Aqueous and Nonaqueous Microemulsion Systems with a Palm Oil-Base Emollient

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ABSTRACT: Microemulsions with a palm oil-based emollient, i.e., medium-chain triglyceride (MCT), and water or glycerol, stabilized by two oppositely charged ionic surfactants and a medium-chain alcohol, were investigated. The results showed that only the water-in-MCT or the glycerol-in-MCT microemulsions were prominent. The maximum solubilization of the MCT emollient was higher in cetyltrimethyl ammonium bromide, i.e., the positively charged surfactant that contained a nitrogen atom, than the negatively charged surfactant sodium dodecyl sulfate. However, the results did not lend themselves for selecting any decisive factor that would explain the different solubilization behavior encountered in the investigated aqueous and nonaqueous systems.

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KEY WORDS: Cetyltrimethylammonium bromide, MCT emollient, microemulsion, palm oil, sodium dodecyl sulfate, solubility.

MCT, an abbreviation for medium-chain triglyceride oil, is an ester oil constituted of glycerol and three fatty acid radicals (1). The fatty acid components are octanoic acid ($C_{8:0}$) and decanoic acid ($C_{10:0}$). This oil is regarded as harmless and safe for internal consumption. Therefore, it is suitable for incorporation in food items or in any topical preparation. In this paper, we present the microemulsion region of the MCT emollient in two oppositely charged ionic surfactants, pentanol and water (or glycerol). The surfactants used are sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB). Microemulsions (2–5) are thermodynamically stable suspensions of two immiscible liquids, generally a hydrocarbon and an aqueous phase. The internal phase is solubilized by particles that range between 10 and 100 nm in size and are composed of surfactant and cosurfactant molecules. It has merits over other vehicles or solvents by both improved stability and solubilization characteristics.

The association phenomenon of ionic surfactants in microemulsions has been extensively investigated, both in aqueous (4–8) and, to a lesser extent, in nonaqueous environments (9,10). However, mainly hydrocarbons were used as the oil components in those studies. Recently, Friberg *et al.* (11) have employed styrene to investigate the composition of water-in-oil microemulsions that had undergone an evaporation process. In another report, Moulik *et al.* (12) used a series of aliphatic and aromatic hydrocarbons to study the acid-base behavior of dye in water-in-oil microemulsions.

We now present the association phenomenon of MCT in such association structures. We hope this paper will contribute to the understanding of the MCT behavior in a microemulsion system.

EXPERIMENTAL PROCEDURES

Materials. The basic materials, sources and purities for the pseudoternary systems were as follows. The CTAB was >99.5% (Sigma Chemical Co., St. Louis, MO), SDS >99% (Fluka, Buchs, Switzerland), glycerol 99.5% (Aldrich, Gillingham, United Kingdom) and pentanol >98% (Fluka). The MCT emollient was obtained from Unichema International (Klang, Selangor, Malaysia) under the commercial name of ESTASAN 3575. The specifications for the MCT emollient are given in Table 1. All of the materials were used as received, and no further purification was performed. The water is doubly distilled.

Determination of phase regions. The phase equilibria are determined by titrating with the smallest amount of the third component to turbidity. The samples were then vortexed (Thermolyne Maxi Mix II; Sybron Corp., Dubuque, IA) for mixing purposes and centrifuged at 5000 rpm. The samples were then allowed to equilibrate in a waterbath at 30°C. The phases were examined visually and between cross polarizers.

TABLE 1
Analysis of the Medium-Chain Triglyceride Oil or Medium-Chain Triglyceride Emollient

Components/properties	Composition/value
Fatty acids	
Octanoic acid, $C_{8:0}$	58.6%
Decanoic acid, $C_{10:0}$	40.7%
Others	0.7%
Iodine value	less than 0.1 g iodine/100 g
Saponification value	331 mg KOH/g

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The region of the phases can be estimated by this method by noting the turbid-to-clear transitions.

RESULTS AND DISCUSSION

Surfactant–pentanol systems. The two oppositely charged surfactants used throughout this investigation are the negatively charged surfactant SDS and the positively charged surfactant CTAB. The solubility regions for the aqueous isotropic solutions are given in Figure 1 for the SDS and CTAB systems. The minimum molar ratio of water-to-surfactant to obtain solubility is similar for both of the aqueous systems, i.e., in the range of 4–5. The maximum solubility of water is significantly higher in the SDS system. This is shown by the continuous solubility region that connects both the normal and inverse micellar regions *via* a narrow bicontinuous channel (Fig. 1). The amount of surfactant needed to obtain solubility is markedly lower in the SDS system than in the CTAB system. A minimum amount of 5 wt% of SDS is needed to obtain solubility at an equal weight ratio of water and pentanol, compared to 21 wt% of CTAB. These findings are consistent as previously reported (11).

