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VEGETABLE OIL IN AQUEOUS AND NONAQUEOUS MICROEMULSION SYSTEMS STABILIZED BY NONIONIC SURFACTANTS

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Nonionic microemulsions with a palm oil-based emollient, i.e. medium chain triglyceride, MCT, stabilized by two nonionic surfactants were investigated in both aqueous and nonaqueous (glycerol and formamide) systems. The results showed the presence of aqueous (or nonaqueous)-in-MCT microemulsions in all the systems investigated. MCT-in-aqueous (or nonaqueous) microemulsions were also observed except the glycerol system. In addition, the results also indicated that the solubilization behaviour encountered in the aqueous and nonaqueous systems investigated was dependent on the surfactant ratio.

INTRODUCTION

One of the striking properties of microemulsions, containing either mixtures of oil/ionic surfactant/cosurfactant/water or oil/nonionic surfactant/water, is their enhanced stability from the thermodynamic perspective (Hoar and Schulman, 1943). Such microemulsions are isotropic and macroscopically homogeneous, consisting of oil and water domains of a typical size of a few tenths of a nanometer. Their vast applications, especially in industry, have attracted much attention to their colloid chemistry. Microemulsions have been proven useful, particularly in the area of enhanced oil recovery (Shah and Schecter, 1977; Taber, 1980). Their latest application is in dye processing, introduced by Barni and co-workers (Barni *et al.*, 1991).

We have recently (Hamdan *et al.*, 1995) demonstrated the formation of both aqueous and nonaqueous microemulsion systems containing a mixture of medium-chain triglycerides (MCT-palm oil emollient), two oppositely charged ionic surfactants and a short-chain alcohol, pentan-l-ol. However, the resulting triglyceride microemulsion systems were only prominent in the water-in-MCT oil and glycerol-in-MCT oil regions. These results indicated that the formation of inverse micelles might be more favoured than that of normal micelle aggregates in such systems. The present work was an extension from this, directed towards the formation of nonionic triglyceride microemulsion systems. These were obtained by employing a mixture of two commercially available nonionic surfactants namely Tween 20 and Tween 80 as emulsifiers, and MCT-palm oil emollient as the triglyceride component.

Nonionic triglyceride microemulsions, apart from being interesting from the fundamental point of view, also have a significant technological potential and especially where environmentally more acceptable formulations are concerned. In addition, many food formulations containing lipids and oils with limited solubility are in increasing demand for the preparation of low-fat products such as sauces and salad dressings (Dickinson and Woskett, 1989). Triglycerides such as those in palm oil or other vegetable oils contain long-chain fatty acids (mainly C_{16} and C_{18}) and hence have large molecules. Such a structure minimizes their solubility in microemulsion systems and consequently liquid crystal mesophases are more readily formed. Recently, Joubran *et al.* (1993, 1994) have demonstrated that the formation of triglyceride micro-emulsions can be achieved by incorporating sucrose and a short-chain alcohol. The synergistic interactions among the alcohol and the sucrose molecules result in the destabilization of the liquid crystalline mesophase, and thus facilitate the formation of the triglyceride microemulsions. Also it has been shown by several pioneering workers (Fletcher *et al.*, 1984; Rico and Lattes, 1984) that nonaqueous solvents such as glycerol or formamide can perturb a colloidal system, resulting in the extension of the microemulsion region.

The present work was undertaken with these in mind, and we now describe the association phenomenon of a medium chain triglyceride (MCT-palm oil) in such systems. We hope this paper will contribute to an understanding of the behaviour of MCT-palm oil in both aqueous and nonaqueous microemulsion systems.

MATERIALS AND METHODS

Materials

The basic materials for the pseudoternary systems were as follows. The nonionic surfactants, polyoxyethylene sorbitan monolaurate and polyoxyethylene sorbitan monooleate were obtained commercially as Tween® 20 (HLB 16.7 ± 1.0) and Tween® 80 (HLB 15.0 ± 1.0), respectively, from Aldrich (Gillingham, United Kingdom). The nonaqueous solvents, glycerol (99.5%) and formamide (99%) were also purchased from Aldrich. The MCT-palm oil emollient was obtained from Unichema International (Klang, Selangor, Malaysia) under the commercial name of ESTASAN 3575. Its specifications are given in *Table 1.* These materials were all used as received and no further purification was performed. The water used was doubly distilled.

