



RHEOLOGY AND STABILITY MECHANISM OF WATER-IN-CRUDE OIL EMULSIONS STABILIZED BY SPAN 83

Sweeta Akbari, Abdurahman Hamid Nour, Saidatul Shima Jamari and Fahim Fayaz

Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Gambang, Pahang, Malaysia

E-Mail: nour2000_99@yahoo.com

ABSTRACT

Water-in-crude oil (W/O) emulsions are found in many industries such as cosmetic, pharmaceutical, and petroleum. The study was aimed to investigate the rheological properties and the stability mechanism of W/O emulsions at different water to oil ratios of (20-80 vol.%) and (40-60 vol.%). The emulsions were stabilized by a non-ionic surfactant (Span 83) at concentrations of 1.5-2.5 vol.%. The heavy and light crude oils were mixed at 50-50 vol.% and characterized in terms of physical and chemical properties. From the results, it was found that the emulsion with higher water volume fraction obtained more viscosity with larger droplet sizes which present low stability. As well as, the higher viscosity was obtained in emulsion with higher emulsifier concentration (2.5 vol.%). However, 20-80 % W/O emulsion and emulsions stabilized with 2.5 % Span 83 produced more stable emulsions as observed through the optical microscopy images. In order to determine the dynamic viscosity, different temperatures from (30 to 90 °C) and spindle rotational speeds from (50 to 250 rpm) were used. Furthermore, all types of prepared emulsions were visually stable over a period of more than one week, where no water separation was observed during this period, besides; they exhibited a non-Newtonian shear thinning fluid behavior.

Keywords: W/O emulsions, span 83, viscosity, stability, crude oil.

INTRODUCTION

The productions of W/O emulsions are of the great interest in many industrial applications such as cosmetic, pharmaceutical, food, and petroleum industries. The stability mechanism of the emulsions differs, in particular industries. In petroleum industries, the emulsified water generally presents in crude oil, and this phenomenon occurs during the production operation due to the existence of natural surfactants such as resin and asphaltenes (Fingas and Fieldhouse, 2004; Rondón *et al.* 2008). Apparently, these surfactants promote the stability of the emulsions by adsorbing at the water-oil interface to form a rigid film surrounding the water droplets. The function of the stabilizers is that the water droplets cannot contact directly to the surface of the transportation pipeline (Ali and Alqam, 2000; Sjöblom *et al.* 2003; Xia *et al.* 2004). Therefore, these stable water droplets prevent the pipeline corrosion.

Surface active materials play a very important role in stability of an emulsion; they lower the interfacial tension between water and oil and hence increase the emulsion stability (Ghannam, 2005; Nesterenko *et al.* 2014). It is generally believed, that the rheological properties and stability of the emulsions are mainly influenced by several factors such as, volume fraction of the dispersed phase, temperature, surfactant concentration, and chemical composition of the crude oil (Derkach, 2009; Aomari *et al.* 1998; Mohammed *et al.* 2009). The emulsifier used in this work is a non-ionic surfactant with hydrophilic-lipophilic balance (HLB) of 3.7. Surfactant molecules with low HLB values are effective for preparing W/O emulsions (Khan *et al.* 2011). The present work is aimed to evaluate the stability mechanism and rheology properties of W/O emulsion stabilized with Span 83 at different water volume fractions and surfactant

concentrations. This work is intended to be the first step in developing W/O emulsion demulsification through the microwave heating technology.

MATERIALS AND METHODS

In this study, two types of different Malaysian crude oils, namely; heavy and light crude oils were used in order to prepare water-in-crude oil emulsions. The heavy and light crude oils were mixed together at a volume ratio of (50-50 %). Table-1 presents the physico-chemical characteristics of heavy-light blended crude oil used in this research.

SARA Fractionation of Crude Oil

The SARA method of analysis was employed to separate the crude oil into four chemical group classes, namely saturates, aromatics, resins, and asphaltenes, through the SARA method of analysis. The Saturates, aromatic, and resin were extracted according to the American Society for Testing and Materials (ASTM D2007) by using open-column liquid chromatography method. Table-2 shows the SARA fractionation of (50-50 vol.%) heavy-light blended crude oil.