Figure 2 provides equivalent information but for the nonaqueous systems. Both of the surfactant systems show an isotropic solution that is extended continuously from the pure glycerol to the pure pentanol in a crescent manner. The maximum solubility of SDS and CTAB are 22 and 30 wt%, respectively. The minimum amount of surfactant needed to obtain solubility is, however, similar for both surfactants.

MCT emollient–SDS microemulsion systems. The pseudoternary phase diagrams for the microemulsion solubility regions are prepared by two simple combinations (Fig. 3). The first combination is by combining water (or glycerol) and

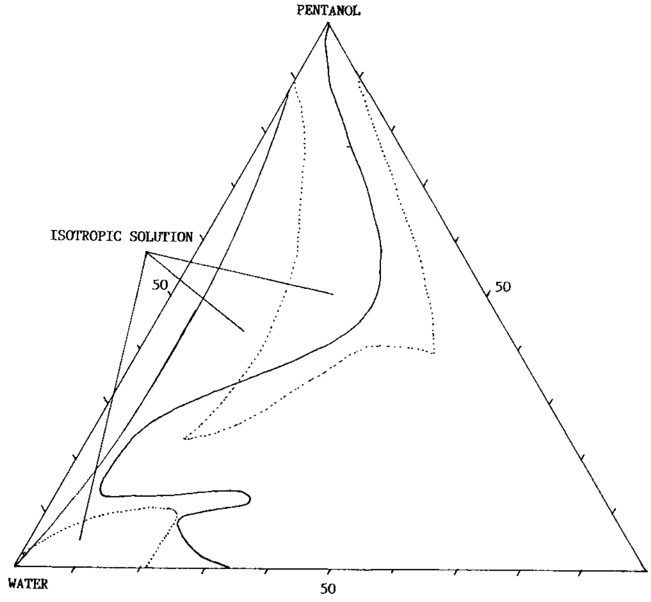

FIG. 1. Ternary phase diagram for water, pentanol and a third component consisting of sodium dodecyl sulfate (—) or centiftrimethyl ammonium (···).

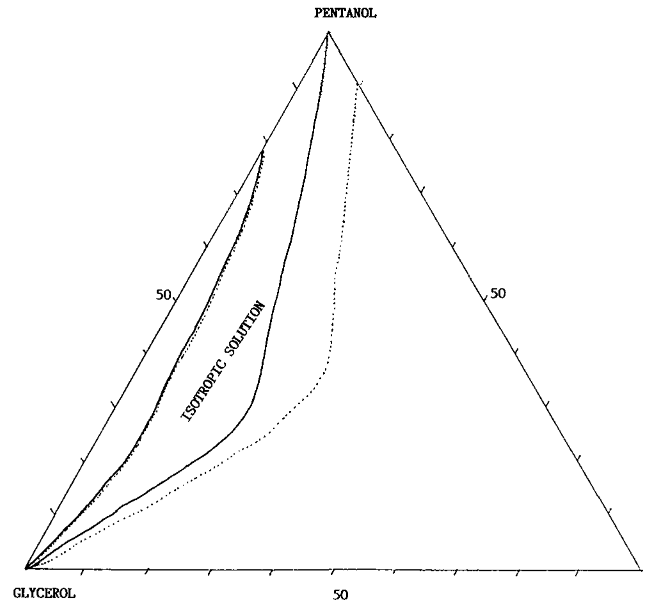

FIG. 2. Ternary phase diagram for glycerol, pentanol and a third component consisting of sodium dodecyl sulfate (—) or cetyltrimethylammonium bromide (···).

