Formulation and phase behavior study of a nonionic triglyceride microemulsion to increase hydrocarbon production

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A R T I C L E   I N F O

Article history:
Received 24 April 2012
Received in revised form 3 July 2012
Accepted 3 July 2012

Keywords:
Microemulsion
Enhanced oil recovery
Chemical flooding
Palm oil
Triglyceride

A B S T R A C T

It is no secret that during microemulsion flooding, the oil entrapped in rock pores can be easily removed when a new Winsor Type III microemulsion is formed in situ. Formulation of an efficient microemulsion in tertiary oil recovery requires good understanding of its phase behavior. This paper presents the phase behavior study of a triglyceride microemulsion before and after n-octane solubilization in formulating an efficient triglyceride microemulsion. The effects of solubilized oil as co-oil, salinity, surfactant concentration and co-surfactant concentration on the phase behavior of a triglyceride microemulsion were investigated. The optimized aqueous phase composition of the triglyceride microemulsion was adjusted at 1 wt% alkyl polyglycosides, 3 wt% glycercyl monooleate, 3 wt% sodium chloride, and 93 wt% de-ionized water. It is concluded that this condition represents the widest range and the maximum volume of Winsor Type III microemulsion that can be achieved for the triglyceride microemulsion after fluid injection.

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1. Introduction

Microemulsions are special formulations consisting of oil and water, stabilized by an amphiphile(s) (Paul and Moulik, 2001). Amphiphile is a substance containing both hydrophilic and hydrophobic parts in its molecular structure. For instance, surfactants and co-surfactants are considered as amphiphiles. Thermodynamic stability, transparency, low stability, ultra-low interfacial tension, large interfacial area, and the capacity to solubilize both aqueous and oil-soluble compounds are some of the unique properties of microemulsions (Paul and Moulik, 2001; Deen and Pedersen, 2008; Sottmann and Stubenrauch, 2009). Due to the typical and distinctive properties of microemulsions, they have attracted a considerable interest in many scientific fields such as enhanced oil recovery over the last decades. Various microemulsion formulations have been widely used in chemical flooding to mobilize the remaining oil in the reservoir by reducing the interfacial tension (IFT) (Putz et al., 1981; Purwono and Murachman, 2001; Bouabiboune et al., 2006; Santanna et al., 2009). As the microemulsion slug is traversing the reservoir, it solubilizes and displaces the remaining oil toward the production well.

Microemulsion in tertiary oil recovery can be prepared either on the surface prior to its injection (Putz et al., 1981; Santanna et al., 2009) or in situ from the injected chemicals and the remaining oil (Zhao et al., 2008; Wang et al., 2010). These two types of microemulsion are different mainly in their oil component. In in situ prepared microemulsion, the oil component must be a hydrocarbon fraction or petroleum which represents the crude oil remaining in the reservoir. However, in a pre-prepared microemulsion, the oil component is not limited to n-alkanes (Putz et al., 1981; Bouabiboune et al., 2006) but it can also be replaced with vegetable oils, which are essentially triglycerides (Santanna et al., 2009).

Many researchers have investigated the application of triglyceride-based microemulsions in areas other than enhanced oil recovery. They have provided substantial information on the formulation, phase diagrams, and microstructure of triglyceride microemulsions (Shinoda et al., 1984; Kunieda et al., 1988; Joubarn et al., 1993; Kahlweit et al., 1995a, 1995b; Hecke et al., 2003; Huang et al., 2004; Komessarukal et al., 2006a, b; Engelskirchen et al., 2007; Do et al., 2009; Fanun, 2010; Phan et al., 2011). Most hydrocarbon-based microemulsion systems exhibit three standard phase behavior types; namely Winsor Type I (oil-in-water microemulsion in equilibrium with an excess oil phase), Winsor Type II (water-in-oil microemulsion in equilibrium with an excess aqueous phase), and Winsor Type III (bicontinuous microemulsion which is the middle phase in equilibrium with both oil and aqueous phases) (Winsor, 1954). In Winsor Type I, the surfactant system has relatively low hydrophobicity, and therefore the surfactant film curves around the oil and the curvature of the surfactant film is considered positive (Winsor, 1954; Komessarukal et al., 2006a). In Winsor Type II, the surfactant system has relatively high in hydrophobicity, and therefore the surfactant film curves...
around the water and the curvature of the surfactant film is considered negative (Winsor, 1954; Komesvarakul et al., 2006a). Bicontinuous or Winsor Type III microemulsion generally occurs when spontaneous curvature of the surfactant film approaches to net zero (Winsor, 1954; Komesvarakul et al., 2006a). Winsor Type IV or one phase microemulsion can be obtained when both the excess oil and water phases of Winsor Type III become soluble in the microemulsion as a result of high surfactant concentration (Winsor, 1954; Komesvarakul et al., 2006a).