Emulsion Preparation

In order to evaluate the effect of different water volume fraction and emulsifier concentration in stability of W/O emulsions the emulsions were prepared in (20-80) and (40-60) vol.% W/O ratios and emulsifier concentrations 1.5 and 2.5 vol.%. For the preparation of the W/O emulsion, the surfactant (Span 83) was added to the crude oil and agitated for 5 minutes under a mechanical agitation of 2000 rpm. Then the dispersed phase (water) was added to the oil phase while mixing in a standard three blade propeller and sheared for another 5



minutes at 30 °C. The type of the prepared emulsions was identified by using the test tube method, whether is the W/O or oil-in-water (O/W) type. For further investigations, the W/O emulsion type was only proceeded.

Emulsion Stability Test

For gravity separation test, the prepared emulsion was placed in a 100 ml graduated cylinder sealed with Para-film and stored for one week (7days). The reading for gravity test was collected every one hour until the sixth hour for the first day, and then it was recorded every 24 hours for a period of more than one week. The samples were verified through the visual observation as there was no water separation observed over in a period of seven days in all types of the samples. Therefore, the stability of the emulsions was observed through the microscopic images just after mixing the emulsions (Figure-4).

Dynamic Viscosity and Microscopic Analysis of the Samples

The viscosity, shear rate, and shear stress measurement for all types of the samples were performed by using Brookfield Rotational Digital Rheometer Model LV/DV-III with UL adaptor and spindles # 31 connected with a heating/cooling water bath. The measurement for viscosity of the samples was performed at different operating temperatures (30, 50, 70, and 90 °C) and different spindle rotational speeds (50, 150, and 250 rpm). The microstructure of the emulsions was observed through an optical microscope (Carl Zeiss, Germany) at a magnification of 10x.

The microscopic images of the emulsions were captured by Dino-Eye camera connected into the computer using Dino-capture 2.0 software. The microstructure of the emulsions analyzed by Image-Pro Plus 6.0 image analyzer software in order to measure the emulsion droplet size (Figure-4).

RESULTS AND DISCUSSION

Factors Affecting Rheological Properties of the Emulsions

The physico-chemical properties and SARA fractionation result of heavy-light blended crude oil are shown in Table-1 and Table-2. It is commonly known that, the viscosity of the emulsion is the most measured rheological property which mainly influenced by some factors such as the volume fraction of the dispersed phase, temperature, chemical composition of each phase (water and oil), as well as the addition of surfactant in the emulsion.

Depending upon an emulsion composition the rheological behavior of an emulsion can be either Newtonian or non-Newtonian (Anisa and Nour, 2010).

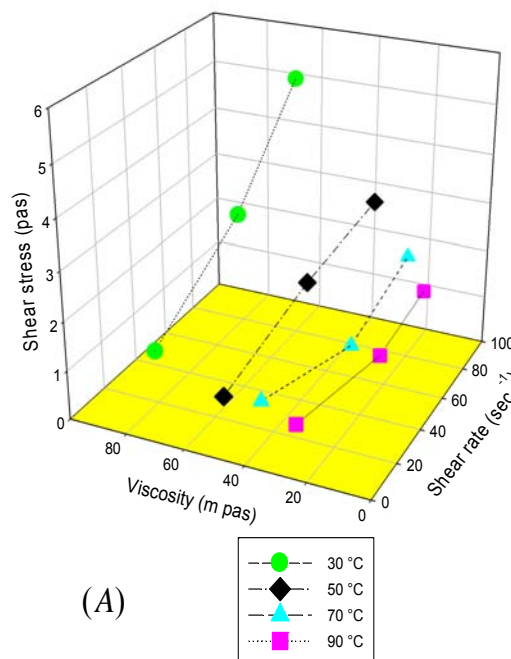
Table-1. Physico – chemical properties of heavy – light blended crude oil.

Density (g/cm ³)	0.8886
Viscosity (N/m ²) at 30 °C	35
API Gravity	28
Surface Tension (mN/m) at 25 °C	26.566
Interfacial Tension (mN/m) at 25 °C	15.831

Table-2. SARA fractionation of heavy – light blended crude oil.

