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Stability of Water-in-Crude Oil Emulsion Using Cocamide Surfactant

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Abstract: The formation of water-in-crude oil emulsion can be encountered in many stages such as drilling, transporting and processing of crude oil. To enhance and control these processes, it is necessary to understand the emulsion mechanisms. In this study, two types of Malaysian crude oil namely; heavy crude oil and light-heavy blended crude oil (40-60 vol%) were characterized physically to use as the oil phase. Cocaamide DEA was used as a natural surfactant. The stability of water-in-crude oil emulsion were investigated at different water volume fractions (50 and 20%) with four volume fractions of Cocamide DEA (0.2 , 0.5, 1 and 1.5%). These emulsions were tested for relative rates of water separation and for rheology studies to demonstrate the viscosity behavior on the emulsion stability. Brookfield Viscometer was used to study the effects of shear rate, temperature, rotation speed (rpm) and water content on the viscosity at varying temperature (30-90°C) and rotation speed (50-250 rpm). Results showed that higher concentration of Cocamide DEA and lower water volume fraction were effective in stabilizing the water-in-crude oil emulsion at room temperature. In addition, the viscosity of the emulsion stabilized by Cocamide DEA showed non-Newtonian behavior.

Key words: Surfactant, cocamide DEA, crude oil, emulsion, stability

INTRODUCTION

Emulsions have long been of great practical interest due to their widespread occurrence in everyday life. It is a fine dispersion of water-in-oil or oil-in-water with drop sizes usually in the micron range (Sjoblom, 2001; Bibette *et al*., 2002; Sunil, 2006). It has the ability to resist changes in its properties over time, the more stable the emulsion, the more slowly its properties changes (McClements, 2005). In the petroleum industry, the method of emulsion and blending with light crude oil have been used as a common method to transport the heavy crude oil through reducing the viscosity as the conventional pipelining from the reservoir to refinery by heating is not a proper approach due to some drawbacks associated in term of operation cost (Ashrafizadeh and Kamran, 2010). However, there are several obstacles with the emulsion approach in term of the selection and the cost of surfactant, efficiency of surfactant in stabilizing the emulsion during transportation and separation once the destination point is reached (Hasan *et al*., 2010). Another difficulty related to emulsions, their formation is costly in term of chemical use, production losses, as well as an environmental problem in case of oil-spillage (Mingyuan *et al*., 1992; Nour *et al*., 2008).

During the preparation of the emulsion system, a surfactant is usually added into the oil-aqueous solution as an emulsifying agent to accomplish two functions; to lower the oil-aqueous solution interfacial tension and to stabilize the presence of the oil droplet phase within the aqueous continuous face to avoid the oil droplet coalescence mechanism (Becher, 1983; Ghannam and Esmail, 1997). Cocamide DEA or cocamide diethanolamine, is a non-ionic, biodegradable and low in toxicity surfactant made by mixing the fatty acids from coconut oils with diethanolamine. It is a viscous liquid (450-850 mPa.sec) that has molecular weight (280-290) with HLB of 13.5. It is used as a foaming agent in cosmetics products like shampoos and hand soaps as an emulsifying agent.

As the new trend in the research work exploration for environmental friendlier compounds and materials are associated by the inspiration of introducing new approaches and materials for saving resources, the present study was performed to investigate the stability of the crude oil emulsions stabilized by the natural surfactant Cocamide DEA which is the first part of an experimental study to demulsify the crude oil emulsions by microwave heating technology. The main point of this investigation is to characterize the crude oil samples and to examine the stability as well as the rheology properties of water-in-crude oil emulsion by investigating various factors affecting the stability and the viscosity of the prepared emulsion.

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MATERIALS AND METHODS

Crude oil: In this study, two types of crude oil samples were collected from Petronas Refinery at Melaka, Malaysia for investigation. The oil samples were marked as crude oil A and crude oil B (40% light crude oil blended with 60% heavy crude oil). Physical characterizations were carried out to identify the behavior of the crude oil before processing as shown in Table 1.