TABLE 1. ANALYSIS OF THE MEDIUM CHAIN TRIGLYCERIDE OIL OR MCT EMOLLIENT

Components/Properties	Composition/Value
Octanoic acid, C8:0	58.6%
Decanoic acid, C10:0	10.7%
Others fatty acids	0.7%
Iodine Value	less than 0.1 g Iodine/100 g
Saponification Value	331 mg KOH/g

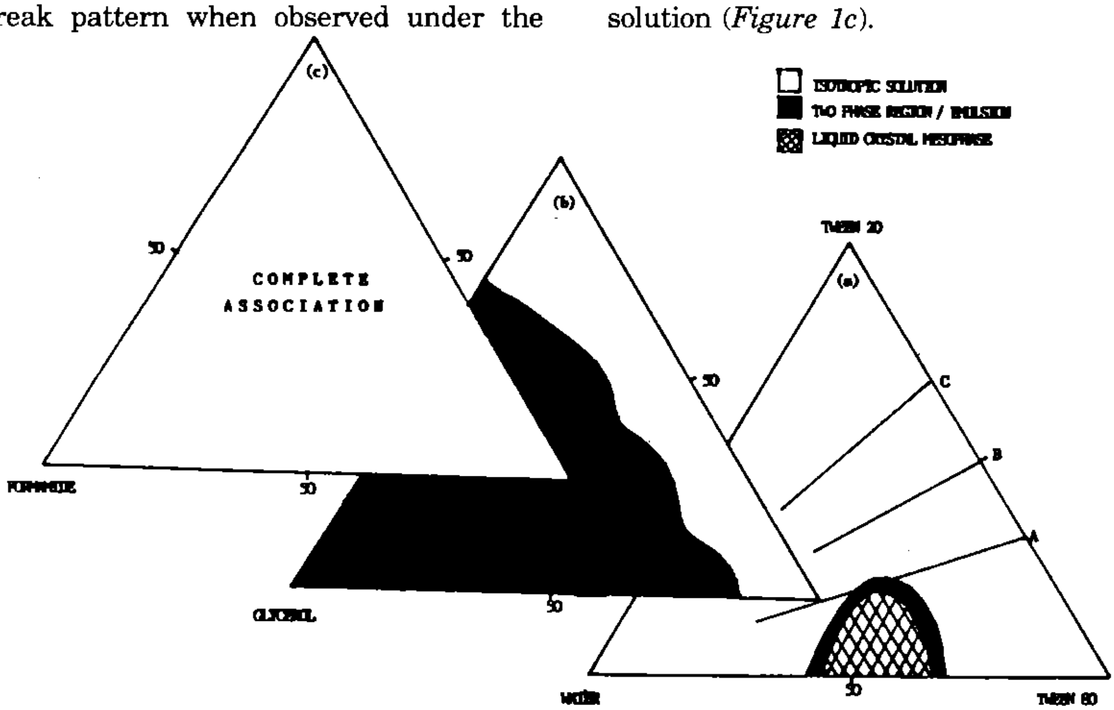
Determination of phase regions

The phase equilibria were determined by mixing two of the components and titrating to turbidity with the minimum amount of the third component. The samples were then thoroughly mixed to homogeneity with a vortex meter (Thermolyne Maxi Mix II) and centrifuged (Rexmed Model DSC-1512SDT) at 5000 rpm. The samples were then allowed to equilibrate in a water bath kept at 30°C. The phases were inspected visually between crossed polarizers and under a polarizing microscope.