Sample Type	Saturated (wt %)	Aromatic (wt %)	Resin (wt %)	Asphaltenes (wt %)
Blended crude oil	65.2	25.1	4.2	5.5

Figures-1 (A) and 1 (B) show the rheological or viscosity behavior of 20 – 80 % W/O emulsion stabilized by 1.5 vol. % and 2.5 vol. % of Span 83, respectively. Figure-1 (A) and Figure-1 (B) indicate that by increasing the spindle rotational speed (shear rate) the emulsion's viscosity decreased while the shear stress increased significantly. The reason behind this was the applied shear force of spindle rotation, which leads to change the emulsion structure and hence the viscosity. This attributed by the hydrodynamic effect which was more dominated at high shear rate.



(A)

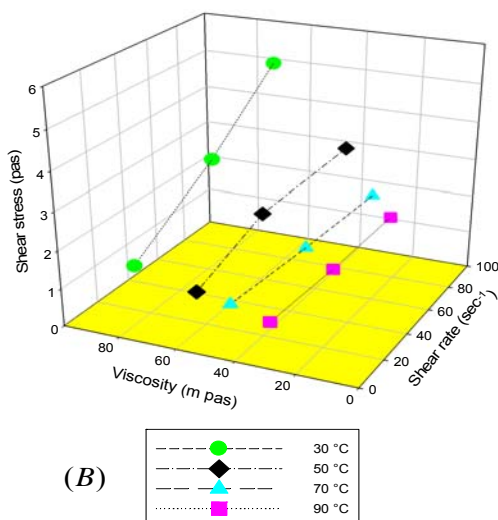


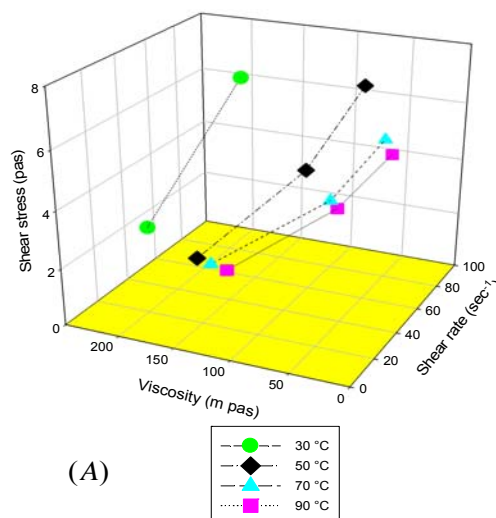
Figure-1. A) Rheological behavior of 20-80 % W/O emulsion stabilized by 1.5 vol.% Span 83. B) Rheological behavior of 20-80 % W/O emulsion stabilized by 2.5 vol.% Span 83.

As shown in Figure-1 (A) by increasing the shear rate from (17 to 85 sec^{-1}) a reduction was observed in viscosity of the emulsion from (79 to 63 mpas) respectively at 30 °C. However, at 90 °C this reduction is more surprising by increasing the shear rate from (17 to 85 sec^{-1}) which was recorded from (31 to 16 mpas).

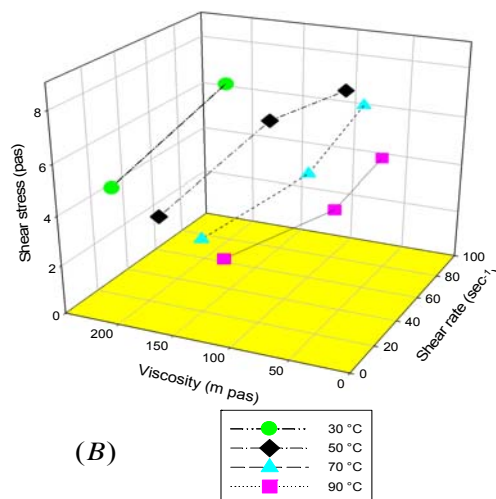
It is also clear from the Figure-1 (A) that increasing the shear rate from (17 to 85 sec^{-1}) caused to an increase in the shear stress from (1.2 to 5.2 pas) at 30 °C and similar behavior was observed for all types of the samples. Therefore, it can be claimed that all samples exhibited a non-Newtonian shear thinning behavior. As shown in Figure-1 (B) altering the spindle rotation from (50 to 250 rpm) was caused to decrease the emulsion viscosity from (83 to 76 mpas) and (36 to 23 mpas) at temperature of (30 to 90 °C) respectively. By applying the shear force, the emulsion alters its structure and leads to viscosity reduction as well as the hydrodynamic effect is more dominant at the high shear rate, where this result is in a good agreement with that found by (Abd *et al.* 2014).

