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FORMATION OF MICROEMULSIONS WITH PALM-BASED OILS STABILIZED BY A NON-IONIC SURFACTANT

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ABSTRACT

There is growing interest to replace petroleum-based ingredients in products with natural-based materials such as palm oil and its derivatives. One of the potential uses of these natural materials is in microemulsion formulations. This paper describes the solubilization and ternary phase behaviour of palm oil and its derivatives with a non-ionic surfactant – coco alcohol (C_{12-14}) ethoxylate with 6.9 moles of ethylene oxides (6.9EO) (also called Imbentin coco 6.9EO).

The capacity of solubilization by Imbentin coco 6.9EO for palm oil methyl esters (POME) ≈ tetradecane > palm kernel oil-medium chain triglycerides (PKO-MCT) and palm olein. The phase inversion temperatures (PIT) for POME, PKO-MCT and palm olein were 59°C, 70°C and 71°C at 2:1, 1:1 and 0.5:1 ratios of oil to surfactant. The PIT for tetradecane, a petroleum-based oil, was 56°C at 1:1 oil to surfactant ratio, but ~73°C at a 2:1 ratio.

The capacities for solubilization and formation of a larger microemulsion region with POME were higher than those with PKO-MCT and palm olein in Imbentin coco 6.9EO systems. The maximum solubilities of POME and PKO-MCT were 2:1 and 1:1 oil to surfactant, both at 60°C, and palm olein 0.5:1 oil to surfactant at 70°C. We indicate that the POME molecules penetrate the liquid crystalline (LC) phase into the palisade layer. They then expand the LC (L_α) region and move to the water-rich axis. However, the micellar solution and/or O/W microemulsion can exist at up to 45% (w/w) surfactant at the lower concentrations of PKO-MCT and palm olein in the ternary systems.

Keywords: palm-based oils, non-ionic surfactant, solubilization, microemulsions, high added value products.

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INTRODUCTION

Microemulsions are isotropic, low viscosity and thermodynamically stable solutions in which two immiscible liquids (for example, water and oil) are brought into a single phase by adding a surfactant or mixture of surfactants and/or co-surfactant (Solan *et al.*, 1997; Evans and Wennerstrom, 1994). Microemulsions contain oil (or water) droplets with radii of <100 nm, surrounded by a surfactant layer, dispersed in a water (or oil) continuous phase. Both oil-in-water (O/W) and water-in-oil (W/O) microemulsions can often occur with the same surfactant but with different compositions and/or at different temperature ranges (Rosano, 1974; Prince, 1977; Overbeek *et al.*, 1984; Friberg, 1985; Langevin, 1986; Shinoda and Lindman, 1987; Aveyard, 1987).

Microemulsions containing aliphatic or aromatic hydrocarbons with low molecular weights have been extensively studied and much data on their

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compositions, properties and structures reported (Shinoda and Friberg, 1986; Aveyard *et al.*, 1987; 1990). There are numerous applications for these, for example, in detergents (Azemar, 1997; Salager, 1999). Under the present washing conditions, liquid crystalline phases and, recently, microemulsions play a predominant role in the mechanisms of soil removal (Azemar, 1997). The most significant properties of microemulsions for detergency are improved solubilization for both polar and non-polar soil compounds, very low interfacial tension between the aqueous and oily phases, and spontaneous formation when the components are brought together. They are also of interest for pharmaceuticals (Gasco, 1997; van Corswant *et al.*, 1998) and cosmetics (Nakajima, 1997; Friberg and Yang, 1997).

Microemulsions are very attractive alternatives to O/W emulsions for agrochemical formulations (Tadros, 1995; 1997). The solutions can be prepared by simply mixing the components without recourse to high energy and expensive equipment. The formulations do not separate in storage, and easily pour and disperse on dilution. Another important attraction of microemulsions is their synergistic effect on the biological efficacy of pesticides by solubilizing the active ingredient (the chemical in pesticide is known as the active ingredient in the terminology) in the microemulsion droplets.

There is a growing interest in replacing petroleum-based ingredients with natural materials, such as long and medium chain triglycerides, and alkyl esters because of their many advantages (Alander and Warnheim, 1989; Joubran *et al.*, 1993; Hamdan *et al.*, 1995; Monig *et al.*, 1996). Natural oils and their derivatives are renewable, biodegradable, harmless to the environment, and less of an irritant to the users (Hamilton, 1993; Leysen, 1992). However, long chain triglycerides, such as those in peanut oil, are considerably more difficult to solubilize in microemulsions than hydrocarbon or alkyl esters (Alander and Warnheim, 1989). Thus, the formulation of microemulsions with long chain triglycerides is expected to be non-trivial.

This paper aims to identify the conditions under which palm oil and its derivatives form microemulsions. It describes an initial investigation of solubilization and microemulsion formation with POME, PKO-MCT and palm olein stabilized by a non-ionic surfactant. We selected a commercial non-ionic surfactant – coco alcohol (C_{12-14}) ethoxylate with 6.9EO (or Imbentin coco 6.9EO) - for initial examination because the surfactant is likely to form microemulsions over at least some of the temperature ranges. The $C_{12}EO_5$, a very common non-ionic surfactant, forms extensive microemulsions with normal alkanes (Shinoda and Friberg, 1986; Aveyard *et al.*, 1987; 1992). Since palm oil and its derivatives are more polar than alkanes, we selected a surfactant with a slightly larger head group than $C_{12}EO_5$. The alkyl and EO distributions of $C_{12-14}EO_{6.9}$ (*Table 1*) are known from recent work (Terry *et al.*, 1999). These findings will provide the basis for formulating microemulsions for high added-value products from palm oil and its derivatives.

MATERIALS AND METHODS

Materials

POME, PKO-MCT and palm olein were supplied by Carotech (M) Sdn Bhd, Unichema International (M) Bhd and Lam Soon (M) Sdn Bhd respectively. The carbon chain lengths of the fatty acids for both POME and palm olein were C_{12-18}, and C_{8-10} for PKO-MCT (*Table 1*). A commercial non-ionic surfactant, Imbentin coco 6.9EO, was used as received from Chemische Fabrik, Hedingen, Switzerland. Tetradecane (99.5% purity) was bought from Sigma-Aldrich, United Kingdom.

