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Investigation of Kinetic and Rheological Properties for the Demulsification Process

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KEYWORDS

Viscosity;
 Surfactants;
 Water in crude oil emulsion;
 Phenol formaldehyde resin;
 Demulsification;
 Coalescence rate;
 Water droplet volume

Abstract Chemical demulsification process is the most widely applied method of treating water in crude oil emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. Hence, five demulsifiers were prepared in two steps. In the first step, the nonyl phenol was polymerized with formaldehyde to obtain five different molecular weights polymers. In the second step, the resulting polymers were ethoxylated with 50 ethylene oxide units and propoxylated with 10 propylene oxide units, yielding (D_1 – D_5). The demulsification efficiency of these demulsifiers was investigated. The influence of viscosity on the droplet diameter for water-in-crude oil emulsion with three different ratios; 30:70, 50:50 and 70:30 (v/v) w/o emulsions were examined. The results showed that, the viscosity of w/o emulsion was strongly augmented by increasing volume of water before reaching the inversion point. The yield point which is required to start the flow decreases with decreasing water percent. The coalescence rate increases with increasing drop size for D_5 as a representative sample. Results show that, the droplet size increases with increasing water content. The efficiency of water separation increases as the molecular weight increase.

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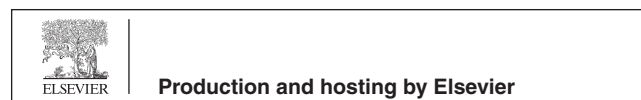
1. Introduction

Crude oil contains sophisticated mixtures of organic chemical structures [1]. Its composition can vary due to its reservoir's place of origin, depth and age [2].

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Crude oil is seldom produced alone because it generally is commingled with water. The water creates several problems and usually increases the unit cost of oil production. The produced water must be separated from oil, treated and disposed off properly. All these steps increase costs. Furthermore, sellable crude oil must comply with certain product specifications, including the amount of basic sediment and water (BS&W) and salt, which means that the produced water must be separated from oil to meet crude specifications. The amount of water that emulsifies with crude oil varies widely from facility to facility. It can be less than 1% and sometimes greater than 80% [3–6]. In the oil industry, water-in-oil emulsions are more common (most produced oilfield emulsions are of this kind); therefore, the oil-in-water emulsions are sometimes referred to as “reverse” emulsions.

The presence, amount and nature of the emulsifier determines, to a large extent, the type and “tightness” of an emulsion. The natural emulsifiers in crude are resident in the heavy fraction. Because there are different types of crudes and because these crudes have different amounts of heavy components, the emulsifying tendencies vary widely. Crude with a small amount of emulsifier forms a less stable emulsion and separates relatively easily. Other crudes contain the right type and amount of emulsifier, which lead to very stable or tight emulsions. Naturally occurring emulsifiers in the crude oil include higher boiling fractions, such as asphaltenes and resins, organic acids and bases. These compounds have been shown to be the main constituents of interfacial films that form around water droplets in many oilfield emulsions. Waxes can also interact synergetically with asphaltenes to stabilize emulsions [7,8].

Emulsion viscosity can be substantially greater than the viscosity of either the oil or the water because emulsions show non-Newtonian behavior. This behavior is a result of droplet crowding or structural viscosity. A fluid is considered non-Newtonian when its viscosity is a function of shear rate. At a certain volume fraction of the water phase (water cut), oilfield emulsions behave as shear-thinning or pseudoplastic fluids (i.e., as shear rate increases, viscosity decreases). An emulsion may also exhibit a yield stress, that is, the shear rate (flow) remains zero until a threshold shear stress is reached “the yield stress”, then pseudoplastic or Newtonian flow begins. The pseudoplastic flow may also be time dependent, or thixotropic, in which case viscosity decreases under constant applied shear rate. The constant values of viscosity for all shear rates, or a slope of zero, indicate that the emulsions exhibit Newtonian behavior [9].

Methods to induce phase separation in water in crude oil emulsions can be classified in three main categories: mechanical, electrical, and chemical. Chemical methods consist of the addition of minute amounts of chemical compounds (usually 10–1000 ppm) to enhance phase separation rates. It is the most economical and commonly used method of dehydration of crude oils. A combination of chemical and mechanical or chemical and electrical is often the best choice for practical applications to neutralize the effects of emulsifying agents to break an interfacial film effectively; without the addition of new equipments or modifications of the existing equipment [7].

The most common method of emulsion treatment is adding demulsifiers. These chemicals are designed to neutralize the stabilizing effect of emulsifying agents. Demulsifiers are surface-active compounds that, when added to the emulsion, migrate to the oil/water interface, rupture or weaken the rigid film, and enhance water droplet coalescence. Optimum emulsion breaking with a demulsifier requires a properly selected chemical for the given emulsion; adequate quantity of this chemical; adequate mixing of the chemical in the emulsion; and sufficient retention time in separators to settle water droplets. It may also require the use of heat, electric grids, and coalescers to facilitate or completely resolve the emulsion. Selection of the right demulsifier is crucial to emulsion breaking. The selection process for chemicals is still viewed as an art rather than a science [10–13]. Amphiphilic molecules with moderate-to-high molecular weight (typically above 3000 Da), such as polyalkoxylated alkylphenolformaldehyde resins and complex block copolymers, are

usually responsible for the separation of a large fraction of the dispersed aqueous phase. For that reason, they are often termed *water droppers*. Several studies suggest that these molecules act by modifying the compressibility and rheological properties of the water-oil interfacial films that stabilize the emulsion in a way that favors the drainage of the thin films between approaching drops and therefore coalescence and phase separation [14].

Through this paper, the rheological properties which affect the destabilization of crude oil emulsion with the newly designed surfactants “ethoxylated and propoxylated poly nonyl phenol formaldehyde” and also comprising their behavior with a commercial surfactant, EPRI 301 and Servo-6603 were studied. Also, the phase ratio will be further investigated and their relative droplet size distribution for w/o emulsion also scrutinized.

2. Materials and methods

2.1. Demulsifiers preparation (preparation of poly nonyl phenol formaldehyde resin)

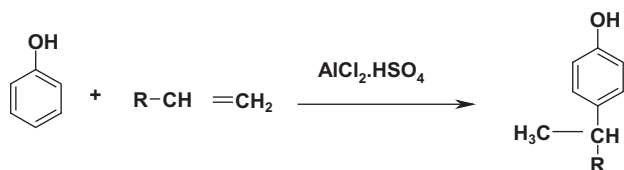
1. The phenol was obtained by the distillation of Coal Tar phenol,
2. Preparation of alkyl phenol.