Figure-2 (A) and Figure-2 (B) show the viscosity behavior of 40-60 % W/O emulsion stabilized with 1.5 and 2.5 vol.% of Span 83 respectively. It can be clearly seen that at high-water volume fraction (40%) the emulsions obtained higher shear stress and viscosity in all shear rates compared to emulsions with 20 % water volume fraction. In fact, the same observation was also reported by (Anisa *et al.* 2010) As shown in Figure-2 (A) the viscosity of emulsion contains 40% water and 1.5 vol.% emulsifier is (193 mpas) at 50 rpm and 30 °C. However, in Figure-2 (B) the viscosity of emulsion stabilized with 2.5 vol. % is significantly high (255 mpas) at the same condition, the reason behind this is the

emulsifier concentration. Increasing the emulsifier concentration increases the viscosity of the emulsion.



(A)



(B)

Figure-2. A) Rheological behavior of 40-60 % W/O emulsion stabilized by 1.5 vol.% Span 83. B) Rheological behavior of 40-60 % W/O emulsion stabilized by 2.5 vol.% Span 83

It can be clearly seen from Figure-1 and Figure-2 the viscosity of the investigated emulsions substantially increased by increasing the water volume fraction from 20% to 40 %, increasing in water content means increasing the water droplets concentration, and these droplets increase the hydrodynamic force and hence the viscosity (Abd *et al.* 2014; Derkach, 2009) . However, further increase of the dispersed phase fraction results in phase inversion of the emulsion from water-in-oil to the oil- in-water (Abdulbari *et al.* 2011; Muzaffar *et al.* 2013). It can be observed that reducing the water volume fraction



from 40% to 20 % resulted in a significant reduction of apparent viscosity from (193 to 79 mpas) at 30 °C, rotational speed of 50 rpm and concentration of 1.5 % Span 83.

However, the viscosity reduction at 90 °C is considerably high which was recorded from (123 to 31 mpas) respectively at the same water oil ratios and rotational speed. The reason behind this is increasing in water molecules. The extensive hydrogen bonding existed in water leads to crowded droplets then to a very viscous system. The water droplets inside the emulsions which are fully emulsified act as solid particles, thereby they tend to increase the emulsion viscosity.

Temperature also has a strong effect on viscosity of crude oil emulsions. As the temperature increases the heavy fractions in crude oil loss the chance of aggregation and thereby the bonds between the solid particles break and thus reduce the oil viscosity (Hasan, Ghannam, & Esmail, 2010). It can be clearly seen from Figures-1 and 2 that the viscosity of all types of emulsions is reduced by raising the temperature from (30 to 90 °C). Figure-1 (A) and Figure-1 (B) demonstrated that by raising the temperature from (30 to 90 °C) the viscosity of the emulsions significantly decreased from (79 to 31 mpas) and following from (83 to 36 mpas) respectively at 50 rpm.

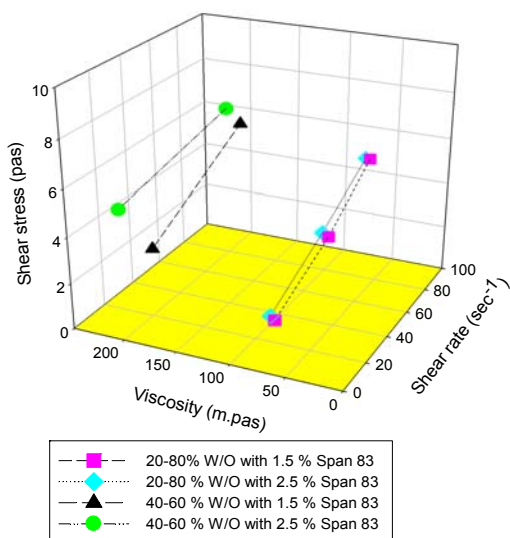


Figure-3. Viscosity behavior of 20-80 % and 40-60% W/O emulsions stabilized with emulsifier concentrations of 1.5 and 2.5 vol.%.

