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Effects of Interfacial Tension Alteration on the Destabilization of Water-Oil Emulsions

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http://dx.doi.org/10.5772/intechopen.74769

Abstract

Resolution of water-in-oil emulsion is a major crude oil processing requirement in oil industry. To improve the quality of the oil and fulfill regulatory requirements numerous chemical demulsifiers of varying efficiencies and effectiveness have been developed over the years. In this study, we have investigated the effects of water content, temperature, and different concentrations of Sodium Methyl Ester Sulfonate (SMES) on emulsion viscosity profiles and stability under distinct levels of salinities. The water content was measured with the American Standard Testing Method ASTM D4928 while SARA analysis was conducted using the ASTM D3279 and ASTM D6591 methods. The density and viscosity of the samples were measured following the ASTM D5002 and ASTM D445 techniques respectively while the emulsion stability was evaluated based on the rate of sedimentation, flocculation and coalescence from Turbiscan classic MA 2000. Refractometer with the aid of a light-emitting diode, a sapphire prism and a high-resolution optical sensor was used to measure the refractive index while interfacial tension was measured with spinning drop tensiometer. The emulsion samples were investigated at 25, 50 and 75°C. Analyses show that the interactions of the constituents of a crude oil system, the produced water system and the emulsion system play major roles in the characterization of water-in-crude oil emulsions. Hence, the stability of water-in-crude oil emulsions is related to the viscous force presented by the continuous phase, water cut and salinity.

Keywords: water-in-oil emulsion, sodium methyl ester sulfonate (*SMES*), demulsifier, Turbiscan MA 2000, ASTM D4928, ASTM D5002, ASTM D6591



1. Introduction

Crude oil is mostly produced as water-in-crude oil emulsion, carrying other dissolved and suspended organic and inorganic substances [1]. It is necessary to dehydrate crude oil before it is transported for refining [2, 3]. Crude oil emulsions are undesirable and can occur in nearly all stages of crude oil production, transport and refining [4, 5]. The emulsified water can occupy significant portions in the crude oil processing facilities, thereby increasing both capital and operating costs. Also, emulsions can lead to various changes in the characteristics and physical properties of the crude oils [6]. Dissolved and suspended materials such as salts, impurities, and finely divided solids, accompanied with produced water can lead to various problems during production and transportation of crude oils. These problems include pumping difficulty due to increased crude oil viscosity, corrosion of pipes and pumps, and poisoning of refinery catalysts [5, 7]. Also, sediments or solids in crude oil can cause equipment damaging, plugging, abrasion, erosion and residual product contamination [7]. Formation damage has also been reportedly caused by emulsions [8].

Pressure drops in flow lines can be high and sometimes cause trips and upsets of wet-crude oil handling equipment due to the presence of emulsified water, which may require an increase in the use of demulsifiers [4]. Unresolved emulsions can enter the oilfield environment, especially on offshore fields causing damage to aquatic lives. Besides, inefficiently dehydrated oil leads to revenue loss due to reduction in the quality of crude oil. Meanwhile, destabilizing water-in-crude oil emulsions remains a continuous challenge in the oil and gas industry due to the encapsulation of water droplets by rigid interfacial films. Understanding the materials responsible for the formation and stabilization of these emulsions is a key step towards efficient demulsification process [9, 10]. Therefore, the effect of water cut and salinity on emulsion resolution as the effect of temperature on interfacial film and the eventual droplet coalescence require detailed investigation. We hypothesize that the deformed interfacial film due to increase in temperature and presence of surfactant is regenerative thereby reducing the possibility of droplets coalescence and maintaining emulsion stability.

2. Emulsion formation and stabilization

Water-in-crude oil emulsions are formed due to high shear stresses at the flow restrictions such as choke valves and the wellhead during transportation of crude oil coupled with produced water [11, 12]. Water disperses in the crude oil forming droplets stabilized by the natural surfactants present in the later [13, 14]. Emulsion droplets undergo spherical to ellipsoidal shape deformation and subsequent break up to smaller drops during flow as shown in **Figure 1** [15, 16]. Droplet deformation is often resisted by the interfacial tension as determined by the Laplace pressure [17]. Thus, the following expression, that is, the capillary number (Ca) is used to determine the morphology of a droplet [15]:

$$Ca = \frac{n_o \dot{\gamma}}{\sigma_{/R}} \tag{1}$$

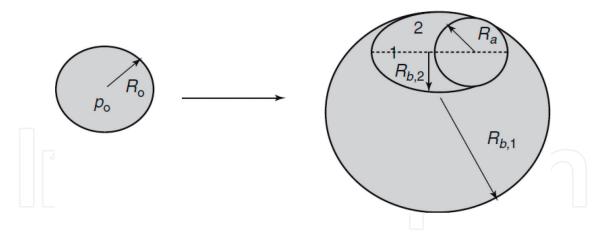


Figure 1. Illustration of increase in Laplace pressure when a spherical drop is deformed to a prolate ellipsoid [15].

where η_o is the viscosity of the medium, $\dot{\gamma}$ is the shear rate, σ is the interfacial tension, and R is the droplet radius.