2.1.1. Preparation of alkylating catalyst

One mole of anhydrous aluminum chloride (133 g) was placed in 1 L beaker and 1 mole of 98% sulphuric acid (98 g) was added to aluminum chloride in three portions at 35°C. The mixture was heated with stirring at 60–70°C using a sand bath, then the flask was placed in cold water to keep the temperature between 100 to 110°C. The dry product $\text{AlCl}_2\cdot\text{HSO}_4$ obtained after the evolution of HCl gas was found to be 197 g. The prepared catalyst was put in a dry container to be used within 3 days only [15].

2.1.2. Alkylation of phenol with α -olefins

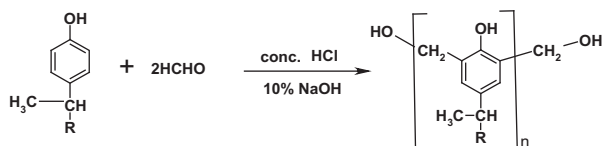
General procedure: Three moles of phenol (282 g) and a certain weight of the catalyst $\text{AlCl}_2\cdot\text{HSO}_4$ (56 g) were charged in a two-liter 3-necked flask fitted with a mercury seal stirrer, a condenser with drying tube and a dropping funnel. The ratio of phenol to catalyst was 1 to 0.2. The contents were heated to 60°C. One mole of α -olefin was added slowly at 60°C with stirring. Then the temperature was raised to 80°C and stirring was continued for 6 h. About 300 ml of diluted HCl (1:1) was added slowly to the hydrolysis of the catalyst. The organic layer was separated and freed from excess phenol by washing 10 times with boiling water. The mixture was then refluxed for 4 h with 200 ml. 95% ethyl alcohol and 100 g 50% aqueous NaOH, about half of ethyl alcohol was removed by distillation under vacuum. After cooling 130 ml of concentrated HCl was added, followed by 400–600 ml of water to dissolve the salt formed. The organic layer was separated, diluted with 500 ml ether and washed with water. The ether was evaporated and the mixture was distilled under reduced pressure to get alkyl phenol [15]. The reaction was completed as per the following equation



2.1.3. Polymerization

One mole of alkylphenol (nonyl) and 1.2 mole of formaldehyde 37% were placed in a 1 L glass flask with four necks, fitted with condenser, a mechanical stirrer, a thermometer and a dropping funnel. An amount equivalent to 2% of the total weight of reactants of concentrated HCl was placed in the dropping funnel. HCl was added dropwise with continuous stirring over a period of 1 h, during which the temperature was maintained at 35°C by cooling, because of the exothermic nature of the reaction. After the addition of HCl was completed, the temperature of the reaction was raised gradually by heating jacket to 110°C. The temperature is maintained at this level for 1 h. A Dien and Stark water collector was then attached to the reactor and connected to a vacuum pump adjusted to 50 mm Hg. The temperature was thus raised to 150°C. The reactants were allowed to stand at this temperature for another 1 h. The product was then cooled and dissolved in benzene, washed with 10% NaOH (sodium hydroxide solution) until neutrality has been reached and then dried after phase separation of aqueous phase over anhydrous sodium sulfate. Benzene was then removed by means of a rotary evaporator. The chemical structure and molecular weight of the prepared polymer are shown in Table 1. The same table shows also their hydrophilic-lipophilic balance (HLB) values as calculated by Griffin's method [16].

The reaction was completed as per the following equation



3. Ethoxylation and propoxylation of the poly nonyl phenol formaldehyde

Into a (1 L) quick fit conical flask connected with a manometer, ethylene oxide/propylene oxide cylinder and nitrogen cylinder, 0.1 M from the poly nonyl phenol formaldehyde was charged into the closed reaction vessel with 0.1 g sodium metal "Na metal" as a catalyst and heated to 150–180°C with continuous stirring while passing a stream of nitrogen gas through the system for 2 min to flush out air. The nitrogen stream was then replaced by ethylene oxide/propylene oxide at a rate, which was regulated by monitoring the Hg level of the manometer. The reaction was carried out for different intervals of time till the desired amount of ethylene oxide/propylene oxide content was obtained (50 ethylene oxide units) (10 propylene oxide units) [17]. The product was then

neutralized with HCl, dissolved in isopropanol, then salted out with supersaturated NaCl solution. The organic layer was then separated and the isopropanol was distilled off. The obtained ethoxylated/propoxylated product showed a brown viscous liquid appearance.

3.1. Hydrophile Lipophile Balance "HLB"

Surface-active ingredients are chemicals that have surface-active properties characterized by hydrophilic-lipophilic balance (HLB) values. The HLB scale varies from 0 to 20. A high HLB value refers to a hydrophilic or water-soluble surfactant.

The HLB of the prepared demulsifiers were calculated according to the most commonly used formula for the non-ionic surfactant;

$$HLB = 20[M_H/(M_H + M_L)]$$

where M_H is formula weight of the hydrophilic portion of the molecules and M_L is the formula weight of the lipophile (hydrophobic) portion of the molecule [18].

The chemical structure of the prepared surfactants, their molecular weight and HLB were represented in Table 1.

3.2. Crude Oil and Sea Water

Crude oil was submitted from the Suez Oil Company (Egypt) without demulsifier treatment and its properties are; specific gravity 0.874 (IP 160), API gravity at 60°F (40.955) (IP 160), kinematic viscosity at 40°C (222.87 cSt) (IP 71), asphaltene content 7.18 wt.% (IP 143), paraffin wax 23.1 wt.% (UOP 46) and water content 0.5 wt.% (IP 74/70).

Sea water was conducted from the Suez Gulf, and have the following physicochemical properties, total dissolved solids 44372 mg/l, resistivity 0.019 Ω at 19°C, conductivity 2.2 μS/m, at 19°C, density 1.032 g/ml, pH 7.74 at 19°C, salinity 39996 mg/l and specific gravity 1.03304.

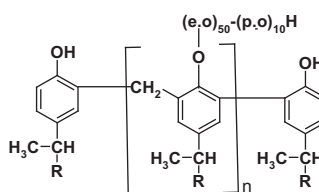
3.3. Preparation of Water in Crude Oil Emulsions

In a 250 ml beaker, the crude oil was stirred at 25°C and 2000 rpm while seawater was added gradually to the crude oil until the two phases became completely homogeneous [19]. The emulsions were prepared at different percentage ratios of water to crude oil (30:70, 50:50, and 70:30). The emulsion was let to stand for about 24 h at 60°C to make sure of its stability and no separation occur to carry out the treatment.

3.4. Bottle Test

The graduated bottle test (Sany glass) was used to estimate the efficiency of the demulsifiers toward resolving W/O emulsions. Each demulsifier was dissolved in xylene (20% active material) and then added to 100 ml of the previously prepared emulsion at different concentrations (ppm). The mixture was added to a 100 ml Sany glass and then was shaken vigorously for 1 min. The bottle was placed in a thermostated water bath at 60°C. Water separation (ml) was observed at different times depending on the efficiency of the demulsifier under investigation. A blank was considered in each set of experiments [20].

