EFFECT OF GLYCEROL DERIVED CO-SURFACANT ON THE TERNARY PHASE BEHAVIOUR OF PALM-BASED MICROEMULSIONS

ABSTRACT

An oil-in-water (O/W) microemulsion was prepared by mixing palm-based methyl esters (PME) with water at a 25:75 by weight ratio. The microemulsion was stabilised with C_{12-14} fatty alcohol ethoxylates (FAE) with 7 and 2 moles of ethylene oxide (EO), and palm-methyl ester sulphonate (MES) as mixed surfactants, and glycerol-derived co-surfactant (GTBE) and conventional 1,2-hexanediol as the co-surfactants. The mixtures were agitated vigorously and then stored at ambient temperature and 45°C. Phase behaviour of the ternary-phase systems was periodically observed using the polarised light sheets. The ternary phase diagrams were then mapped. The physical characterisations of any stable microemulsions, such as the conductivity and viscosity solutions were also determined. The optimum concentrations of mixed surfactants (MES/FAE 7/FAE 2) and GTBE to form stable microemulsions were 20% (w/w) and 10% (w/w), respectively. A larger microemulsion region was also obtained for other system consisting of mixed surfactants (FAE 7/FAE 2) and GTBE with the optimum concentrations of mixed surfactants and co-surfactant for producing full microemulsions were 15% (w/w) and 10% (w/w), respectively. Physical characterisations of the stable microemulsion solutions showed that the conductivity values depended on the content of aqueous solution, while the viscosity values on the physical structures of microemulsion formation.

Keywords: glycerol-derived co-surfactant (GTBE), palm-based microemulsions, household and industrial applications.

INTRODUCTION

Over these last few decades, microemulsions have found increasing use in many fields ranging from enhanced oil recovery (Santanna et al., 2009; Nguyen et al., 2008) to pharmaceutical (Laurence and Rees, 2000; Kohsaku and Takayoshi, 2002; Ke et al., 2005). Here, we studied the suitability of glycerol derived co-surfactant (GTBE) as a co-surfactant for producing oil-in-water (O/W) microemulsion for diverse applications such as agrochemicals for crop care and public health sectors, liquid cleaners containing natural insect repellents, etc.

Generally, a microemulsion is formed when the correct mixture of oil, water and amphiphiles are mixed together under appropriate agitation conditions. The size of a microemulsion droplet...
is within the range of ~10 -100 nm, thus making the microemulsion essentially transparent. The inclusion of co-surfactant into these systems reduces the interfacial tension to spontaneously form thermodynamically stable, low viscosity and optically clear solution. The role of medium chain alcohols in microemulsions is to destructure any liquid crystalline phases and to increase the fluidity of the interfacial layer separating the oil and water (Fanun, 2008).

Surfactant acts as a stabiliser in a microemulsion system. Selection of a correct surfactant is crucial to obtain the low interfacial tension. However, a high concentration of surfactant is not preferable since it can cause bioincompatibility problems such as skin irritation (Alany et al., 2000). Therefore, a co-surfactant can be included to lower the concentration of the surfactant used in the microemulsion system (Prince, 1977). Kahlweit et al. (1995; 1996) and Alany et al. (2000) found that many short-chained aliphatic alcohols are regarded as toxic to end-users and aquatic organisms. However, their study showed that 1,2-hexanediol, which has similar properties to aliphatic alcohols, was an excellent co-surfactant in the formation of stable microemulsions, and also it was less toxic to end users. The potential of 1,2-hexanediol as an alternative to replace medium chain aliphatic alcohols was also investigated by Raman et al. (2008).