TABLE 1. FATTY ACID COMPOSITIONS OF PALM-BASED OILS AND IMBENTIN COCO 6.9EO

	Fatty acid								
Oil	**C_8**	**C_{10}**	**C_{12}**	**C_{14}**	**C_{16}**	**C_{18}**	**C_{18-1}**	**C_{18-2}**	**Others**
POME	-	-	0.2	0.9	38.9	4.9	42.8	11.4	0.9
PKO-MCT	66.9	33.1	-	-	-	-	-	-	-
Palm olein	-	-	0.3	1.0	38.7	4.0	44.0	11.2	0.8
Imbentin coco 6.9 EO*	-	0.75	72.3	26.4	0.55	-	-	-	-

Source: *Terry *et al.* (1999).

Solubilization of the Oils in Imbentin Coco 6.9EO

This procedure was adopted from previous work (Rosano *et al.*, 1988; Wolf *et al.*, 1989). The palm-based oils were mixed with 20% (w/w) Imbentin coco 6.9EO at 0:1, 0.5:1, 1:1, 1.5:1 and 2:1 oil:surfactant ratios into small glass bottles and stirred with a magnetic stirrer at room temperature (RT) until homogenous. Then water was added to make 100% (w/w) mixtures. The mixtures were closed tightly and stirred at ~ 500 rpm while heating on a hot plate from RT to ~80°C at ~1.0°C per minute.

The physical appearance of the mixtures [cloudy, translucent or transparent] was observed during the heating to determine the solubilization and cloud point of the solutions. Transparent and clear regions indicate that a swollen micellar solution and/or microemulsion had been formed.

Determination of Ternary Phase Diagrams

The ternary phase behaviour of palm oil and its derivatives in Imbentin coco 6.9EO solutions was investigated using a method adopted from Broze (1997). Forty-five samples containing certain amounts of oil and water were mixed with 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70% and 80% (w/w) surfactant in test tubes and closed tightly. The samples were incubated in a water-bath for about 2 hr at 50°C, then mixed again for ~1 to 2 min. The mixtures were equilibrated overnight at 30°C, 40°C, 50°C and 60°C. The phases were observed under polarized light for birefringent layers, and the specific liquid crystal types determined using a polarizing microscope, Olympus Model AX70.

RESULTS AND DISCUSSION

Solubilization of Palm-Based Oils in Imbentin Coco 6.9EO

This was exploratory work for obtaining the triangular phase diagram for the water-oil-surfactant systems. *Figure 1* shows the solubilization and cloud point curves of tetradecane, a hydrocarbon derived from petroleum, in 20% (w/w) Imbentin coco 6.9EO solution.

A clear and low viscosity isotropic solution was produced when 20% (w/w) Imbentin coco 6.9EO was dissolved in 80% (w/w) distilled water. When the temperature was raised, the surfactant solution remained isotropic until 58.8°C when it became cloudy (turbid). This was due to phase separation into surfactant-rich and surfactant-lean phases. This temperature is defined as the *cloud point*. According to Corti and Degiorgio (1981), the turbidity is usually due to an increasing dominance of critical fluctuation. The growth in micelle size is very small, but the intermicellar interaction increases rapidly.

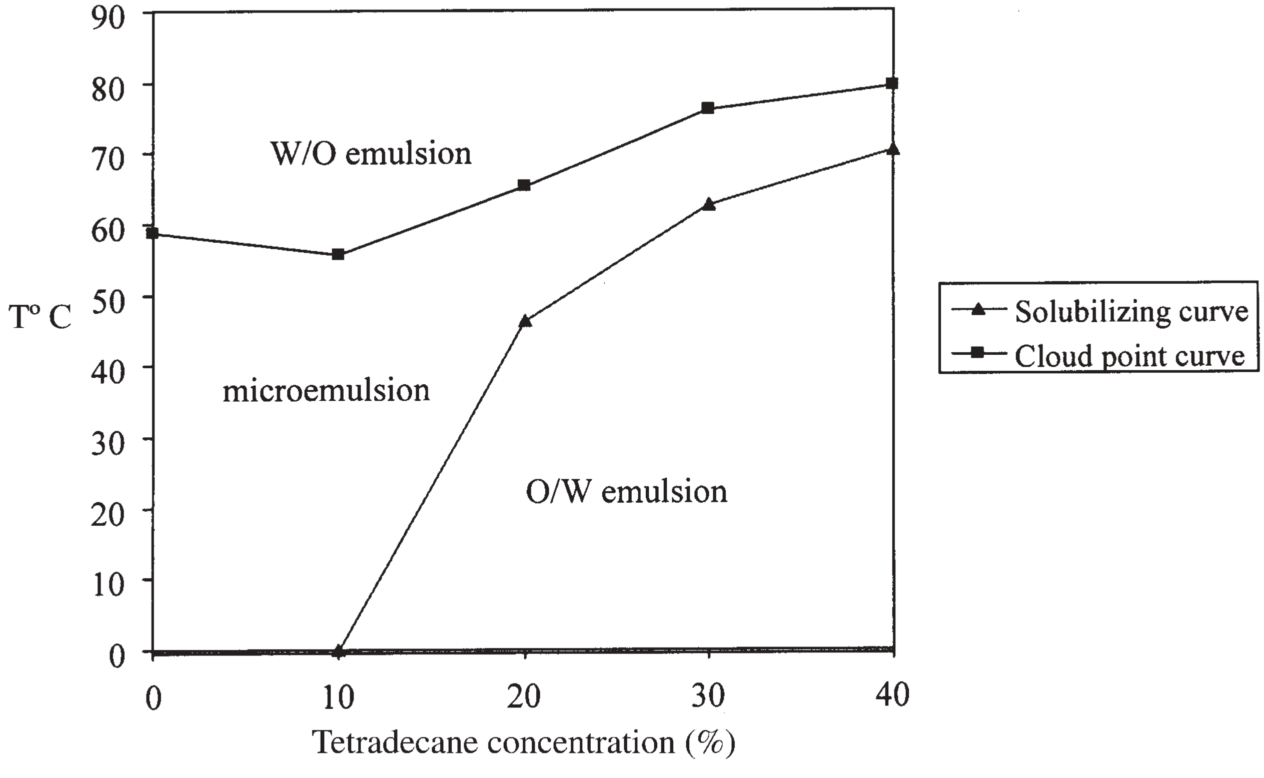

Figure 1. Solubilization of tetradecane in 20% (w/w) Imbentin coco 6.9EO solution.