It has been previously reported that Winsor Type III phase behavior rarely occurs for a triglyceride-based microemulsion in the absence of salts, co-oil, and co-surfactants such as short-chain alcohols at room temperature (Hecke et al., 2003; Huang et al., 2004; Komesvarakul et al., 2006a). For the application of a triglyceride-base microemulsion in tertiary oil recovery, the phase behavior of the prepared microemulsion prior to the injection is not a major concern. However, it is essential that the injected microemulsion forms Winsor Type III microemulsion in situ because the bicontinuous microemulsion provides ultra-low interfacial tension and very large solubility of hydrocarbon (Shinoda et al., 1984). While the injected triglyceride microemulsion is traversing the oil reservoirs and solubilizing the remaining hydrocarbon, the oil phase composition of the microemulsion is changing because the solubilized oil plays the role of co-oil in the newly in situ prepared microemulsion. Thus the oil phase of the prepared microemulsion in the reservoir contains not only triglycerides but also the solubilized hydrocarbon oil. The oil composition in the microemulsion is continuously changing by solubilizing additional hydrocarbons. Therefore, the phase behavior of the microemulsion is altered along the reservoir since the curvature of the surfactant film depends both on the nature of the surfactant(s) and the composition of the aqueous and oil phases (Hyde et al., 1997; Komesvarakul et al., 2006a,b). Winsor Type III microemulsion may form if the hydrophilic–lipophilic property of the surfactant system is balanced by the addition of co-oil (Shinoda et al., 1984). Therefore, it is crucial to study the phase behavior of a prepared microemulsion after solubilization of the model hydrocarbon oil, which is n-octane in this study, to formulate an appropriate triglyceride microemulsion to increase hydrocarbon production in tertiary oil recovery. N-octane was used as the model hydrocarbon oil because it is considered good to represent the crude oil in reservoirs (Green and Willhite, 1998).

The main objective of this paper is to study the change in the phase diagrams of triglyceride microemulsions during a tertiary recovery process. Palm oil is used as the oil phase of the triglyceride microemulsion. Alkyl polyglycosides (APGs) and glyceryl monooleate (GM) were used as the surfactant and co-surfactant of the triglyceride microemulsion, respectively. In this study, different Winsor Type I triglyceride microemulsions were prepared at various salinities, surfactant and co-surfactant concentrations of the aqueous phase. The phase behaviors of all the triglyceride microemulsion samples before and after the n-octane solubilization were investigated. The range and the volume of bicontinuous (Winsor Type III) microemulsion region after n-octane solubilization are the two essential criteria considered in the selection of the aqueous phase composition of the triglyceride microemulsion. Based on the phase behavior results, the composition of the aqueous phase of the triglyceride microemulsion was optimized to ensure both the Winsor Type III microemulsion occurs at a wide range of n-octane concentration and considerable volume of the in situ middle phase microemulsion is achieved.

2. Experimental tests

2.1. Materials

The surfactant used in this work was Glucopon 650EC, a mixture of APGs having an average alkyl chain length of 11, hydrophilic–lipophilic balance (HLB) of 11.9, and critical micelle concentration (CMC) of 0.073 g/L at 37 °C (Jurado et al., 2007). It was provided by Cognis (Malaysia) Sdn Bhd which is now part of BASF Chemical Company. The active percentage of the surfactant solution is 50–53 weight percent (wt%).