A series of glycerol alkyl ether was studied by Blute et al. (1998) and Fukuda et al. (1993; 2001). In these studies, the branched alkyl tail was believed to inhibit the formation of liquid crystal and formed thermodynamically stable microemulsion at low concentrations of surfactant. In this study, a glycerol derivative (defined as GTBE) was used as the co-surfactant because of its branched structured molecule. This branched molecular co-surfactant was obtained from the etherification process of short chain polyols with monohydric alcohols in the presence of a catalyst under pre-determined pressure and temperature (Yusrabbil, 2007). It is a water-soluble compound (pH ~5-6) and consists of 55%-80% GTBE and 30%-35% unreacted glycerol. Purification of this product gave 75%-80% GTBE and ~5% glycerol. According to this invention, GTBE is non-irritant to skin hence safe to end-users.

This study aims to determine the suitability and potential application of GTBE as an alternative co-surfactant derived from natural-based glycerol in oil-in-water (O/W) microemulsion for diverse applications such as agrochemicals for crop care and public health sectors, liquid cleaners containing natural insect repellents, etc. In addition, the potential application of GTBE as cost-effective co-surfactant in palm-based O/W microemulsion for practical applications will be determined. The physical properties of the microemulsions such as their conductivity and viscosity are also reported.

### MATERIALS AND METHODS

#### Materials

Palm fatty acid methyl esters (PME) were supplied by Carotech (M) Sdn Bhd. The alkyl alcohol ethoxylates (FAE 7 and FAE 2) were provided by Emery Oleochemicals (M) Sdn Bhd [formerly known as Cognis Oleochemicals (M) Sdn Bhd], and the 1,2-hexanediol (AR grade) as the conventional co-surfactant was purchased from Chemmart Asia Sdn Bhd (manufactured by Sigma-Aldrich). Alpha-methyl ester sulphonate (µ-MES) as the surfactant and glycerol derivative, GTBE, as co-surfactant were synthesised in a laboratory of the Advanced Oleochemicals Technology Division (AOTD), MPOB.

#### Methods

The O/W microemulsions were prepared by mixing palm oil-based methyl esters (PME) with 0.01M NaCl solution that was filtered first as the aqueous phase at 25:75 ratio. The microemulsions were formed by palm-based methyl ester sulphonate (MES) and fatty alcohol ethoxylates (FAE) with 7 and 2 moles of ethylene oxide (EO) as mixed surfactants, and GTBE as a natural-based co-surfactant. The 1,2-hexanediol, the conventional co-surfactant was also used as a comparison.

The formation of O/W microemulsion was also studied without the addition of MES. The mixtures were mixed vigorously and incubated in water bath at 50°C for 2 hr and then kept at ambient temperature and 45°C for one month. The phase behaviour of the ternary-phase systems was observed using polarised light sheets periodically under room temperature and 45°C. The ternary phase diagrams were then mapped. Later, the full microemulsion samples were subjected to conductivity and viscosity measurements to determine their physical characteristics.

### RESULTS AND DISCUSSION

#### Ternary Phase Diagram of PME/Water/[FAE 7+FAE 2]/1,2-Hexanediol and PME/Water/[FAE7 + FAE2 + MES]/1,2-Hexanediol

Figure 1 presents the effect of 1,2-hexanediol on the ternary phase diagram of PME/[FAE 7+FAE 2] water at 25°C and 45°C. The ternary phase diagram shows that the minimum concentration of mixed surfactant and 1,2-hexanediol to form microemulsion solution was 10% (w/w) and 15% (w/w) at 25°C (Figure 1a). While at 45°C, the minimum mixed surfactants and 1,2-hexanediol concentrations required were 15% (w/w) and 20% (w/w),
respectively to form stable microemulsion (Figure 1b). The optimum concentrations of surfactant and co-surfactant required to form stable microemulsions were 20% (w/w) and 10% (w/w), at 25°C, and 15% (w/w) and 20% (w/w) at 45°C, respectively. It is shown from the ternary phase diagrams that two/multiple-phases (or emulsions) region enlarged when the temperature was increased a little at water-rich corner from room temperature to 45°C. The transition phase from microemulsion region to two/multiple-phases (or emulsions) region after the increase in temperature is due to low concentration of surfactant in the microemulsion solution (Ismail, 2006). This leads to increasing dominance of critical fluctuation, i.e., the growth in micelles size is very minor but the intermicellar interactions increase markedly (Corti and Degiogio, 1985; Conroy et al., 1990). However, liquid crystal region was about the same after the increase of temperature.