Tetradecane was added to 20% (w/w) Imbentin 6.9EO solution at 0.5:1, 1:1, 1.5:1 and 2:1 ratios of oil to surfactant. At RT (~25°C), the 0.5:1 ratio was transparently bluish but milky white in the medium-low viscosity emulsions of 1:1, 1.5:1 and 2:1 ratios. When the temperature was raised, the milky white solutions changed into clear microemulsion regions. The curve of the transition is termed the *solubilization curve* (Shinoda and Friberg, 1986; Aveyard *et al.*, 1990; Tadros, 1995).

The solubilization of tetradecane increased considerably from 0.5:1 to 1:1 then plateaued to a gentler increase from 1:1 to 2:1 oil to surfactant ratio. The microemulsion region was larger at the water-rich end and narrow at the oil-rich region as shown in *Figure 1*. The cloud point curve fell a little at 0.5:1 then increased steadily from 0.5:1 to 2:1 oil to surfactant ratio. Cloudy O/W and W/O emulsions were observed under the solubilizing and above the cloud point curves, respectively.

POME was also mixed with 20% (w/w) Imbentin 6.9EO solution at 0.5:1, 1:1, 1.5:1 and 2:1 ratios of oil to surfactant (*Figure 2*). The solubilizing curve was approximately similar to that for tetradecane.

The solubilization of POME increased greatly when POME was added to the surfactant solution at 0.5:1 to 1:1 ratios of oil to surfactant and produced a larger microemulsion region. From 1:1 to 2:1 ratio of oil to surfactant, the POME solubilization increased gradually, with a narrow microemulsion region produced. The microemulsion turned cloudy again at just above the *cloud point*, so termed as the point of phase separation for W/O emulsions.

Figures 3 and *4* show the solubilization of PKO-MCT and palm olein in 20% (w/w) Imbentin coco 6.9EO solution. A microemulsion region was also formed with PKO-MCT and palm olein, but only up to the 1:1 and 0.5:1 ratios for PKO-MCT and palm olein to surfactant at ~70°C. The cloud point curves for both PKO-MCT and palm olein (*Figures 3* and *4*) were also higher than that for the POME system.

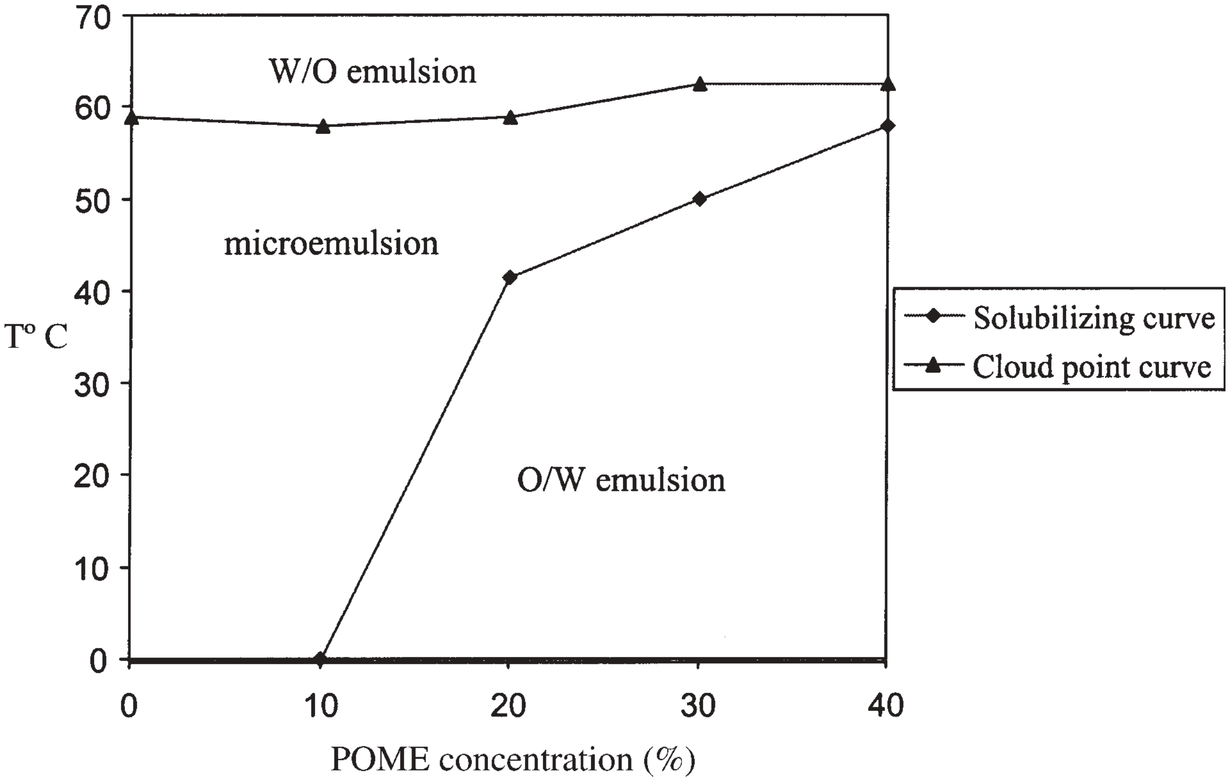

Figure 2. Solubilization of palm oil methyl esters (POME) in 20% (w/w) Imbentin coco 6.9EO solution.