RESULTS AND DISCUSSION

Surfactant-solvent systems

The two nonionic surfactants used throughout this investigation were Tween 20 and Tween 80. The location of the solubility regions is shown in a phase diagram for systems containing Tween 20, Tween 80 and three different solvents namely water, glycerol and formamide (*Figure 1*). The aqueous system (*Figure 1a*) shows the existence of one homogeneous isotropic solution and one mesophase. The mesophase region was identified as a typical lamellar liquid crystal – or D phase (Ekwall, 1975 –) by its exhibiting an oily streak pattern when observed under the polarizing microscope. This mesophase region extends from the Tween 20-free axis, with the water content ranging between 35.0% and 56.0%. It retains its structure up to about 20.0 weight per cent of Tween 20. The homogeneous isotropic solution covers the remainder of the phase diagram and is separated from the liquid crystalline phase by a narrow two-phase region (*Figure 1a*). *Figure 1b* shows equivalent information for a nonaqueous solvent, glycerol. The solubility region displays a different association phenomenon. The isotropic solution was found to be projecting from the glycerol-free axis in a zig-zag manner towards the glycerol apex. A maximum glycerol solubility of 19.0 weight per cent of glycerol (*Figure 1b*) is observed at two Tween 20/Tween 80 weight ratios of 50/50 and 20/80. The liquid crystalline mesophase was not observed in this system, however. The solubility of another nonaqueous solvent, formamide, in the nonionic surfactants shows a complete association resulting in only an isotropic solution (*Figure 1c*).



Series	Tween 20/ Tween 80 (w/w)
A	32/68
B	50/50
C	68/32

Figure 1. Effect of solvent on the association structure for ternary phase diagram of Tween 80, Tween 20 and a third component consisting of a) water, b) glycerol and c) formamide.

MCT oil-surfactant microemulsion systems

The pseudoternary phase diagrams for the microemulsion solubility region are prepared by two simple combinations (*Figure 2*). The first combines aqueous solvent (water) or nonaqueous solvent (glycerol or formamide) and MCT-palm oil emollient, followed by titration with a third component, an emulsifier which contains a mixture of Tween 20 and Tween 80. The second combination is made by fixing MCT-palm oil emollient and Tween 20 as separate apexes, while the third apex consists of a mixture of Tween 80 and water (or glycerol or formamide) at a weight ratio of 20:80.

The solubility regions prepared by the first combination in both the aqueous and nonaqueous systems are investigated in three series, selected with varying solvent content, but with constant Tween 20/Tween 80 weight ratios (*Figure 1a*). The surfactant ratios are chosen from the surfactant line and extend to the solvent apex. Series A is chosen to be near the liquid crystalline mesophase of 32/68 weight ratio. This is because Friberg *et al.* (1969) have shown that liquid crystals are an essential feature for increasing the stability of an emulsion. The other two series, B and C, are chosen with higher Tween 20/Tween 80 ratios of 50/50 and 68/32 respectively (*Figure 1a*).

It is observed that the isotropic solution regions, obtained from combination 1 for the aqueous system, curve towards the emulsifier (Tween 20/Tween 80) apex in all the series investigated (*Figures 3(a), (b), (c)*). However, the regions taper off through a narrow channel, about 2 weight per cent of MCT-palm oil, to the water apex. The solubility of MCT-palm oil is also observed to be inversely dependent on the emulsifier ratios: a higher solubility with a lower emulsifier ratio.

Figures 4 and *5* show equivalent information but for the nonaqueous counterparts, *i.e.* glycerol and formamide respectively. Once again the isotropic solution covers mainly the emulsifier apex. The narrow channel observed in the water system (*Figure 3*) is not seen in the glycerol systems (*Figures 4(a), (b), (c)*). However, for the formamide systems the narrow channel

