ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785
(ISRA), Journal Impact Factor: 2.114

IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

THE INFLUENCE OF PROCESS PARAMETERS ON STABILITY OF WATER-IN-CRUDE OIL EMULSION STABILIZED BY SPAN 80

Sweeta Akbari*, N.H. Abdurahman, Fahim Fayaz
* Faculty of Chemical and Natural Resources Engineering, University Malaysia Pahang-UMP
Faculty of Chemical and Natural Resources Engineering, University Malaysia Pahang-UMP
Faculty of Chemical and Natural Resources Engineering, University Malaysia Pahang-UMP

ABSTRACT
There is a wide range of scientific literature related to emulsion stability, most of them dealt with water-in-oil (W/O) or oil-in-water (O/W) type. The present work is aimed to investigate the stability mechanisms of water-in-crude oil emulsion stabilized by a non-ionic emulsifier (Span 80). The blending of (50-50 vol. %) heavy and light crude oil was first characterized in terms of physico-chemical properties. The emulsion was stabilized by (1.5 and 2.5 vol. %) emulsifier at different water: oil ratio of (20-80 vol. %) and (40-60 vol. %). According to the result of microscopy images, the steric stability was obtained in low water volume fraction content (20%), with the smaller droplet sizes and at higher surfactant concentration (2.5%). The emulsions stabilized with Span 80 obtained a visually stable emulsion in both concentrations of emulsifier and volume fractions of dispersed phase (water) in a period of one week, and there was no water separation was observed in this period. To determine the dynamic viscosity rate, the temperature was varied from 30 ºC to 90 ºC and shear rate from (17 to 85)1/sec respectively. Moreover, the emulsion with the higher water volume fraction (40%) and emulsifier concentration of 2.5 % indicated higher dynamic viscosity. However, in all types of the samples, the dynamic viscosity decreased by increasing the shear rate. The results obtained in this study have exposed the capability of the chosen emulsifier as another promising method for stabilizing w/o emulsions. Further works are, nevertheless, required to provide deeper understanding of the mechanisms involved to facilitate the development of an optimum system applicable to the industry.

KEYWORDS: W/O emulsions, Stability, Span 80, rheology, Droplet size.

INTRODUCTION
An emulsion is defined as the mixture of two immiscible liquid phases which one phase is dispersed into another [1]. Around 80 % of exploited crude oils exist in the form of emulsion in the worldwide. In petroleum industries, the emulsion of water-in-crude oil (W/O) is more common than the oil-in-water (O/W) type. W/O emulsion is the type of emulsions which the continuous phase is oil and the dispersed phase is water [2]. Generally, the presence of emulsifying agents which are naturally existed in crude oil play a very important role in stability and characterization of W/O emulsion. Therefore, the emulsion of W/O are usually very stable due to the presence of these surface active agents such as asphaltenes and resins. The surface active materials form a rigid film surrounding the water droplets and avoid the mechanism of coalescences [3, 4]. In fact, there are several other important industrial processes that deal with the production of stable emulsions, such as food industry, cosmetic, pharmacy, and agriculture [5].

The formation of W/O emulsion is of great interest in several industrial and environmental applications for example, in the case of crude oil spillage, pipeline transportation, and storage of crude oil. Therefore, the rheological study of the emulsion has a great importance in order to understand the formation and stability mechanism of an emulsion. Several studies have investigated that the rheological properties of emulsions and their stability are essentially influenced by many factors for example; temperature changes can influence the emulsion stability and viscosity [6]. The high water volume fraction as a dispersed phase is effective in breakup and mobility of water droplets because the droplets become more compact which finally can dispose the mechanism of coalescence and hence increases the viscosity [7, 8, 9]. A lowering of the interfacial tension between water and crude oil which can increase interfacial

ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785
(ISRA), Journal Impact Factor: 2.114

film strength, prevent the coalescence mechanism of the water phase and consequently leads to a stable emulsion [5, 10].

The emulsifying agent used in this research is a non-ionic surfactant. Span 80 or sorbitan monooleate is obtained from a reaction between sorbital and fatty acid [11]. The present study is focused on many significant points in order to come up with a good understanding of those factors that affect the rheology of water-in-crude oil emulsion. The effect of surfactant concentration and water volume fraction on stability and properties of W/O emulsions was investigated. As well as, the rheological and morphological properties of emulsions was evaluated through the measurement of emulsion flow behavior and the optical microscopic analysis of droplet size.

MATERIALS AND METHODS

In the present work, the blending of two different types of Malaysian crude oil that is, heavy and light crude oils were collected from Petronas Refinery at Melaka. The heavy and light crude oils were blended together with a volume ratio of (50-50 %), and characterized in terms of physico – chemical properties, as shown in Table 1.