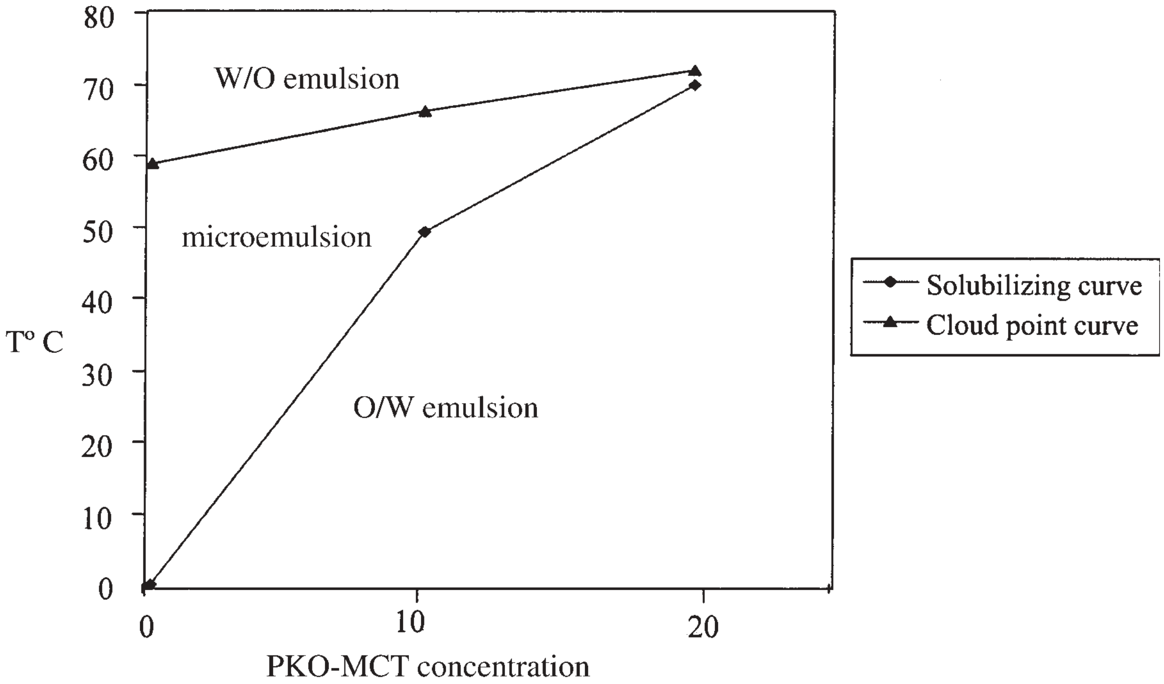

Figure 3. Solubilization of palm kernel oil-medium chain triglycerides (PKO-MCT) in 20% (w/w) Imbentin coco 6.9EO solution.

In *Figures 1* to *4*, the maximum solubilizations for both tetradecane and POME were 2:1 of oil to surfactant, but for PKO-MCT and palm olein were 1:1 and 0.5:1 of oil to surfactant at 20% (w/w) of Imbentin coco 6.9EO. The phase inversion temperature (PIT) or hydrophile-lipophile balance (HLB) temperature lies somewhere in the middle of the three-phase region (Aveyard *et al.*, 1987;1990). The PITs were estimated at 51°C and 56°C, and 59°C and 73°C for the 1:1 or 2:1 ratios of oil to surfactant for POME and tetradecane, respectively. However, the PITs were estimated at 70°C and 71°C with 1:1 and 0.5:1 ratios of oil to surfactant for PKO-MCT and palm olein. In addition, the PIT changes with the type of microemulsion obtained in the equilibrium systems (and also with the emulsion obtained if two phases are shaken together). If the temperature (T) < PIT, an O/W microemulsion or O/W emulsion is obtained. However, a W/O microemulsion or emulsion is obtained if T > PIT (*Figures 1* to *4*).

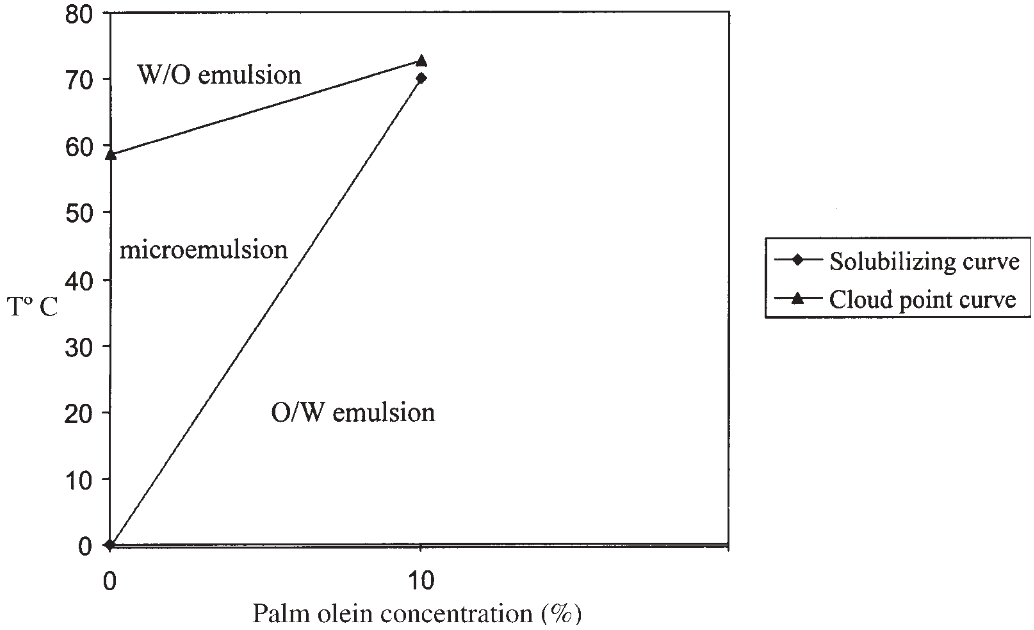

Figure 4. Solubilization of palm olein in 20% (w/w) Imbentin coco 6.9EO solution.