Table 1 Designation, molecular weight and HLB of the ethoxylated poly nonyl phenol formaldehyde surfactant.

Demulsifier designation	Chemical structure	Molecular weight		HLB
		Without (E.O.)	With 50 unit (E.O.) + 10 unit (P.O.)	
D ₁		840	3620	12.1
D ₂		940	3720	11.8
D ₃		1060	3840	11.4
D ₄		1730	4510	9.7
D ₅		2040	4820	9.1

Ethylene oxide units (E.O.) = 50 units
 Propylene oxide units (P.O.) = 10 units
 n = Repeating unit of poly nonyl phenol formaldehyde

3.5. Rheological Behavior

Oil viscosity was measured using Haak viscometer model Rotovisco RV12 with a heating/cooling water bath. The crude oil used in this study was considered as non-Newtonian fluid because the viscosity of the crude oil changes while being measured with a rheometer at different speed rotation. The viscosity measurement started from low shear rates. The shear rate was then increased at constant temperature (60°C). The rheological properties were measured over a shear range of 1–1200 s⁻¹. The flow curve can be analyzed using the Herschel–Bulkley equation [21–22]:

$$\tau = \tau_B + kD^m$$

where τ is the shear stress; τ_B is the dynamic yield stress “Bingham yield value”; k is the consistency index; m is the shear thinning index and D is the shear rate. The Bingham yield value (τ_B) can be obtained from the intercept of the graph relation between shear rate and shear stress. On the other hand, the linear line from the relation between shear rate and viscosity give us the dynamic “apparent” viscosity.

The rheology parameters were obtained from the following equations:

$$\text{Shear stress, } \tau = A \cdot S \text{ (Pa)}$$

$$\text{Viscosity, } \eta = G \cdot S/n \text{ (mPa s)}$$

$$\text{Shear rate, } D = M \cdot n \text{ (s}^{-1}\text{)}$$

where, n = number of revolution, rpm; S = torque; $M = 2.34$ (min/s); $A = 3.22$ (Pa/S K t) and $G = 1347$ (mPa s/S K t min).

3.6. Photography and Kinetic Study of the Demulsification Process

One demulsifier (D₅) was chosen for this purpose on the basis of its high demulsification efficiency compared with the other prepared demulsifiers. The 70% w/o emulsion was kept overnight at room temperature to get a stable emulsion without treatment. Photographic microscopy studies were carried out at 60°C for treated and untreated emulsions. The treated and untreated emulsion samples were taken at different times with a Teflon stick for analysis. An emulsion droplet was spread on a glass slide and covered with a Teflon layer. The slides were photographed under an Olympus binocular microscope; model

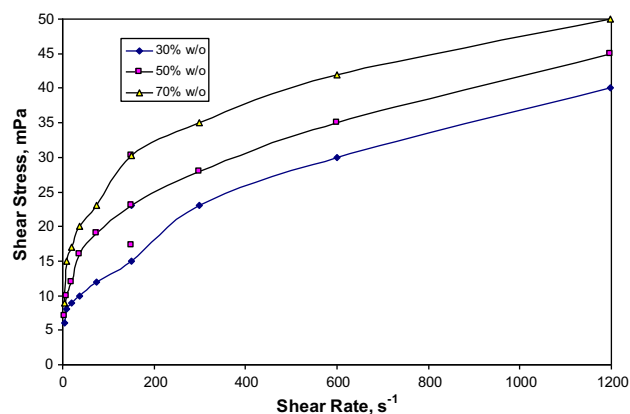


Figure 1 Relation between shear rate and shear stress for the untreated crude oil emulsions.

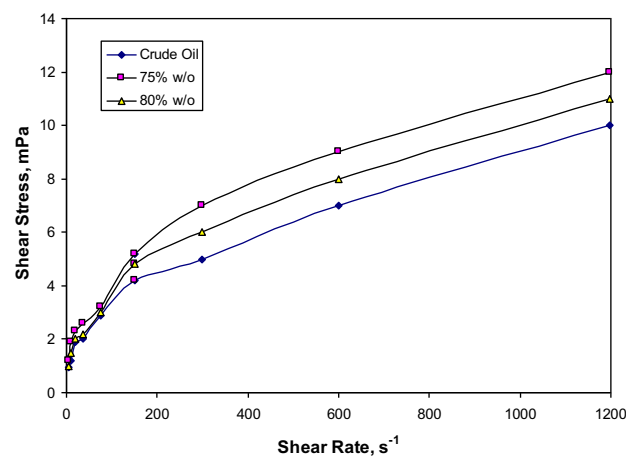
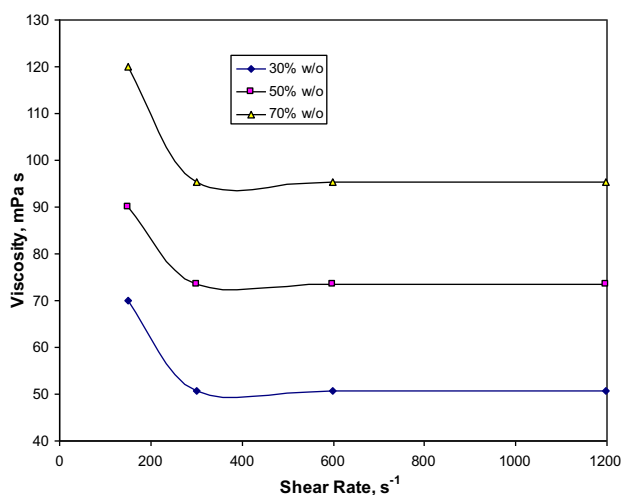
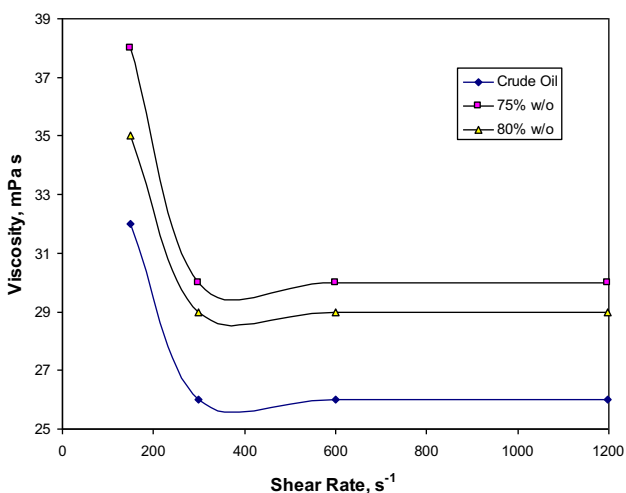


Figure 2 Relation between shear rate and shear stress for the untreated dry crude oil and the inverted emulsions.