In **Figure 1**, the radius of curvature (Ra) exists only near 1. However, two radii ($R_{b,1}$ and $R_{b,2}$) of curvature are present near 2. Therefore, smaller droplets require more stress to deform. Generally, the surrounding liquid transmits the needed stress through agitation. The magnitude of the transmitted stress depends on the level of agitation. Vigorous agitation will transmit high stress which will supply more energy to produce smaller drops. Emulsion formation is highly affected by the presence of surfactants in the system. Surfactants lower the interfacial tension and therefore the internal pressure leading to reduced stress required to break up a droplet. Surfactants also prevent new droplets from coalescing. Emulsification involves various processes such as droplet deformation, surfactant adsorption and droplet collision. These processes are illustrated in **Figure 2**. The thin lines depict the droplets while heavy lines and dots depict the surfactants.

Developing techniques for preventing and destabilizing crude oil emulsions requires adequate knowledge of the major properties of petroleum and the dispersed water which dictate the ultimate stability of the emulsion; the functional groups in the stabilizers which contribute to their interfacial activity; the interactions between the interfacially active components which are responsible for the stability of the emulsion [18, 19]. Asphaltenes have been reported to form aggregates which have an adsorbed covering sheath of aromatic resins as a stabilizing layer around dispersed water droplets in crude oil [11, 20–22].

Droplets in crude oil emulsions can be compared to colloidal particles in dispersion that frequently collide with each other which show that they are in Brownian motion. Hence, these droplets interact during such collision and this determines the stability of the system. The interactions can be in two forms which are attractive and repulsive. The droplets will coalesce and adhere together when the electrostatic dipole attraction between the water and oil molecules is high; however, the emulsion becomes stable if like charges exist as neighbors and the repulsive forces between the ions dominates [23]. Van der Waals forces constitute the main source of attraction between droplets or particles in colloidal systems since the particles are similar. Therefore, an emulsion can be said to be stable only if sufficient repulsion counteracts the attractive force between the droplets. The magnitude and range of only the van der Waals London

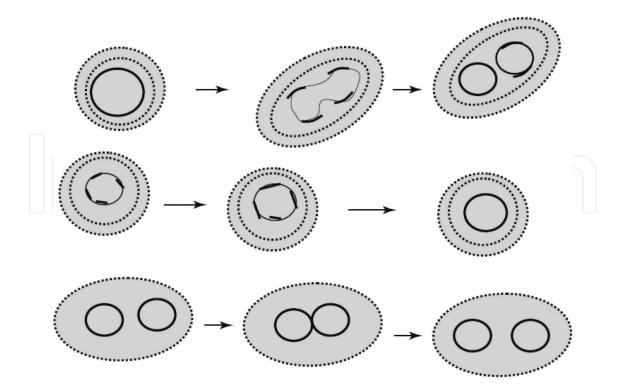


Figure 2. Schematic representation of the various processes occurring during emulsion formation [15].

(VDWL) attraction are the main determinants of how stable emulsion droplets can be due to the contribution of London forces to long-range attractions between emulsion droplets [24–26].

Coalescence occurs in three steps: (1) approach of the droplets through the continuous phase; (2) deformation of the droplets to form a thin film between them; and (3) thinning of this film to a critical thickness, below which the droplets coalesce [27, 28]. The suspension of droplets in a non-flowing continuous phase can be described as unsteady moving body in stationary fluid. The hydrodynamics of such droplets involves at least four forces: viscous force due to the viscosity of the continuous phase which describes the amount of friction between nearby regions of the fluid moving at different velocities; force of gravity which is a function of the composition of the droplets, force of attraction between the droplets (Van der Waal forces); and shearing forces which is the resultant of all the three forces [29]. Consequently, the hydrodynamics of emulsions lead to at least four mechanisms by which emulsions are stabilized. They are: Electrostatic repulsion; Steric repulsion; Thin film stabilization and; The Marangoni-Gibbs effect. In an emulsion stabilized with a surfactant, the homogeneous distribution of surfactant molecules on the surfaces of the drops is perturbed by the drainage of the liquid in the interfacial film [30]. The resulting non-homogeneous distribution of adsorbed surfactant molecules leads to the appearance of interfacial tension gradients. This non-equilibrium situation tends to be compensated by the migration of the surfactant molecules towards the interior of the interfacial film. This motion drags part of the liquid of the interface inside the interfacial film, producing a stabilizing effect that competes with the Van der Waals attraction between the drops surfaces. This work investigates the effect of interfacial tension alteration on the resolution of water-oil emulsions to pave way for formulation of environmentally friendly chemical demulsifiers.

3. Methodology

3.1. Material

The crude oil samples used for this research were obtained from PETRONAS, Melaka. The properties of the crude oil were determined according to standard procedures. Sodium Methyl Ester Sulfonate (*SMES*) is anionic surfactant produced by oil and fat obtained from green plants and animals. It has several properties which include good wetting ability, hard water resistance and softening, good solubility and highly degradable. It has also been used as an emulsifier with little stimulation to skin but high frothing ability. *SMES* has been synthesized from vegetable oil such as palm and jatropha oil [31]. Its toxicity and biodegradability have been tested [32, 33] and found to be comparatively better than most available anionic surfactants. Thus, *SMES* is well suited for environmentally friendly applications.

3.2. Water content measurement

The water content of the crude oil was determined by standard test method. This measurement was necessary to ascertain the dryness of the crude oil and be able to correctly analyze any effects of water content on the stability and destabilization of its emulsions. Volumetric Karl Fischer titration (ASTM D4928) was used since water content in dry crude oil specification falls between 0.1 and 100%. The Karl Fischer (K-F) method is based on sulfur dioxide oxidation reaction by iodine in a methanoic hydroxide solution.