In general, the microemulsion droplets are curved and stabilized by the surfactant monolayer with the droplet size largely determined by the spontaneous curvature of the surfactant layer (Aveyard *et al*., 1987; 1990). As increasing the temperature reduces the curvature of the oil droplets in water, a three-phase region (bicontinuous phase) is formed and can be loosely regarded as infinite-sized surfactant aggregates. The temperature at which the three-phase occurs is termed the PIT, or HLB temperature.

At T ≈ PIT, the surfactant has an equal affinity for solubilizing the oil and water. Thus, a microemulsion can be obtained at the maximum solubilization of oil and water. Therefore, the PIT, interfacial tension and solubilization are interrelated through the effective molecular geometry of the surfactants.

The solubilization phenomenon can also be interpreted using the packing constraint concept (PCC). The rise in temperature dehydrates the surfactant head groups, reducing their effective area, a_h, and increasing the PCC value from <1 (which forms O/W microemulsions) to 1 (which forms bicontinuous microemulsions) and >1 (which forms W/O microemulsions). In conclusion, the degree of solubilization of hydrocarbons in non-ionic surfactants is mainly related to the chemical structures and hydrophilicity of the solubilizates, and to the spontaneous curvature of the surfactant layers and/or packing parameters of the surfactants. The capacities for solubilization with Imbentin coco 6.9EO systems were POME ≈ tetradecane > PKO-MCT > palm olein.

Ternary Phase Diagram of Palm-Based Oils in Imbentin coco 6.9EO

A triangular phase diagram was used to document the changes in composition and temperature for the three- or four-components system. Ternary phase behaviour studies were carried out on the palm-based oils/surfactant/water mixtures, and the phase diagrams constructed at 30°C, 40°C (45°C for palm olein), 50°C and 60°C.

The phase behaviour of POME, Imbentin coco 6.9EO and water over a range of temperature (30°C, 40°C, 50°C and 60°C) is shown in *Figures 5a* to *5d*. W and S indicate water and the surfactant components, and I, II, III, IV and V define the aqueous phase (micellar solution and/or O/W microemulsion), an emulsion (two- and/or three-phase), a liquid crystalline region (LC), oil-continuous micellar solution and/or W/O microemulsion and bicontinuous microemulsion, respectively.

At 30°C, the clear O/W microemulsion region close to the water axis had a maximum solubility of POME of 0.5:1 (ratio of oil to 20% surfactant solution). The ratio increased to 1:1 and 2:1 at 40°C and 50°C. The separate clear region V in *Figures 5c* and *5d*, which contained 2:1 to 2.5:1 POME to surfactant at 50°C and 60°C, respectively, indicate a bicontinuous region. This region is also termed the middle or *Winsor III* phase. In this temperature range, the maximum solubilization of POME and water occurred, and the temperature is termed the hydrophile-lipophile balance temperature or the phase inversion temperature. As discussed in the section on solubilization above, the PIT of POME in 20% (w/w) Imbentin coco 6.9EO (at 1:1 ratio of oil to surfactant) was about 50°C.

The LC region did not change much at 30°C, but started to destabilize and move to the water corner at 40°C. At 60°C, the LC region became smaller, but both emulsions (II) and (IV) expanded as shown in *Figure 5d*. The LC regions in *Figures 5a* to *5d* consisted of a lamellar phase, or L_α, that mixed with the emulsion (two- or three-phase) at the higher amounts of oil. H_1 did not occur in all the ternary phase diagrams because it had been destabilized by the temperature and POME to form the L_α phase.