Upon addition of MES into PME/[FAE 7+FAE 2]/water system, we can see in Figure 2 that the minimum mixed surfactants required was 15% (w/w) and 5% (w/w) of co-surfactant at 25°C and 45°C, respectively. On the other hand, the optimum concentration of mixed surfactants and co-surfactant required to form microemulsion were 15% (w/w) and 10% (w/w), respectively at both temperatures. Comparing Figures 2a and 2b, it was shown that the liquid crystal region destabilised to form microemulsions when the temperature was increased to 45°C. The enlargement of microemulsion region after the rise of temperature is due to

![Figure 1](image1.png)  
![Figure 2](image2.png)
EFFECT OF GLYCEROL DERIVED CO-SURFACTANT ON THE TERNARY PHASE BEHAVIOUR OF PALM-BASED MICROEMULSIONS

The formation of mixed micelles in the mixed surfactants system. This result is supported by a research conducted by Lim (2001) where enlargement of the isotropic solution upon increasing the temperature was noted. The isotropic region of sodium salts of alpha-sulphonated methyl esters derived from palm stearin (α-SMEPS)/commercial surfactants/water (H2O) systems above 50 w/w% H2O was constructed at different temperature (15°C, 20°C, 25°C, 30°C and 40°C). The incorporation of commercial surfactants has increased the solubility of α-SMEPS.

The ternary phase diagrams show larger microemulsion regions were formed with the addition of MES in the system (Figure 2) compared to the system without MES (Figure 1). Anionic surfactant, MES was used in the mixture of surfactants because it gives good detergency performance (Schambil and Schwuger, 1990) and good biodegradability (Steber and Wierich, 1989). It is widely used in detergents, shampoos and other cleaning products (Maurad et al., 2006). Larger microemulsion regions in Figure 2 indicated that MES gave better synergistic effect in the mixed surfactants system and 1,2-hexanediol to form microemulsions.

**Ternary Phase Diagram of PME/Water/(FAE 7+FAE 2)/GTBE and PME/Water/(FAE 7+FAE 2+MES)/GTBE**

Figure 3 shows the effect of glycerol-derived co-surfactant on the ternary phase diagrams of PME/(FAE 7 + FAE 2)/water at 25°C and 45°C. The minimum concentration of mixed surfactants and co-surfactant required to form microemulsion were 15% (w/w) and 10% (w/w), respectively at 25°C. The same concentrations were also required to form microemulsion at 45°C. However, the optimum mixed surfactants required to form microemulsion was 15% (w/w) and 10% (w/w) at 25°C and 45°C, respectively. Figures 3a and 3b also showed that a slight destabilisation occurred in the liquid crystal region, thus small broadening in the microemulsion region was observed after the increase in temperature. The increase in temperature also slightly narrowed the region of two/multiple-phases (or emulsions).

The ternary phase diagram of Figure 4 shows PME/water/(FAE7+FAE 2+MES)/GTBE at 25°C and 45°C. The minimum concentrations of mixed surfactants and GTBE required to form microemulsion were 20% (w/w) and 10% (w/w), respectively at 25°C. While at 45°C, the minimum mixed surfactants and GTBE concentrations required were 15% (w/w) and 20% (w/w), respectively to form microemulsion. The optimum concentrations to form microemulsions were also the same as the minimum concentrations at 25°C and 45°C. From the ternary phase diagram, it is shown that there was a slight expansion in microemulsion regions.

In Figure 4, we can see that inclusion of MES increased the surfactant concentration to 20% (w/w) compared to without MES. Nevertheless, GTBE gave comparable result to 1,2-hexanediol as co-surfactant. A series of alkyl glycerol ether was investigated by Blute et al. (1998) and Fukuda et al. (1993; 2001). According to these studies, the branched alkyl tail was believed to restrain the formation of liquid crystals to form thermodynamically balanced microemulsions at low surfactant concentrations.

