Effect of Native Solids Sizes and Concentrations on the Kinetic Stability of Water-In-Oil Emulsions

Adamu Bello\textsuperscript{1} and Abubakar A Umar\textsuperscript{2}
\textsuperscript{1, 2} Department of Petroleum Engineering, Abubakar Tafawa Balewa University, Bauchi, NIGERIA.

E-mail: \textsuperscript{1}belloadmu@gmail.com, \textsuperscript{2}drhidima5050@gmail.com

Abstract. The mingled production of oil and water, in the presence of other surface active agents (surfactants), either indigenous in the crude oil aid the formation and stabilization of emulsion. Colloidal particles behave like surfactants molecules, mostly when they adsorb to a fluid-fluid interface. With adequate coverage of these particles at the interface, they act as barriers against droplet coalescence and enhance emulsion stability. This study investigate the effect of certain native solids on the kinetic stability of W/O emulsions. The effect of their sizes and concentrations was studied. Conventional batch test, coupled with Turbiscan were used for the stability measurements. It was found out that the particle type (physico-chemical properties), concentration of the particles at the interface and their sizes are important measures of emulsion stability.

Keywords: Emulsions, Emulsion Stability, Pickering Emulsions, Kinetic Stability, Solids

1. Introduction
Emulsions are, from a thermodynamic point of view, generally unstable because liquid/liquid systems have the natural tendency to separate into the different phases, reduce the interfacial area (and thus the interfacial energy). Petroleum Emulsions however, demonstrate kinetic stability due to the presence of surface active agents that adsorb at the liquid/liquid interface; reduce interfacial tension and form thick films that prevent coalescence. The formation and subsequent stabilization of petroleum emulsion is a costly problem, both in terms of chemicals used and the production lost \cite{1, 2}. The stability of these thick films that form at the interface, thus, the emulsion stability, depends on several factors; like asphaltene, resins, waxes (heavy materials in the crude oil), clays, scales, corrosion products, etc. \cite{1-3}.

The emulsion types that are stabilized by the attachment of fine particles at the water-oil interface are called Pickering Emulsions, or Particles-Stabilized Emulsions \cite{4}. A variety of particles, including clays and silica, can be used to stabilize these types of emulsions. For solid particles to stick to and be collected at the surface of dispersed droplets in an emulsion, the solid material (powder) had to be wetted by both liquids. Generally, particles would have preference for one of the two liquids and would therefore reside longer in that liquid \cite{5-7}. Hydrophilic particles would tend to stabilize O/W
emulsions while W/O emulsions are stabilized by oil-wettable particles. The free energy of emulsion formation is expressed by:

$$\Delta G_{\text{Formation}} = \Delta A \gamma_{12} - T \Delta S$$  \hspace{1cm} (1)

Where, $\Delta A$ is the change in interfacial area, $\gamma_{12}$ is interfacial tension, $\Delta S$ is change in entropy and $T$ is the temperature of the system. In most cases, $\Delta A \gamma_{12} \gg T \Delta S$ and $\Delta G_{\text{formation}}$ is positive.

Therefore, when there is no stabilization mechanism (surface active agent presence), the formed emulsion would become unstable. Surfactants are amphiphilic molecules and they have a natural tendency to go to oil-water interface. They reduce the oil-water interfacial tension; thereby minimizes the energy required for emulsion formation. The adsorbed surfactant molecules at the interface act as electrostatic or steric barriers against droplet coalescence and increase the emulsion stability. Hydrophilic to hydrophobic balance of the surfactant molecules dictate the nature of the emulsion (O/W or W/O) being formed [8-10]. Colloidal particles behave in many ways like surfactant molecules, particularly if adsorbed to a fluid/fluid interface. However, certain differences in behaviors are unavoidable. For instance, individual particles do not form aggregates by assembling in the same way surfactant molecules do, by forming micelles. Hence the absence of solubilization in particle stabilization mechanism [3,11,12,19]. The ability of a particle to adsorb at an interface depends on how partly wetted it is by both phases [13, 14]. For a particle residing at an oil/water interface, the contact angle $\theta$, measured through the aqueous phase is below 90°, which means the particle is favorably wetted by the water (preferentially hydrophilic in nature). However, a particle with a contact angle $\theta$, above 90° is preferentially wetted by the oil (i.e. hydrophobic). A particle with contact angle of 90° is correspondingly wetted by both phases, and is considered at the point of inversion [5,10,14]. The kinetic stability of emulsions is imparted by particles majorly through a steric barrier, which forms at the interface. If a certain particles concentration is present at that interface, a close packed network is generally formed, increasing the stability of the emulsion [15, 16].