BHSP with a camera, and the droplets were counted with the help of a Digitat 5050-R (EPRI, Egypt).

Table 2 Rheological parameters for dry crude oil and freshly prepared w/o emulsions at 60°C without demulsifier additive.

W/Oil emulsion	Dynamic “apparent” viscosity, η_{app} (mPa s)	Dynamic yield value, τ_B (Pa)
Crude oil (dry)	26	4.2
Emulsion 30% (w/o)	50.6	17.3
Emulsion 50% (w/o)	73.6	23.1
Emulsion 70% (w/o)	95.3	30.2
Emulsion 75% (w/o)	30	5.2
Emulsion 80% (w/o)	29	4.8

**Figure 3** Relation between shear rate and viscosity for the untreated crude oil emulsions.**Figure 4** Relation between shear rate and viscosity for the untreated dry crude oil and the inverted emulsions.

4. Results and Discussion

4.1. Rheological Behavior of the Studied Emulsions

The experimental results revealed that these emulsions exhibit a shear thinning behavior “pseudoplastic” and followed a power law model. The studied crude oil emulsion system shows a dynamic yield value followed by a shear thinning behavior. This was clear in Figs. 1 and 2.

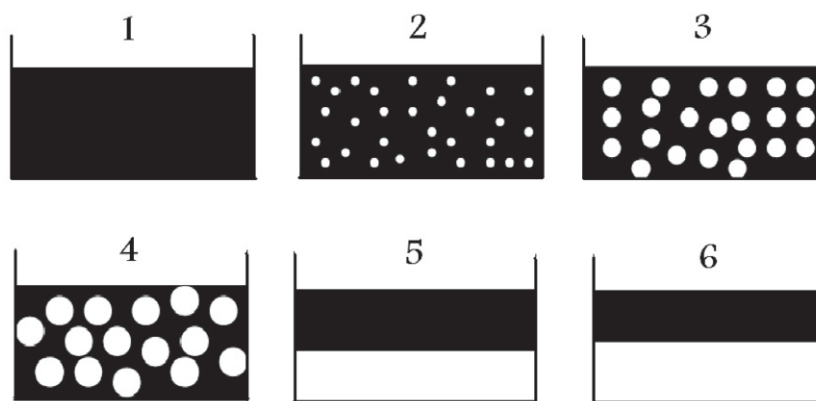
It was clear from Table 2 and Figs. 3 and 4 that, the viscosity of water in oil emulsion increases with increasing water cut before reaching what is called inversion point beyond which the continuous phase changes to water. The viscosity increased linearly with increasing the water cut due to the increase of hydrogen bonds, leading to decrease in the molecular distances of the emulsion system as well as an increase of resistance to flow. In other words, the increase in the emulsion viscosity was mainly due to the increase in the continuous phase viscosity. This behavior may be due to the increase of water content in the emulsion which leads to increase of the number and volume of dispersed water droplets in the continuous phase (oil). The viscosity of the emulsion increases with increasing the number and volume of water droplets. The increasing of viscosity is related to the internal pressure of water droplet P_1 which is accompanied by decreasing the outer pressure of continuous phase P_0 (oil) [23]. This behavior was clearly shown in Sketch 1.

The yield stress is defined as a limiting stress below which a sample behaves as a solid. At low stress, the elastic deformation takes place, which disappears when the applied stress is released. The relationship between the elastic deformation and the applied stress is linear. However, above the yield stress point, the applied stress leads to unlimited deformation which causes the sample to start flow [24]. It can be observed that the yield point which is required to start the flow decreases with decreasing water percent. The yield point of the dry crude oil reaches a value of 4.2 Pa at 60°C and it increases to 30.2 Pa when the water percentage reaches 70%. This was due to the increase of viscosity due to the increase of water volume. The Bingham yield value was again decreased to become near that of the dry crude oil as the inversion point was reached since the continuous phase became water.

From data in Table 2, it was found that, the dynamic “apparent” viscosities (η_{app}) were 50.6; 73.6 and 95.3 mPa s against 30%, 50% and 70% w/o emulsion, while the dynamic “apparent” viscosities (η_{app}) of dry crude oil was 26 mPa s. On the other hand, the Bingham yield value of dry crude oil (τ_B) was 4.1 Pa but it was 17.3, 23.0 and 30 against 30%, 50% and 70% w/o emulsion. These results are consistent with Sketch 1. At water content 75% and 80%, the emulsions were going to phase inversion point and then complete separation occurred. The apparent viscosities (η_{app}) and Bingham yield value (τ_B) for 75% and 80% w/o emulsions were (30 and 29 mPa s) and (5.2 and 4.8 Pa), respectively as shown in Figs. 7 and 8.

4.2. Demulsification Process

Demulsification involves two steps. First, there must be agglomeration or coagulation of droplets. Then, the agglomerated droplets must coalesce. Only after these two steps can



Where :

- 1) Dry Crude Oil
- 2) 30% Water $P_0 > P_i$
- 3) 50% Water $P_0 \geq P_i$
- 4) 70% Water $P_0 \leq P_i$
- 5) 75% Water $P_0 < P_i$ (Phase inversion)
- 6) 80% Water $P_0 < P_i$ (Phase inversion)

Where P_0 is the outer pressure of the continuous phase and

P_i is the internal pressure of the dispersed water droplet phase.

Sketch 1 Phase volume inversion.

complete phase separation occur. The only clear generalization regarding demulsifiers is that they have a high molecular weight (about the same as natural surfactants) and, when used as emulsifying agents, they tend to establish an emulsion opposite in type to that stabilized by natural surfactants [9].

The process of chemical demulsification of a water-in-crude oil emulsion involves the acceleration of the coalescence as well as the film rupture process [25].

When two droplets approach each other, the thickness of the interfacial film decreases as the liquid flows out of the film. This sets up an IFT gradient with high IFT inside the film and low IFT outside the film. The interfacial viscosity is very high because of the adsorbed natural surfactants (asphaltenes). Demulsifier molecules must have a higher surface activity than natural surfactants and, therefore, replace them at the interface. When demulsifier molecules are adsorbed in the spaces left by the natural surfactants, the IFT gradient is reversed, film drainage is enhanced and the interfacial viscosity is reduced. This causes the film to become very thin and collapse, resulting in droplet coalescence. Besides displacing the natural surfactants at the interface (breaking the rigid film), many chemical additives reduce or inhibit the rate of buildup of interfacial films. The best demulsifiers should possess both types of film modifying behavior: displacement of components in rigid interfacial films and inhibition of the formation of the rigid films [9].

