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Triglyceride Microemulsion Systems with Palm Oil

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ABSTRAK

Mikroemulsi dengan minyak sawit RBD dan RPO, dan pelarut, distabilkan dengan dua surfaktan ionik bertentangan cas dan alkohol berantai sederhana telah dikaji. Keputusan menunjukkan bahawa hanya mikroemulsi pelarut dalam minyak yang jelas. Kelarutan maxima terhadap kedua-dua minyak sawit RBD dan RPO adalah lebih tinggi dalam surfaktan bercas positif yang mengandungi atom nitrogen berbanding dengan surfaktan yang bercas negatif. Walaubagaimanapun, keputusan tidak memberikan apa-apa rumusan muktamat tentang kesan pelarut, jarak rantai hidrokarbon untuk asid lemak dan kehadiran pigmen terhadap kawasan mikroemulsi dalam semua sistem yang dikaji.

ABSTRACT

Microemulsions with refined, bleached and deodorized (RBD) and red palm oil (RPO), and solvents, stabilized by two oppositely charged ionic surfactants and a medium chain alcohol, were investigated. The results showed that only the solvent-in-oil microemulsions were prominent. The maximum solubilization of the both RBD and RPO were higher in the positively charged surfactant containing nitrogen atoms than in the negatively charged one. However, the results did not lend themselves to any decisive factor about the effect of solvents, length of hydrocarbon chain of the fatty acids or the presence of pigment on the microemulsion region in all systems investigated.

Keywords: palm oil, microemulsion, phase equilibria, sodium dodecyl sulphate, cetyltrimethylammonium bromide, glycerol

INTRODUCTION

Microemulsions (Hoar and Schulman 1943; Schulman and Riley 1948; Schulman and Friend 1949; Friberg 1976) are thermodynamically stable

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suspensions of two immiscible liquids, generally a hydrocarbon and an aqueous phase. The internal phase is solubilized by particles ranging between 10 and 100 nm in size and composed of surfactant and co-surfactant molecules. It merits over other vehicles or solvents by both improved stability and solubilization characteristics.

The association phenomenon of ionic surfactants in microemulsion has been extensively investigated both in water (Schulman and Friend 1949; Friberg 1976; Podzimek and Friberg 1980; Clausse *et al.* 1988) and to a lesser extent in waterless environment (Fletcher *et al.* 1984; Rico and Lattes 1984). However, mainly hydrocarbon was used as the oil component in those studies, an obvious trend with regard to the importance of microemulsions in tertiary oil recovery (Shah and Schechter 1977). Recent interest has focused on microemulsion systems based on the triglycerides (Joubran *et al.* 1993, 1994). This is primarily due to the growing awareness of environmentally more acceptable formulations.

Our recent contribution (Hamdan *et al.* 1995) presented the microemulsion systems with a medium chain triglyceride (MCT) palm oil emollient. The fatty acid components of MCT are octanoic acid, C8:0 and decanoic acid, C10:0 and are derived mainly from the kernel of oil palm fruits. The mesocarp, however, produces oil which contains equal percentages of palmitic acid, C16:0 and oleic acids, C18:1. This oil, used mainly as cooking oil, is called refined, bleached and deodorized (RBD) palm oil. A more recent development in the palm oil industry is the production of a new generation cooking oil called red palm oil (RPO), with the pigment carotene retained in the oil. Therefore, the variations in the hydrocarbon chain length of the fatty acids and the presence of pigments should exhibit interesting colloidal association behaviour in surfactant systems. In addition, Joubran *et al.* (1994) have demonstrated that the formation of triglyceride microemulsion could be achieved by incorporating sucrose and short-chain alcohol. The synergistic interactions among the sucrose and alcohol molecules resulted in the destabilization of liquid crystal mesophase, thus facilitating the formation of microemulsions. It has also been shown by several workers (Fletcher *et al.* 1984; Rico and Lattes 1984), in their pioneering contributions, that replacement of water with polar solvents such as glycerol and formamide, thus giving a waterless environment, could perturb a colloidal system, resulting in the extension of the microemulsion phase.

