfactant + cosurfactant) is optimum. Practically, droplets in the emulsions are not completely dispersed in liquid crystal when the surfactant concentration is low (7%). That is why coalescence or creaming takes place. This drawback is overcome by

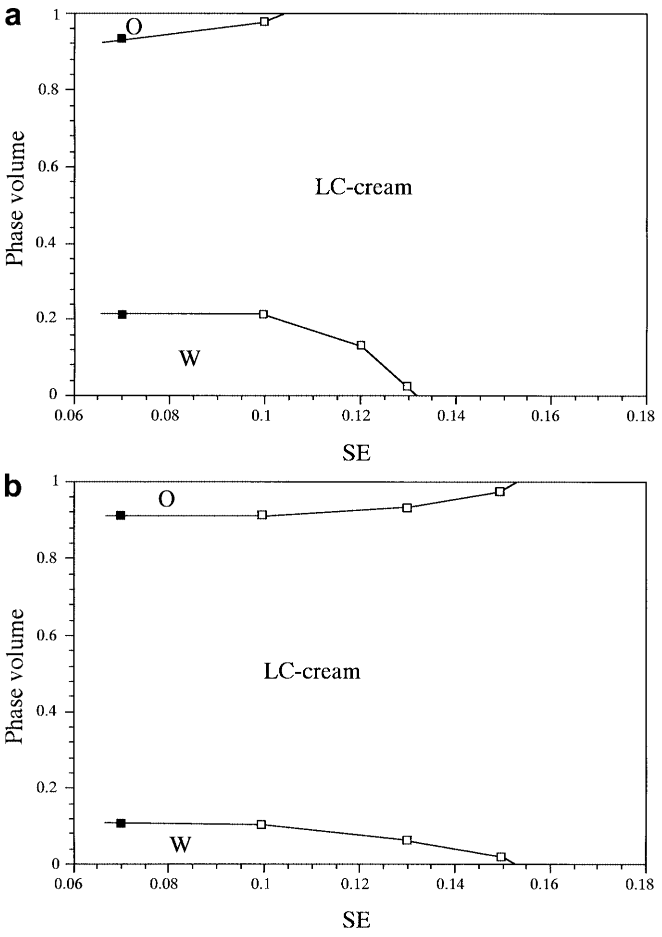

Fig. 6a–b. Emulsion stability as a function of SE concentration after keeping in the thermostat for 1 h at 25 °C for **(a)** water/ SE/ octanol/ decane system and **(b)** water/ SE/ decanol/ decane system. Water/oil weight ratio is 50/50. LC-cream is the milky-viscous liquid crystal-present region. W, O indicate water and oil phases in the equilibrium-state. *Filled squares* indicate 7 wt% surfactant

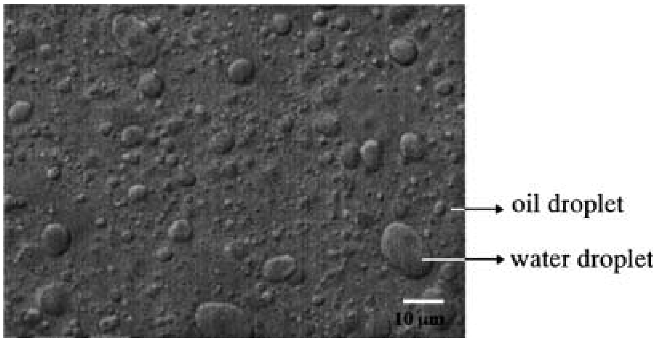

Fig. 7. VEM image of the droplets dispersed in lamellar liquid crystal at 25 °C in water/ SE/ decanol/ decane system. Large and small droplets are water and oil, respectively. The water/oil ratio is 50/50. SE concentration is 20 wt%

facilitating the abundant growth of lamellar liquid crystal with increasing the surfactant concentration at the balanced state. Consequently, the test of emulsion stability was performed along the LC-present region at 25 °C in the water/ SE/ octanol/ decane and water/ SE/ decanol/ decane systems and shown in Fig. 6a and 6b.

Both cases represent the gradual expansion of LC-present region since, water and oil droplets are properly dispersed in the lamellar liquid crystal, which was confirmed by microscopy. The phase separation does not take place when the whole phase volume is covered with the viscous-milky LC-cream. The type of droplets in LC-cream, was distinguished by the Becke line effect [12, 13] while doing microscopy (VEM). Figure 7 shows the type and size of droplet, dispersed in the lamellar liquid crystal.

Conclusion

The effect of adding cosurfactants and oils on the phase behavior and the emulsion stability has been studied in water/ SE/ cosurfactant/ oil systems. Both the short-chain cosurfactants (pentanol, hexanol) and oil (*m*-xylene) form middle-phase microemulsion, whereas the long-chain cosurfactants (heptanol, octanol, decanol) and oils (decane, hexadecane) form lamellar liquid crystal at the balanced state. In the LC-present region, water and oil droplets are dispersed in a lamellar liquid crystal. It is considered that the emulsion stability is highly dependent on the chain length of the cosurfactant as it forms liquid crystal with water and oil droplets when the HLB of the mixture (surfactant + cosurfactant) is optimum. But due to the insufficient volume of liquid crystal in the dilute region, water and oil droplets cannot properly be dispersed and there is a phase separation after some time. The liquid crystal can be entirely spread over the whole emulsion body by increasing the surfactant concentration (SE). Thus emulsions become stable in a long-chain amphiphile (surfactant/ or cosurfactant) system. Consequently, emulsions are not always unstable at PIT or HLB composition.

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