The two reactions involved in K-F titration are:

1. Where an alcohol (usually methanol or ethanol), sulfur dioxide (SO₂) and a base (RN) react to form an alkylsulfite intermediate:

$$CH_3OH + SO_2 + RN \xrightarrow{yields} [RNH]SO_3CH_3$$
 (2)

2. Where the alkylsulfite reacts with iodine (I_2) and the water from the sample.

$$[RNH]SO_3CH_3 + I_2 + H_2O + 2RN \xrightarrow{yields} [RNH]SO_4CH_3 + 2[RNH]I$$
 (3)

Since water and I_2 are consumed in equimolar amounts in reaction 2, if the amount of I_2 consumed is known, the amount of water that was present in the sample would be known.

3.3. SARA analysis

SARA analysis is important to determine the tendency of the crude oil to precipitate asphaltenes by calculating the asphaltene to resin (A/R) ratio, colloidal instability index (CII) and refractive index (RI) of the crude oil. The stability of resulting emulsions can also be estimated by applying the correlations among the various components of the crude oil. These determinants are necessary to study the behavior of the interfacial film between the crude oil and water droplets.

Asphaltene was removed by diluting the crude oil with n-heptane using a standard method prescribed in ASTM D3279 since asphaltenes are insoluble in liquid paraffins. The remaining components, saturates, aromatics and resins collectively known as maltenes are separated by polarities using ASTM D6591. The maltene with heptane was pumped through a chromatographic packed column of Agilent 1260 Infinity equipment for separation. The column contains silica and amine which have more affinity to more polar components. Resins which are the most polar of the maltenes are adsorbed on the column earlier thereby limiting heptane from pushing them through. Both the saturates and aromatics are pushed through the column by heptane but saturates would flow pass quicker due to their less polar nature. Thus, saturates are detected by the Refractive Index Detector (RID) of the equipment at a shorter time (retention time) than the aromatics which are more polar. The eluent (heptane) was replaced with Dichloromethane (DCM) to push out the resins using back flush since the resins are stuck near the top end of the column. Ultraviolet (UV) signals also record retention time for UV active components. In this case, only the aromatics are UV active and UV will only confirm the results of RID.

3.4. Density measurement

Density is a fundamental physical property that can be used in conjunction with other properties to characterize crude oil sand other substances present in crude oil emulsions. It is useful when the hydrodynamics of emulsion droplets are discussed and can also help to investigate impact of particle collisions. Digital density analyzer was used to measure the densities in this study according to ASTM D5002. The density is measured with a U-shaped hollow glass tube, which is put into oscillation. The oscillation frequency of the tube filled with the sample is measured. The higher weight of the sample the lower the frequency. The density is calculated with the measured frequency. The density values of the crude oil, castor oil, fresh water, and two brine solutions (20 and 40 g/L) were obtained at room temperature, 50 and 70°C. Viscous force is an important phenomenon that prevents emulsion droplets from falling free when suspended in fluids. Standard method ASTM D445 was used to measure the viscosity of the crude oil. The EV 1000 instrument was used and it is based on a simple and reliable electromagnetic concept. Two coils move the piston back and forth magnetically at a constant force which could be likened to the movement of emulsion droplets under hydrodynamic and gravitational forces.

3.5. Refractive index and interfacial tension measurements

Dissolution of salts (e.g. NaCl) in water involves a process whereby Na $^+$ and Cl $^-$ break free from the crystal-lattice structure of the solid. This process can be captured by examining the optical density of the aqueous solution. The index of refraction value of a material is a number that indicates the number of times slower that a light wave would be in that material than it is in a vacuum. A vacuum is given an n value of 1.0000. The n values of other materials are calculated from Eq. (4):

$$n_{material} = \frac{3.00 * 10^8 \, m/s}{V_{material}} \tag{4}$$

Refractometer with the aid of a light-emitting diode, a sapphire prism and a high-resolution optical sensor is used to measure the refractive index. The sample is put on the prism and

the measurement started. From a certain angle of incidence—the so-called critical angle—the ray no longer penetrates the sample but is fully reflected from its surface and is detected by the optical sensor. The refractive index is calculated from this critical angle. Emulsification is affected by interfacial tension and the separating potential between two or more phases. Interfacial tension is the work done to expand the interface between two non-mixing adjacent phases. At the separating boundary, the sum of cohesive forces is greater than the adhesive forces between the two phases. Accordingly, molecules at the interface have fewer attractive interacting partners than in the bulk phase. The phases therefore form the smallest possible interface without the action of external force.