Sodium chloride (NaCl, A.R. grade) was supplied by LGC Scientific, Malaysia. Furthermore, n-octane and GM were supplied by Sigma–Aldrich. Palm kernel oil was purchased from Delima Oil Products Sdn. Bhd. in Malaysia. All of the materials were used as supplied without further purification.

2.2. Triglyceride microemulsion preparation

Triglyceride microemulsion was prepared by mixing 230 g of the oil phase with 230 g of the aqueous phase. The aqueous phase comprised of surfactant, co-surfactant, sodium chloride, and de-ionized water at various compositions. The oil phase was pure palm oil. After adding all the components at their desired fractions, the sample was shaken with orbital shaking motion. Lab Companion SL-300 Benchtop Shaker at low shaking frequency of 100 rpm was used to avoid the appearance of emulsion phase. The triglyceride microemulsion sample was shaken for at least an hour to ensure a well-mixed and uniform mixture because of quite low aqueous solubility of APG, low frequency of mixing, and the relatively large volume of the samples. The sample was then poured into a separating funnel and left undisturbed for at least one week for equilibrium. Since palm oil is a natural component, to avoid the possibility of degradation, sample bottles used during the mixing were sealed with Viton lined screw caps. In addition, separating funnels used in the resting step were sealed with tight lubricated Teflon stopper. The microemulsion phase formed after the equilibrium was noted to be Winsor Type I or lower phase microemulsion. Then the microemulsion phase was separated from the upper (excess oil) phase in the separating funnel and was used in the next phase behavior studies. The volumes of the triglyceride microemulsion and the excess oil phase were recorded to depict phase diagram of the triglyceride microemulsion before n-octane solubilization.

2.3. Optimization of the aqueous phase composition of the triglyceride microemulsion by phase behavior studies

2.3.1. Optimization of salinity

Five Winsor Type I triglyceride microemulsion samples were prepared at various salinities of 1, 3, 6, 9, and 12 wt% of the aqueous phase. The concentration of APG (surfactant) and GM (co-surfactant) were fixed at 1 and 2 wt% of the aqueous phase. All of the 5 measured volume fraction data sets of the excess oil and prepared microemulsion were presented in a phase diagram against the concentration of NaCl to show the phase behavior of the triglyceride microemulsion as a function of NaCl concentration prior to n-octane solubilization.
To investigate the phase behavior of the triglyceride microemulsion after n-octane solubilization, 1, 2, 3, 4, 5, 6, 7, 8, and 9 ml of n-octane was added to each of the microemulsion samples while maintaining the total volume of n-octane and microemulsion prior to mixing at 10 ml. After being shaken for a minimum period of an hour, all of the 9 mixtures of constant aqueous phase salinities were poured into burettes and left undisturbed for about one week to make sure equilibrium was reached. Then the volumes of the aqueous, microemulsion, and oil phases were measured and presented as phase diagrams. The phase behavior study after n-octane solubilization was repeated twice for all the 45 prepared samples to ensure reproducibility of the measured data. The average of the two experimental data was used for phase diagram presentations. The optimum concentration of NaCl in the aqueous phase is the salinity at which the phase behavior shows the appearance of Winsor Type III microemulsion in a wider range of n-octane concentrations.

2.3.2. Optimization of co-surfactant concentration

Five Winsor Type I triglyceride microemulsion samples were prepared at various GM concentrations of 0.5, 1, 2, 3, and 4 wt% of the aqueous phase. The concentration of APG was fixed at 1 wt% of the aqueous phase. All of the samples were prepared at the determined optimum salinity. All of the 5 measured volume fraction data sets of the excess oil and prepared microemulsion were presented in a phase diagram against the concentration of GM to show the phase behavior of the triglyceride microemulsion as a function of GM concentration prior to n-octane solubilization.

