

Role of Asphaltene in Stability of Water-in-oil Model Emulsions: The Effects of Oil Composition and Size of the Aggregates and Droplets

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Abstract

Water-in-oil (W/O) emulsions are the most common type of emulsions handled in petroleum processes. It is thought that the field emulsions are primarily stabilized by asphaltene-resin micelles and several research works have studied the stability mechanisms of asphaltene in crude emulsions. However, there is still plenty of research gaps and unanswered questions in this area due to the complexity of the problem and difficulty of access and crude emulsions processing. These challenges can be addressed by investigating the effect of asphaltene on the model emulsions' kinetic stability. This study introduces a model W/O emulsion prepared by a new stabilizer (Gilsonite) that contains asphaltenes and resins in combination with a non-ionic surfactant (Span 83). The colloidal characterization of the asphaltene aggregates in the mineral oil and oil blend of Toluene and mineral oil was carried out. The size of the asphaltene aggregates in the mineral oil was found to increase with the added Gilsonite concentration because of asphaltene precipitation and the process of smaller aggregates clumping together, forming flocs. Gilsonite was also found to precipitate and stabilize the W/O emulsions with the mineral oil as the external phase where the asphaltene precipitation was most severe. The emulsions' least kinetic stability was measured when Toluene was added in the oil blend (50% volume fraction), where 100% water phase separation was observed with 0.25% Gilsonite concentration. However, the dilute Emulsion (10% water content in the emulsion) samples with 25% Toluene revealed higher stability in terms of water phase separation than the case with 12.5% Toluene with 20.83% less water separation in a 3-day storage period. This observation contradicts the expected outcome in a thermodynamic perspective where the W/O emulsion stability is thought to be merely dependent on the asphaltene precipitation. The dilute emulsion with 12.5% Toluene contained asphaltene aggregates larger than the emulsion droplets, which cannot contribute to the stability process. The ratio of mean aggregate size to the mean droplet size was 133% larger for the dilute emulsion with a smaller fraction of Toluene in the oil blend for this case. Therefore, the aggregates' size to droplet size misalignment resulted in less stability for this emulsion than the emulsion with higher aromaticity of the oil blend despite the very high precipitation rate. This paper presents observations of the effects of the asphaltene precipitation rate, size of the aggregates, and size distribution of the emulsion droplets on the model W/O emulsions' stability. The significance of the results is in revealing the importance of Integrating the thermodynamical and colloidal viewpoints to describe the role of asphaltene in stabilizing emulsions. This approach leads to the conclusion that besides the asphaltene precipitation, the aggregates' size distribution in relation to the size of the emulsion droplets is a critical factor in stabilizing the emulsions. Results presented in this study can be used in the design of solvents in enhanced oil recovery, producing model emulsions replicating oil reservoir in-situ emulsion features, synthesis of demulsifiers for the emulsions stabilized with

asphaltene-resin micelles, and other industrial applications. Additionally, Gilsonite was introduced as a new additive that can be used to study the role of asphaltene in stabilizing model emulsions.

Keywords:

Water-in-oil emulsion; Gilsonite; Asphaltene; Asphaltene precipitation; Emulsion stability

1. Introduction

Emulsions are part of a broader mixture system known as the colloids. An emulsion is a dispersed system of immiscible liquids with water as the internal phase and oil as the external phase in a Water-in-oil (W/O) emulsion [1-3]. Oil-in-Water (O/W) emulsions have been investigated broadly. In contrast, W/O emulsions are not characterized comparably, which is likely due to the issues with the stability of this type of emulsion [4]. This is the case despite the importance of W/O emulsions, particularly in the petroleum industry.

Gilsonite (Asphaltum) is a naturally occurring form of asphalt (bitumen), which is soluble in aromatics [5]. This solid hydrocarbon mineral is widely used in many products in various industries, including oil well cements and drilling fluids, printing inks and paints, and asphalt modifiers, among others [5]. Literature indicates Gilsonite is an effective fluid-loss control agent in the water-based drilling muds and an excellent shale stabilizer in the oil-based drilling muds [6,7]. Moreover, several patents claim Gilsonite can be used as an asphalt modifier and emulsion pavement sealer [8-10]. To the authors' knowledge, Gilsonite has never been used in model W/O emulsions. This is the first study suggesting the use of this type of mineral to study the role of asphaltenes in stabilizing the W/O emulsions.