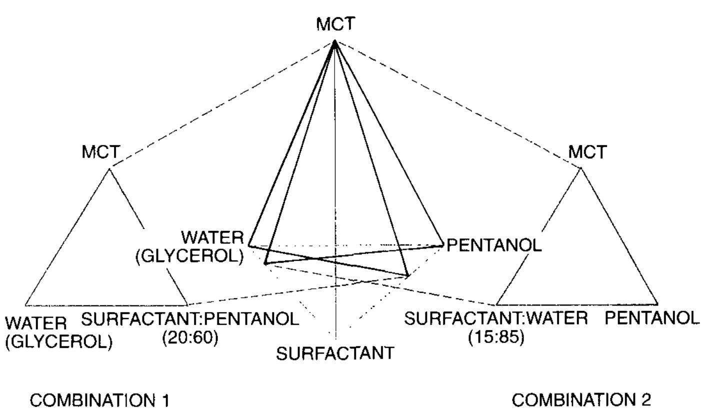

FIG. 3. Combinations taken for the construction of pseudoternary phase diagrams for the four-component systems of water or glycerol, pentanol, medium-chain triglyceride (MCT) emollient and sodium dodecyl sulfate or cetyltrimethylammonium bromide.

MCT emollient and titrating with a third component, which contains a mixture of SDS and pentanol (20:80, wt/wt); and provides an infinite water solubility. The second combination is by fixing the MCT emollient and pentanol as separate apexes while the third apex consists of a mixture of SDS and water or glycerol at a weight ratio of 15:85.

Figure 4 shows the solubility region prepared by the first combination. The aqueous system shows an isotropic solution region that protrudes between 28 and 90% of SDS/pentanol (20:80) up to about 53% of MCT emollient. The minimum water content to achieve this region is a straight line at about 7% of water. This minimum value is, however, shifted

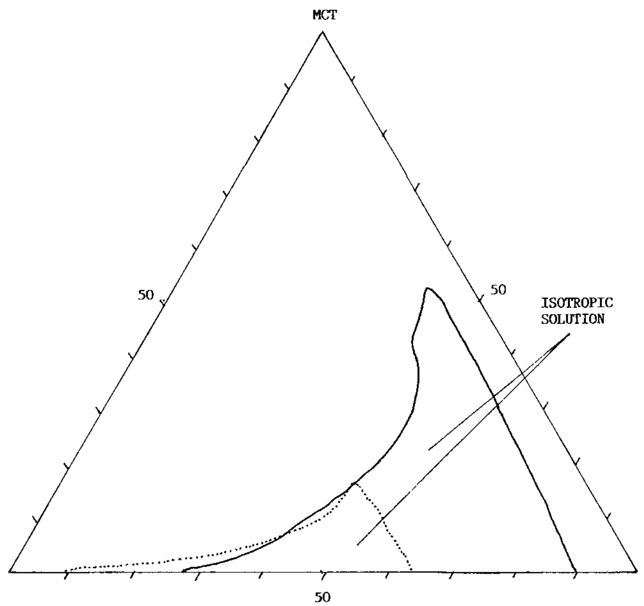

FIG. 4. Pseudoternary phase diagram for medium-chain triglyceride, sodium dodecyl, sulfate/pentanol (20:80) and a third component consisting of water (—) or glycerol (···).

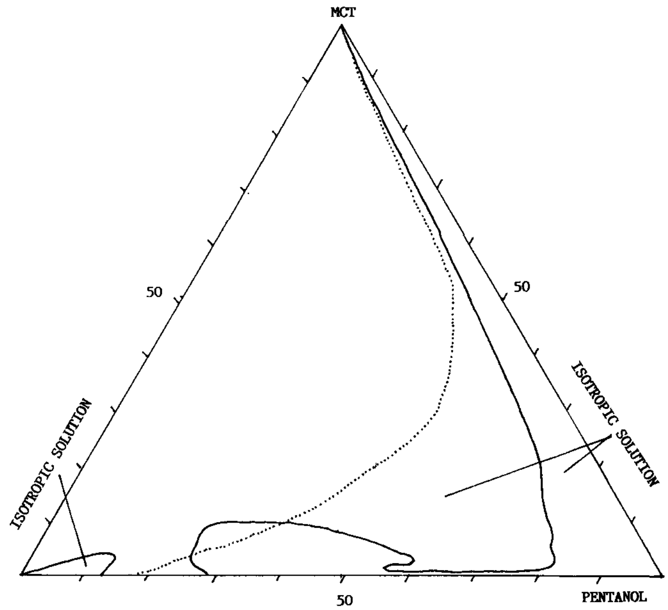

FIG. 5. Pseudoternary phase diagram for the MCT, pentanol and a third component consisting of a mixture of sodium dodecyl sulfate and water (—) or glycerol (...) at a weight ratio of 15:85. See Figure 3 for abbreviation.

to a higher value of about 35% when the water is replaced with an equal amount of glycerol, shown as dotted lines in Figure 4. The solubility region for the nonaqueous system is smaller, with a region projecting from the MCT-free axis up to 17% of MCT content. The shift in the minimum glycerol phase and the decrease in size of this region may be explained by the difference in the solubility of SDS in water and glycerol, respectively. Water and SDS display a mutual solubility to about 60% by weight of SDS, while its corresponding solubility in glycerol is less than 1%.