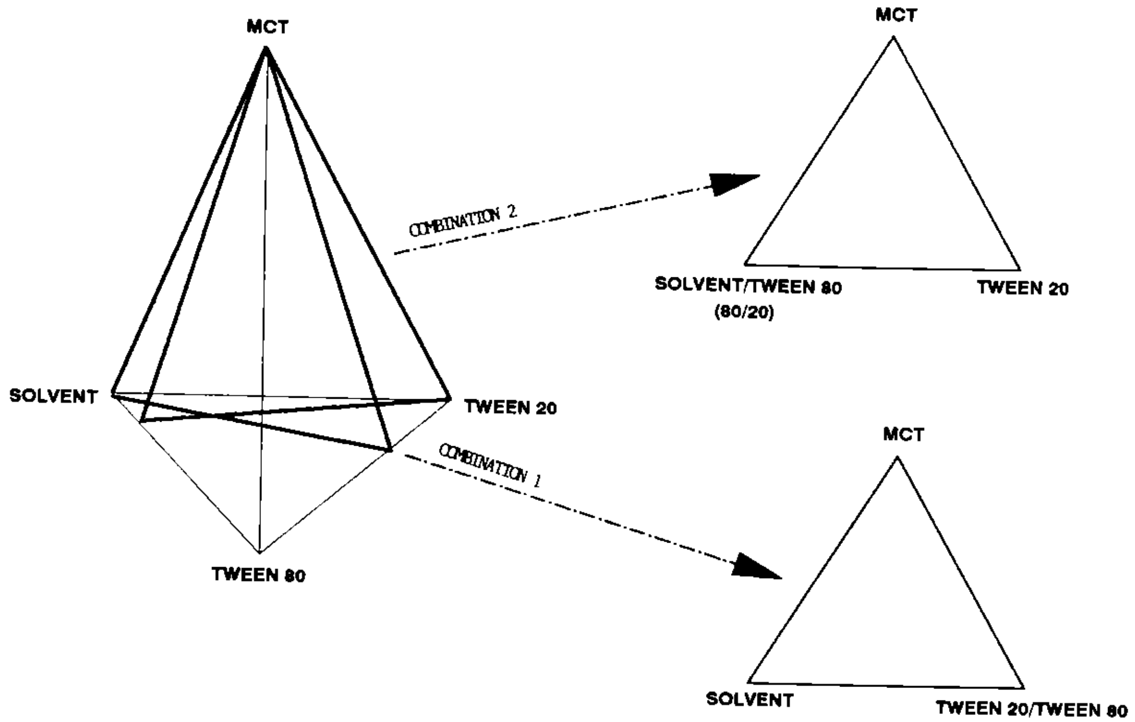


Figure 2. Combination taken for the construction of pseudoternary phase diagrams for the four-component systems of solvent, Tween 20, Tween 80 and medium-chain triglyceride (MCT) palm oil.

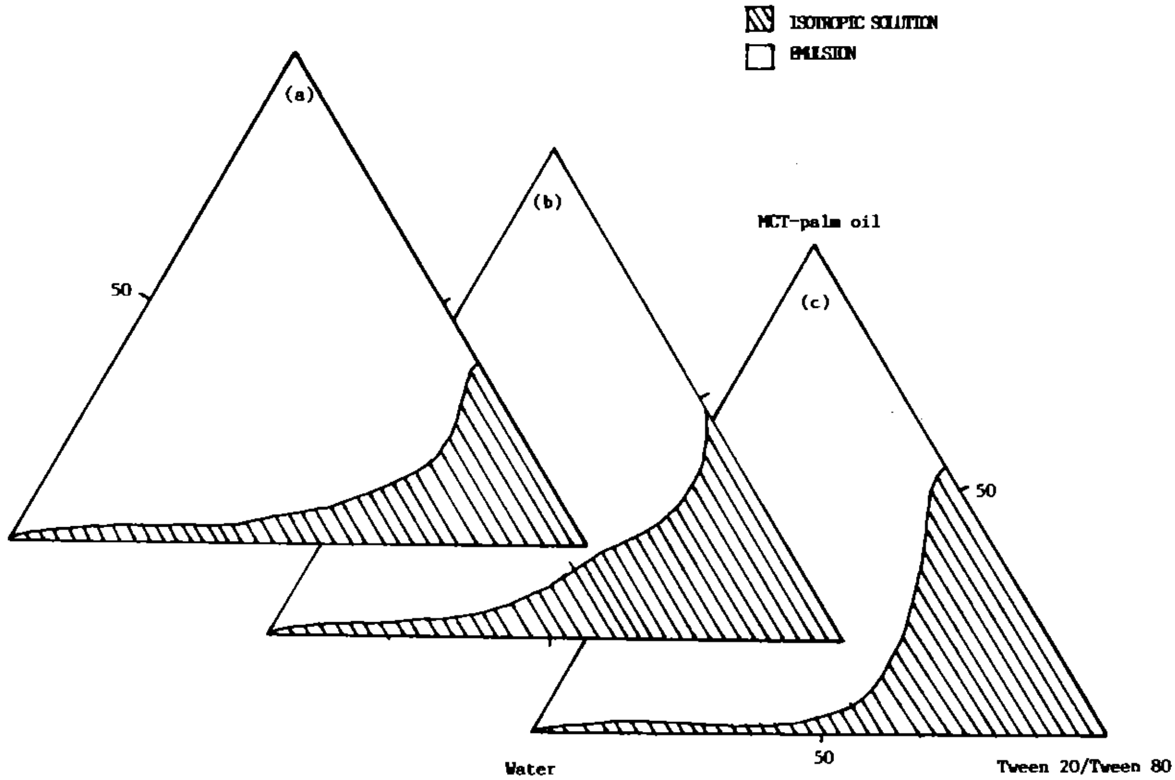


Figure 3. Pseudoternary phase diagram for water, MCT and a third component consisting of mixtures of Tween 20 and Tween 80 at weight ratios of a) 32/68, b) 50/50 and c) 68/32.