The demulsifiers used in this study were ethoxylated/propoxylated poly nonyl phenol formaldehyde. They were oil soluble nonionic polymeric surfactants. Their interfacial properties were controlled by the relative amounts of the hydrophilic ethylene oxide attached to the poly nonyl phenol formaldehyde hydrophobic end of the demulsifier. Hence, the HLB term emerged. In general, natural emulsifiers that stabilize water-in-oil emulsion exhibit an HLB value in the range of 3 to 8.5. Thus, demulsifiers with higher HLB value will destabilize these emulsions. The demulsifiers act by total or partial dis-

placement of the indigenous stabilizing interfacial film components (polar materials) around the water droplets. This displacement also brings about a change in properties such as interfacial viscosity or elasticity of the protecting film, thus enhancing destabilization. These demulsifiers contain a phenol structure with an aromatic ring and polarity which have stronger affinity with asphaltene and resin. The investigated demulsifiers were very interfacially active and have relatively large interfacial molecular areas; they therefore affect spreading and migration of molecules to and from the interface.

D_5 with a high EO/PO/NPF molecular weight and HLB 9.1 was provided with a superior lipophilic property. Its molecular structure can be easily adsorbed on the interface of oil water through the oil phase, which peptizes the hydrophobic film surrounding the water droplets in the emulsion and weakens the rigidity of the interfacial film by a diffusion partitioning process. While, demulsifiers D_1 , D_2 , D_3 and D_4 formed multipoint adsorption on the interface of water oil emulsion, which affected the coalescence of the brine droplets, the dehydration rate was slower. This may be owing to the low hydrophobicity compared to D_5 since, the less hydrophobic molecule will not favor the crude oil hydrophobic system but will favor being on the interface.

Due to the previous discussion D_5 was selected to further investigate the rheological behaviour and the coalescence parameters with concentration of 100 ppm and at different w/o ratios, 30%, 50% and 70%.

4.3. Rheological Behavior in Relation to Demulsification Efficiency of the Studied Emulsions with D_5 Demulsifier

In the demulsification process, the bulk viscosity of the emulsion is one of the factors affecting the emulsion stability. Oil with high viscosity has the ability to hold up more and larger water droplets than oil with lower viscosity. The application of heat, the addition of diluents, or the addition of chemicals can

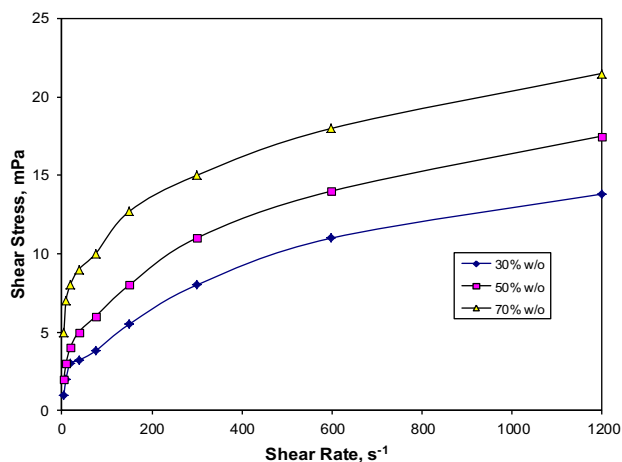


Figure 5 Relation between shear rate and shear stress for the treated crude oil emulsions with 100 ppm D_5 .

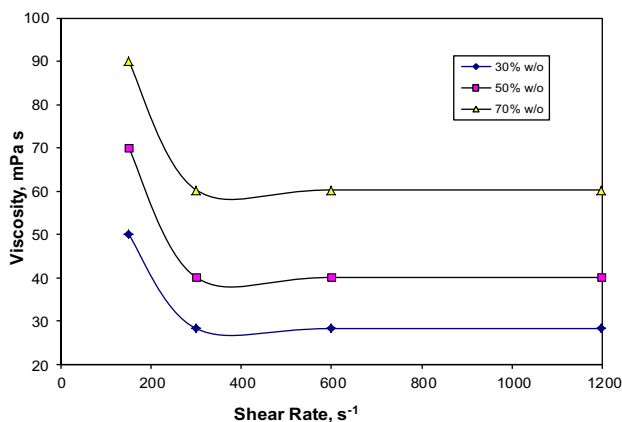


Figure 6 Relation between shear rate and viscosity for the treated crude oil emulsions with 100 ppm D_5 .

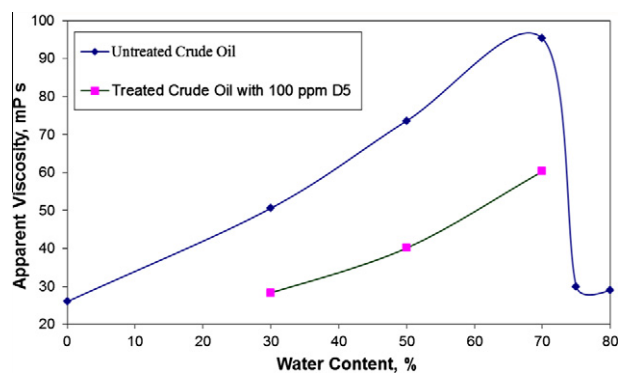


Figure 7 The relation between the apparent viscosity and water content of w/o emulsion.

reduce the viscosity of oil. Lowering the viscosity increases both the rate at which water droplets settle and the mobility of water droplets and thereby leads to collision, coalescence and a further increase in the rate of separation.

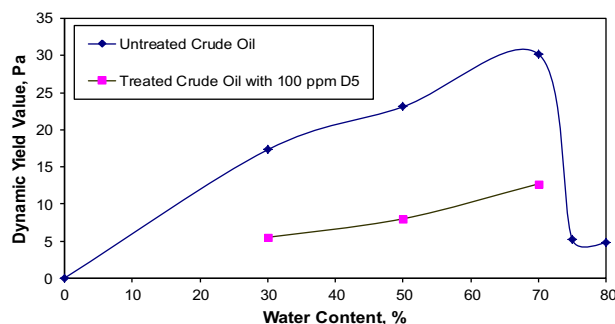


Figure 8 The relation between the dynamic yield value and water content of w/o emulsion.

The presence of surfactants in the continuous phase of emulsion can affect the rheology of emulsions in two ways: (a) it alters the rheology of the continuous phase; and (b) it can induce flocculation of droplets via depletion and bridging mechanisms [26].