Figure 5 shows the pseudoternary diagram prepared by the second combination. A different behavior is observed for both of the aqueous and nonaqueous systems in the presence of MCT molecules. The MCT emollient is completely miscible in pentanol. The resulting solution in the aqueous system is able to solubilize all of the SDS/water (15:85) component. The solubility region can be divided into three main subregions. The smallest subregion is at a low content of pentanol between 0 and 13%, followed by a medium subregion ranging, from 29 and 57% of pentanol, and an extended subregion with a pentanol content ranging from 82% onward. The nonaqueous system (Fig. 5) shows a larger solubility region that curves toward the pentanol apex. The solubility of the SDS/glycerol mixture in pentanol is reduced to 17% of the mixture. This is probably due to the fact that the mixture of SDS and glycerol at the weight ratio of 15:85 does not produce micelle aggregates and hence exhibits lower solubilization capabilities than the water counterpart.

MCT emollient–CTAB microemulsion systems. It has been pointed out that positively charged surfactants (13) give a high solubilization of water in water-in-oil microemulsions at high oil content. It has also been suggested that a combination of an alcohol with a nitrogen-containing surfactant may be highly desirable to achieve the abovementioned behavior. With that in mind, we employed CTAB in place of SDS for investigating the association phenomenon of the previously discussed microemulsion systems. Figure 6 shows an equivalent phase diagram for the CTAB system as was shown in Figure 4. The isotropic solution region for the aqueous system protrudes upward from 79 to 98% of the mixture of CTAB

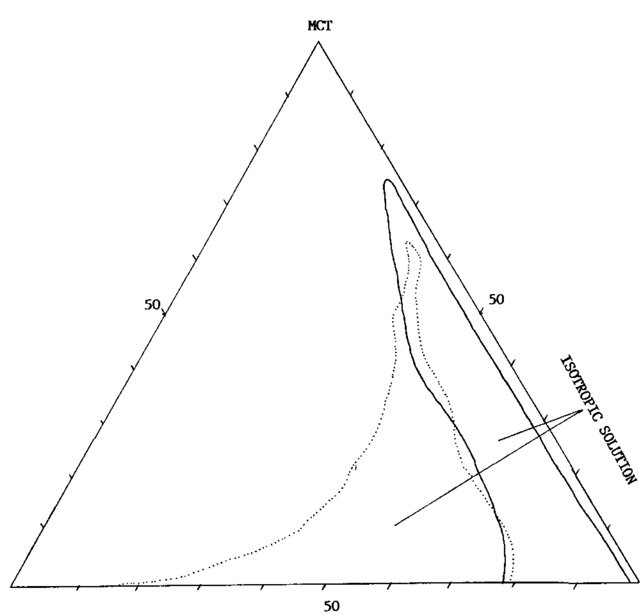

FIG. 6. Pseudoternary phase diagram for MCT, cetyltrimethylammonium bromide/pentanol (20:80) and a third component consisting of water (—) or glycerol (···). See Figure 3 for abbreviation.

and pentanol to about 74% of the MCT emollient. The solubilization of the MCT emollient is higher if compared to the SDS system. However, the maximum and minimum water contents to achieve the solubility in the CTAB system are greatly reduced, to about 2 and 15%, respectively. These results did not seem to show the superiority of CTAB to SDS as mentioned earlier (13) in combination with pentanol for microemulsions containing MCT emollient. However, when a different weight ratio of CTAB and pentanol is used, i.e., 40:60 by weight, which exhibits a maximum water solubility, a larger region is observed in this new system (Fig. 7). Therefore, we suggest that caution should be practiced before making such conclusions as put forth in a previous paper by Chew *et al.* (14) on microemulsion systems that consists of water-soluble glycol derivatives, hydrocarbon, water and both SDS and CTAB.