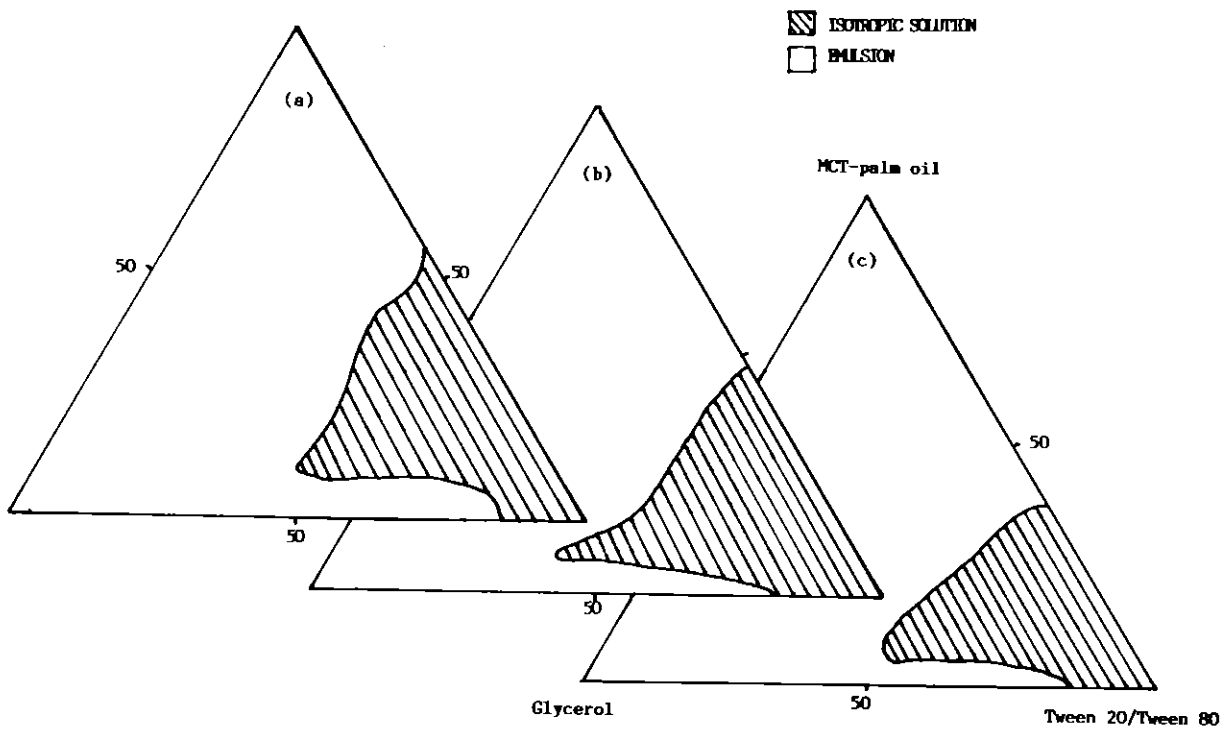


Figure 4. Pseudoternary phase diagram for glycerol, MCT and a third component consisting of mixtures of Tween 20 and Tween 80 at weight ratios of a) 32/68, b) 50/50 and c) 68/32. See Figure 2 *for abbreviation.*

opens up and covers the formamide apex, with series A exhibiting the largest solubility area (*Figures 5(a), (b), (c)*). These observations suggest that normal micelles may form in the water and formamide systems but are not favoured in the glycerol environment. In order to clarify these observations, an investigation of the microemulsion system at high solvent content was conducted. The location of the microemulsion region was readily determined by fixing solvent/Tween 80 (80:20 w/w), Tween 20 and MCT-palm oil as separate axes, as in the second combination in *Figure 2*.