Figure 3. Effects of glycerol-derived co-surfactant (GTBE) on the triangular phase diagrams of palm-based methyl ester (PME)/fatty alcohol ethoxylates (FAE) [(FAE) 7+FAE 2] / water at i) 25°C and ii) 45°C. The II, III, and I are the two/multiple-phases (or emulsions), liquid crystals, and oil-in-water (O/W) and/or water-in-oil (W/O) microemulsions, respectively. The ratio of PME to water was 25:75.

243
Physical Characterisation

Conductivity. The electrical conductivity of the microemulsions was measured with a Cole Palmer Conductivity meter at 25.0 ± 0.1°C. The electrode probe was calibrated using an aqueous standard solution with 1413 μS/cm conductance at 25°C. Electrical conductivity measures the ability of ions to move in aqueous phase on the local charge droplets (Georges and Chen, 1986). Conductivity measurements were only done on visibly transparent and clear solutions obtained that had been vortexed to homogenise and left for one to two days at ambient temperature for equilibrium.

Figure 5a shows the conductivity curves for microemulsions formed with 1,2-hexanediol as the co-surfactant and (FAE 7 + FAE 2 + MES) as the mixed surfactants. The curves showed a decrease in conductivity with the increase in co-surfactant concentrations. For 10% (w/w) and 30% (w/w) of mixed surfactants, the slope of the conductivity curves decreased gradually until 40% (w/w) of co-surfactant. The curves decreased obviously from 40% (w/w) of co-surfactant onwards where the slope was steeper. Meanwhile, for 20% (w/w) mixed surfactants, the slope of the conductivity curve decreased gradually until 30% (w/w) of co-surfactant and the slope slightly decreased from that point onwards.

These results show that phase transition occurred from normal micellar and/or O/W microemulsion to inverse micellar and/or water-in-oil (W/O) microemulsion for 10%, 20% and 30% (w/w) of surfactant. The optimum concentration of co-surfactant in which the phase transition occurred was at 40% (w/w) for 30% (w/w) and 40% (w/w) of mixed surfactants. However, no obvious phase transition had occurred for 40% (w/w) of mixed surfactants. Conductivity curves for microemulsions formed with 1, 2-hexanediol as the co-surfactant and (FAE 7 + FAE 2) as the mixed surfactants without inclusion of MES are illustrated in Figure 5b. The conductivity slopes gradually decreased for 10% (w/w) mixed surfactants up to 40% (w/w) of co-surfactant and rapidly decreased from there onwards. The conductivity slopes gradually decreased for 20% and 30% (w/w) of mixed surfactants up to 30% (w/w) of co-surfactant and rapidly decreased from there onwards. The slope decreased gradually for 40% (w/w) of surfactant from 20% to 50% (w/w) concentrations of co-surfactants.

Figure 6a shows the curves for microemulsion formed with GTBE as the co-surfactant and (FAE 7+FAE 2+ MES) as the surfactant. The steepness of the conductivity curves decreased gradually for 10% (w/w) of surfactant up to 70% (w/w) of co-surfactant and suddenly decreased from 70% (w/w) onwards. As for 20% of mixed surfactants, the conductivity slope decreased up to 30% (w/w) of co-surfactant and slightly decreased from 40% (w/w) onwards. For 30% and 40% (w/w) of mixed surfactants, the conductivity slope decreased up to 30% (w/w) of co-surfactant and rapidly decreased from 30% (w/w) of co-surfactant onwards.

These results show that phase transitions from normal micellar and/or O/W microemulsion to inverse micellar and/or W/O microemulsion for 10%, 20% and 30% (w/w) of mixed surfactants occurred at 40%, 30% and 30% (w/w) co-surfactant, respectively. On the other hand, phase transition had not occurred obviously for 40% of mixed surfactants.