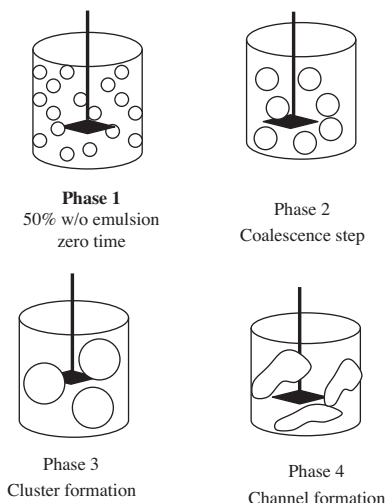
By comparing the data before and after demulsifier treatment, it was found that the demulsifier caused acute depression of the dynamic “apparent” viscosity η_{app} and the dynamic yield value τ_B at the same water content. This was clear in Figs. 1–8. Tables 2 and 3 indicate that the overall reduction in viscosity with surfactant was about 20–25 times smaller than those compared with the untreated crude oil emulsions and the overall reduction in the dynamic yield value was about 10–18 times smaller than those compared with the untreated crude oil emulsions. This may be attributed to the efficiency of the designed surfactant molecules in reducing the interfacial tension of the adsorption film in emulsion, making deformation of the dispersed phase easier.

From Table 3 and Figs. 1–8, it was also observed that, the viscosity of all the treated and untreated emulsion systems was generally higher than that of the dry crude oil. This is attributed to the impedance to laminar flow exerted by the dispersed water droplets [27].

The untreated emulsion takes a long time for separation, i.e. 30% water in oil emulsion took 35 days at 60°C to separate 20% of water content and. The treated 30% w/o emulsion using D_5 at 100 ppm at 60°C, exhibited 100% demulsification after 40 min only. From these data, it can be concluded that, the demulsifier molecule plays an axial role in decreasing the emulsion viscosity which then facilitates and accelerates the demulsification process. The mechanism of decreasing viscosity as a result of demulsifier treatment was shown in Sketch 2. Sketch 2 clears that, in phase 1, at zero time of treatment, the droplets size were nearly equal. By passing time, they coalesce to make the coalescence step as shown in phase 2. By dynamic rotation (using dynamic viscometer RV12 model), the dragging of water droplets occurred and it was accompanied by decreasing the dynamic viscosity and the yield value. This behavior continuously occurred until the formation of micro water clusters as shown in phase 3. Every two clusters or more combine to form a macro cluster which further grows and elongates to form channels as shown in phase 4. Due to this step, the viscosity of the phase dropped to be equal to that of the original dry crude oil and the complete demulsification process occurred.

Table 3 Rheological parameters for the freshly prepared crude oil emulsions treated with 100 ppm D_5 at 60°C.

W/Oil emulsion	Dynamic “apparent” viscosity, η_{app} (mPa s)	Dynamic yield value, τ_B (Pa)
Emulsion 30% (w/o)	28.3	5.5
Emulsion 50% (w/o)	40.1	8
Emulsion 70% (w/o)	60.3	12.7

**Sketch 2** Mechanism of decreasing viscosity as the result of demulsifier treatment.

4.4. Photography and Kinetics of the Demulsification Process

The demulsifier molecule develops high surface pressure (minimum interfacial tension) at crude oil /water interface [28]. It results in replacement of the rigid film of asphaltene and resins by a film, which is conducive to coalesce the water droplets. The coalescence of water droplets was studied for D_5 demulsifier as a representative sample at 100 ppm on the basis of emulsion volume (water: oil content). From Tables 4–7 and Figs. 9–13, one can observe that, the size of the water droplet increases with time and water content.

The increased water droplet radius leads to an increase in the coalescence rate. These data can be analyzed through the plotting of the specific surface area of the water droplet against time, as shown in Figs. 9–12. These plots can be conveniently split into two or three segments and each line of the straight segments is described by a first order rate equation as follows:

$$\log S = -kt + c$$

where s is the interfacial area per gram of the dispersed phase (cm^2/g); t is the time taken for separation; c is a constant and k

Table 4 Coalescence parameters for Water Droplets in 30% untreated w/o emulsion at 60°C.

Time, day	r^a (dm)	Water droplet volume (dm^3)	No. of water droplets	Surface area of water droplet (dm^2)	Total surface area of water droplet (dm^2)	S^b (cm^2/g)	Log(S)
0	0.000596	8.86354×10^{-10}	3.38465×10^{13}	4.46151×10^{-6}	151006711	5033.56	3.70187
5	0.00086	2.61678×10^{-9}	1.14645×10^{13}	9.18167×10^{-6}	105263158	3508.77	3.54516
10	0.00092	3.30282×10^{-9}	9.08316×10^{12}	1.07234×10^{-5}	97402597.4	3246.75	3.51145
15	0.00095	3.55564×10^{-9}	8.43729×10^{12}	1.12639×10^{-5}	95036958.8	3167.9	3.50077
20	0.00096	3.75059×10^{-9}	7.99874×10^{12}	1.1672×10^{-5}	93360995.9	3112.03	3.49304
25	0.00103	4.54829×10^{-9}	6.59589×10^{12}	1.32732×10^{-5}	87548638.1	2918.29	3.46513
30	0.00126	8.45492×10^{-9}	3.5482×10^{12}	2.0067×10^{-5}	71202531.6	2373.40	3.37537
35	0.00159	1.67973×10^{-9}	1.786×10^{12}	3.1713×10^{-5}	56639395.8	1887.98	3.27602

^a r : Radius of water droplet.

^b S : Specific surface area of the dispersed water phase = area of the dispersed phase/mass of the dispersed phase.

Table 5 Coalescence parameters for water droplets in 30% w/o emulsion treated by 100 ppm D_5 at 60°C.

Time (min)	r (dm)	Water droplet volume (dm^3)	No. of water droplets	Surface area of water droplet (dm^2)	Total surface area of water droplet (dm^2)	S^* (cm^2/g)	Log(S)
0	0.000596	8.86354×10^{-10}	3.38465×10^{13}	4.46151×10^{-6}	151006711	5033.56	3.70187
10	0.00082	2.33382×10^{-9}	1.28544×10^{13}	8.50725×10^{-6}	109356015	3645.2	3.56172
20	0.00124	8.02109×10^{-9}	3.74014×10^{12}	1.93746×10^{-5}	72463768.1	2415.46	3.383
30	0.00131	9.43358×10^{-9}	3.18013×10^{12}	2.15871×10^{-5}	68649885.6	2288.33	3.35952
40	0.00142	1.19623×10^{-8}	2.50787×10^{12}	2.52903×10^{-5}	63424947.1	2114.16	3.32514
50	0.00369	2.10695×10^{-7}	1.42386×10^{11}	17.1204×10^{-5}	24377031.4	812.568	2.90986
60	0.00624	1.01773×10^{-6}	2.947748×10^{10}	48.9213×10^{-5}	14420765.9	480.692	2.68187

* Specific surface area of the dispersed water phase = area of the dispersed phase/mass of the dispersed phase.