In the present comparative studies among triglyceride microemulsion of various palm oil fractions, we extend our previous work (Hamdan *et al.* 1995) to the association behaviour of microemulsions with RBD and RPO. The effect of solvents (water, sucrose and glycerol) and ionic surfactants on the microemulsion phase will also be presented.

MATERIALS AND METHODS

Materials

The basic materials, source and purity for the pseudoternary systems are listed as follows. The cetyltrimethylammonium bromide, CTAB >99.5% (Sigma), sodium dodecyl sulphate, SDS > 99% (Fluka), sucrose 95% (Sigma), glycerol 99.5% (Aldrich) and pentanol >98% (Fluka). The red (RPO) palm oil was prepared following the previously described method (Zaizi *et al.* 1996). The pigment was removed by activated clay to give refined, bleached and deodorized (RBD) palm oil. The fatty acid content was analysed by gas-liquid chromatography (Table 1). The colour measurement for the RPO was performed using Lovibond Tintometer in a 5.25" Lovibond cell, giving a value of 54R; and the pigment (carotene) content was 242 ppm. The water was doubly distilled and deionized.

TABLE 1
Fatty acid composition of palm oil

Fatty acid		%
Lauric	C12:0	0.2
Myristic	C14:0	0.9
Palmitic	C16:0	41.0
Stearic	C18:0	3.2
Oleic	C18:1	45.1
Linoleic	C18:2	8.9
Linolenic	C18:3	0.3
Arachidic	C20:0	0.4

Determination of Phase Regions

The phase equilibria are determined by titrating with the smallest amount of the third component to turbidity. The samples are then vortexed (Thermolyne Maxi Mix II) for mixing purposes and centrifuged at 5000 rpm. The samples are then allowed to equilibrate in a water bath kept at 30°C. The phases are examined visually and between cross polarizers. An estimated region of the phases can be made by this method by noting the turbid/clear transitions.

RESULTS AND DISCUSSSION

Surfactant-pentanol Systems

The two oppositely charged surfactants used throughout this investigation are a negatively charged surfactant SDS and a positively charged surfactant CTAB. Their solubility regions for the isotropic solutions with water (or glycerol) have been described previously (Hamdan *et al.* 1995).

RBD-SDS and RPO-SDS Microemulsion Systems

The pseudoternary phase diagrams for the microemulsion solubility region are prepared by two simple combinations (*Fig. 1*). The first combination is the solvent and palm oil fractions titrated with a third component containing a mixture of SDS and pentanol (20:80, w:w). The second combination is made by fixing palm oil fractions and pentanol as separate apexes, and the third apex consists of a mixture of SDS and solvent at a weight ratio of 15:85.

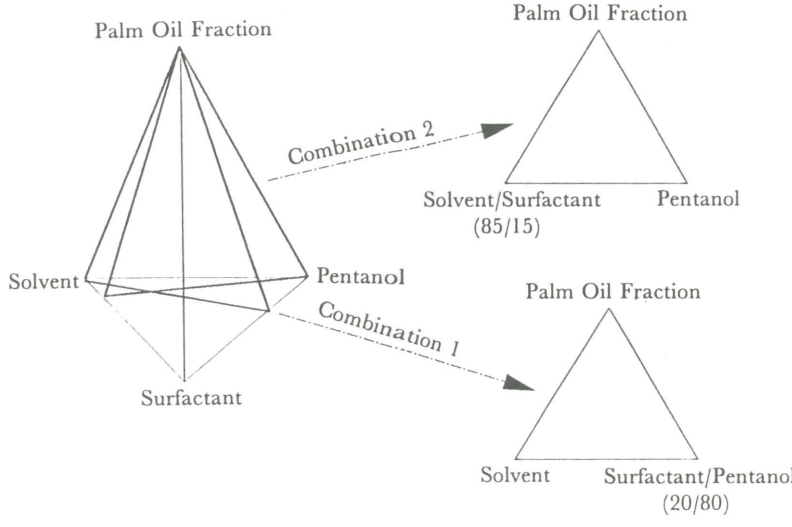

Fig. 1. Combinations taken for the construction of pseudoternary phase diagrams for the four component systems of water or glycerol or sucrose, pentanol, palm oil fractions and SDS or CTAB