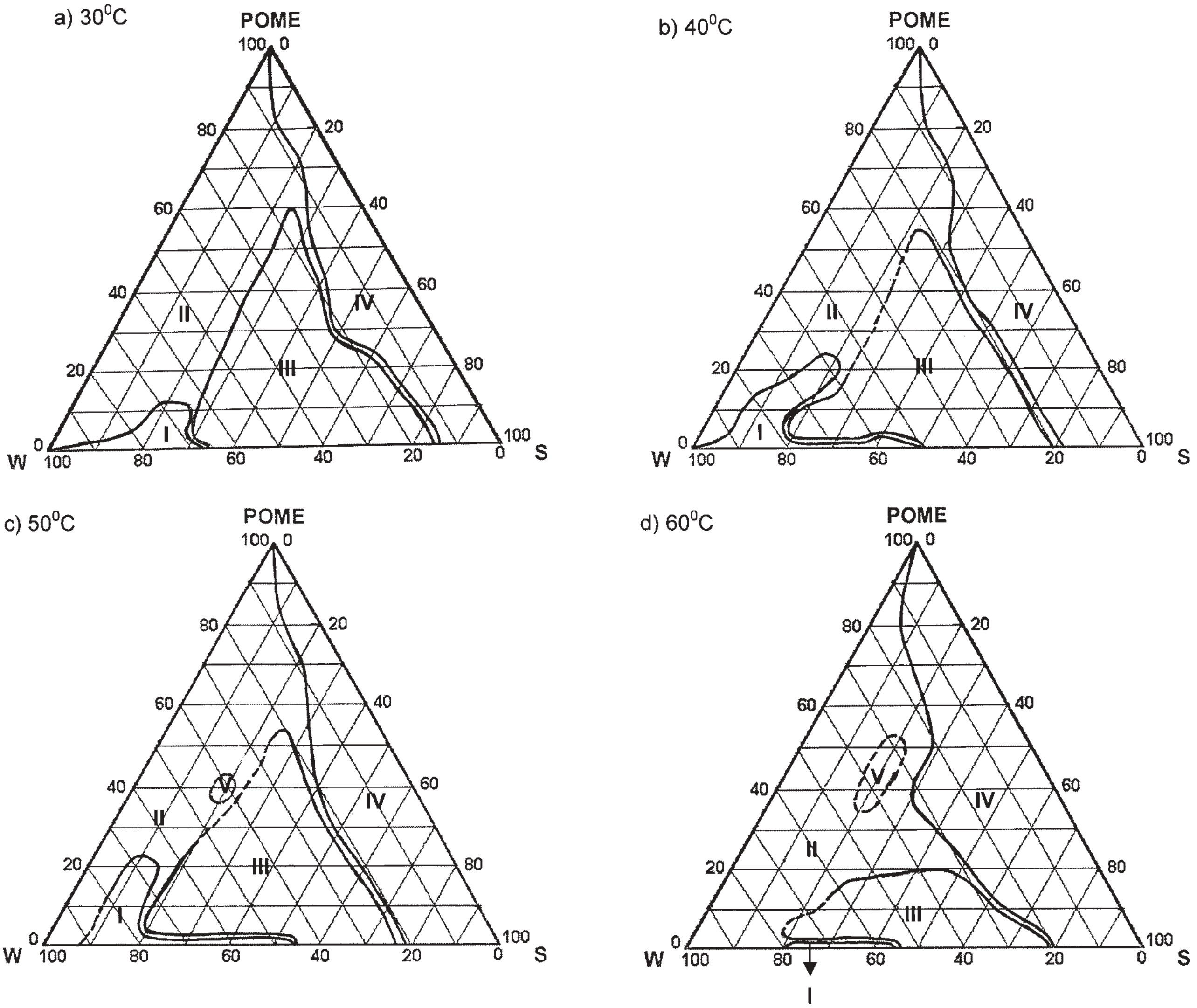

Figure 5. Ternary phase diagrams of palm oil methyl esters (POME) in Imbentin coco 6.9EO solution at (a) 30°C, (b) 40°C, (c) 50°C and (d) 60°C. I, II, III, IV and V indicate the aqueous phase (micellar solution or o/w microemulsion), emulsion (two- or three-phase), liquid crystalline region (LC), oil-continuous micellar solution and/or w/o microemulsion, and microemulsion, respectively. W and S are the water and surfactant components.

Figure 6 presents the phase behaviour of PKO-MCT in mixture with Imbentin 6.9EO at 30°C (a), 40°C (b), 50°C (c) and 60°C (d). At 30°C, the micellar solution and/or O/W microemulsion region had a high water content as <10% of the PKO-MCT had dissolved in the surfactant solution. The solubility of PKO-MCT increased a little at 1:3 ratio of oil to surfactant at 40°C and 50°C. A microemulsion region was obtained only up to ~ 1:1 ratio of PKO-MCT to surfactant at 70°C. This indicated that the PIT of PKO-MCT in Imbentin 6.9EO solution was higher than at 60°C. In fact, the PIT of PKO-MCT in 20% (w/w) Imbentin coco 6.9EO (at 1:1 ratio of oil to surfactant) was about 70°C as discussed in the section on solubilization above. In addition, PKO-MCT has three fatty acids attached to the glycerol structure, so the total carbon chain is longer and its chemical structure more bulky than those in POME. Therefore, the solubilization capacity of PKO-MCT in Imbentin 6.9EO micelles is lower than that of POME.

The emulsion region was larger in the PKO-MCT system, but the inverted micellar solution and/or W/O microemulsion region smaller at 30°C and 40°C compared to the POME system. The LC region also did not change much between 30°C and 40°C. However, it only appeared above 45% (w/w) Imbentin 6.9EO at the water-surfactant axis. At 50°C and 60°C, the LC region was destabilized and formed a larger emulsion (or two/three-phase) and an oil-continuous micellar solution and/or W/O microemulsion region as shown in *Figures 6c* and *6d*. In addition, the LC region moved towards the water-rich region at 50°C and 60°C.