Figure 6 shows the pseudoternary diagram prepared using the second combination. A similar but smaller solubility region is observed for the aqueous and nonaqueous systems. The solubility region is largest for the aqueous systems with two maxima at 24.0 and 35.0 weight per cent of MCT-palm oil. Both the Tween 20 and water (formamide)/Tween 80 (80:20,w:w) show mutual solubility (*Figures 6(a),(b)*). The solubility region in the glycerol system is modest, with an extension of only about 17.0 weight per cent from the Tween 20 apex (*Figure 6(c)*). This further substantiates the earlier observation that normal micelles are not formed in the glycerol system. This phenomenon is attributed to the difference in the Krafft point of the nonionic surfactants in both the aqueous and nonaqueous solvents at the temperature investigated (Rico and Lattes, 1984).

In summary, the present results demonstrate that nonionic triglyceride microemulsions and especially the solvent-in-MCT oil microemulsion do exist in the systems investigated. Also a combination of surfactants, which in this case are both hydrophilic emulsifiers (HLB values of 14–18), must be taken into consideration for the system behaviour. A more systematic approach,

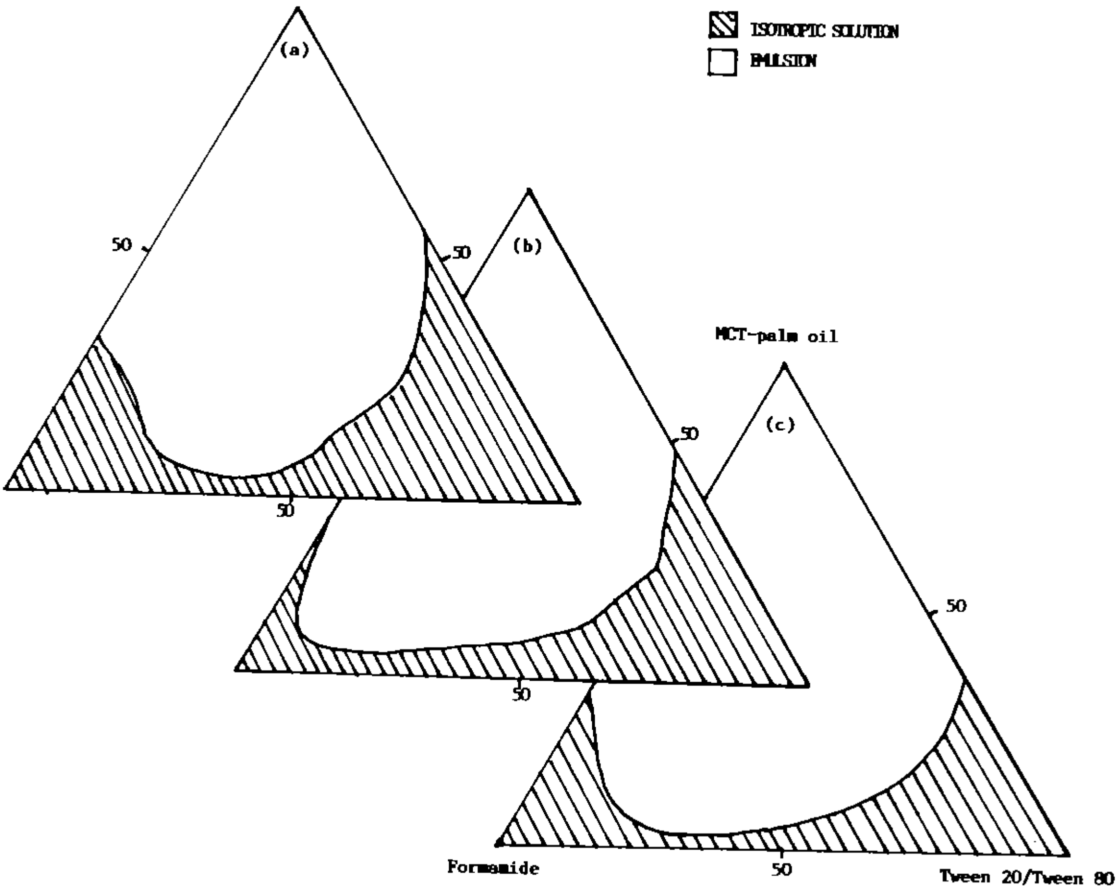


Figure 5. Pseudoternary phase diagram for formamide, MCT and a third component consisting of mixtures of Tween 20 and Tween 80 at weight ratios of a) 32/68, b) 50/50 and c) 68/32. See Figure 2 *for abbreviation.*