Fig. 2(a) shows the solubility region prepared by the first combination with RBD. The system with water shows an isotropic solution region protruding 31-95% SDS:pentanol (20:80) up to about 63% RBD. The minimum water content to achieve this region is found at about 3% water. This minimum value, however, shifts to a higher value of about 26% when the water is replaced with an equal amount of glycerol, shown as solid lines in *Fig. 2(a)*. The solubility region for the glycerol system is found to be smaller with a region projecting with a saddle from the RBD-free axis up to 7 and 10% RBD content. The shift in the minimum glycerol phase and the decrease in size of this region, as explained earlier (Hamdan *et al.* 1995), are due to the difference in the solubility of SDS in water and glycerol, respectively. Water displays a higher solubility of SDS than the corresponding glycerol. The dotted lines in *Fig. 2(a)* show similar information but with 10% sucrose as the solvent. The solubility region resembles that of the

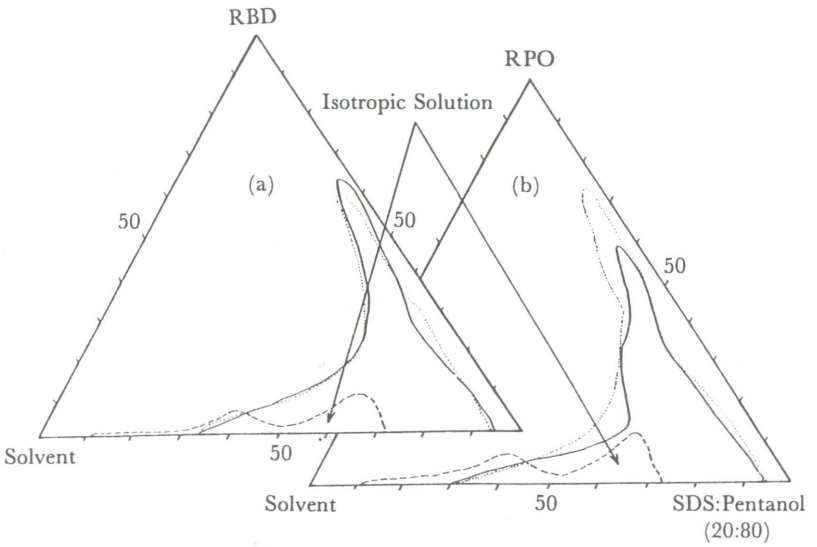

Fig. 2. Pseudoternary phase diagram for (a) RBD and (b) RPO with SDS:pentanol (20:80) and a third component consisting of water or glycerol (——) or 10% sucrose (.....)

water counterpart, but with a lower ability to solubilize the RBD molecules ($\sim 59\%$).

Fig. 2(b) shows the solubility regions with RPO. It is observed that the region covers the phase diagram in the same manner as those of RBD, but with one prominent difference, that is, the solubility region with sucrose exhibits the largest region. This indicates the superiority of sucrose to water and glycerol with regard to the solubilization of RPO.

Fig. 3 shows the pseudoternary diagram prepared by the second combination. A different behaviour is observed for all water, glycerol and sucrose systems in the presence of RBD (or RPO) molecules. The RBD (or RPO) is found to be completely miscible in pentanol. The resulting solutions in the water and sucrose systems are able to solubilized up to about 27% of the SDS:water (or sucrose) (15:85) component and are limited to only lower water (or sucrose) and RBD (or RPO) content. The glycerol system (broken lines, *Fig. 3*) shows a larger solubility region curving towards the pentanol apex. The solubility of the SDS:glycerol mixture in pentanol is reduced to 23% of the mixture. The absence of a solubility region emanating from the solvent corner is probably due to the fact that the mixture of SDS, and the respective solvents at the weight ratio of 15:85, does not produce micelle aggregates and hence exhibits a low solubilization capabilities. This is an understandable result due to the long hydrocarbon chain of the fatty acids (C16 and C18) which does not favour the formation of micelles.