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

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

The emulsifier was sorbitan monooleate (Span 80) having a hydrophilic – lipophilic balance (HLB) value of 4.3. The emulsifier was used in concentrations of (1.5 and 2.5 vol. %) in order to prepare the emulsions of water-in-crude oil, and it was kindly provided by Sigma-Aldrich, USA.

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. Saturates, aromatics, and resin were extracted according to American Society for Testing and Materials (ASTM D2007) by using open-column liquid chromatography.

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

Sample Type	Saturated (wt %)	Aromatic (wt %)	Resin (wt %)	Asphaltenes (wt %)
Heavy and light blended crude oil	65.2	25.1	4.2	5.5

Emulsion Preparation

Emulsions were prepared at two volume ratio of water-oil 20-80 %, and 40-60 %. In order to evaluate the effect of Span 80 and its concentration in stability of water-in-crude oil emulsion, it was used with different concentration of 1.5 vol.% and 2.5 vol.% . For the emulsion preparation, the Span 80 was dissolved into the crude oil and vigorously sheared for 5 minutes. 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 with mixing speed of 2000 rpm at 30ºC .Consequently, the emulsion type was identified by using the test tube method whether is the W/O or O/W type.

ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785
(ISRA), Journal Impact Factor: 2.114

Evaluation of Emulsion Stability

The prepared emulsions was placed in graduated cylinders 100 ml. The reading for emulsion stability was recorded after each one hour until six hours for the first day. Then the reading was collected every 24 hours for a period of one week. While, there was no water separation remarked through the visual observation in this period. Therefore, the stability of the emulsions was observed by microscopic image of an optical microscope (carl zeiss, Germany) just after mixing the emulsions.

Dynamic Viscosity of the Samples

The dynamic viscosity for all type of the samples was determined by using Brookfield Rotational Digital Rheometer Model LV/DV-III with UL adaptor and spindles # 31 connected with a heating/cooling water bath. The viscosity of the emulsions was measured at different rotational speeds (50, 150, and 250 rpm), while temperature was applied at (30, 50, 70, and 90 ºC) respectively at approximately 10 ml of each sample.

Microscopic Analysis of Droplet Size

The droplet size of the emulsions was observed through the Carl Zeiss research optical microscope. The microscopic images of the emulsions were captured by Dino-Eye camera connected to the computer using Dino-capture 2.0 software. The microstructure of the emulsions analyzed by Image-Pro Plus 6.0 image analyzer software.

RESULTS AND DISCUSSION

Effect of Phase-Volume Ratios, Surfactant Concentration, and Droplet size on Stability of W/O emulsion

It is clear from the Table 3 that emulsion with high-volume fraction of the dispersed phase (40-60% W:O ratio) presented high droplet size (low stability) compared to the low-water content emulsion (20-80 %). This is due to the high mobility of the water droplets through the gravity force. As well as, the extensive hydrogen bonding existed in water is responsible for lowering the emulsifier power which can lead to a crowded droplet then to a very viscose system. The specific gravity of water is higher than oil so the water droplets at the top of the emulsion are inclined to migrate toward the bottom and finally aggregate to a separate layer. Increasing the water content in an emulsion can increase the water droplets and therefore, the mechanism of sedimentation, flocculation, and coalescence can easily occur. It can be observed from the Table 3 that lowering the water content of the emulsion leads to smaller water droplets, which finally present more stability. Anisa et al., 2010 found that the smaller the droplet size the more sable the emulsion.

Table 3. Effect of emulsifier concentration on droplet size of W/O emulsion

		20 – 80 % W/O	40 – 60 % W/O
Emulsifier	Emulsifier Concentration (vol.%)	Mean Droplet Diameter (µm)	Mean Droplet Diameter (µm)
Span 80	1.5	88	100
	2.5	80	90

Moreover, it can be noted from the result that increasing the concentration of the emulsifier (from 1.5 to 2.5) % reduced the droplet size of emulsion, which could enhance the emulsion stability. In the case of droplet size, 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 neighbours and form larger droplets. 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.

It is clear from the result shown in Table 3 and microscopy images of Fig. 1 and Fig. 2 that Span 80 formed the smaller droplet in 2.5 % of concentration and water volume fraction of 20-80 %. In water content of (20 %) the droplet size of emulsion with Span 80 is in the range of (80 – 88) µm in concentrations of (2.5 and 1.5 %) respectively with composed of spherical small droplets. While, changing the dispersed phase volume fraction from 20% to 40% is caused to the greater droplet diameter in all emulsions shown in Figs. 1 and 2.

ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785
(ISRA), Journal Impact Factor: 2.114

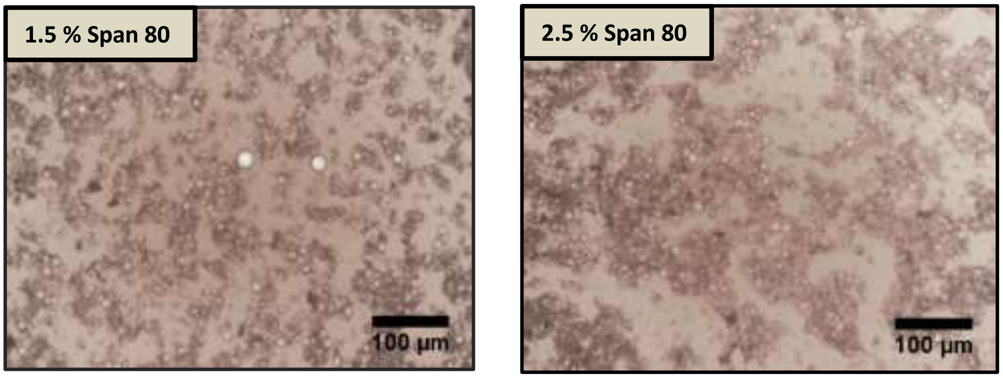

Fig.1. Optical microscopy images of 20 – 80% water-in-crude oil emulsions

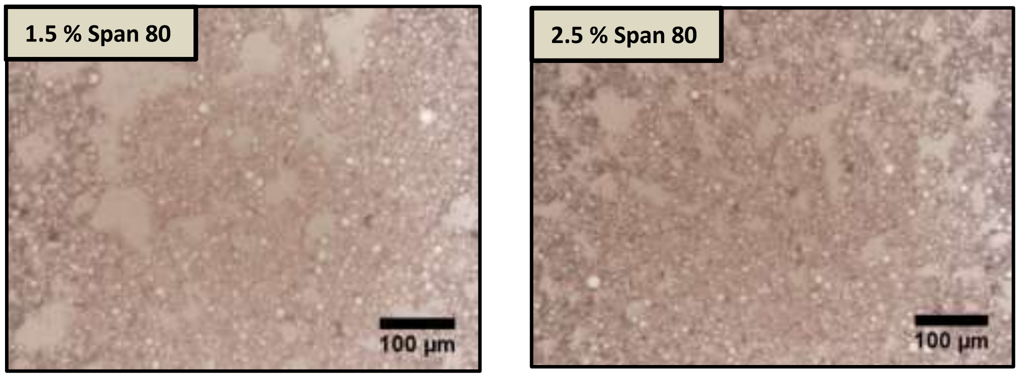

Fig.2. Optical microscopy images of 40 – 60% water-in-crude oil emulsions

It is clearly observed that, by raising the emulsifier concentration (from 1.5 to 2.5 %) the droplet size of the emulsions dropped significantly and the reason is the sufficient amount of emulsifier which could support all the droplets to be covered by Span 80.

Compared to the 20 % water content emulsion, the mean droplet diameter of emulsion with 40 % water volume fraction is relatively high. It can be found from the Table 3 in 40 % water content the mean droplet diameter of emulsion stabilized with Span 80 is (100 and 90 µm) at concentrations of (1.5 and 2.5 %) respectively. It was found from the experimental results that by using 20 – 80 % and 40 – 60 % W/O emulsion in the presence of (1.5 and 2.5 %) emulsifier at 30 ºC and mixing speed of 2000 rpm can produce visually stable emulsions for a period of one week where there was no water separation appeared in this period. However, to reveal the emulsion stability the microstructure and morphology of the emulsions were observed through the optical microscopy image of W/O shown in Fig. 1 and Fig. 2. Hence, it can be claimed that reducing the water volume fraction and increasing the emulsifier concentration could enhance the emulsion stability.

Rheological Properties of the Samples

There are several factors that influence on rheological properties of an emulsion such as water volume fraction, temperature, shear stress, and shear rate. Moreover, the rheological behavior of an emulsion can be either Newtonian or non-Newtonian depending upon emulsion composition. Regarding to the crude oil rheology, Fig. 3 shows the effect of temperature, shear rate, and shear stress on dynamic viscosity of (50 – 50) % blending of heavy and light crude oil, which is used for preparing the W/O emulsions. As shown in Fig. 3 (a) increasing the temperature from 30 ºC to 90 ºC is caused to the viscosity reduction in all rotational speeds (50 rpm – 250rpm). The reason is when the temperature increases the thermal energy and frequency of the droplet collision increase as well hence reduce the viscosity. Moreover, it is observed that apparent viscosity decreases by raising the shear rate. Thus, the crude oil shows a non-Newtonian flow behavior. Fig. 3 (a) exhibit by changing the temperature from 30 ºC to 90 ºC the viscosity of crude oil is changed from (35 to 8.7 m.pas) respectively in 50 rpm. In addition, Fig. 3 (b) describes the effect of shear rate on viscosity of crude oil where by varying the shear rate from (17 to 85 sec-1) the viscosity reduction was recorded at