Cocamide DEA: The non-ionic surfactant Cocamide Diethanolamine (Cocamide DEA) was used in this study as natural emulsifying agent at varying doses (0.2, 0.5, 1 and 1.5 vol%) to investigate the rheology properties and the stability of Malaysia crude oil emulsions.

Emulsion preparation: About 24 samples of water-in-crude oil emulsion samples at different fractions by volume of water and oil phases (50-50% and 20-80%) were prepared and characterized with respect to hydrocarbon chain distribution, surfactant type and concentration, as well as viscosity dependence. In 500 mL graduated beakers, the crude oil sample (continues phase) was mixed with the Cocamide DEA (stabilizer) then agitated vigorously. After that, water (dispersed phase) was added gradually and slowly to the mixing phase (oil and stabilizer). The preparation process was achieved using a standard three blade propeller at a different speed from (1500-1800 rpm) at 30°C for 10 min. The prepared emulsions were examined by filter paper as well as by test tube methods to identify the type of emulsion (water-in-oil or oil-in-water).

Stability test: Gravity separation test took place to measure the stability of prepared emulsions by observing the amount of water separated. The emulsion was placed in graded cylinder and left for settling by gravity forces for one week. The percentage of water separated (W%) was calculated as separation efficiency as illustrated in the following equation:

$$W\% = \frac{\text{Vol. of water layer (mL)}}{\text{Original amount of water (mL)}} \times 100$$

Apparent dynamic viscosity: The dynamic viscosity of prepared emulsions was determined by Brokfeild Rotational Digital Viscometer Model LV/DV-III with UL adapter and spindle # 31. The viscometer was connected with a water bath thermostat. Viscosity measurements were achieved with different rotation speed 50, 100, 150 and 250 rpm and different temperature 30, 50, 70 and 90°C.

RESULTS AND DISCUSSION

Crude oil properties: Depend on the physical properties, it was found that sample A behave as heavy crude oil whereas sample B behave as medium crude oil, as shown in Table 1.

Effect of emulsifier concentration and water content on the emulsion stability: The effect of Cocamide DEA concentration on the stability of Malaysian crude oil samples is presented in Fig. 1 and 2. The purpose of using DEA as a stabilizer for the recovery in the refinery

Table 1: Physical properties of the crude oil samples

Crude oil	Crude A	Crude B
Density (g cm^{-3})	0.947	0.893
Viscosity (mPa sec)	298.700	19.100
API Gravity	17.130	26.120

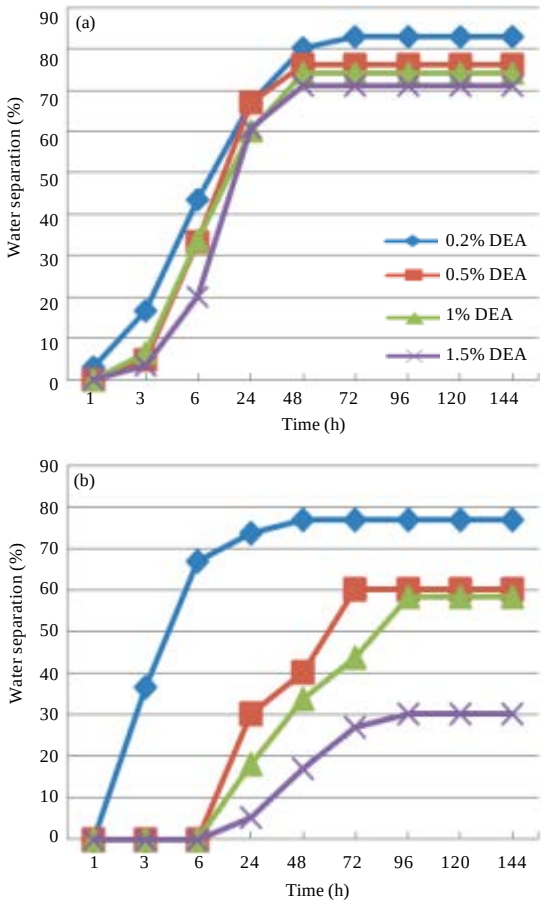

Fig. 1(a-b): Effect of DEA concentrations on (50-50%) w/o emulsion of (a) Heavy crude oil and (b) Blend crude oil