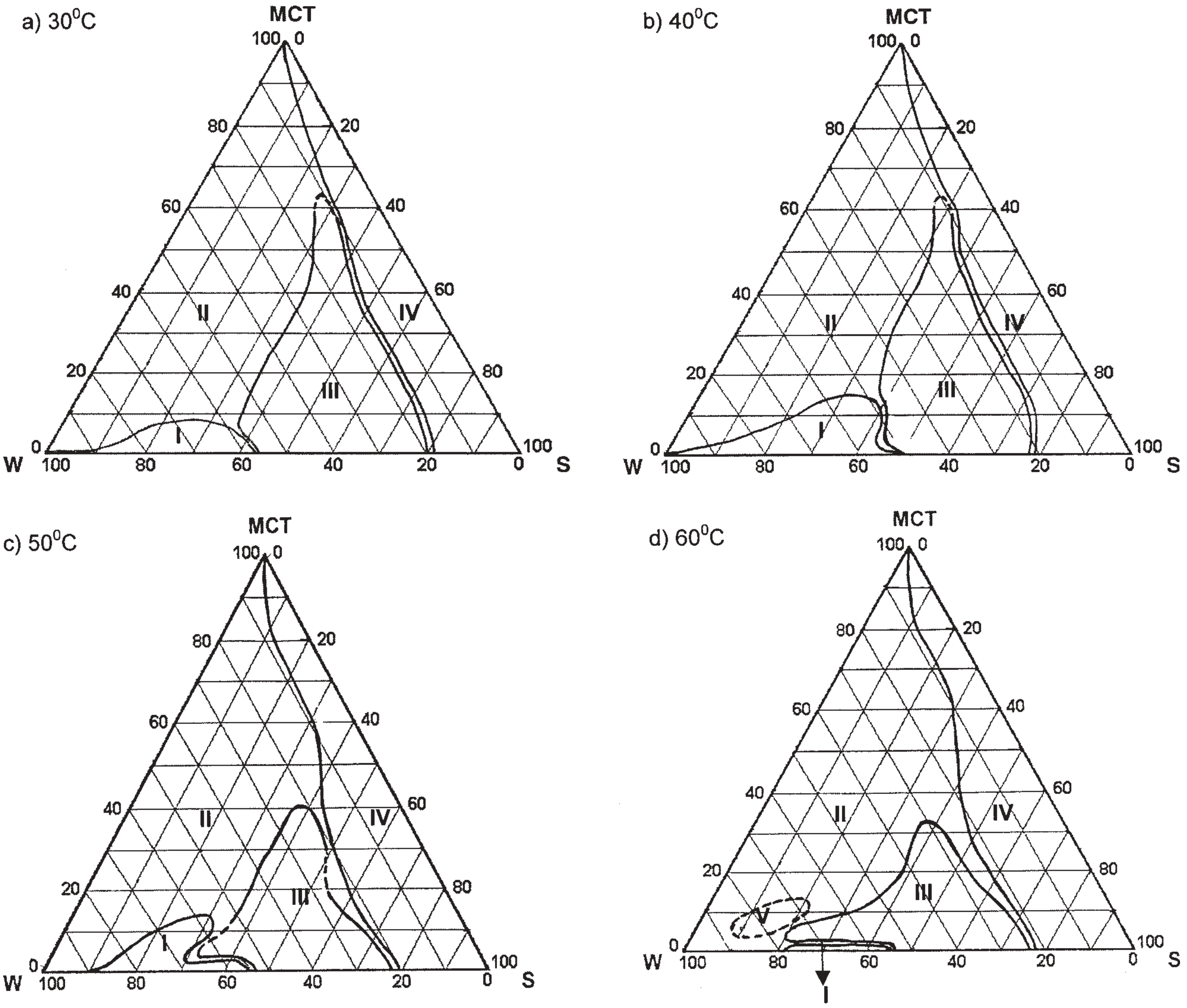

Figure 6. Ternary phase diagrams of palm kermel oil-medium chain triglycerides (PKO-MCT) in Imbentin coco 6.9EO solution at (a) 30°C, (b) 40°C, (c) 50°C and (d) 60°C. I, II, III, IV and V indicate the aqueous phase (micellar solution or o/w microemulsion), emulsion (two- or three-phase), liquid crystalline region (LC), oil-continuous micellar solution and/or w/o microemulsion, and microemulsion, respectively. W and S are the water and surfactant components.

The ternary phase diagrams for palm olein are presented in *Figures 7a* to *7d*. There are only four phases in these triangular diagrams, *i.e.*, the micellar solution or O/W microemulsion, LC region and inverse micellar solution, or W/O microemulsion. The micellar solution and/or O/W microemulsion at the water-rich axis were smaller at 30°C and 40°C, *i.e.*, less than a 1:3 ratio of oil to surfactant (*Figures 7a* and *7b*). At 30°C and 40°C, the LC region (III) also did not change much, and the oil-continuous micellar solution and/or O/W microemulsion were similar to those in the PKO-MCT-ternary phase diagrams. However, the LC region only existed above 45% (w/w) Imbentin 6.9EO at the water-surfactant axis.