Work must be done to expand the interface. Hence, cohesive and adhesive forces are critical to interfacial tension. The interfacial tension (IFT) of the crude oil in fresh water and the prepared brine solutions was determined using the spinning drop tensiometer. A horizontal capillary filled with a bulk phase and a drop phase is set in rotation. The diameter of the drop which is elongated by centrifugal force correlates with the interfacial tension. When a heavy bulk phase and a light drop phase are situated in a horizontal, rotating capillary, the drop radius perpendicular to the axis of rotation depends on the interfacial tension γ between the phases, the angular frequency ω of the rotation and the density difference $\Delta \varrho$. Thus, with a given speed of rotation and with known densities of the two phases, the interfacial tension can be calculated from the measured drop diameter d (=2r) in accordance with Vonnegut's equation:

$$\gamma = \frac{r^3 \cdot \omega^2 \cdot \Delta \rho}{4} \tag{5}$$

3.6. Emulsion samples preparation

The kinetics of emulsion stability involves considerations on droplets interactions in the crude oil. The intra-actions within the droplets that are responsible for the droplets' momentum are also important. Thus, fresh water and brine solution formed droplets were examined in this study. Water-in-oil emulsions were prepared by mixing crude oil with fresh water and synthetic brine solutions in turn (volume/volume). Two brine solutions were prepared by diluting 20 grams and 40 grams of NaCl in a liter of distilled water to make 20 and 40 g/L aqueous solutions respectively. 20, 40 and 50 ml of fresh water were mixed with 80, 60 and 50 ml of crude oil respectively to make 20, 40 and 50% fresh water-in-crude oil emulsions. Similarly, 20, 40 and 50% brine-in-crude oil emulsions were prepared. These water cuts were chosen to capture the significance of droplets interactions in the crude oil since lower water cuts might defy resolution with the about-to-be tested demulsifiers. The two phases were homogenized using Hamilton constant mixer. No external emulsifier was used since the aim was to achieve natural emulsifier-stabilized emulsions. Agitation was allowed to take place for 5 minutes to achieve stable emulsions. About 100 ml of emulsion was prepared at a time for uniformity and repeatability purpose.

3.7. Emulsion stability measurement

Measuring the ability of a solution to conduct electric current is a crucial step in determining the presence of interfacial films especially when the phases involved have non-similar electrical conductivity values. Sulaimon and Bamikole [34] used the Turbiscan classic MA 2000 to

investigate the effect of stability on the aging of water-in-oil (w/o) emulsions for proper characterization and resolution. They concluded that the Turbiscan is a robust, accurate and automatic multiple light scattering technique for characterizing w/o emulsion stability. Through this method, the concentration of ions in brine solutions can be determined. The presence of interfacial films can easily be noted since crude oil does not conduct electricity. The effect of temperature on the conductivity of materials is significant. Conductivity measurements are taken at 25°C since the ionic activity increases with temperature. The electrical conductivity of the fresh water, two brine solutions, crude oil and the resulting emulsions were measured an electrical conductivity meter.

Measuring cylinders, 10 ml, were filled with emulsions and incubated in an oven at 25, 50 and 70°C for 5 days. Thereafter, the cylinders were removed, and the amount of separated water was recorded. This test was carried out using emulsions with all salinities and water cuts. Turbiscan classic MA 2000 was used to monitor the rate of sedimentation, flocculation and coalescence to determine the degree of stability of each emulsion composition formed. The testing tube was filled with 10 ml of emulsion and 10 acquisitions were made at room temperature. The autoscan was set to obtain a scan acquisition at every 2 minutes. Subsequently, the emulsions were heated to 50 and 70°C for 6 hours in a water bath and 10 acquisitions were also made at 2 minutes interval for comparison. Understanding the impact of collisions among emulsion droplets is important to study the destabilization of crude oil emulsions. Rotational viscometer was used to measure the deformation of the emulsion droplets under shearing forces. Rotational rheometry is most suited to very low shear rate / viscosity measurement, determining changes in structural properties via low amplitude and controlled strain oscillatory measurements. Double-gap plate was used since it has highest sensitivity for low viscous samples, lower inertia compared to other plates, nearly no impact on loading errors. The rheology was measured at 25, 50 and 70°C and the shear rate was varied from 1 to 1000 per second.

4. Results and discussion

4.1. Density and SARA analysis

The crude oil originally contained 0.2% water. This shows that the crude oil was within the specified limit of BS&W. Removing this intrinsic water content is difficult and may not be achieved with current dehydration techniques. Then, the crude oil (CO) was considered dry. The crude oil was then mixed with fresh water (SAL-0), 20,000 ppm aqueous solution of NaCl (SAL-1) and 40,000 ppm aqueous solution of NaCl (SAL-2) for this work. There exists a proportionate increase in density according to salt content in water as shown in **Table 1** since total pressure corresponds to the amount or number of particles present in the system. Solvation of NaCl crystal in water produced Na⁺ and Cl⁻(ions) surrounded by water molecules and the ions gained energy to move more freely. An increase in the number of salt particles led to more frequent collisions in the system. Obviously, fresh water has the lowest density while 40,000 ppm brine has the highest density. This observation can be explained by the amount of the average kinetic energy possessed by the particles in the liquids [35]. The particles in the crude oil gained more kinetic energy to move faster since there is no difficult barrier to

S/N	Temperature (°C)	Density (g/cc)				
		SAL-0	SAL-1	SAL-2	CRO	
1	25	0.99704	1.0138	1.0258	0.9079	
2	50	0.98803	1.0048	1.0163	0.8909	
3	70	0.97776	0.9972	1.0083	0.8767	

Table 1. Sample density.

overcome to do so. Perhaps, all the particles in the crude oil responded uniformly to temperature change. Dissociation of sodium chloride in water leads to encapsulation of Na⁺ and Cl⁻in water molecules. Water molecules possess low kinetic energy and therefore prevented the salt ions from fully responding to temperature change. The ions, therefore, assumed the kinetic energy of the water molecules.