In order to investigate the phase behavior of the triglyceride microemulsion after n-octane solubilization, 1, 2, 3, 4, 5, 6, 7, 8, and 9 ml of n-octane was added to each of the microemulsion samples while maintaining the total volume of n-octane and microemulsion before mixing at 10 ml. After being shaken for a minimum period of an hour, all of the 9 mixtures of constant GM concentrations were poured into burettes and left undisturbed for about one week to make sure equilibrium was reached. Then the volumes of the aqueous, microemulsion, and oil phases were measured and presented in phase diagrams. The phase behavior study after n-octane solubilization was repeated twice for all the 45 prepared samples to ensure reproducibility of the measured data. The average of the two experimental data was used for phase diagram presentations. The optimum concentration of NaCl in the aqueous phase is the salinity at which the phase behavior shows the appearance of Winsor Type III microemulsion in a wider range of n-octane concentrations.

2.3.3. Optimization of surfactant concentration

Four Winsor Type I triglyceride microemulsion samples were prepared at various APG concentrations of 0.5, 1, 1.5, and 2 wt% of the aqueous phase. The concentrations of GM and NaCl in the aqueous phase were fixed at their optimum values. All of the 4 measured volume fraction data sets of the excess oil and prepared microemulsion were presented in a phase diagram against the concentration of APG. This is to show the phase behavior of the triglyceride microemulsion as a function of APG concentration prior to n-octane solubilization.

In order to investigate the effect of n-octane on the phase behavior of triglyceride microemulsions, 1, 2, 3, 4, 5, 6, 7, 8, and 9 ml of n-octane was added to each of the microemulsion samples. The total volume of the n-octane and microemulsion prior to mixing was maintained at 10 ml. After being shaken for a minimum period of an hour, all of the 9 mixtures of constant APG concentrations were poured into burettes and left undisturbed for about one week to make sure equilibrium was reached. Then the volumes of aqueous, microemulsion, and oil phases were measured and presented in phase diagrams. The phase behavior study after n-octane solubilization was repeated twice for all the 36 prepared samples to ensure reproducibility of the measured data. The average of the two experimental data was used for phase diagram presentations. The optimum concentration of APG in the aqueous phase is the concentration at which the phase behavior shows the appearance of Winsor Type III microemulsion in a wider range of n-octane concentrations.

3. Results and discussion

3.1. Optimization of salinity by phase behavior study

Fig. 1 shows the two photos of the Winsor Type I triglyceride microemulsion samples in separating funnels as an example to visually recognize the phase behavior. The Winsor Type I (lower phase) microemulsion samples of (a) and (b) in Fig. 1 were observed to be in equilibrium with the excess oil phase (upper phase). The salinities of the aqueous phase in the prepared triglyceride microemulsion samples of (a) and (b) in Fig. 1 are 1 and 3 wt%, respectively. It is apparent that the microemulsion and oil phase are separated distinctly. Sample of the microemulsion and oil phase can be obtained opening the valve of the separating funnel.

The transparency of some of the prepared microemulsion samples after separation was compared visually against de-ionized water in Fig. 2. Sample bottles (b)–(e) in Fig. 2 contain the triglyceride microemulsion samples at various salinities of 1, 3, 6, 9 wt% of the aqueous phase, while sample bottle (a) contains de-ionized water. The concentrations of APG and GM in microemulsion samples (b)–(e) are all the same and equal to 1 and 2 wt% of the aqueous phase, respectively. Since all the fluids inside sample bottles (b)–(e) in Fig. 2 are transparent, it is concluded that the prepared samples are not emulsions but they are microemulsions. The yellowish color of microemulsion samples compared to the de-ionized water is due to the solubilized palm oil.

The volume fractions of the excess oil and prepared microemulsion samples at various salinities were obtained from the experiments. The phase behavior of the triglyceride microemulsion as a function of NaCl concentration prior to n-octane solubilization is shown in Fig. 3. It is observed that the volume fractions of the oil and microemulsion phases remain almost constant at various NaCl concentrations. Thus the phase behavior of the triglyceride microemulsion prior to n-octane solubilization was found to be independent of salinity. This is because the nature of the microemulsion samples is intrinsically nonionic (Iglauer et al., 2010).