Moreover, in 40-60 % W/O emulsions, as shown in Figure-2 (A) and Figure-2 (B) the viscosity of the emulsions changed gradually and significantly from (193 to 123 mpas) and (from 225 to 125 mpas) respectively at 50 rpm. Figure-3 shows a very clear result of emulsions viscosity at different water volume fraction (20-80) % and (40-60) % and emulsifier concentrations of 1.5 and 2.5 vol.%. The high viscosities are obtained in high water

volume fraction (40%) and emulsifier concentration (2.5 vol.%) and it is supported by emulsified water droplets which act as solid particle inside the emulsion thus they increase the emulsion viscosity.

Stability Mechanism of the Emulsion

It is clear from Table-3 and Figure-4, by increasing the water content from 20% to 40 %, the droplet size of the emulsions increased as well. The specific gravity of water is higher than oil so the water droplets at the top of the emulsion were inclined to migrate to the bottom and form larger droplets which finally aggregate to a separate layer. Increasing the water content in an emulsion can increase the water droplets and its sizes. Therefore, the mechanism of sedimentation, flocculation, and coalescence can easily occur. As shown in Table-3, by increasing the volume fraction of the dispersed phase from 20 to 40 %, the droplet size of the emulsions increased from (97 to 108 μm) at emulsifier concentration of 1.5 vol.%. Furthermore, the droplet size of W/O emulsion containing 2.5 vol.% and Span 83 increased from (82 to 103 μm) respectively. Thereby, it can be claimed from the results that the emulsions with higher water volume fractions (40%) obtained low stability with larger droplet sizes compared to lower dispersed phase volume (20%). The reason is the high amount of water droplets which can reduce the ability of emulsifier to cover all droplets thereby the water droplets inclined to coalesce with their neighbours and form larger droplets (Akbari, Abdurahman, & Fayaz, 2015).

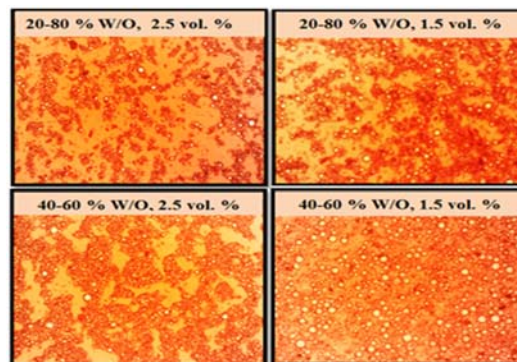


Figure-4. Optical microscopy images of W/O emulsions, the scale bar is 100 μm .

Table-3. Droplet size of W/O emulsions stabilized by Span 83.

Emulsifier	Emulsifier Concentration (vol.%)	20-80 %W/O 40-60%W/O	
		Mean Droplet Diameter (μm)	Mean Droplet Diameter (μm)
Span 83	1.5	97	108
	2.5	82	103



Surface active materials play an important role in stability of water-in-crude oil emulsion. The function of emulsifiers is to lower the interfacial film between water and crude oil and to form a cohesive interfacial film around the droplets hence preventing the coalescence of water droplets, which finally leads to a stable emulsion. Moreover, the amount of emulsifiers is also effective in the stability mechanism of W/O emulsions. As shown in Table-3 increasing the concentration of emulsifier (from 1.5 to 2.5) % reduced the droplet size of emulsion from (97 to 82 μm) in emulsion contained 20 % water, which could enhance the emulsion stability. In fact, if the concentration of emulsifier is low, the ability of covering the droplets is low as well, thereby the droplets are likely to coalesce with their neighbors and form larger droplets.

CONCLUSIONS

The results from this study support the conclusion that the emulsion stability is affected by the surfactant concentration and volume of the dispersed phase (water). The more stable emulsion was obtained in emulsions with lower water content (20%) and higher Span 83 concentration (2.5%). However, emulsions with higher water contents (40%) and Span 83 concentration (2.5%) provided more viscous emulsions. It is also found that all emulsions were exhibited the non-Newtonian shear thinning fluid behavior.

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