(35, to 23 m.pas) and (8.7, to 5.8 m.pas) at 30 ºC and 90 ºC respectively. By applying the shear force, the emulsion alters its structure and leads to viscosity reduction. As shown in Fig. 3 (c) the shear stress increased gradually and significantly with the shear rate which indicates crude oil exhibiting non-Newtonian of shear thinning behaviors the reason behind this is the hydrodynamic effect is more dominant at the high shear rate.

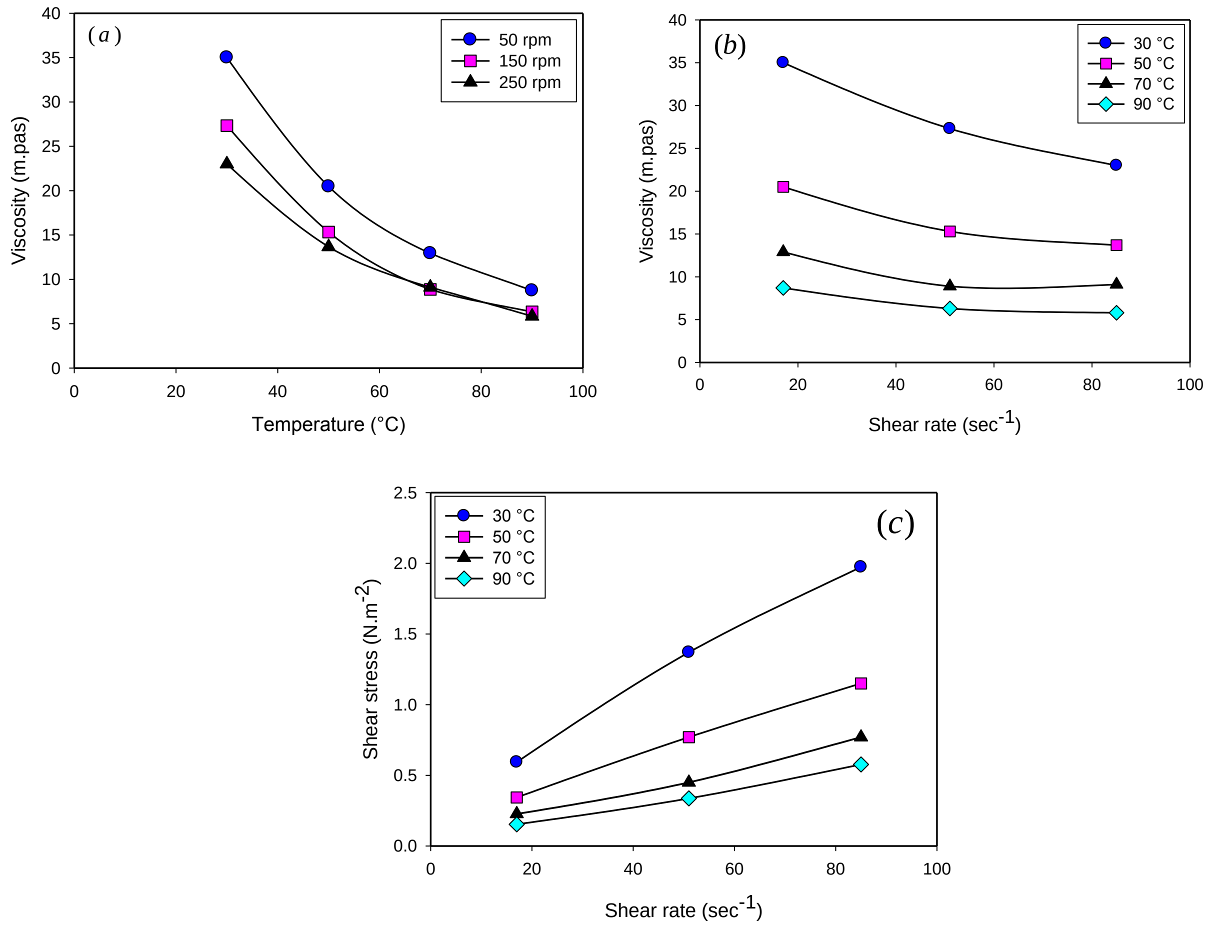

Fig.3. Effect of temperature, shear rate, and shear stress on viscosity of 50 – 50 % heavy and light blended crude oil