Table 6 Coalescence parameters for water droplets in 50% w/o emulsion treated by 100 ppm D₅ at 60°C.

Time (min)	r (dm)	Water droplet volume (dm ³)	No. of water droplets	Surface area of water droplet (dm ²)	Total surface area of water droplet (dm ²)	S* (cm ² /g)	Log(S)
0	0.000596	8.86354 × 10 ⁻¹⁰	5.64109 × 10 ¹³	4.46151 × 10 ⁻⁶	251677852	5033.557	3.701875
3	0.001185	6.96664 × 10 ⁻⁹	7.17706 × 10 ¹²	1.76371 × 10 ⁻⁵	126582278	2531.646	3.403403
6	0.001779	2.3572 × 10 ⁻⁸	2.12116 × 10 ¹²	3.97504 × 10 ⁻⁵	84317032	1686.341	3.226945
9	0.002174	4.30177 × 10 ⁻⁸	1.16231 × 10 ¹²	5.9362 × 10 ⁻⁵	68997240	1379.945	3.139862
12	0.002765	8.85021 × 10 ⁻⁸	5.64958 × 10 ¹¹	9.6024 × 10 ⁻⁵	54249548	1084.991	3.035426
15	0.003162	1.32359 × 10 ⁻⁸	3.7776 × 10 ¹¹	12.5578 × 10 ⁻⁵	47438330	948.7666	2.977159
18	0.004887	4.88647 × 10 ⁻⁷	1.02323 × 10 ¹¹	29.9968 × 10 ⁻⁵	30693677	613.8735	2.788079
21	0.006075	9.38658 × 10 ⁻⁷	5.32676 × 10 ¹⁰	46.3535 × 10 ⁻⁵	24691358	493.8272	2.693575

* Specific surface area of the dispersed water phase = area of the dispersed phase/mass of the dispersed phase.

Table 7 Coalescence parameters for water droplets in 70% w/o emulsion treated by 100 ppm D₅ at 60°C.

Time, min	r (dm)	Water droplet volume (dm ³)	No. of water droplets	Surface area of water droplet (dm ²)	Total surface area of water droplet (dm ²)	S* (cm ² /g)	Log(S)
0	0.000596	8.86354 × 10 ⁻¹⁰	7.89752 × 10 ¹³	4.46151 × 10 ⁻⁶	352348993	5033.557	3.701875
3	0.001192	7.0908 × 10 ⁻⁹	9.8719 × 10 ¹²	1.7846 × 10 ⁻⁵	176174497	2516.821	3.486782
6	0.001531	7.3077 × 10 ⁻⁸	9.579 × 10 ¹¹	8.4514 × 10 ⁻⁵	80956052	1156.534	3.292146
9	0.006025	9.15671 × 10 ⁻⁷	7.64467 × 10 ¹⁰	4.55936 × 10 ⁻⁴	34854772	497.9253	2.697164
12	0.008392	2.47437 × 10 ⁻⁶	2.829 × 10 ¹⁰	8.84546 × 10 ⁻⁴	25023832	357.4833	2.553256
15	0.010388	4.69315 × 10 ⁻⁶	14915363174	0.001355356	20215633	288.7948	2.460589

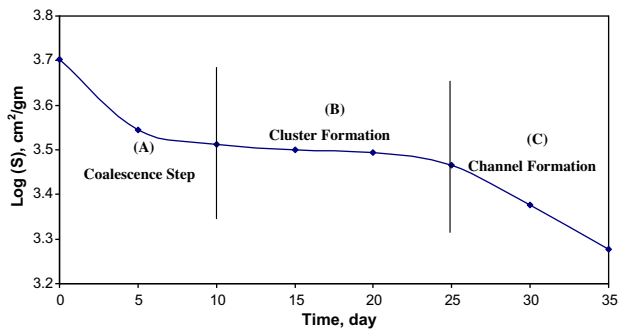


Figure 9 Time taken for demulsification process against log(S) for the untreated 30% w/o emulsion at 60 °C.

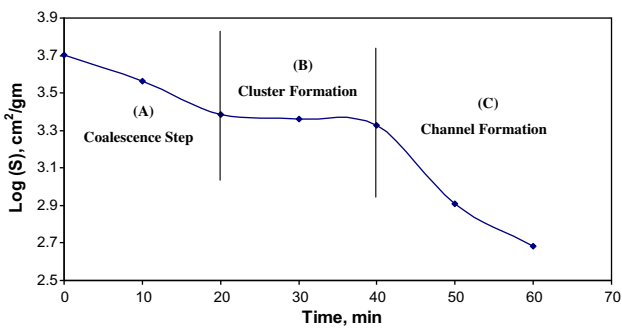


Figure 10 Time taken for demulsification process against log(S) for the treated 30% w/o emulsion with 100 ppm D₅ at 60 °C.

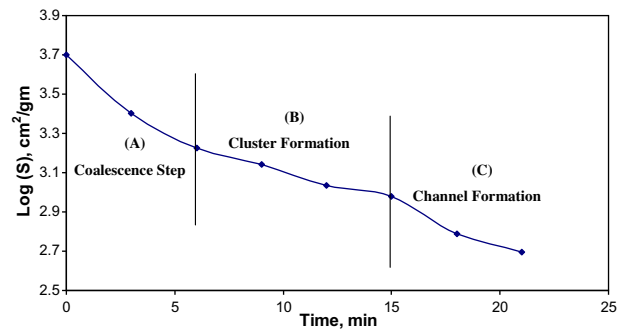


Figure 11 Time taken for demulsification process against log(S) for the treated 50% w/o emulsion with 100 ppm D₅ at 60 °C.

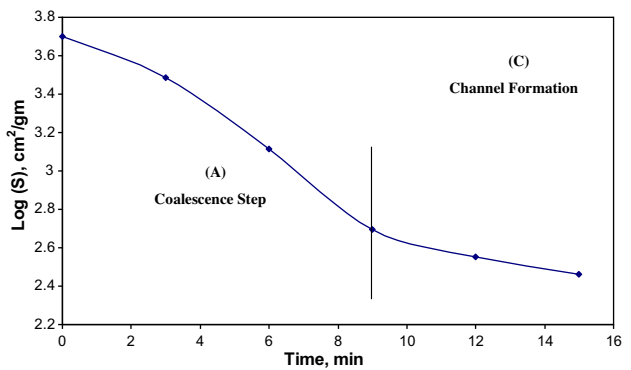


Figure 12 Time taken for demulsification process against log(S) for the treated 70% w/o emulsion with 100 ppm D₅ at 60 °C.