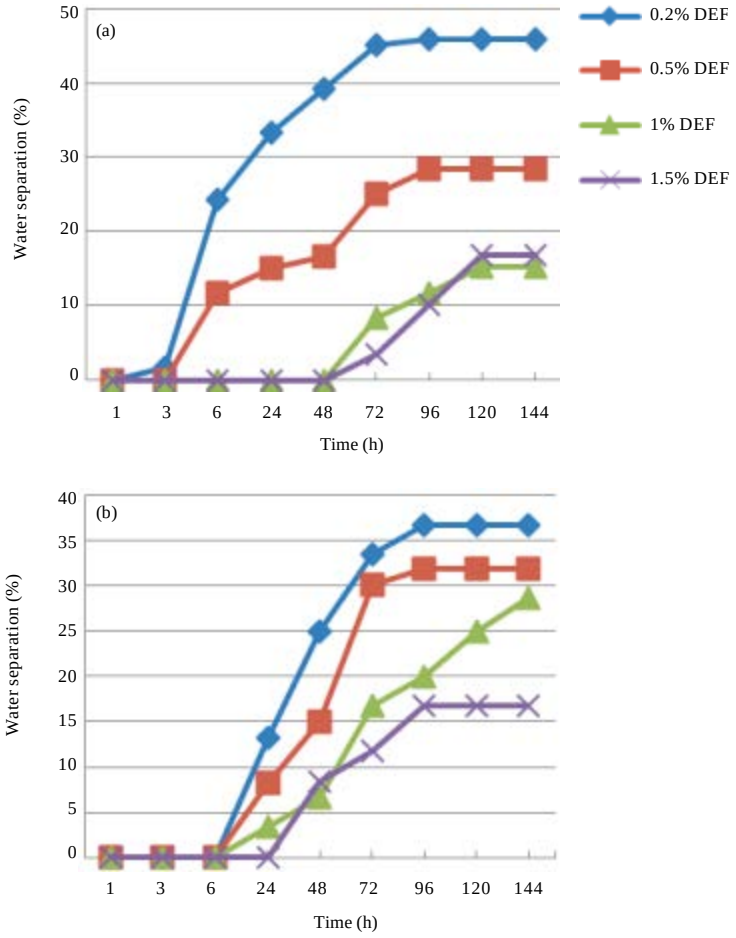

Fig. 2(a-b): Effect of DEA concentrations on (20-80%) w/o emulsion of (a) Heavy crude oil and (b) Blend crude oil

compared to other agents is much easier. The dosages of Cocamide DEA were varied (0.2, 0.5, 1 and 1.5 vol%) for screening purpose. Stability was evaluated by percentage of water separated from the emulsion which was measured from the cylinder and reading were collected after 1, 3 and 6 h for the first 24 h and later the readings were collected after each 24 h over period for one week. The main purpose of this screening process was to find the best formulation in terms of emulsifier concentration, since concentration is very significant from an economic point of view. Generally, in every experimental emulsification study, stability test is required to find out the best and reliable emulsion at lower cost (Zaki *et al*., 1996).

Figure 1a shows the stability progress of the heavy crude oil emulsion contains (50 vol%) of water. It can be observed that in the first 24 h coalescence was occured and the percentage of water separated was between 60-66%. However, after 24 h, the separation percentage was increased up to 71-83%. Besides, it can be noted that increasing the concentration of the emulsifier reduced the coalescence of water droplets and gives better stability of the emulsion.