Regarding to the rheology properties of W/O emulsions Fig.4 (a) and Fig. 4 (b) shows the effect of shear rate and shear stress on viscosity of 20 – 80 % W/O emulsion stabilized by 1.5 vol.% of Span 80. It can be observed from the Fig. 4 (a) that the shear stress increased gradually and significantly with the shear rate and the reason behind this is the hydrodynamic effect increase by increasing the shear rate and hence the shear stress. Fig. 4 (a) shows that increasing the shear rate from (17 to 85 sec-1) caused to an increase in the shear stress from (1.46 to 6.36 pas) at 30 ºC. Similar effect was observed for all types of the samples Fig. 5 to Fig. 7. Therefore, it can be claimed that all of the samples behaved as a non- Newtonian shear thinning. Moreover, it is shown in Fig. 4 (b) that the shear rate is also effective on viscosity of the emulsions. Raising the shear rate from (17 to 85 sec-1) is reduced the viscosity from (90.4 to 73 m.pas) at temperature of 30 ºC respectively. This may be attributed to the breakup of flocculated particles caused by the force carried by the shear rate and thus reduced the viscosity.

It should be noted that temperature also has a strong effect on viscosity and viscous behavior of petroleum products. 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 [12]. Moreover, increasing the temperature in an emulsion increases the mobility of water droplets and finally leads to the viscosity reduction. As shown in Fig. 4 (b) by varying the temperature from (30 to 90 ºC) a viscosity reduction was observed from (90.4 to 33 m.pas) at shear

ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785
(ISRA), Journal Impact Factor: 2.114

rate of 17 sec-1respectively.

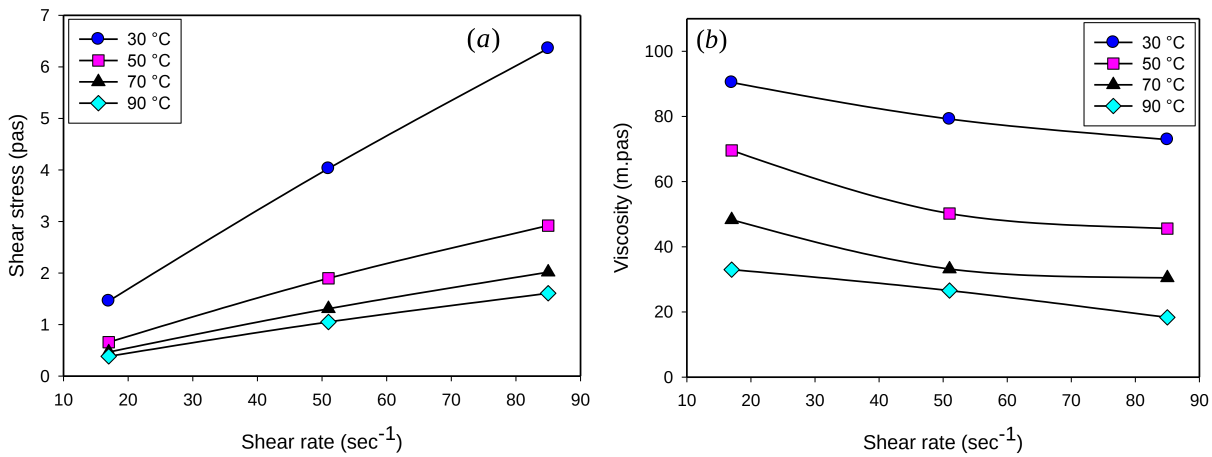

Fig. 4. Effect of shear rate and shear stress on viscosity of 20 – 80 % W/O emulsion stabilized with 1.5 vol.% Span 80

Fig. 5 shows the effect of shear rate and shear stress on viscosity of 20 – 80 % W/O emulsion stabilized with 2.5 vol.% of Span 80. The rheological behavior of emulsion shown in Fig. 5 is similar to Fig. 4. However, Fig. 4 (b) and Fig. 5 (b) exhibits that by increasing the concentration of Span 80 from (1.5 to 2.5 vol.%) is caused to an increase in viscosity from (90.4 to 101.8 m.pas) at 17 sec-1 shear rate and 30 ºC respectively.