It was also observed that the triglyceride microemulsion samples at various NaCl concentrations experienced a phase transition by addition of n-octane. Fig. 4 presents the phase inversion in the new microemulsions as a function of n-octane concentration for all the triglyceride microemulsion samples at various aqueous phase salinities. A typical behavior was observed in Fig. 4 for all triglyceride microemulsion samples at various aqueous phase salinities. It was perceived that by increasing the volume of n-octane, the volume of the middle phase oil-in-water microemulsion increases to a maximum value before it starts to reduce gradually to zero.

Microemulsion phase transition can be achieved in several ways, depending on the type of surfactant. For instance, for nonionic surfactants, different microemulsion types (Winsor Types I–IV) can be formed by varying the temperature, addition of co-oil or hydrophilic/lipophilic linkers (Komesarukh et al., 2006b). The addition of co-oil to a triglyceride microemulsion, in this study, induces the appearance of Winsor Type III in room temperature (Fig. 4). When palm oil is the only oil component in the composition of the microemulsion (in the absence of n-octane), a Type I microemulsion is observed (Fig. 3). This suggests that the surfactant system is relatively hydrophilic (low hydrophobic), resulting
in a positive curvature of the surfactant film with the oil droplets. A Winsor Types I–III transition can be achieved in at least two ways: increasing the hydrophobicity of the surfactant system (aqueous phase) or increasing hydrophilicity of the oil (Komesvarakul et al., 2006b). Since n-octane with carbon number of 8 is more hydrophilic than palm oil with equivalent alkane carbon number of 16 (Phan et al., 2009), addition of n-octane to a triglyceride microemulsion leads to an increase in the hydrophilicity of the microemulsion oil phase, which consequently makes a balance between the hydrophilicity of the oil phase to the aqueous phase.
The hydrophobicity–hydrophilicity balance leads to an increase in penetration of the surfactant film into the oil phase, a decrease in the curvature from positive values (Type I) to zero (Type III), and an increase in the flexibility of the film (Komesvarakul et al., 2006b). The addition of n-octane to the microemulsion as co-oil is effective until the concentration of n-octane in the microemulsion reached a value (about 40–60 vol%) at which a maximum amount of oil-in-water microemulsion appears. When the concentration of n-octane in the microemulsion exceeds beyond this limit, the surfactant film becomes very flexible inducing a change in the microstructure of the microemulsion from an oil-in-water to water-in-oil type. Thus, after a certain value of n-octane concentration (about 40–60 vol%), the volumes of aqueous and oil-in-water microemulsion phases are decreasing and the volume of oil containing water-in-oil microemulsion is increasing simultaneously. This phase transition continues until n-octane concentration reaches 80 vol%, where all the aqueous phase is solubilized in the oil phase to form water-in-oil microemulsion.

The phase transition indicates that the prepared triglyceride microemulsion has the capability to solubilize n-octane by forming oil-in-water (Winsor Type III) microemulsion along the reservoir until the concentration of n-octane in the new in situ microemulsion reaches a value at which the microstructure of the microemulsion is altered to water-in-oil. The same phase transition was typically occurred for all triglyceride microemulsion samples at various aqueous phase salinities. Since the phase behavior of the microemulsion was observed to be quasi-independent of salinity even after n-octane solubilization, the salinity of the microemulsion formulation can be adjusted at any value within the studied range. Thus in this study the salinity of 3 wt% NaCl was selected and taken as the optimum salinity of the microemulsion.

![Fig. 3. Phase behavior of the triglyceride microemulsion as a function of NaCl concentration before n-octane solubilization. The concentrations of APG and GM are 1 and 2 wt% of the aqueous phase, respectively.](image)