Compare to the emulsion of blend crude oil sample, Fig. 1b, at the same water content of (50 vol%), the coalescence was occured after 24 h and the separation was between 30.4-76.8%. Particularly (0.5, 1 and 1.5 vol%) of DEA were significant in stabilizing the emulsion where there was no separation occurred at all after 6 h. Even though the coalescence was occurring, but it was between 5.4-30% only.

As a result, the gravity separation test of (50-50 vol%) emulsion showed that DEA concentration of (1.5 vol%) gave better stability for the medium crude oil

emulsion. Compared with the stability of the heavy crude oil emulsion, Cocamide DEA at this concentration was insufficient in stabilizing the w/o emulsion and the DEA concentration should be increased higher than (1.5 vol%) in order to get an emulsion with better stability.

Figure 2a and b presents the stability of heavy and blend crude emulsions contain (20 vol%) of water stabilized by Cocamide DEA. In Fig. 2a, it can be seen that using 1 and 1.5 vol% of DEA were significant in stabilizing the heavy crude oil emulsion for 50 h where there was no water separated at all. Even though after 50 h of processing time there was a coalescence occurred, but it considered trivial and the percentage of water separated were 15.2 -16.9%. In contrast, using 0.2 and 0.5 vol% of DEA were insufficient in stabilizing the emulsion as the coalescence occured after 3-6 h of settling and separations were between 28.4-45.9%.

Compare with the separation progress of the blend crude oil emulsion Fig. 2b, it was found that using (1.5 vol%) of DEA was sufficient to produce stable emulsion where there was no separation occurred during the first 24 h. After 24 h, coalescence was occurred to give 16.8%. However, using (0.2, 0.5 and 1 vol%) of DEA the coalescence occurred and the percentage of water separation was 36.7, 31.8 and 28.6%, respectively.

Therefore, the gravity separation test of (20-80 vol%) w/o emulsion showed that 1 and 1.5 vol% of DEA gives better stability for heavy crude oil emulsion up to 50 h. Whereas, for blend crude oil emulsion, Cocamide DEA at 1.5 vol% was sufficient in stabilizing the emulsion and the stability could be increased if the DEA concentration increased more than 1.5 vol% in order to produce high stable emulsion.

It can be concluded that increasing the surfactant concentration enhance the emulsion stability due to increase the surfactant molecules adsorbed at the water/oil interface that can result in intermolecular interactions, which will work against any strain on the interface (Gibbs-Marangoni Effect) and providing an electrostatic and steric barrier to coalescence mechanism among the water droplets due to their non-ionic nature and stabilizing the system (Zaki, 1997; Filho *et al*., 2012). Moreover, the most stable emulsion was noted at a water volume fraction of 20% and the Cocamide DEA showed better stability of emulsion at room temperature with all concentrations which considered as tight emulsion. Compared to the 50% volume fractions of water, this emulsion was stable for a few hours before water was a coalescence as a separate layer down the emulsion which considered as a medium or loose emulsion. Thus, it is clear evidence that reducing the volume fraction of water and increasing the concentration of Cocamide DEA will give a better stabilized w/o emulsion at room temperature.

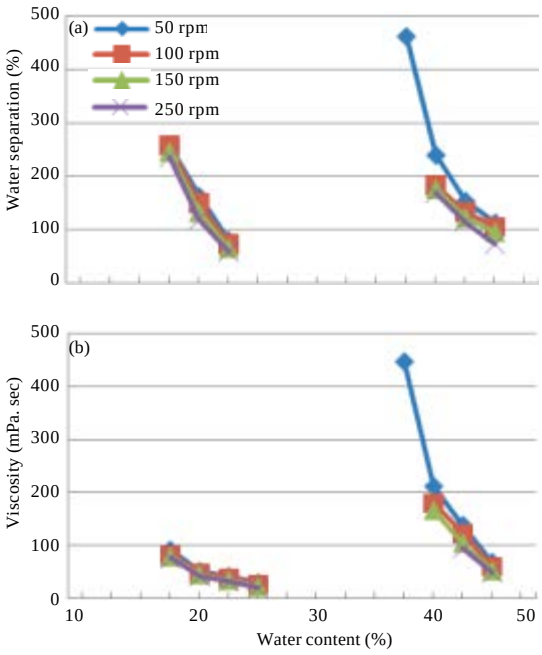

Fig. 3(a-b): Effect of water content on viscosity of w/o emulsion stabilized with DEA (1.5 vol%) at different temperature and rpm, (a) Heavy crude oil and (b) Blend crude oil