This study examines the effects of eight (8) native solids extracted from field operations. Solids are of different sizes were used to prepare model emulsions, and of varied concentrations. Batch testing (static bottle test) and the Dynamic Light Scattering method (Turbiscan) - were used to study the stability of synthetic emulsions prepared using castor oil.

2. Methodology
The following step by side methods were followed in order to achieve the objective of this study:

2.1. Oil Samples
For this study, a model emulsion was used. It is prepared using castor oil as the continuous phase. The Castor oil was purchased from a local vendor Avanti’s chemicals Sdn Bhd, Malaysia. Before usage, the density, viscosity, color, and specific gravity of the castor oil were determined.

2.2. Preparation of Native Solid Particles
The method employed by [8] in separating the asphaltenes and solids was used in this study. The asphaltene/solids mixture extracted from the well was dissolved in toluene in a ratio of 100 cm$^3$ toluene per gram Asphaltene/Solids. The mixture was sonicated for a period of 40 minutes so that the asphaltene dissolve completely and to ensure that the solids are dispersed. The mixture was left for 1 hour undisturbed, and then centrifuged at 4000 rpm (1640 RCF) for 6 min.

Recovering the asphaltene from the mixture requires decanting the supernatant and evaporating the solvent until only dry asphaltene was left. The solids that remained in the centrifuge tube before they are being dried are called “wet” solids. To obtain “dry” solids, the wet solids were dried in a fume hood at 22 °C until the mass was invariant. Dry solids were employed for particle size determinations while the fresh solids were employed for emulsion stability experiments.
2.3. Preparation of Model Emulsion
Emulsions used in this study were prepared using water-to-oil ratios of 40/60 (v/v). Distilled water was used as the aqueous phase and Castor oil of density 0.9570 g/cc as the continuous phase. For every 60mL of the oil phase, an equivalent 40mL of the aqueous phase was added, into a 100mL plastic centrifuge bottle with a Wheaton adjustable pipet. Prior to mixing the oil and water, different amounts (0, 0.3, 0.4, and 0.5 w/w% concentrations) were added into the castor oil and mixed with a homogenizer for few minutes. The oil containing the solids and deionized water were then mixed with a Cyclone IQ Homogenizer. The homogenization was performed for 10 000 rpm for a period of 8 min, ensuring that the homogenization effect was felt at the oil/water interface and at the bottom of the bottle, by shifting the shaft up and down during homogenization process. After homogenization, the prepared emulsions were transferred into the Turbiscan bottle for stability measurements, while some were kept in a 100mL glass tubes and aged for 72 hours at 60°C.

2.4. Emulsion Types Determination
Since we cannot be certain of which emulsion type forms after the homogenization, it is important that we check the type of emulsion using any of the methods available. The filter paper method was adopted. In this method, the emulsion to be checked was taken and dropped on a filter paper. Some of the emulsions move up the paper (spread up the filter paper), indicating that they are O/W emulsion. Those that did not spread on the filter paper were considered to be W/O emulsions and were selected for this study.

2.5. Batch Test- Emulsion Stability Measurement
The Bottle Test is the most common method used to investigate the stability of emulsion. In this study, it is employed to assess the stability of the prepared emulsions at room at 60oC. This phenomena is controlled by the gravity separation, where the amount of water separated is being observed with time, and used as a measure of the stability. All prepared emulsions were kept in a calibrated plastic centrifuge bottle in a water bath of 60oC, and aged for one week. The percentage of water separated was calculated, and plot against time. The results are shown in section 3.

2.6. Emulsion Stability – Multiple Light Scattering
The Turbiscan is a relatively recently developed technique, which allows for the scanning of the turbidity profile of an emulsion along the height of a glass tube filled with the emulsion, following the fate of the turbidity profile over time. The reading head is composed of a pulsed near-IR light source (l = 850 nm) and two synchronous detectors. The transmission (T) detector receives the light, which goes through the sample (0°), while the backscattering (BS) detector receives the light back-scattered by the sample (135°). The Turbiscan head acquired T and BS data every 40 mm along the vertical length of the cell. Therefore, the scan of a 60-mm height sample provides patterns, including 1,500 points of measurement, in less than 20s. Thus, by repeating the scan of a sample at different time (t) intervals, the stability or instability of dispersions can be studied in details.