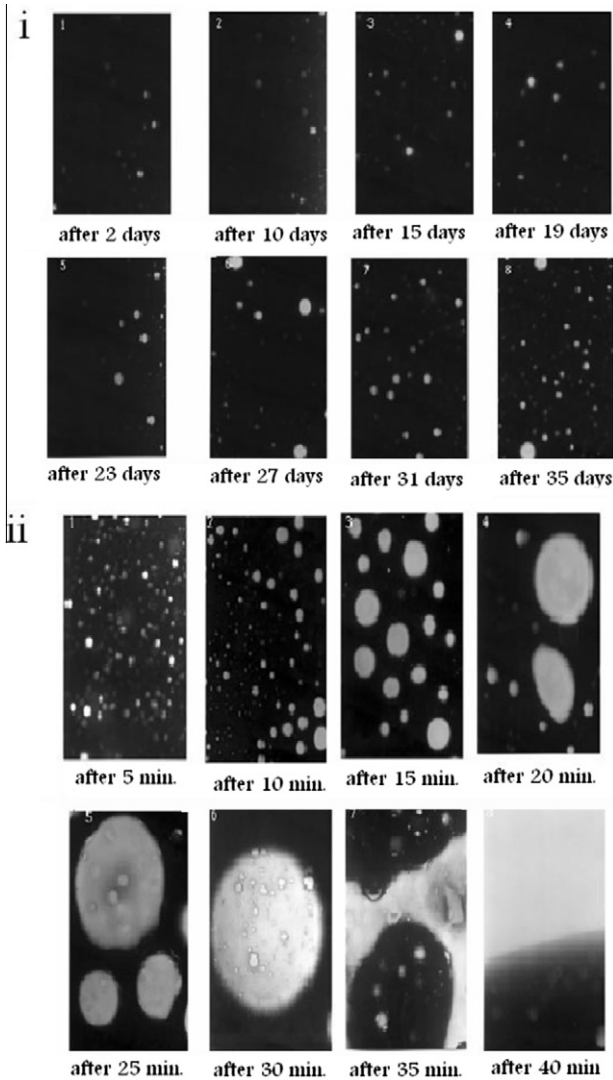


Figure 13 Photos of W/O untreated emulsion (I) and emulsion treated with D_5 . (1) Dry crude oil, (2) 30% water $P_0 > P_i$, (3) 50% water $P_0 \geq P_i$, (4) 70% water $P_0 \leq P_i$, (5) 75% water $P_0 < P_i$ (phase inversion), (6) 80% water $P_0 < P_i$ (phase inversion), where P_0 is the outer pressure of the continuous phase and P_i is the internal pressure of the dispersed water droplet phase.

is the slope of each line and is measured by the coalescence rate during that period:

$$k = d \log s / dt$$

The water droplet diameter of the untreated crude oil emulsion (30% w/o) increases with increasing time by days as shown in Table 5 and Fig. 8. The water droplet grew slowly up to 25 days, and then it slightly increased till 35 days at which 20% of the water content separated. This may be due to the mechanical stability character of asphaltene and resins on the interface film which impede the drainage of two neighbor water droplets to coalesce. When the 30% w/o emulsion was treated by 100 ppm of D_5 , the demulsification time was taken by minutes as clear in Table 5 and Fig. 10. The diameter of water droplets increased slowly from 0 time up to 60 min (at which 73% of water was separated), then the radius increased

Table 8 Coalescence rate constant of water droplets for the dry crude oil and for 30%, 50% and 70% w/o emulsions treated by 100 ppm of D_5 60°C.

Sample	Coalescence rate constant (k) ^a		
	(A) Coalescence step	(B) Cluster formation	(C) Channel formation
Control sample	1.3×10^{-5}	2.1×10^{-6}	1.4×10^{-5}
Emulsion 30%	1.6×10^{-2}	2.8×10^{-2}	3.2×10^{-2}
Emulsion 50%	5.9×10^{-2}	2.1×10^{-2}	3.5×10^{-2}
Emulsion 70%	1.1×10^{-1}		3.95×10^{-2}

^a k is ($\text{cm}^2/(\text{g day})$) for the dry crude oil and ($k, \text{cm}^2/(\text{g min})$) for the treated crude oil.

rapidly and after 85 min, all water in the emulsion separated. This means that, the complete deployment of the demulsifier molecules on the interface reached the maximum at 60 min. The tension of the interface became very low, at which the interface rupture and the coalescence increased rapidly (Table 5 and Fig. 10). The same behavior was observed for the 50% and 70% w/o emulsions, which were also, treated with the same demulsifier (D_5). This was clear in Tables 6 and 7 and Figs. 11 and 12. In these figures, a complete deployment of the demulsifier molecules was obtained within 28 and 15 min, respectively for 50% and 70% water content. From the above-mentioned results, it can be concluded that, the increase of water content of an emulsion increases the tendency of water droplets to coalesce.

By analyzing the data in Tables 4–7 and the illustrations in Figs. 9–12, we have found that the demulsification process can be divided into two or three main segments. The segment (A) points to the rate of coalescence formation, but segment (B) indicates the rate of cluster formation, while segment (C) denotes to water channel formation. At the end of this step complete water separation was pronounced. The values of coalescence rate (k) for the untreated 30% w/o emulsion, treated 30%, 50% and 70% w/o emulsions by D_5 were listed in Table 8. The control sample exhibited a very slow rate of coalescence (1.3×10^{-5}), cluster formation (2.1×10^{-6}) and channel formation (1.4×10^{-5}) after 25 days incubation period at 60°C. In the same sample which was treated by 100 ppm D_5 demulsifier (30% and 50% water content), the rate of coalescence (k) increased in order of 10^{-2} , while the rate of coalescence of 70% w/o emulsion was very rapid (10^{-1}). From the curve in Fig. 12, there were two segments, the first denotes the coalescence and cluster formation ($k = 1.1 \times 10^{-1}$) and the second segment denotes the channels formation ($k = 3.95 \times 10^{-1}$). In this instance, the coalescence and clustering were mixed in one fast step.

5. Conclusion

Results from this study have shown that:

- The viscosity of emulsions increases as the water cut increase.
- The flow behaviour of the dry crude oil exhibits a dynamic yield stress of 4.2 Pa, whereas in the case of treated 30% w/o emulsion, the yield stress was 17.3.

- The apparent viscosity for w/o emulsion increases as the water cut increase till the inversion point was reached where the water becomes the continuous phase and the viscosity decrease to become near that of the dry crude oil.
- The demulsifier usually has a higher surface activity than these natural emulsifiers, so it can displace them and weaken the film, thereby promoting the droplets of brine to coalesce when they contact each other.
- The coalescence rate increases with increasing drop size, as observed experimentally.

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