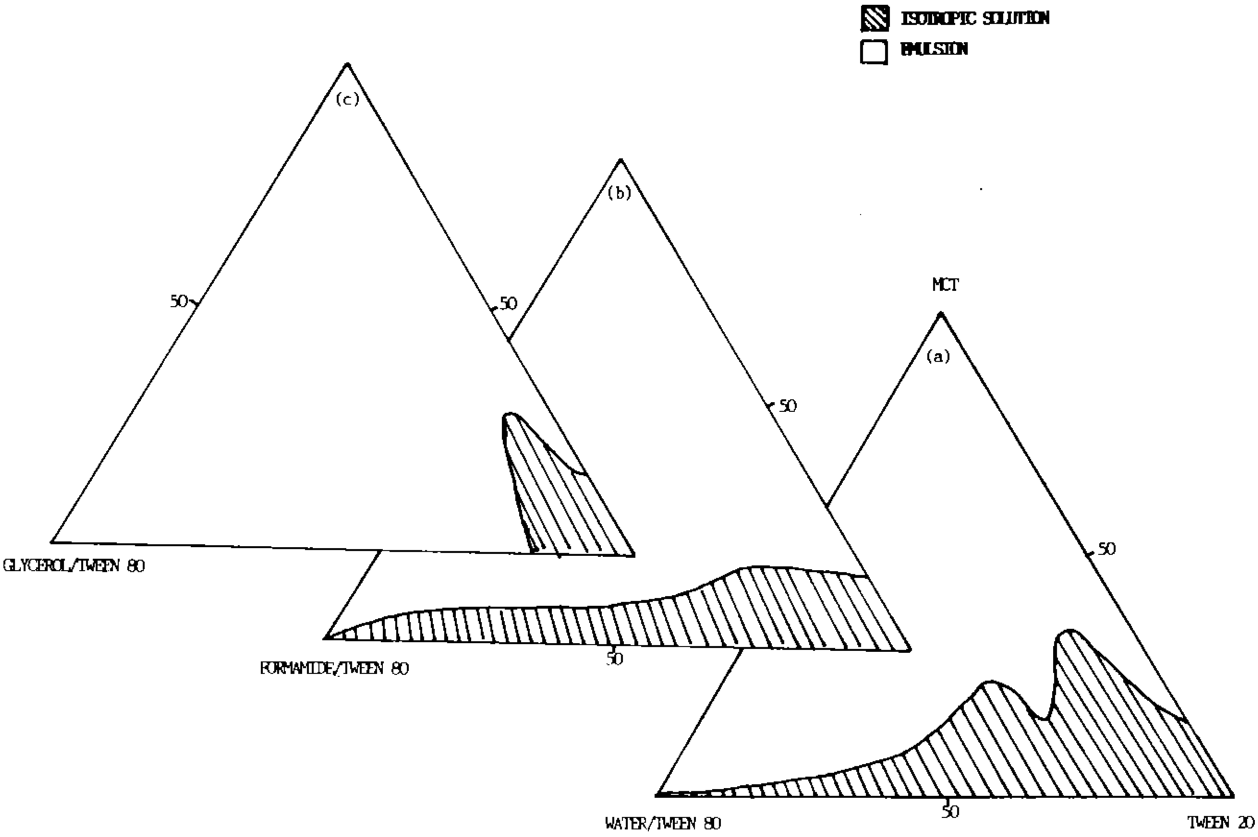


Figure 6. Pseudoternary phase diagram for MCT, Tween 20 and a third component consisting of a mixture of Tween 80 with a) water b) formamide and c) glycerol at a weight ratio of 80/20. See Figure 2 *for abbreviation.*

i.e. employing a binary mixture of hydrophilic and lipophilic emulsifiers is in progress in our laboratory to investigate the MCT oil-in-solvent microemulsion. We are also using light scattering measurements (Sjoblom and Friberg, 1978) in order to investigate further the existence of the microemulsion systems *per se* and to determine the presence of micellar aggregates in these systems before attempting final conclusions.

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