The dotted lines in Figure 7 show the nonaqueous counterpart of the systems with a mixture of CTAB and pentanol at a weight ratio of 40:60. A slightly larger region is observed when compared to the corresponding SDS systems (Fig. 4) with a maximum solubility of 20% of the MCT emollient. This region extends upward between 4 and 60% of the mixed CTAB and pentanol (40:60). This region is smaller than that of the system containing a mixture of CTAB and pentanol at a weight ratio of 20:80 (compare the dotted lines of Figs. 6 and 7). Obviously, the ratio of CTAB and pentanol also plays an important role in the association phenomenon of this particular investigated system.

Figure 8 shows the pseudoternary phase diagram prepared for the CTAB system by the second combination. The association phenomenon in both aqueous and nonaqueous systems shows a similar trend as those of the SDS systems. The medium subregion observed in the SDS aqueous system (Fig. 5) is, however, not present in the corresponding CTAB system. The solubility region for the nonaqueous CTAB systems is smaller but curves toward the pentanol apex in the same fashion as those of the SDS system.

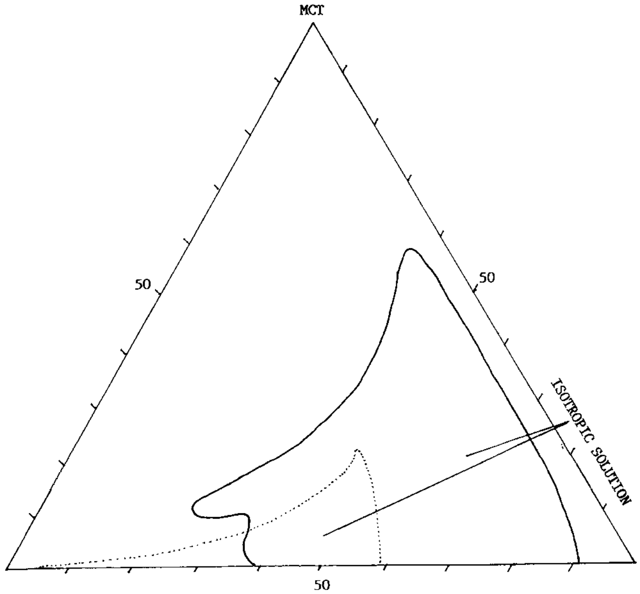

FIG. 7. Pseudoternary phase diagram for MCT, cetyltrimethylammonium bromide/pentanol (40:60) and a third component consisting of water (—) or glycerol (···). See Figure 3 for abbreviation.

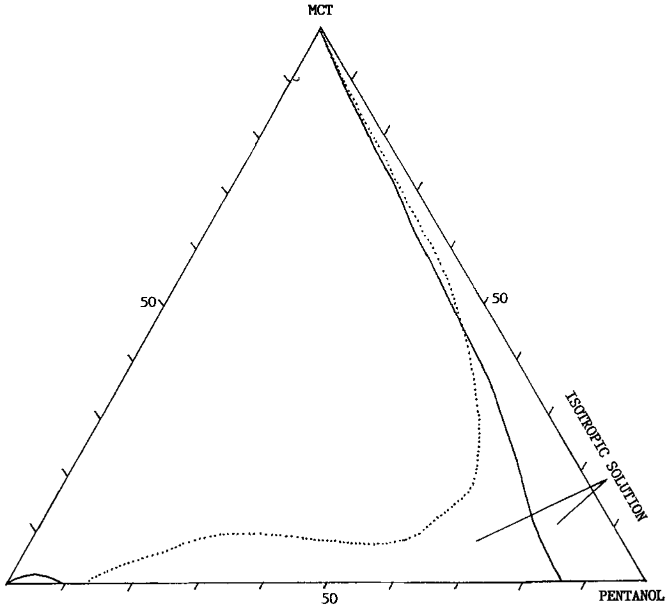

FIG. 8. Pseudoternary phase diagram for the MCT, pentanol and a third component consisting of a mixture of cetyltrimethylammonium bromide and water (—) or glycerol (···) at a weight ratio of 15:85. See Figure 3 for abbreviation.

In summary, the present results demonstrate that microemulsions, especially in the water-in-MCT emollient or glycerol-in-MCT emollient systems, do exist but are only limited to lower water or glycerol contents. Also, a specific combination of certain types of surfactants or of the surfactant and cosurfactant ratio cannot be treated individually but they should rather be considered in terms of the systems behavior. More work must be carried out, such as light scattering (15), to further verify the existence of the microemulsion systems and to determine the presence of inverse micelles in these systems, prior to making any final conclusions.

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