Effect of water content and shear rate on the viscosity and the stability of W/O emulsions: Several factors namely; temperature, rotation speed (rpm) and shear rate were considered to investigate the effects of the water content and the shear rate on the viscosity and further on the stability of w/o emulsions to provide complete information about non-Newtonian or Newtonian behavior of the system. As reported in a previous study stability of emulsions relates to their bulk phase elastic behavior. The Viscoelastic fluids are a common form of non-Newtonian fluid. Typically, fluids that have a high molecular weight are usually having this behavior (Donald, 2012). In fact, each emulsion investigated has a viscosity more than the viscosity of the continuous phase (oil).

Figure 3a and b demonstrated the effects of the water content on the viscosity of w/o emulsions of both crude oil samples stabilized with DEA (1.5 vol%) at different rotation speed and temperature. For the heavy crude oil emulsion, the viscosity of emulsion contains (50 vol%) water was high between (100-300 mPa.sec). However, when the water content reduced to 20 vol%, reduction in viscosity was occurring between (60-280 mPa.sec), as shown in Fig. 3a. Similarly, for blend crude oil emulsion, using 20 vol% of water resulted in low viscosity

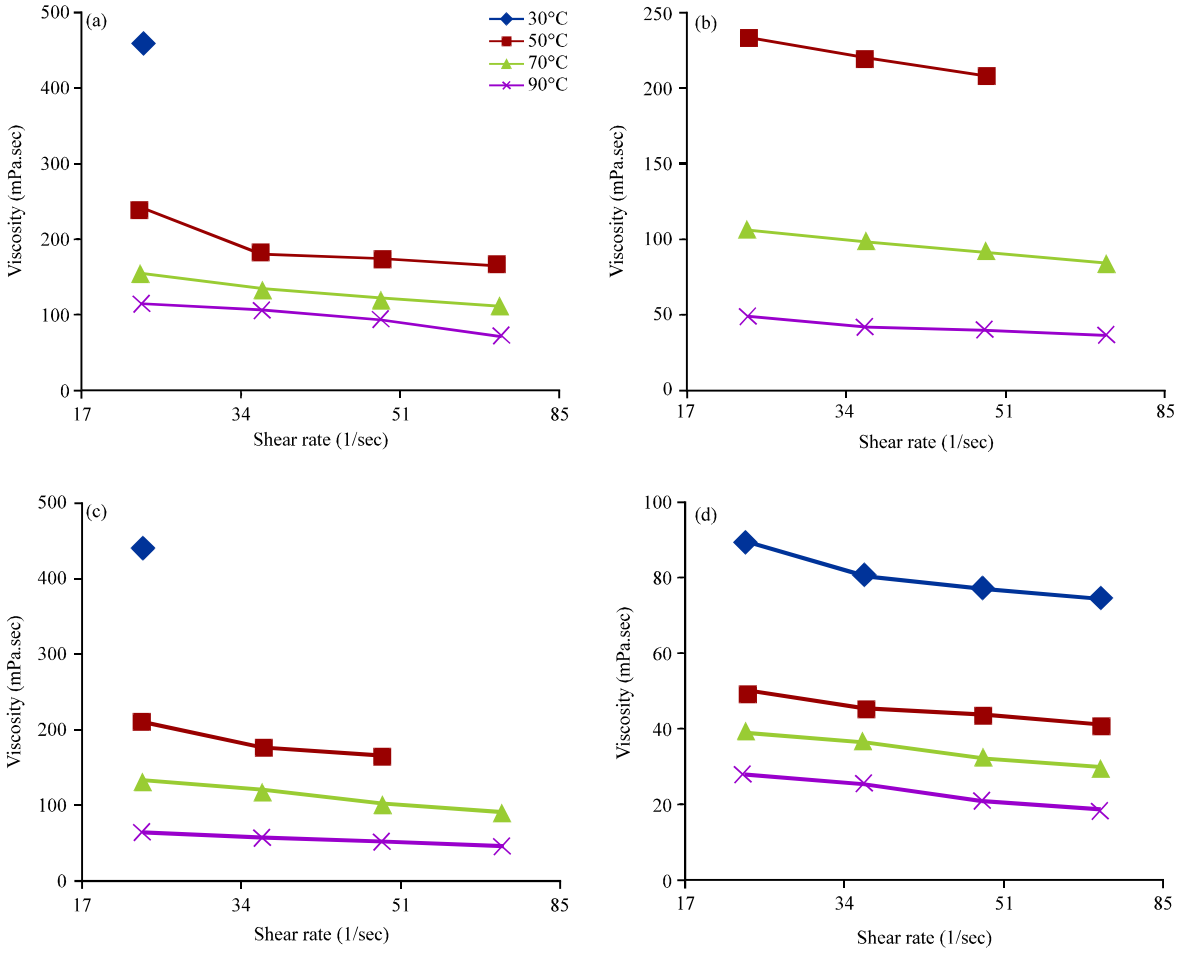

Fig. 4(a-d): Effect of shear rate on viscosity emulsion at different temperatures using DEA 1.5 vol% for, (a) Heavy oil emulsion with 50 vol% of water, (b) Heavy oil emulsion with 20 vol% of water, (c) Blend oil emulsion with 50 vol% of water and (d) Blend oil emulsion with 20 vol% of water

between (10-90 mPa.sec) while the viscosity increased up to (50-450 mPa.sec) when the water volume fraction increased up to 50 vol%, as showen in Fig. 3b. In fact, increase the viscosity with increase the water volume fraction (dispersed phase) resulted in faster coalescence due to the presence of the hydrogen bond which means the inter droplet distance is higher therefore the droplet stay close to each other and thus the effect of hydrodynamic forces increased as well as the deformation is increased (Anisa and Nour, 2010; Sunil, 2006).