There was a corresponding decrease in viscosity with temperature due to easier movement of particles at elevated temperature. At low temperature, the particles are closely-packed, and their movement is restricted. Some components of the crude oil such as waxes are dissolved back into the bulk crude oil at higher temperature than their cloud points and thereby leaving other components which are resistant to heat such as asphaltene particles to move more freely. This phenomenon brings about easy flow of fluid and any other particle such as water droplets, introduced into the crude oil would move more freely and interact with the asphaltene particles. The SARA content of the crude oil is presented in **Table 2**. The crude oil contained 2.09% asphaltenes and 26.3% resins.

4.2. Effects of SMES on the intermolecular interactions and emulsion stability

Interfacial tension (IFT) of the crude oils SAL-0, SAL-1 and SAL-2 are presented in **Table 3**. Obviously, IFT decreases with temperature and it is highest in SAL-0 and lowest in SAL-1. Theoretically, IFT is a function of pressure, temperature and composition. The pressure exerted on the interfacial films was highest in SAL-1 and lowest in SAL-0 due to salt particles solvation forces acting in the aqueous solutions. The pressure is reduced in SAL-2 due to less collision impacts of the particles caused by incomplete solvation. Hence, the work required to break the interfacial films encapsulating resulting emulsion droplets would be highest for SAL-0 and least for SAL-1 droplets.

Component	Amount (%)
Asphaltene	2.09
Resin	26.30
Saturate	53.21
Aromatics	18.40

Table 2. SARA content of the crude oil.

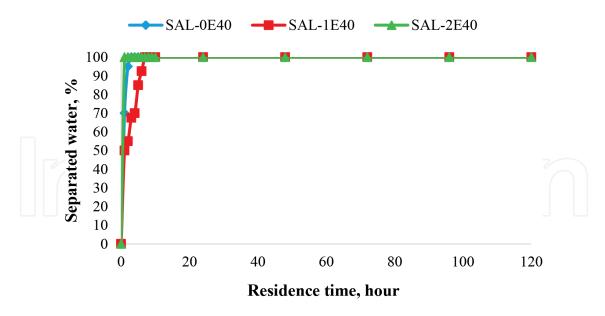


Figure 18. Phase separation at 150 g/L of SMES in emulsions with 40% water cut.

the repulsion presented by the ions present in the dispersed phase. Full phase separation occurred within 1 hour, 3 hours and 8 hours in SAL-2E40, SAL-0E40 and SAL-1E40 respectively. Subsequent increase in dosage to 250,000 ppm *SMES* led to 100% water separation within 1 hour in SAL-0E40 and 3 hours in SAL-1E40 (**Figure 19**).

The distance (Derby length) between the emulsions droplets was longer at 20% water cut. The droplets required adequate momentum to overcome the Derby length. Demulsification proceeded fastest in SAL-1E40 at 50000 ppm *SMES* (**Figure 20**) since it possessed highest momentum. Increase in dosage to 150,000 and 250,000 ppm brought about 100% phase separation in all the emulsions since adequate quantity of *SMES* was available to destabilize the droplets as depicted in **Figures 21** and **22**.

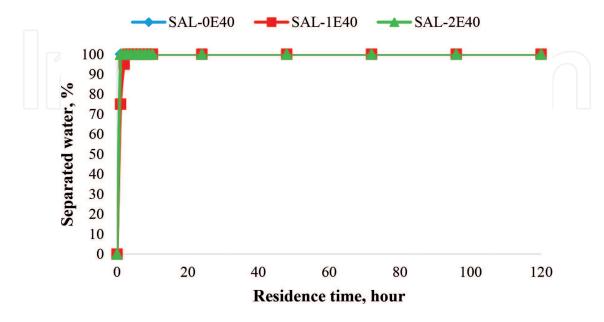


Figure 19. Phase separation at 250 g/L of SMES in emulsions with 40% water cut.

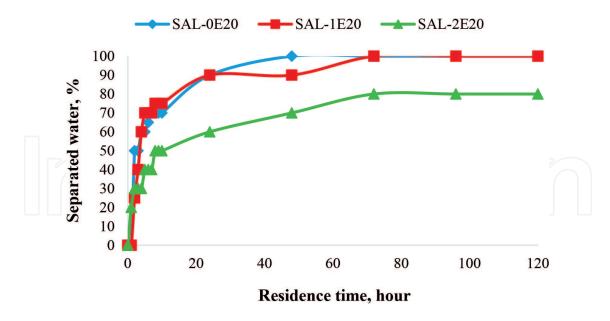


Figure 20. Phase separation at 50 g/L of SMES in emulsions with 20% water cut.