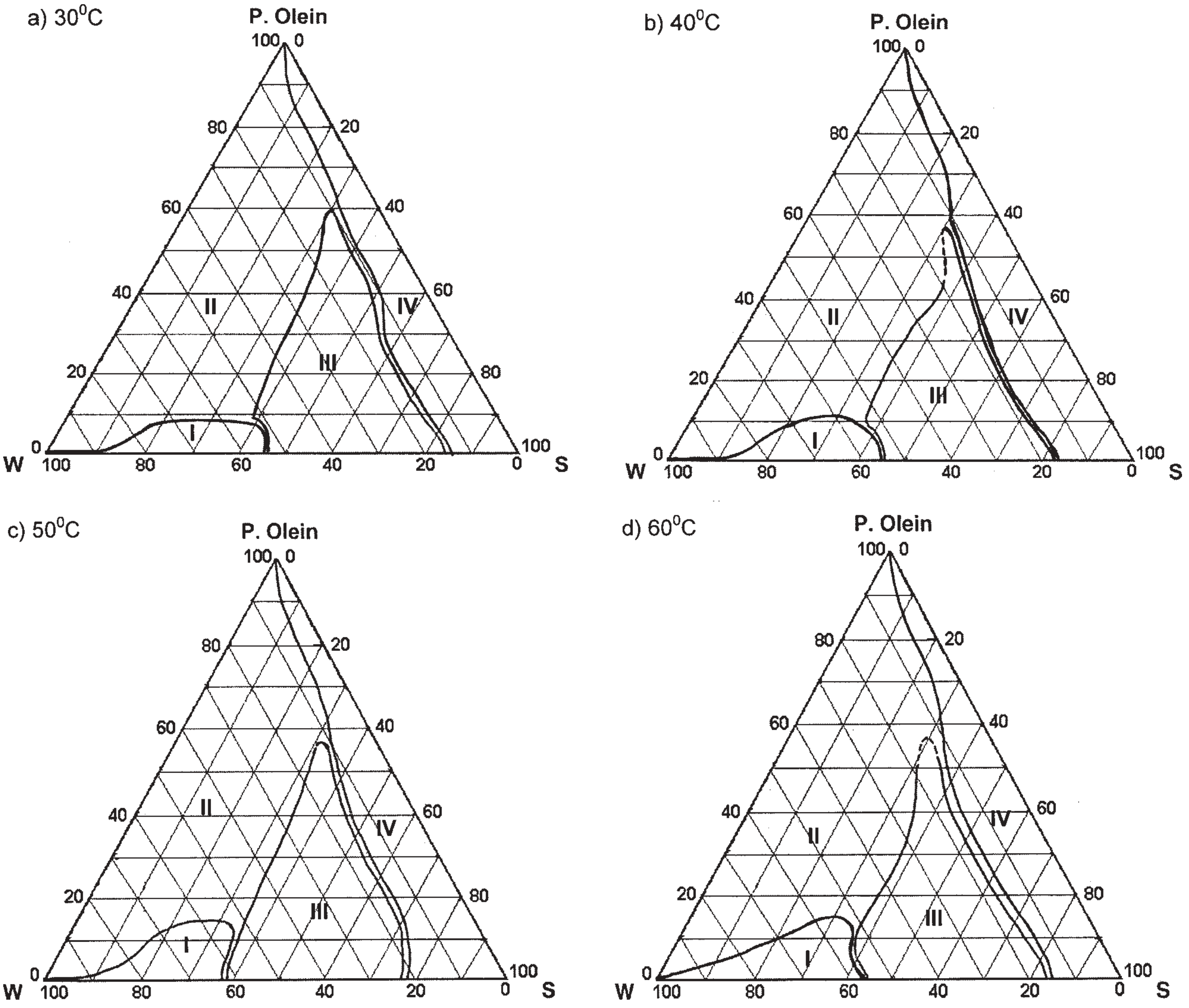

Figure 7. Ternary phase diagrams of palm olein in Imbentin coco 6.9EO solution at (a) 30°C, (b) 40°C, (c) 50°C and (d) 60°C. I, II, III, IV and V indicate the aqueous phase (micellar solution or o/w microemulsion), emulsion (two- or three-phase), liquid crystalline region (LC), oil-continuous micellar solution and/or w/o microemulsion, and microemulsion, respectively. W and S are the water and surfactant components.

The solubility of palm olein only increased slightly in a 1:3 ratio of oil to surfactant (*i.e.* 10% oil to 30% surfactant) at 50°C and 60°C. As discussed in the section on solubilization, the PIT of palm olein in the Imbentin coco 6.9EO system was also higher at 70°C. There was also not much change in the other phases (LC and W/O microemulsion) in the palm olein-ternary phase diagrams at 50°C and 60°C. These indicate that the solubilization capacity of palm olein in the Imbentin coco 6.9EO system was lower than that of PKO-MCT and POME.

The ternary phase behaviour of palm-based oils in Imbentin coco 6.9EO systems indicates that solubilization of the oils in non-ionic surfactants and the formation of microemulsions are mainly related to their chemical structures, hydrophilicity of the solubilizates and the spontaneous curvature of the surfactant layer and/or packing parameters of the surfactants. POME has C_{12-18} chain with one methyl group attached to the ester linkage, PKO-MCT three fatty acid esters with C_{8-10} chains, and palm olein also three fatty acid esters, all with a C_{18-1} chain. Thus, the capacities for solubilization and microemulsion formation with Imbentin coco 6.9EO systems are higher for POME than those of PKO-MCT and palm olein.

Alander and Warnheim (1989) stated that the molecular size of solubilizates, their polarity expressed as interfacial tension, dipole moment or polarizability and the structure of the resulting microemulsions are some factors determining the solubilization capacity of a given system. Warisnoicharoen *et al*. (2000) suggested that based on cloud point/PIT temperature experiments, the higher molecular volume oils are incorporated differently into microemulsions prepared using polyoxyethylene (POE)-based surfactants from the smaller molecular volume oils. These suggest that the smaller molecular volume oils, such as the fatty acid esters, act in the same way as a co-surfactant in interchelating with their hydrophilic group in the surfactant head group region of POE-based surfactants. Thus, the curvature and interfacial tension of the oil droplets in water are reduced, increasing the solubilization capacity of the surfactants.

Other researchers have previously stated that the short and/or medium chain alkanes or aromatic hydrocarbons of oils penetrate the surfactant palisade layer (Kuneida *et al*., 1998; 2000; Ozawa *et al*., 2001). Thus, the curvature of the surfactant layer is less positive or more negative. On the other hand, the oils with long chain and/or bulky alkanes solubilize and penetrate deeply into the surfactant aggregates. The difference in oil penetration causes the difference in phase transition of the liquid crystals. For example, the H_1 phase changes to L_α on addition of an aromatic hydrocarbon or short/medium chain alkanes, and to a discontinuous micellar phase with long and/or bulky chain oils (Kuneida *et al*., 2000; Ozawa *et al*., 2001).

We conclude that the POME molecules (at lower concentrations) may penetrate the LC phase in the water-rich region and locate themselves in the palisade layer (*Figures 5b* to *5d*). They expand the LC (L_α) region and move to the water-rich axis. However, at lower concentrations, the PKO-MCT (*Figures 6b* to *d*) and palm olein molecules (*Figures 7b* to *7d*) may solubilize and locate themselves in the interior of the H_1 phase to form the micellar solutions and/or microemulsions.

CONCLUSION

The capacity for solubilization of palm-based oils with non-ionic surfactants system is mainly related to their chemical structures and hydrophilicity and also to the spontaneous curvature of the surfactant layer and/or packing parameters of the surfactants. For example, the smaller molecular volume oils, such as the fatty acid esters, act as a co-surfactant in that they interchelate with their hydrophilic group in the head group region of POE-based surfactants. Thus, the curvature and the interfacial tension of the oil droplets in water are reduced to increase the solubilization capacity of the surfactants. The capacities of solubilization were POME ≈ tetradecane > PKO-MCT > palm olein in Imbentin coco 6.9EO systems.

The ternary phase behaviour of palm-based oils in Imbentin coco 6.9EO systems also indicate that the degree of solubilization of palm oil and its derivatives in non-ionic surfactants and the formation of microemulsions are mainly related to the chemical structures and hydrophilicity of the solubilizates, and also to the spontaneous curvature of the surfactant layer and/or packing parameters of the surfactants. We conclude that the POME molecules (at lower concentrations) may penetrate the LC phase in the water-rich regions and enter the palisade layer. They then expand the LC (L_α) region and move to the water-rich axis. However, the PKO-MCT and palm olein molecules (at lower concentrations) may solubilize and locate themselves in the interior of the LC (H_1) phase to form micellar solutions and/or microemulsions.

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