![Fig. 4. Phase behavior of the in situ microemulsion as a function of n-octane concentration. The concentrations of APG and GM are 1 and 2 wt% of the aqueous phase. The salinity of the samples are different: (a) 1 wt%, (b) 3 wt%, (c) 6 wt%, (d) 9 wt%, and (e) 12 wt% of the aqueous phase.](image)
Another interesting observation from the phase behaviors of Fig. 4 is that all volumes in the phase diagrams reach only 95% level. Although the total volume of n-octane and microemulsion before mixing was 10 ml, it is observed that the total volume of the new microemulsion prepared after the addition of n-octane to the triglyceride microemulsion is less than 10 ml (about 9.5 ml). This may be due to the change in the packing parameter. Packing parameter provides a simple effective way to predict the shape of microemulsion droplet (Tchakalova et al., 2008). The molecular geometry is supposed to determine certain physical properties of surfactant aggregates such as their size, without needing detailed information about the intermolecular forces involved (Tchakalova et al., 2008). After n-octane solubilized in the triglyceride microemulsions, new Winsor Type III microemulsions appeared. Compared to the triglyceride molecule, n-octane molecules are smaller and can be placed in the smaller surfactant aggregates, in which triglyceride molecules is not able to be placed. Therefore, many smaller microemulsion droplets appeared in the new microemulsion. Thus the packing parameter of the new microemulsion decreases by addition of n-octane. The reduction in the packing parameter of the microemulsion leads to a decrease in the volume of the microemulsion and consequently a decrease in the total volume of the system.

3.2. Optimization of co-surfactant concentration by phase behavior study

Fig. 5 shows the photos of the prepared triglyceride microemulsion samples at various GM concentrations after being separated from the excess oil phase. Sample bottles (a)–(d) shown in Fig. 5 contain the triglyceride microemulsion samples at GM concentration of 3, 2, 0.5, 1 wt% of the aqueous phase, respectively. The concentrations of APG and NaCl in all the samples are 1 and 3 wt% of the aqueous phase, respectively. The prepared samples in sample bottles (a) and (b) were transparent, while the prepared samples in sample bottles (c) and (d) were translucent. In a transparent fluid, light is able to completely pass through the medium, and the objects behind the medium can be seen clearly. A translucent fluid only allows some or a small percentage of light to pass through, and therefore the objects behind the medium can be seen but they are not clearly visible. Although the transparencies of the samples were different, all of them remained stable for more than 3 months in the sealed bottles without any separation and precipitation. The stability observations indicate that all of the prepared samples are microemulsions and not emulsions.

The volume fractions of the excess oil and prepared microemulsion samples at various GM concentrations were also obtained from experiments. The phase behavior of the triglyceride microemulsion as a function of GM concentration prior to n-octane solubilization is shown in Fig. 6. It can be seen that the volume fraction of the microemulsion phase is around 0.45 for GM concentration less than 3 wt% and drops to about 0.4 at GM concentration of 4 wt% of the aqueous phase.

The GM, used as co-surfactant in this study, is a lipophilic linker (Komesvarakul et al., 2006b). The lipophilic linkers, which are chemical additives in surfactant systems, are shown to absorb at the palisade layer of the interface (oil side of the surfactant layer), promoting the local order and enhancing the interaction between the surfactant tail and the oil phase (Gracia et al., 1993; Acosta et al., 2003; Komesvarakul et al., 2006a). Lipophilic linker(s) enhances the solubilization in a microemulsion system with the assistance of hydrophilic linker(s) (Acosta et al., 2003). Above a certain concentration, the lipophilic linker becomes inefficient because it partitioned preferentially into the excess oil phase (Acosta et al., 2002, 2003). This phenomenon is more vital if the oil is polar such as triglycerides (Acosta et al., 2002, 2003). Therefore, the decrease in the amount of the microemulsion above GM concentration of 3 wt% as shown in Fig. 6 is due to the inefficiency of the co-surfactant and its preference to partition more into the excess of oil phase.
Fig. 7 presents the phase inversion in the new microemulsions as a function of n-octane concentration for all triglyceride microemulsion samples at various GM concentrations in the aqueous phase. When n-octane was added to the triglyceride microemulsion samples at various GM concentrations, different phase behaviors occurred. Addition of lipophilic linker and co-oil are the two governing parameters, which influenced the occurrence of a wide variety of phase behaviors.