When added to emulsions, *SMES* dissociates into its anion and sodium salt action. It is adsorbed to the interface between the droplets and the crude oil with some preferential orientation according to the relative polarity of the interfacial film. Adsorption of surfactants is a dynamic occurrence which is prevented by another process that is responsible for surfactant transfer into the bulk phase. This phenomenon occurs rapidly. Consequently, equilibrium is attained after certain period depending on the concentration of the surfactant in the bulk phase. According to Salager [25], the free energy of the absorbed molecules of surfactants is lower compared to the

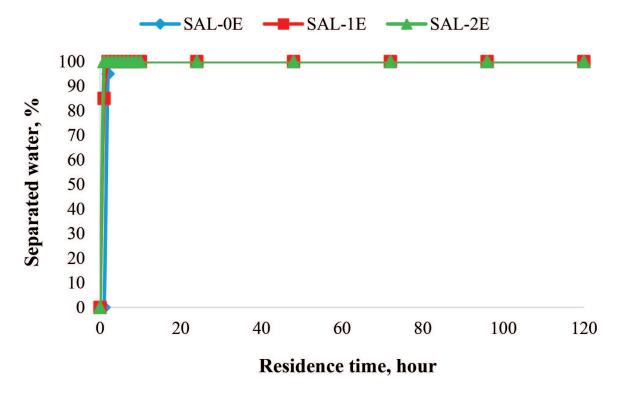


Figure 21. Phase separation at 150 g/L of SMES in emulsions with 20% water cut.

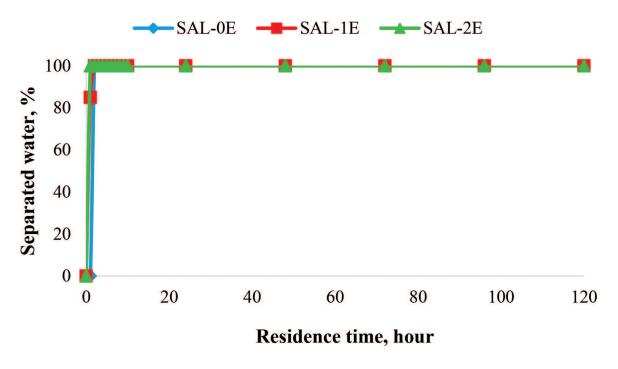


Figure 22. Phase separation at 250 g/L of SMES in emulsions with 20% water cut.

freer molecules in the bulk phase. Hence, the equilibrium is very much displaced towards the adsorbed state. Subsequently, a monolayer of the surfactant rapidly occupies the interface and the molecular arrangement of the surfactant depends its structural and geometrical properties.

In the presence of *SMES*, the cohesion between the droplets is substantially modified since this force action is very short, compared to the accumulating rate of the surfactant monolayer. The hydrophobic tail of the surfactant is adsorbed at the nonpolar phase leaving the hydrophilic head in the bulk phase. The anions are fixed to the interface, while the cations (Na+) are subjected to random molecular motion. There is uniform distribution of the cations in the system and there exists a Coulomb attractive force between the adsorbed anions and the wandering cations. The Coulomb force prevents the cations from separating far away from the interface making them to form a layer located near to the interface. The stable dispersion experience in the emulsions with 20 percent water cut even in the presence of demulsifier was due to large Derby length that prevented the short-range forces from acting on the droplets. Increasing the concentration of electrolytes in the system will shorten the Derby length, especially the polyvalent electrolytes. Reducing the Debye length will lead to a shorter distance of potential overlapping, and thereby encouraging the short-range forces (cohesion and adhesion) to disrupt the emulsions. The steric repulsion among asphaltenes and resins (responsible for emulsion stability) is broken by this process.

5. Conclusion

There was a corresponding increase in pressure with water content and consequently, higher shearing force was required to make emulsions flow. Comparison of emulsion rheology profiles with shear rate shows the progressive increase in viscosity according to water content.

Collision impact, especially at elevated temperature was high enough to break the droplets but unable to destroy the interfacial film and, flocculation of the droplets was therefore impossible. The films encapsulating the emulsion droplets possess elastic properties that facilitated surface reconstruction of the interfacial films to compensate for "dimples" created after droplet deformation. Thus, it has been established that the interactions of the constituents of the crude oil system, the produced water system and the emulsion system play major roles in characterizing water-in-crude oil emulsions. The presence of interfacial films and the deviation of the emulsions from being Newtonian towards pseudo plastic behavior with respect to water cut and salinity suggest the breakage of emulsion droplets due to shear stress. Meanwhile, interfacial films possess surface reconstruction capability which ensures dimples coverage after collision impact. It was shown that the ease or difficulty with which droplets break depend largely on water cut and salinity. Hence, the stability of water-in-crude oil emulsions is related to the viscous force presented by the continuous phase, water cut and salinity.

Acknowledgements

The authors would like to thank the University Technology PETRONAS (UTP) for providing the grant used for this study and the permission to present the research findings.

Nomenclature

API America petroleum institute

Ast transformed resin content, %

BO butylene oxide

BS 4708 method for determination of viscosity of transparent and opaque liquids

(kinematic and dynamic viscosities)

BS back scattering

BS & W basic sediment and water

Ca capillary number

CII colloidal instability index

CRO crude oil

ASTM D2500 standard test method for cloud point of petroleum product

ASTM D3279 standard test method for n-heptane insolubles

ASTM D445 standard test method for kinematic viscosity of transparent and opaque

liquids (and calculation of dynamic viscosity

ASTM D4928 standard test method for water in crude oils by Coulometric Karl Fischer

Titration

ASTM D5002 standard test method for density and relative density of crude oils by digi-

tal density analyzer

ASTM D6591 standard test method for determination of aromatic hydrocarbon types in

middle distillates-high performance liquid chromatography method with

refractive index detection

ASTM D93 standard test methods for flash point by Pensky-Martens closed cup tester