2.7. Emulsion Stability- Droplet Size Distribution (DSD)
Conventional measurements of particle size (sometimes together with zeta potential) usually involve light scattering or sedimentation techniques and necessitate serious dilution of the emulsion samples. Diluting the sample would usually temper with both the size distribution and zeta potential of the sample, as a result changing the exact information required from the measurement. The major advantage that an acoustic spectroscopy has over other spectroscopic methods is its ability to characterize concentrated dispersed systems without dilution. The frequency dependence of the sound attenuation is the normal experimental output of this measurement. In this study, the Acoustic
Electroacoustic Spectrometer was used to determine the droplet size distribution (DSD) of the emulsions. Two statistically illustrative distributions are considered by the spectrometer software: log-normal and bimodal particle size distribution (the later defined as the superposition of two log-normal distributions with the same standard deviation). The results are reported based on the type of distribution that minimizes the fitting error of the predictive theory to the measured acoustic spectrum. The instrument measures the particle size for system containing particles within the 5 nm to 1 mm size range [17].

2.8. Emulsion Bulk Rheology

Emulsion rheology, or the flow properties of emulsions is one major property of an emulsion. Emulsion rheology is defined as the study of the deformation and flow of emulsions. The rheological properties of emulsions, especially its viscous behavior, is very vital in handling produced crude oil that normally come along with water especially in mature oil field. Rotational rheometry is a powerful technique for the measurement of complex shear rheology across all material types. It is ideal for discerning structural and compositional changes of materials, which can be critical controlling factors in flow and deformation properties, and ultimately product stability and performance. In this study, the MCR 301 Anton Paar HPHT Rotational Rheometry at EOR Laboratory, Universiti Teknologi PETRONAS was used. The MCR viscometer is very easy and user friendly to measure shear stress and shear rate at specific rotational speed and plot the flow curve automatically by the Rheoplus software.

3. Main Results

3.1. Oil samples

The properties of the continuous phase (castor oil) were measured, as presented in Table 1. As mentioned earlier, Castor oil was used as the dispersed phase. The color of the oil is pale yellow. Therefore, in order to differentiate the color of the two phases farther, a non-reactive dye was added to the castor oil and stirred for some time.

| Properties       | Values | Units       |
|------------------|--------|-------------|
| Density          | 0.9570 | g/cc        |
| Viscosity        | 0.6500 | Pa.S        |
| Color            | Yellow | -           |
| pH               | 3.4    | -           |
| Specific gravity | 0.9550 | @24°C       |

3.2. Native Solids

After the treatments of the solids used for this study as discussed earlier, they were classified into fine and coarse. Those with diameters <4µm were classified as fine solids, while those with diameters from 8µm and above were classified as coarse. The solids when adsorbed on the interface or on an existing emulsion film can create a steric barrier between adjacent water drops, hindering collision between the drops, effective film drainage, and subsequent coalescence. This would increase the stability of the emulsion. The native samples used are as shown in Figure 3.
3.3. Emulsion Stability Measurement- Batch Test and Turbiscan

This is the most popular technique used in determining the stability of emulsions in the oil field and in most simple laboratory procedures. It is done by measuring the amount of water resolved from the emulsion over time. Transparent and graduated plastic or glass bottles are used. In this procedure, a centrifugal bottle was used. However, the Turbiscan (Light scattering) technique is a more valid and more accurate method of determining emulsion stability when compared to the bottle test. Both methods were used in this study. As mentioned in section 2.3, emulsions were prepared with the same water cut (40/60 vol %), in the presence of different native solids and different concentrations.

Figures 2(A) and (B) illustrate the effect of increasing solid particles concentrations (w/w) (BT08, BA3L, BT53 BR001 on BR002) water-in-oil emulsions stability. From the figures, the least stable emulsion is one formed with the most coarse solids (those sized above 15µm) (Figure 2B), while the most stable emulsions are those formed by the finest solids. Figure 2(B) however are emulsions prepared by slightly coarse solids, and it can be observed that the most stable emulsions in the figure are those prepared by the most concentrated samples (0.3, 0.4 and 0.5).

Generally, it can be observed from these figures that higher concentrations of solids leads to higher degree of stability of the emulsions formed. Increasing the concentration of the solids led to a decrease in the amount of water resolved from emulsion upon centrifugation and heating. It can be deduced that small-sized inorganic particles enhance water-in-oil emulsion stability. The stabilization mechanism is believed to be steric stabilization, emanating from the interfacial barrier created by the solids. Steric stabilization is as a result of a physical barrier to contact and coalescence. For instance, high-molecular weight surface active agents have the ability to adsorb on the surface of the dispersed phase droplets and spread considerably into the continuous phase. This can provide a volume restraint or a physical barrier for particle interactions. As droplets coated by the surface-active agents approach, the surfactants would forcefully go closer, thereby resulting to repulsive forces, and droplets are kept farther apart. Many researchers ascribe emulsion stability to the viscoelastic interfacial film that forms around the dispersed droplet. This film is believed to be formed through the interactions of the surface-active molecules (mainly asphaltenes and resins). Solids however can potentially stabilize emulsions by adsorbing onto the water/oil interface directly or by adsorbing onto a film already formed by a surfactant.
Figure 2. (A) Emulsions with fine solids and diff concentrations (0.5, 0.4, 0.3, 0.1 w/w), and (B) Emulsions with very coarse solids and diff concentrations (0.5, 0.4, 0.3, 0.1 w/w).