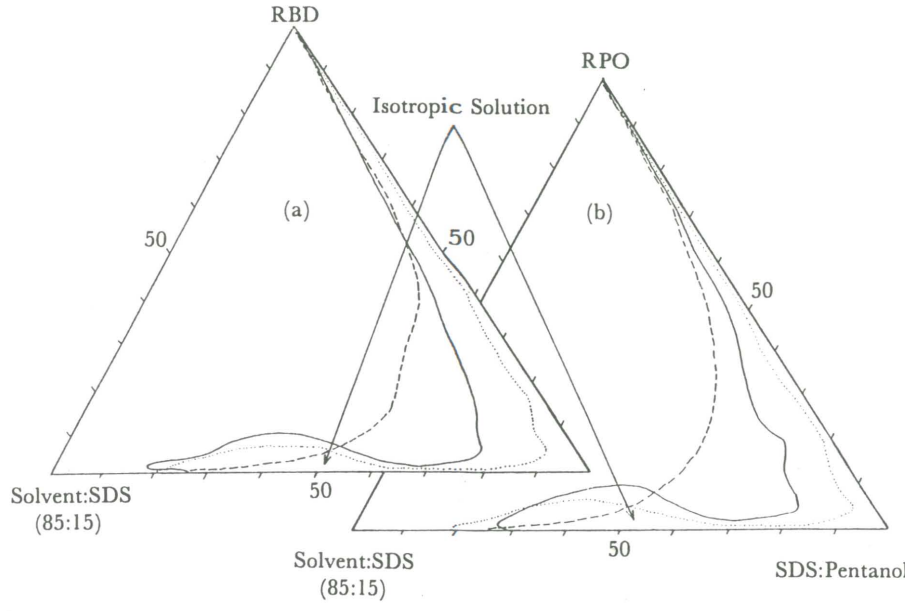

Fig. 3. Pseudoternary phase diagram for (a) RBD and (b) RPO with pentanol and a third component consisting of a mixture of SDS and water or glycerol (——) or 10% sucrose (.....) at a weight ratio or 15:85

RBD-CTAB and RPO-CTAB Microemulsion Systems

Fig. 4(a) shows an equivalent phase diagram as was shown in *Fig. 2(a)*, but for the CTAB system. The isotropic solution region for the aqueous system is observed to be protruding upwards by 77-99% of the mixture of CTAB and pentanol to about 80% of RBD. The solubilization of RBD is higher than the SDS system. However, the maximum water content to achieve solubility in the CTAB system is greatly reduced, to about 23%. These results did not seem to show the superiority of CTAB over SDS as shown previously by Venable and Viox (1984) in combination with pentanol for the microemulsion containing RBD. A similar phenomenon was observed in our previous work (Hamdan *et al.* 1995) and therefore precautions should be taken before making such a conclusion.

The dotted lines in *Fig. 4(a)* show the waterless counterpart of the systems with a mixture of CTAB and pentanol at a weight ratio of 20:80. A larger region is observed than in the corresponding SDS systems (broken lines, *Fig. 2(a)* with an ability of solubilizing RBD better than 59%. This region extends upwards by 19-80% of the mixed CTAB and pentanol (20:80). The solubility region with the equivalent system, but containing 10% sucrose, is shown by the dotted lines in *Fig. 4(a)*. The maximum solubility of RBD is found at 70%; a decrease of 12.5% from the one with water. Similar dependency of the solubility region on the solvents is