DBSA dodecylbenzene sulfonic acids

DCM dichloromethane

DLVO Derjaguin, Landau, Verwey and Overbeek

GCMS gas chromatography mass spectrometry

HLB hydrophilic-lipophilic balance

HPLC high performance liquid chromatography

IFT interfacial tension

K-F Karl Fischer

MLS multiple light scattering

NaCl sodium chloride

NIR near infrared

RI refractive index

RID refractive index detector

S&W sediment and water

SAL-0 fresh water

SAL-0E20 20% SAL-0 cut-in-crude oil emulsion

SAL-0E40 40% SAL-0 cut-in-crude oil emulsion

SAL-0E50 50% SAL-0 cut-in-crude oil emulsion

SAL-1 brine solution (20000 ppm salinity)

SAL-1E20 20% SAL-1 cut-in-crude oil emulsion

SAL-1E40 40% SAL-1 cut-in-crude oil emulsion

SAL-1E50 50% SAL-1 cut-in-crude oil emulsion

SAL-2 brine solution (40000 ppm salinity)

SAL-2E20 20% SAL-2 cut-in-crude oil emulsion

SAL-2E40 40% SAL-2 cut-in-crude oil emulsion

SAL-2E50 50% SAL-2 cut-in-crude oil emulsion

SARA saturates, aromatics, resins and asphaltenes

SG specific gravity

SMES sodium methyl ester sulfonate

UV ultra-violet

VDWL Van Der Waals London

Visc untransformed natural logarithm of viscosity

 Δp pressure change

 $\Delta \varrho$ density difference

μS/cm micro-Siemens per centimeter

1/k extension of double layer

1/s per second

Å angstrom

Cl- chlorine ion

cP centipoise

 $\varepsilon_{_{0}}$ relative permittivity

 ϵ_{r} permittivity of free space

g asymmetry factor

g/cc, g/cm³ gram per cubic centimeter

n refractive index

Na⁺ sodium ion

nm nanometer

 $n_{_{\scriptscriptstyle 0}}$ number of ions per unit volume of each type present in bulk solution

°C degree Celsius

Qs scattering efficiency

 $R_{a'} R_{b,1'} R_{b,2}$ radius of curvature

T absolute temperature

x particle diameter

ý shear rate

Zi valency of the ions

γ interfacial tension

φ concentration

 ω angular frequency

 ℓ^* photon transport mean free path

 η liquid dynamic viscosity $\eta_{\rm o}$ viscosity of a medium $\kappa_{\rm B}$ Boltzmann constant ΣW summation of water separation

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References

- [1] Kaiser A. Environmentally Friendly Emulsion Breakers: Vision or Reality? SPE International Symposium on Oilfield Chemistry. Woodlands, Texas, USA: Socienty of Petroleum Engineers Inc.; 2013
- [2] Oriji A, Appah D. Suitability of local demulsifier as an emulsion treating agent in oil and gas production. Paper SPE 162989 presented at the SPE Nigeria Annual international conference and exhibition (NAICE). Abuja, FCT, Nigeria; August 6-8 2012
- [3] Abdel-Aal H, Aggour M, Fahim M. Petroleum and Gas Field Processing. New York, BASEL: Marcel Dekker, Inc.; 2003
- [4] Kokal S. Crude Oil Emulsions. Petroleum Engineering Handbook General Engineering. Vol. 1. Texas, USA: Society of Petroleum Engineers; 2006. pp. 533-570
- [5] Becker J. Crude Oil Waxes, Emulsions, and Asphaltenes. Tulsa, Oklahoma: PennWell Books; 1997
- [6] Othman A. Study on Emulsion Stability and Chemical Demulsification Characteristics. Bachelor Degree Thesis. Pahang: Universiti Malaysia Pahang; 2009
- [7] Stewart M, Arnold K. Emulsions and Oil Treating Equipment: Selection, Sizing and Troubleshooting. New York: Gulf Publishing, Elsevier; 2009
- [8] Zhou H, Dismuke K, Lett N, Penny G. Development of more environmentally friendly demulsifiers. In: I SPE 151852 Presented at the SPE International Symposium and Exhibition on Formation Damage Control. Kuala Lumpur, Malaysia: Society of Petroleum Engineers, Inc; February 15-17 2012
- [9] Koshelev V, Klimova L, Starikov V, Nizova S. New demulsifiers for petroleum preparation processes. Chemistry and Technology of Fuels and Oils. 2000;36(2)