At low concentration of GM (0.5 wt% of the aqueous phase), a Type I microemulsion is observed (Fig. 7(a)) and it is in equilibrium with excess oil. This suggests that the surfactant system is relatively hydrophilic (low hydrophobic), resulting in a positive curvature of the surfactant film with the oil droplets. GM is more lipophilic (or more hydrophobic) than APG, which is the surfactant. Thus, the hydrophobicity of the surfactant system, which is the mixture of APG and GM, increases with the concentration of GM in the microemulsion. Therefore, middle phase (Winsor Type III) microemulsion starts to appear at GM concentration of 1 wt% (Fig. 7(b)). Furthermore, the range of middle phase microemulsion tends to expand more with the increase of GM concentration in the aqueous phase (Fig. 7(c)–(e)). Although the widest range of the microemulsion phase occurs at GM concentration of 4 wt% (Fig. 7(e)), it is not the most favorable phase behavior. Compared to Fig. 7(c) and (d), the amount of the middle phase microemulsion in Fig. 7(e) is insignificant at the first concentrations of n-octane.

When the prepared triglyceride microemulsion is traveling along the reservoir and solubilizing the model oil, n-octane, the concentration of n-octane in the new in situ prepared microemulsion is not very significant. Thus the first concentrations of n-octane are the most dominant range in selecting the optimum GM concentration. Therefore, Fig. 7(d) shows the most optimum phase behavior condition because the microemulsion range is wider in Fig. 7(d) than in Fig. 7(c). On the other hand, the volume of the microemulsion at the first n-octane concentrations is greater in Fig. 7(d) than in Fig. 7(e). Finally, based on the phase behavior studies, GM concentration of 3 wt% of the aqueous phase was selected as the co-surfactant composition of the triglyceride microemulsion.

3.3. Optimization of the concentration of surfactant by phase behavior study

Fig. 8 shows the photos of the prepared triglyceride microemulsion samples at various APG concentrations after they are separated from the excess oil phase. Sample bottles (a) and (b) shown in Fig. 8 contain the triglyceride microemulsion samples at APG concentration of 1.5 and 2 wt% of the aqueous phase, respectively. The concentrations of GM and NaCl in the samples are 3 and 3 wt% of the aqueous phase, respectively. Fig. 5(a) shows the photo of the triglyceride microemulsion at APG concentration of 1 wt% and the same NaCl and GM concentrations. The prepared samples in
Fig. 8. The photos of two of the triglyceride microemulsion samples after being separated from the excess oil phase. Sample bottles (a) and (b) contain the triglyceride microemulsion samples at APG concentration of 1.5 and 2 wt% of the aqueous phase. The concentrations of GM and NaCl in the samples are 3 and 3 wt% of the aqueous phase, respectively.

Fig. 9. Phase behavior of the triglyceride microemulsion as a function of APG concentration before n-octane solubilization. The concentrations of GM and NaCl are 3 and 3 wt% of the aqueous phase, respectively.

Figs. 5(a) and 8(a) were transparent and stable, indicating that they are microemulsions not emulsions.

The volume fractions of the excess oil and prepared microemulsion samples at various APG concentrations were obtained from the experiments. The phase behavior of the triglyceride microemulsion as a function of APG concentration before n-octane solubilization is shown in Fig. 9. It can be observed that the volume fraction of microemulsion phase stayed around 0.45 at all APG concentrations except 1 wt%, at which the volume fraction of microemulsion phase falls to a minimum of about 0.395. It shows that at APG concentration of 1 wt%, the surfactant mixture (APG and GM) has the tendency to partition more into the oil phase and thus the volume fraction of microemulsion reduces. It implies the weak degree of interaction between triglyceride (oil) and the nonpolar part of the surfactant mixture (APG and GM) at APG concentration of 1 wt%.

Fig. 10 presents the phase inversion in the new microemulsions as a function of n-octane concentration for all triglyceride microemulsion samples at various APG concentrations in the aqueous phase. Different phase behaviors occurred when n-octane was

Fig. 10. Phase behavior of the in situ microemulsion as a function of n-octane concentration. The concentrations of GM and NaCl are 3 and 3 wt% of the aqueous phase. The APG concentration of the samples are different: (a) 0.5 wt%, (b) 1 wt%, (c) 1.5 wt%, and (d) 2 wt% of the aqueous phase.
added to the triglyceride microemulsion samples at various APG concentrations. A variety of phase behaviors can be explained considering the considerable effects of hydrophilic surfactant and co-oil on the triglyceride microemulsions.