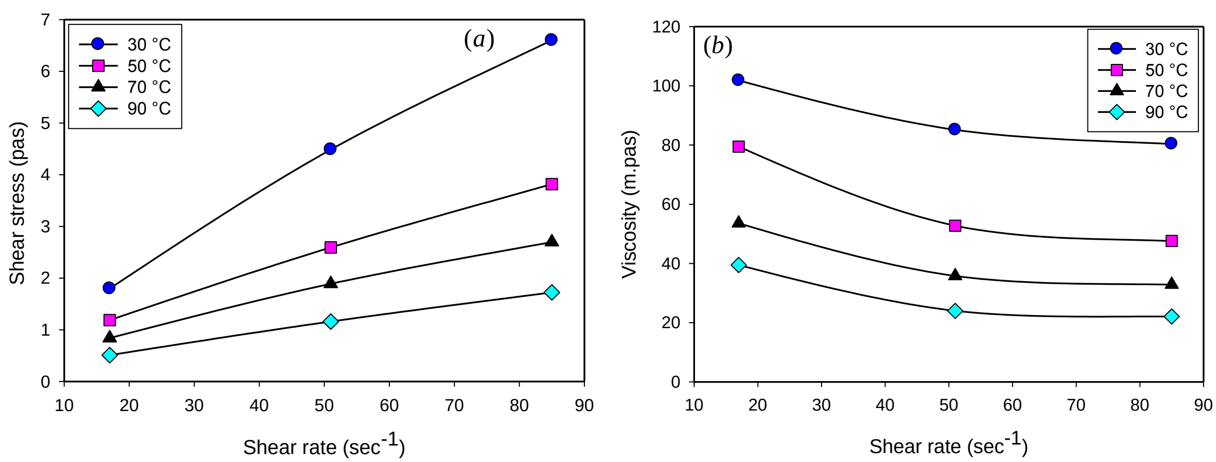

Fig. 5. Effect of shear rate and shear stress on viscosity of 20 – 80 % W/O emulsion stabilized with 2.5 vol.% Span 80

Figs. 6 and 7 show the effect of shear rate and shear stress on viscosity of 40 – 60 % W/O emulsions stabilized by 1.5 and 2.5 vol.% of Span 80 respectively. Compared to the Fig. 4 and Fig. 5 with 20 % water, the 40 % water volume fraction is more dominated on rate of viscosity and shear stress. Where, the emulsions with high water volume fraction obtained higher shear stress and viscosity with the shear rate. Fig. 6 (a) and Fig. 7 (a) exhibit that by increasing the shear rate from (17 to 85 sec-1) the shear stress for both of the samples obtained more than (9 pas) as the reason was described before. On the other hand, Fig. 6 (b) and Fig. 7 (b) show that increasing the water content to 40 % is resulted to higher viscosity compared to 20 % water. Means that the viscosity for higher water content is in the range of (242 to 280 m.pas) at 50 rpm and 30 ºC

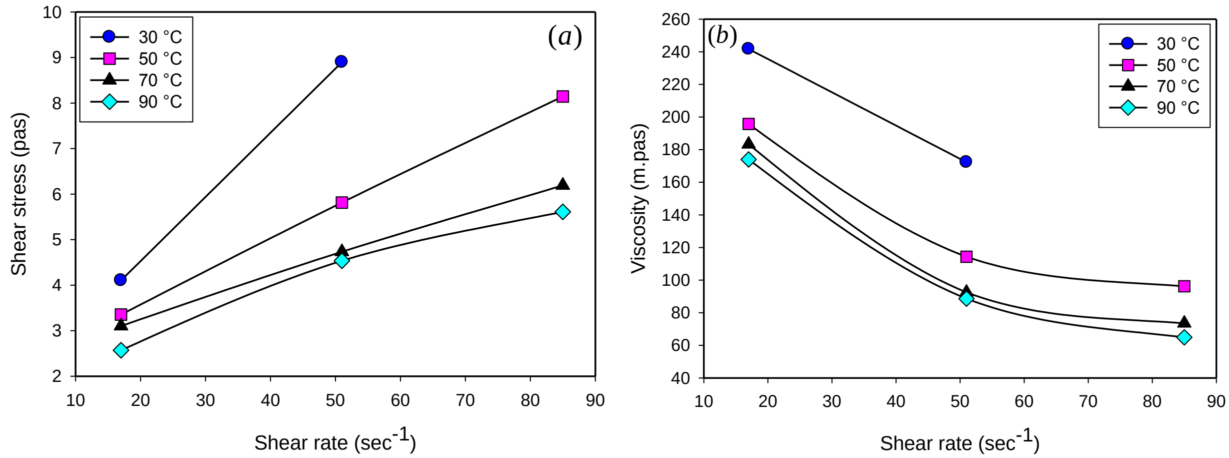

Fig. 6. Effect of shear rate and shear stress on viscosity of 40 – 60 % W/O emulsion stabilized with 1.5 vol.% Span 80