- [10] Stout C, Nicksic S. Separation and gel permeation analysis of natural emulsion stabilizers. In: SPE 42nd Annual Fall Meeting. Vol. 243. Houston, Texas: American Istitute of Mining, Metallurgical, and Petroleum Engineers, Inc; October 1-4 1967. pp. 253-259
- [11] Nghiem L, Hassam M, Nutakki R, George A. Efficient Modelling of Asphaltene Precipitation. Paper SPE 26642 presented at the SPE Annual Technical Conference and Exhibition. 1993;5:375-384
- [12] Sjoblom J, Urdahl O, Borve K, Mingyuan L, Saeten J, Christy A, et al. Stabilization and destabilization of water-in-crude oil emulsion from the Norwegian continental shelf. Correlation with model systems. Advances in Colloid and Interface Science. 1992;41:241-271
- [13] Fingas MF. Water-In-Oil Emulsions: Formation and Prediction. Handbook of Oil Spill Science and Technology. Toronto, Canada: John Wiley & Sons; 2014
- [14] Fingas M, Fieldhouse B. A review of knowledge on water-in-oil emulsions. AMOP. 2006:1-26
- [15] Tadros TF. Emulsion Formation, Stability, and Rheology. Applied Surfactants. Germany: Wiley-VCH Verlag GmbH; 2005
- [16] Eley D, Hey M, Symonds J. Emulsions of water in asphaltene-containing oils 1. Droplet size distribution and emulsification rates. Colloids and Surfaces. 1988;32:87-101
- [17] Gurkov TD, Basheva ES. Hydrodynamic Behaviour and Stability of Approaching Deformable Drops, "Encyclopedia of Surface and Colloid Science". New York: Marcel Dekker; 2002
- [18] Yarranton HW, Alboudwarej H, Jakher R. Investigation of Asphaltene association with vapor pressure Osmometry and interfacial tension measurements. Industrial and Engineering Chemistry Research. 2000;39(8):2916-2924
- [19] McLean JD, Kilpatrick PK. Effects of Asphaltene solvency on stabibility of water-in-crude-oil emulsions. Journal of Colloid and Interface Science. 1997;189:242-253
- [20] Al-Jarrah M, Al-Dujaih A. Characterization of some Iraqi asphalts II. New findings on physical nature of asphaltenes. Fuel Science and Technology International. 1989;7(1):69-88
- [21] Sztukowski D, Jafari M, Alboudwarej H, Yarranton H. Asphaltene self-association and water-in-hydrocarbon emulsions. Journal of Colloid and Interface Science. 2003; **265**(1):179-186
- [22] Jamalluddin A, Nazarko T, Hills S, Fuhr B. Deasphalted oil: A natural asphaltene solvent. Journal of SPE Production & Facilities. Paper SPE 28994 presented at the 1995 SPE International Symposium on Oilfield Chemistry held in San Antonio, Feb. 14-17. Texas, USA: SPE International Symposium on Oilfield Chemistry; 1996
- [23] Sato T, Ruch R. Stabilization of Colloidal Dispersions by Polymer Adsorption. New York: Marcel Dekker Inc.; 1980

- [24] Claesson PM, Blomberg E, Poptoshev E. Surface Forces and Emulsion Stability. Encyclopedic Handbook of Emulsion Technology. New York: Marcel Dekker, Inc.; 2001; pp. 305-326
- [25] Salager JL. Interfacial Phenomena in Dispersed Systems. Laboratory of Formulation, Interfaces Rheology and Processes, FIRP Booklet # E120-N. Teaching Aid in Surfactant Science & Engineering. Universidad De Los Andes FacultadDe Ingenieria Escuela De Ingenieria Quimica; 1994
- [26] Mackor EL, Van der Waals JH. The statistics of the adsorption of rod-shaped molecules in connection with the stability of certain colloidal dispersions. Journal of Colloid Science. 1952;7:535
- [27] Zapryanov Z, Malhotra AK, Aderangi N, Wasan DT. Emulsion stability: An analysis of the effects of bulk and interfacial properties on film mobility and drainage rate. International Journal of Multiphase Flow. 1983;9:105
- [28] Pichot R. Stability and Characterisation of Emulsions in the presence of Colloidal Particles and Surfactants. A PhD thesis submitted to the University of Birmingham, Department of Chemical Engineering, School of Engineering; 2010
- [29] Dukhin SS, Sjoblom J, Saether O. An experimental and theoretical approach to the dynamic behavior of emulsions, chap. 1. In: Sjoblom J, editor. Emulsions and Emulsion Stability. Boca Raton: CRC Press and Taylor & Francis Group; 2006
- [30] Miller DJ, Böhm R. Optical studies of coalescence in crude oil emulsions. Journal of Petroleum Science and Engineering. 1993;9(1):1-8
- [31] Elraies K, Tan M, Awang M, Saaid I. The synthesis and performance of sodium methyl ester sulfonate for enhanced oil recovery. Petroleum Scienceand Technology. 2010;28(17): 1799-1806
- [32] Razmah G, Salmiah A. Biodegradability and Ecotoxicity of palm stearin-based methyl Ester Sulphonates. Journal of Oil Palm Research. 2004;16(1):39-44
- [33] Masuda M, Odake H, Miura K, Oba K. Effects of 2-sulphonatofatty acid methyl ester (α-SFME) on aquatic organisms and activated sludge. Journal of the American Oil Chemists' Society (Yukagaku). 1994;**43**(7):551-555
- [34] Sulaimon AA, Adeyemi BJ. Investigating the kinetics of water-in-crude oil emulsion stability. ARPN Journal of Engineering and Applied Sciences. 2015;**10**(16):7131-7136
- [35] Chugh KL. ISC Chemistry: General and Physical Chemistry Part 1. 9th ed. Kalyani Publishers; 2014
- [36] Aveyard R, Binks BP, Fletcher PDI. The resolution of water-in-crude oil emulsions by the addition of low molar mass demulsifiers. Journal of Colloid and Interface Science. 1990;139(1):128-138
- [37] Chhabra RP. Non-Newtonian Fluids: An Introduction. SERC School-Cum-Symposium on Rheology of Complex Fluids. India: Indian Institute of Technology Madras; Jan 1-4, 2010

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