At APG concentration of 0.5 wt%, middle phase (Winsor Type III) microemulsion is observed (Fig. 10(a)) at a wide range of n-octane concentration below 80 vol%. The appearance of Winsor Type III implies that the existence of hydrophobicity–hydrophilicity balance of the surfactant layer as a result of an increase in the hydrophilicity of the oil mixture phase by the addition of n-octane to the triglyceride microemulsion.

When APG concentration in the aqueous phase of the triglyceride microemulsion rises to 1 wt% (Fig. 10(b)), the range of middle phase microemulsion reduces to maximum 70 vol% n-octane concentration. However, the volume of the microemulsion phase is increased significantly, specifically at low values of n-octane concentration. This may be due to an enhancement in hydrophobicity–hydrophilicity balance of the surfactant layer by APG addition because the surfactant mixture (APG and GM) shows the tendency to partition more into microemulsion phase rather than the oil phase.

By increasing the APG concentration to 1.5 wt% of the aqueous phase of the triglyceride microemulsion, the range of middle phase microemulsion shrinks to a limited range of n-octane concentration between 20 and 80 vol%. This is because the surfactant mixture tends to be more hydrophilic by the addition of APG. Therefore, the curvature of the surfactant film with the oil droplets increases from about zero to some positive values imposing Winsor Type I in some regions of n-octane concentrations. Middle phase (Winsor Type III) microemulsion region disappears thoroughly by further increase in the concentration of APG to about 2 wt% of the aqueous phase (Fig. 10d). Winsor Type I phase behavior is dominating in the whole range of n-octane concentration because the curvature of the surfactant film with the oil droplets is very positive and the surfactant mixture is highly hydrophilic.

Based on these phase behavior studies, APG concentration of 1 wt% of the aqueous phase was selected as the optimum surfactant composition of the triglyceride microemulsion because of both relatively large range of middle phase microemulsion and considerable volume of microemulsion particularly at low values of n-octane concentration.

4. Conclusion

The results of this study showed that triglyceride microemulsion could be used effectively in enhanced oil recovery because Winsor Type III microemulsion could be prepared in situ. This can be achieved by the addition of n-octane to the Winsor Type I triglyceride microemulsion at certain compositions. Aqueous phase salinity change is not able to alter the phase diagram of the microemulsion significantly even after n-octane solubilization. This is due to the nonionic nature of the triglyceride microemulsion. Winsor Type III microemulsion could also be obtained over a wide range of n-octane concentration at all aqueous phase salinities. Thus the composition of NaCl in the triglyceride could be assigned at any value, such as 3 wt%, of the aqueous phase. At low GM concentration of 0.5 wt% of the aqueous phase, no middle phase microemulsion was observed after n-octane solubilization. However, Winsor Type III started to appear at GM concentration of 1 wt% of the aqueous phase and its range continued to expand by the addition of GM. Since at low n-octane concentrations, the volume of the middle phase microemulsion at GM concentration of 3 wt% was more than GM concentration of 4 wt%, concentration of 3 wt% of the aqueous phase was considered as the optimum composition of GM. By increasing the concentration of APG in the aqueous phase, the region of middle phase microemulsion was shrinking and tended to disappear completely at high APG concentration of 2 wt% of the aqueous phase. Relatively large range of middle phase microemulsion and considerable volume of microemulsion are observed, especially at low values of n-octane concentration, at APG concentration of 1 wt%. Thus 1 wt% of the aqueous phase was selected as the optimum surfactant composition of the triglyceride microemulsion. The formulation of the aqueous phase composition, concentration of a triglyceride microemulsion at the determined optimum values ensures favorable phase behavior in situ prepared microemulsion flooding.

Acknowledgements

The authors would like to acknowledge the financial support of the Bright Sparks Program at University of Malaya. They also would like to acknowledge the support of University of Malaya IPPP grant, project number: PV021/2011B.

References