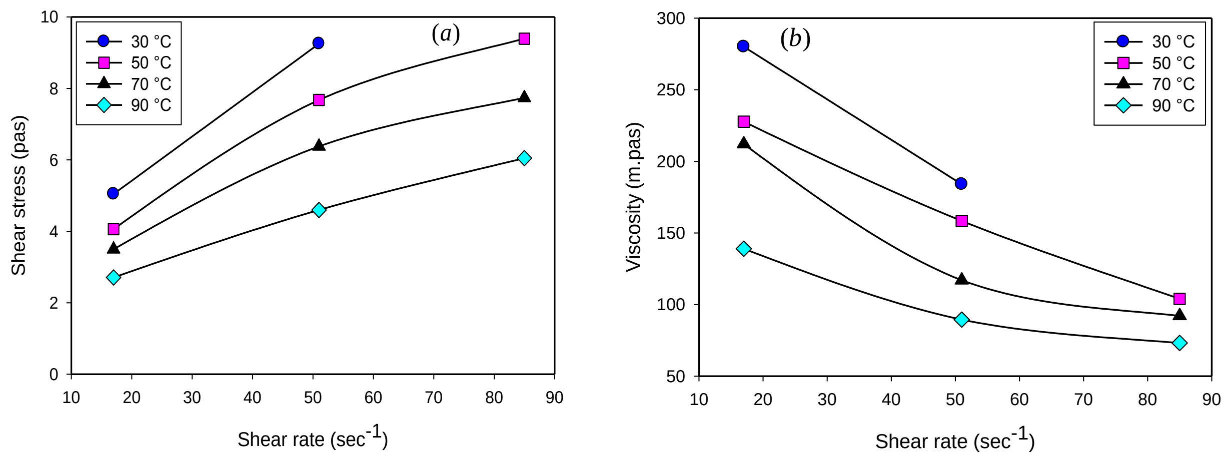

Fig. 7. Effect of shear rate and shear stress on viscosity of 40 – 60 % W/O emulsion stabilized with 2.5 vol.% Span 80

Fig. 8 illustrates the viscosity behavior of 20 – 80 % and 40 – 60 % Water-in-crude oil emulsions stabilized by 1.5 and 2.5 vol.% of Span 80. It can be clearly seen, 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 [13]. However, further increase of the dispersed phase fraction results in phase inversion of the emulsion from water-in-oil to the oil-in-water [14]. It can be observed that reducing the water volume fraction from 40% to 20 % resulted in a significant reduction of apparent viscosity from (241.7 to 90.4 m.pas) at 30 ºC, rotational speed of 50 rpm and concentration of 1.5 % Span 80. However, the viscosity reduction at 90 ºC is considerably high which is recorded from (174 to 33) m.pas respectively at the same water oil ratios and rotational speed.

ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785
(ISRA), Journal Impact Factor: 2.114

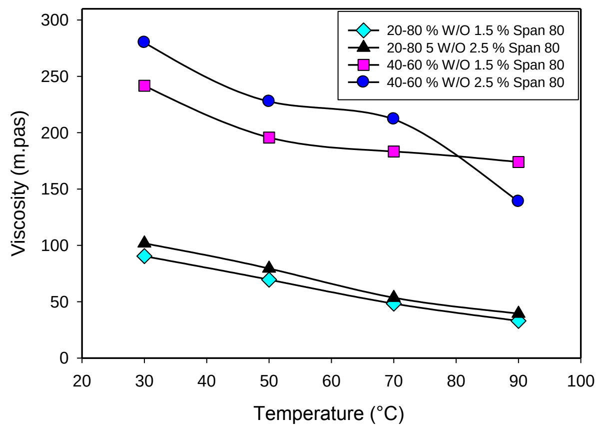

Fig. 8. Viscosity behavior of 20-80 % and 40-60 % phase ratios stabilized with 1.5 vol.% and 2.5 vol.% Span 80

It is also obviously shown in Fig. 8 that emulsions prepared with higher emulsifier concentration (2.5%) obtained more viscosity compared to (1.5%) emulsifier. It is believed that, increasing the emulsifier concentration will result in more stability and smaller droplet sizes which are fully emulsified and leads to reduce the surface tension in emulsion. In fact, the emulsified water droplets act as a solid particle in the system which can further increase the attraction force between the emulsion particles and hence the viscosity [15, 16]. As shown in Fig. 8 in 40 % water content emulsions and emulsifier concentrations of (1.5 and 2.5 vol.%) the viscosity is recorded at (242 and 280 m.pas) respectively at 30 ºC. It is generally accepted that the viscosity measurements were not constant with the shear rate; therefore, all emulsions act as a non-Newtonian pseudo plastic (or shear-thinning) manner.