Figure 6a shows the curves for microemulsion formed with GTBE as the co-surfactant and (FAE 7+FAE 2+MES) as the surfactant. The steepness of the conductivity curves decreased gradually for 10% (w/w) of surfactant up to 70% (w/w) of co-surfactant and suddenly decreased from 70% (w/w) onwards. As for 20% of mixed surfactants, the conductivity slope decreased up to 30% (w/w) of co-surfactant and slightly decreased from 40% (w/w) onwards. Finally, for 30% and 40% (w/w) of mixed surfactants, the conductivity slope decreased up to 30% (w/w) of co-surfactant and rapidly decreased from 30% (w/w) of co-surfactant onwards.

The phase transition from normal micellar and/or O/W microemulsion to inverse micellar and/or
or W/O microemulsion for 10% (w/w) of mixed surfactants occurred approximately at 70% (w/w) of co-surfactant. For 20% (w/w) of mixed surfactants, the phase transition occurred at 40% (w/w) of co-surfactant. Lastly, the phase transition of 30% and 40% (w/w) of mixed surfactants from normal micellar and/or O/W microemulsion to inverse micellar and/or W/O microemulsion occurred at 30% (w/w) of co-surfactant. Thus, the optimum concentrations for the phase transition occurred at 70%, 40%, 30% and 30% (w/w) of co-surfactant for 10%, 20%, 30% and 40% (w/w) of mixed surfactants, respectively.

The conductivity slopes for microemulsion system with GTBE as the co-surfactant and (FAE 7+FAE 2) as the mixed surfactants are graphically depicted in Figure 6b. The curves show that the conductivity slope decreased for 10% (w/w) of mixed surfactants up to 60% (w/w) of co-surfactant and decreased rapidly from 60% (w/w) onwards where the slope is steeper. For 20% of mixed surfactants, the conductivity slope decreased up to 50% (w/w) of co-surfactant and decreased rapidly from 50% (w/w) of co-surfactant onwards. The conductivity slope decreased up to 40% (w/w) of co-surfactant for 30% and 40% (w/w) of mixed surfactants and decreased rapidly from 40% (w/w) of co-surfactant onwards.

The phase transition from normal micellar and/or O/W microemulsion to inverse micellar and/or W/O microemulsion for 10% (w/w) of surfactant occurred at 60% (w/w) of co-surfactant. For 20% (w/w) of mixed surfactants, the phase transition occurred at 50% (w/w) of co-surfactant. As for 30% and 40% (w/w) of mixed surfactants, the phase transition occurred at 40% (w/w) of co-surfactant from normal micellar and/or O/W microemulsion to inverse micellar and/or W/O microemulsion. Hence, the optimum concentrations for the phase transitions occurred at 60%, 50% and 40% (w/w) of co-surfactant for 10%, 20%, 30% and 40% (w/w) of mixed surfactants, respectively.

Figure 5. The conductivity curves for microemulsion systems with 1,2-hexanediol as the co-surfactant with mixed surfactants systems (a) fatty alcohol ethoxylates [fatty alcohol ethoxylates (FAE) 7+FAE 2 + MES] and (b) (FAE7 + FAE2).
The results showed that the conductivity values were dependence on the water content in the microemulsion solutions. As the concentrations of the co-surfactant increased and the water compositions decreased, the conductivity values decreased significantly. Therefore, the electrical conductivity and ionic motion were affected by the water composition in the system. Additionally, conductance in microemulsion solutions was low at water-less region than at the water-rich region, indicating that higher conductivity values were likely a continuous phase (O/W microemulsion) and transit to bicontinuous and / or W/O microemulsion as the aqueous content decreased (Fanun, 2008; Ismail, 2006; Lim, 1999; 2006). Elevated values of conductivity can be explained by phenomenon of hydration of the surfactant head groups (Baker et al., 1984). The results obtained were also in agreement with previous studies conducted by Pons et al. (2003), and Aveyard et al. (1989).