The effects of shear rate data on viscosity of (50 vol% and 20 vol%) w/o emulsions are plotted in Fig. 4a-d. It is clear that over a range of shear rate (from 17-85) 1/sec, the apparent viscosity was a function of the shear rate as it decreased with increasing temperature (from 30-90°C). The reason behind decreasing the viscosity when the shear rate increased is due to destroy the molecules of the emulsion at the moment of turning the viscometer`s spindle. So the hindering to the shear rate will decrease and therefore the high shear rate will be, the more the structure is destroyed and the lower viscosity will be.

Generally, all emulsions were found to follow shear thinning behavior (pseudo plastic) or non-Newtonian behavior. However, emulsion with 50% volume fraction of water in both crude oil samples had elastic behavior higher than emulsion with 20 vol% of water.

It can be concluded that the emulsion with lowest water volume fraction (20%) exhibited the lowest viscosity values and characterizing less elastic behavior compared with highest water volume fraction (50%) of each crude oil sample.

CONCLUSION

The present study demonstrated viscosity behavior and water contents on stability of w/o emulsion stabilized by Cocamide DEA. These effects were investigated using several factors namely: Shear rate, temperature and stirring speed of Brookfield Viscometer. The findings of this study were highlighted as; high concentration of (1.5 vol%), Cocamide DEA was a good natural surfactant that had ability to stabilize the w/o emulsion kinetically and thermodynamically for both crude oil samples at room temperature. Low water volume fraction was effective in stabilizing the w/o emulsion of Malaysian crude oil through reducing the viscosity that resulted inhibition in the coalescence process. All w/o emulsions investigated were found to follow shear thinning behavior (pseudo plastic) or non-Newtonian behavior.

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