CONCLUSION

In this investigation, the experimental study was conducted to evaluate the stability, rheology, and droplet size of the emulsions in varied water volume fraction, and emulsifier concentration. According to the experimental results, it was found that lower water volume fraction (20%) and higher emulsifier concentration (2.5%) were effective to obtain more stable emulsions with smaller droplet sizes as observed through the optical microscopy images. Therefore, it can be claimed that the smaller the droplet size the more stable the emulsion. It was also found that, higher water volume fraction (40%) and concentration of emulsifier (2.5%) resulted in more viscous emulsions. As a result of emulsions flow behavior all emulsions behaved as a non-Newtonian shear thinning manner.

ACKNOWLEDGEMENTS

This section should be typed in character size 10pt Times New Roman, Justified.

REFERENCES

[1] H. Lee, M. J. Mccarthy, and S. R. Dungan, "Experimental characterization of emulsion formation and coalescence by nuclear magnetic resonance," J. Am. Oil Chem. Soc., vol. 75, no. 4, pp. 463–475, 1998.
[2] Barkat Ali Khan, "Basics of pharmaceutical emulsions: A review," African J. Pharm. Pharmacol., vol. 5, no. 25, pp. 2715–2725, 2011.
[3] L. Xia, S. Lu, and G. Cao, "Stability and demulsification of emulsions stabilized by asphaltenes or resins.," J. Colloid Interface Sci., vol. 271, no. 2, pp. 504–6, Mar. 2004.
[4] M. T. Ghannam, "Water-in-crude oil emulsion stability investigation," Pet. Sci. Technol., vol. 23, no. January 2014, pp. 649–667, 2005.
[5] S. Ghosh and D. Rousseau, "Fat crystals and water-in-oil emulsion stability," Curr. Opin. Colloid Interface Sci., vol. 16, no. 5, pp. 421–431, 2011.
[6] N. I. Anisa, A. H. Nour, and A. Material, "Affect of viscosity and droplet diameter on water-in-oil (w / o) emulsions : An experimental study," World Acad. Sci. Eng. Technol., vol. 4, no. 2, pp. 691–694, 2010.
[7] R. M. Abd, A. H. Nour, and A. Z. Sulaiman, "Kinetic stability and rheology of water-in-crude oil emulsion stabilized by cocamide at different water volume fractions," Int. J. Chem. Eng. Appl., vol. 5, no. 2, pp. 204–

ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785
(ISRA), Journal Impact Factor: 2.114

209, 2014.
[8] B. Xu, W. Kang, X. Wang, and L. Meng, "Influence of water content and temperature on stability of W/O crude oil emulsion," Pet. Sci. Technol., vol. 31, no. 10, pp. 1099–1108, 2013.
[9] N. H. Abdurahman and W. K. Mahmood, "Stability of water-in-crude oil emulsions : Effect of cocamide diethanolamine (DEA) and Span83," Int. J. Phys. Sci., vol. 7, no. 41, pp. 5585–5597, 2012.
[10] J. Jiao and D. J. Burgess, "Rheology and stability of water-in-oil-in-water multiple emulsions containing Span 83 and Tween 80.," AAPS PharmSci, vol. 5, no. 1, p. 12, Jan. 2003.
[11] M. K. Naskar, A. Patra, and M. Chatterjee, "Understanding the role of surfactants on the preparation of ZnS nanocrystals," J. Colloid Interface Sci., vol. 297, no. 1, pp. 271–275, 2006.
[12] S. W. Hasan, M. T. Ghannam, and N. Esmail, "Heavy crude oil viscosity reduction and rheology for pipeline transportation," Fuel, vol. 89, no. 5, pp. 1095–1100, May 2010.
[13] S. R. Derkach, "Rheology of emulsions," Adv. Colloid Interface Sci., vol. 151, no. 1–2, pp. 1–23, 2009.
[14] F. Muzaffar, U. K. Singh, and L. Chauhan, "Review on microemulsion as futuristic drug delivery," Int. J. Pharm. Pharm. Sci., vol. 5, no. 3, pp. 39–53, 2013.
[15] M. A. R. Mohammed, S. Ali, and A. Mohammed, "Effect of additives on rheological properties of invert emulsions," Iraqi J. Chem. Pet. Eng., vol. 10, no. 3, pp. 31–39, 2009.
[16] M. Eftekhardadkhah and S. H. Hashemabadi, "Influence of salinity, surfactants and power of ultrasonic homogenizer on droplet size distribution of crude oil/water emulsions," Iran. J. Chem. Eng., vol. 8, no. 3, pp. 55–63, 2011.