### Viscosity

Viscosity measurements were carried out by using Rheometer Physica MCR at 25.0 ± 0.1°C. The same prepared samples, which had been vortexed and left for equilibrium for one to two days at ambient temperature, were used to measure their viscosity. Figure 7a shows the viscosity curves for microemulsion system with 1,2-hexanediol as Co-S and [FAE 7+FAE 2+MES] as mixed surfactants. As for 10% and 20% (w/w) of mixed surfactants, the viscosity curves showed that the slopes decreased up to 20% (w/w) of co-surfactant and shifted up at about 20% (w/w) of co-surfactant onwards. As for 30% and 40% (w/w) of mixed surfactants, the slopes also decreased up to 30% (w/w) of co-surfactant and increased from about 30% (w/w) of co-surfactant onwards.

Figure 7b shows the viscosity curves for microemulsion system with 1,2-hexanediol as the
co-surfactant and (FAE 7+FAE 2) as the mixed surfactants. The viscosity curves decreased up to 30% (w/w) of co-surfactant and increased gradually from 30% (w/w) of co-surfactant onwards for 20%, 30% and 40% (w/w) of mixed surfactants. As for 10% (w/w) of mixed surfactants, the viscosity slopes increased gradually from 20% (w/w) co-surfactant onwards.

Figure 8a shows the viscosity curves for microemulsion system with 1,2-hexanediol as the co-surfactant with mixed surfactants systems (a) fatty alcohol ethoxylates (FAE7)+ FAE 2 + methyl ester sulphonate (MES) and (b) (FAE7 + FAE2).

It was observed from the viscosity curves that the kinematic viscosity of the microemulsion solutions decreased gradually and reached the transition phase, and then increased obviously from the transition phase onwards as shown in Figures 7 and 8. The increase in kinematic viscosity leads to increasing the diameter of droplets and promoting to aggregation of continuous form of microemulsion collapsing into bicontinous or W/O microemulsion system (Fanun, 2008). This is fairly in agreement with other studies investigated by
Ismail (2006) and Lim (1999; 2006). In addition, the viscosities of the microemulsion systems with GTBE as the co-surfactant were relatively higher than the microemulsion systems with 1, 2-hexanediol as the co-surfactant. This might be due to the molecular weight of GTBE, which is larger than the 1, 2-hexanediol. This is in agreement with a previous study which confirmed that the structure of co-surfactant essentially influenced the viscosity of microemulsions (Lim, 1999).

CONCLUSION

According to the ternary phase diagrams, which contained $\alpha$-MES, the optimum concentration of 1,2-hexanadiol as a co-surfactant was 10% (w/w) that had formed stable microemulsion. Meanwhile, for the ternary phase diagrams, which did not contain $\alpha$-MES, the optimum concentration of 1,2-hexanadiol was 15% (w/w). On the other hand, the formation of stable microemulsion with incorporation of GTBE as a co-surfactant, which contained $\alpha$-MES, the optimum concentration of GTBE was 20% (w/w). For formation of stable microemulsion without $\alpha$-MES, the optimum concentration of GTBE was 15% (w/w). The results determined that $\alpha$-MES gives better synergistic effect with 1,2-hexanadiol compared to GTBE as the co-surfactant because it formed larger microemulsion region in the ternary phase diagram studied.

From the physical characterisation analyses, it can be concluded that conductivity and viscosity values depend on the content of aqueous and non-aqueous solutions. Also, viscosity values depend on the chemical structure of the substances for formation of microemulsion. Nevertheless, the increase of conductivity values correlate with decreasing viscosity values of the microemulsion solutions. Conductivity and viscosity studies are important since they give information on the internal structures of water solubilised in the microemulsion systems (Bisal et al., 1990). These mean that phase transitions of microemulsion can...
be investigated using electrical conductivity and viscosity measurements to distinguish formation of O/W, bicontinuous and or W/O microemulsions. We therefore conclude that GTBE could be used as a potential alternative co-surfactant for producing palm-based O/W microemulsion products such as agrochemicals for crop care and public health sectors, liquid cleaners consisting natural insect repellent, aerosol-insecticides, etc.

ACKNOWLEDGEMENT

The authors wish to thank the Director-General of MPOB for the approval to publish this article.

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