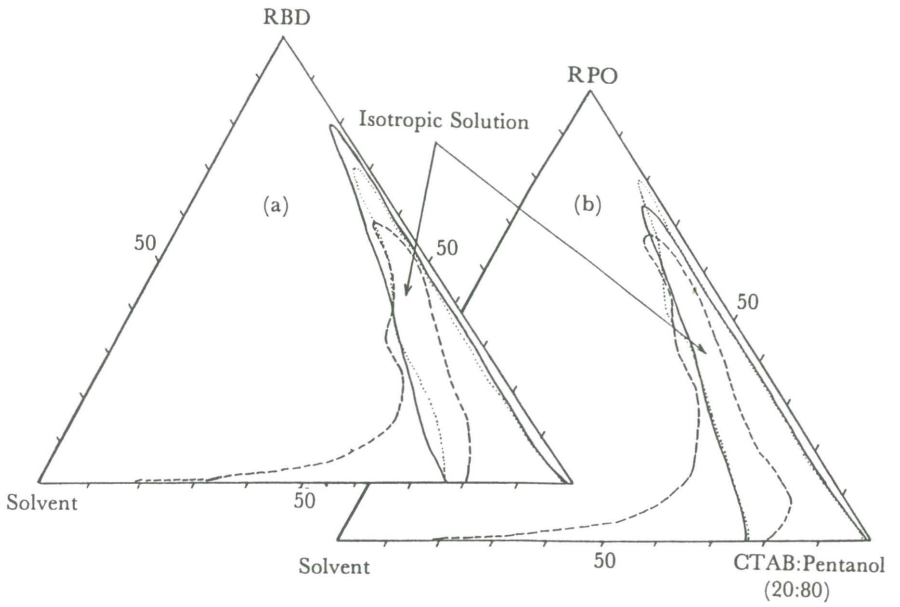

Fig. 4. Pseudoternary phase diagram for (a) RBD and (b) RPO withCTAB:pentanol (20:80) and a third component consisting of water or glycerol (——) or 10% sucrose (.....)

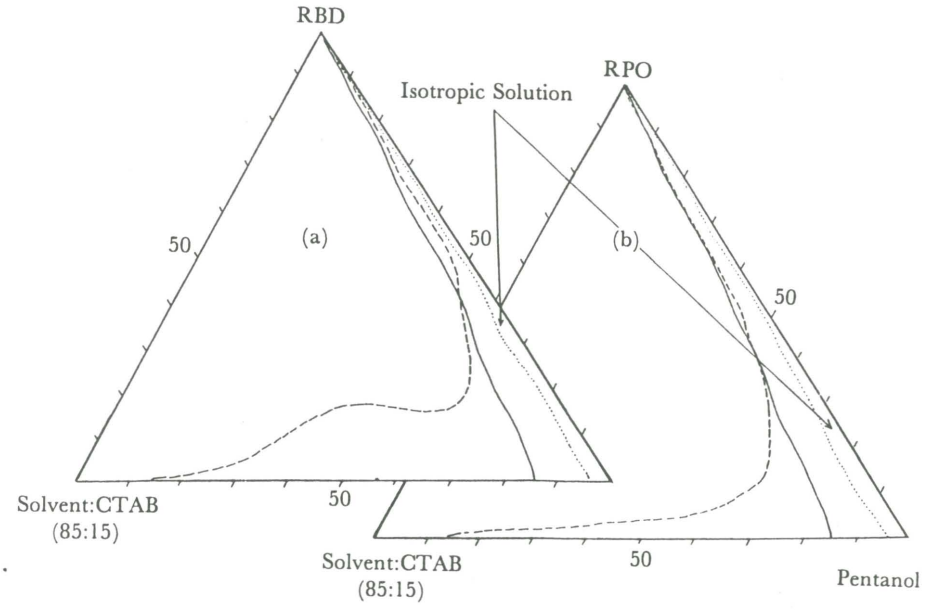

Fig. 5. Pseudoternary phase diagram for the (a) RBD and (b) RPO with pentanol and a third component consisting of a mixture of CTAB and water (——) or glycerol (.....) or 10% sucrose (.....) at a weight ratio of 15:85

observed when RBD is replaced with RPO (*Fig. 4(b)*). The maximum RPO solubility is, however, found to be highest in the sucrose solution.

Fig. 5 shows the pseudoternary phase diagram prepared on the CTAB system by the second combination. The association phenomenon in all solvent systems shows a similar trend to those of the SDS systems. The region, emanating from the intermediate range of water (or sucrose): surfactant and pentanol observed in the SDS aqueous system (*Fig. 3*) is, however, not present in the corresponding CTAB system. The solubility region for the glycerol systems in the CTAB system is retained and curves towards the pentanol apex in the same fashion as those of the SDS system.

In summary, the present results demonstrate that microemulsions and especially the solvent-in-palm oil fractions microemulsion do exist in these investigated systems but are limited to lower solvent content. The results do not seem to show any direct dependency of the microemulsion region on the solvents used, nor on the length of the hydrocarbon chain of the fatty acids and the pigment (carotene) present in the oil.

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