As shown in Figures 3 through 6, those emulsions prepared without solids (blank samples) separated very fast, indicating that the two immiscible phases would separate immediately in the absence of a surface-active agent. However, those emulsions that have different concentrations of the solids exhibit stability based on the concentration, as well as the ability of the solid to be wetted by both phases. As shown in Fig. 3, all the 5 native coarse solids formed an emulsion that is slightly stable. BT08 and BA3L are more stable, with BT08 showing zero water separation up till 6 hours after preparations. Figure 6 are emulsions prepared by the finest solids (with diameters <2µm). As can be seen on the figure, almost all the emulsions were stable for more than 6 hours at 60°C. For such fine solids, even BR002 that begin to separate in less than 2 hours for emulsions with coarse solids, took nearly 5 hours to start separating when the sizes are smaller. This is a clear indication that, as particles sizes decrease, emulsion stability increases.

Figure 5 shows the relationship between solids concentrations and emulsion stability. It can be seen that, the higher the concentration of the solids, the more interfacial coverage of the droplet, hence the more hindrance to coalescence.
The Turbiscan MA2000 optical analyzer allows the estimation of sedimentation behavior, in the white opaque column, where the emulsion shows a visual consistency. This behavior is shown by the Transmission and Backscattering profiles. From the profiles, similar behavior as indicated by the bottle tests were seen. The most stable emulsions are those formed by the finest solids, while the most concentrated samples also give most stable emulsions.

Figure 3. Emulsions with different coarse solids.

Figure 4. Emulsions with different fine solids.
3.4. Emulsion Bulk Rheology

The relationship between the shear rate and shear stress for four emulsions prepared with the finest solids were investigated. As shown in Figure 9, the relationship between shear rate and shear stress for stable emulsions formed from finest solids near linear with BR 001, suggesting a Newtonian flow. A similar behavior is displayed by BA 03L. This indicate that, stable emulsions behave like Newtonian fluids. Shear thinning was observed for less stable emulsions prepared with coarse solid particles. BT08 and BT153 are less stable emulsions, and exhibit non-newtonian flow behavior (shear thinning). In general, it can be concluded that while stable emulsions behave like Newtonian fluids, unstable emulsions behave like non-newtonian fluids.
3.5. Emulsion Stability – Backscattering
The Backscattering profiles are generated for different emulsions prepared with different types and varying sizes of solids. As earlier established from the bottle test stability determinations, emulsions prepared with the finest solids are more stable than those prepared with coarse solids. Figures 8 to 11 show different backscattering profiles for emulsions prepared with different concentrations of the fine, coarse and very coarse solids. However, as shown in Figures 8 to 11, the effect of concentration is not very much felt for very fine solids. In the figures, almost all the concentrations for fine solids show a significant backscattering, indicating that there is no separation and the emulsion remain stable for that period under investigation.

However, subsequent solids sizes of coarse and very coarse show significant effect in concentration. Although the emulsions prepared with the highest concentration of 0.5wt% were used for testing the stabilities, the water separated faster in the coarse and very coarse samples, thereby having less backscattering compared to the fine-solids emulsions.

Figure 7. Flow behavior of 4 emulsions formed by the finest solids.

Figure 8. Backscattering profiles of emulsions prepared with 0.5wt% of fine solids.
4. Conclusion

Figure 9. Backscattering graphs of Emulsions prepared with fine solids 0.4wt%.

Figure 10. Backscattering graphs of Emulsions prepared with coarse solids of concentrations 0.5wt%.

Figure 11. Backscattering graphs of Emulsions prepared with very coarse solids of concentrations 0.5wt%.
Native solids extracted from some Malaysian petroleum emulsions were used to carry out an investigation into the role of solid particles in the stabilization of water-in-model oil emulsions. The investigation revealed that while certain native solids form w/o emulsions, some can only form an o/w emulsion. Fine solids adsorb at the oil/water interface and prevent droplets coalescence, thereby increasing the emulsions stability. The stability of these emulsions is due to steric effect originating from particles adsorbed at the oil/water interface.

The study also revealed the role of increase in solids concentrations to the emulsion stability. The free energies of adsorption to interfaces of solids can be very high (thousands of kT), and they can consequently be assumed to be effectively irreversibly adsorbed. This irreversible adsorption has a major consequence on the long-term stability of emulsions formed in the presence of solids since it is possible to completely prevent coalescence.

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