Asphaltene is the heaviest and a polarizable fraction of the crude oil with a complex structure [11]. Studies show that the asphaltenes precipitate into solids and deposit either due to the change in the field conditions (change in pressure and temperature) or the oil composition [12-14]. Many problems have been linked to the precipitation of asphaltenes in both upstream and downstream facilities of the oil industry [15]. Moreover, the formation of crude emulsions is thought to be mainly a result of natural emulsifiers, such as asphaltenes in the oil reservoir [16-19].

Kokal and Al-Dokhi demonstrated that crudes with a higher tendency of asphaltene precipitation are more likely to form kinetically stable emulsions [20]. Several other research works emphasize the crucial role of asphaltene in stabilizing crude emulsions and present the hypothesis that asphaltenes could also adsorb on the reservoir minerals and contribute to the stability of emulsions [21-23]. Generally, asphaltene precipitation is described by two modelling approaches [11]. One is the thermodynamic model that assumes asphaltene as a part of the non-ideal mixture, which precipitates when solubility values fall below specific values. The other approach is the colloidal model that considers asphaltene as colloidal particles surrounded by adsorbed resins. In this modelling approach, precipitation is assumed to be non-reversible. However, asphaltene precipitation's reversibility is still an area of debate and controversy [11].

Overall, the consensus is that the crude blend's increased aromaticity lowers the emulsion stability, and the kinetic stability is often explained through a thermodynamical lens [23-25]. The colloidal modelling approach states that the asphaltenes and resins form aggregates, and the aggregates clump together, establishing micelles. These micelles cover the droplets' interfacial area and

stabilize the emulsions by steric hindrance primarily [26]. Previous studies demonstrate asphaltene materials as hydrophilic functional groups could potentially produce aggregates at the oil-water interface and form viscoelastic interfacial films around the water droplets [27-29]. However, the mechanism and influencing factors are still not fully understood. There is a substantial gap in the literature regarding the identification of the factors that impact the stability of the emulsions by asphaltenes. This study incorporates both approaches and attempts to describe W/O emulsions' stability by the effect of asphaltene precipitation and the colloidal characterization of the aggregates in terms of the relative size of the aggregates to emulsion droplets.

A model W/O emulsion was prepared with Gilsonite, which contains asphaltene in large fractions at ambient temperature and pressure. Initially, the asphaltene's colloidal behavior was investigated in the mineral oil and oil mixtures (mineral oil and Toluene). Moreover, the thermodynamical viewpoint was accounted for in terms of asphaltene precipitation rate, which is a function of the asphaltene solubility in oil. Finally, the model emulsions' stability in terms of water phase separation was evaluated in dilute and concentrated emulsions for different oil compositions. The results clarify some crucial effects of the oil composition, size of the aggregates, and size distribution of the water droplets in the stability of W/O emulsions by asphaltene.

A better understanding of emulsion stability with asphaltene-resin micelles is essential to handle field emulsions produced in the petroleum industry and this work attempts to clarify some aspects of mechanisms through which the emulsions are stabilized. The significance of this study is adopting an integrated colloidal-thermodynamics approach in the analysis of the kinetic stability results. The findings presented in this study are useful in the design of solvents utilized in the enhanced oil recovery, producing model emulsions to characterize the flow behavior of the oil field in-situ emulsions, and designing demulsifiers. Moreover, Gilsonite is introduced as a new stabilizing agent for the W/O emulsions which mimics the asphaltene features.

2. Materials and Methods

Mineral oil and Toluene were used in different fractions to prepare the model emulsions and investigate the asphaltenes' colloidal behavior in oil. This study's mineral oil contains 96.5 wt% saturate mixtures and 3.5 wt% aromatics with a specific gravity of 0.85 at 15 °C and Toluene's specific gravity is 0.86 with a dynamic viscosity of 0.59 mPa.s at 20°C. Toluene is an aromatic hydrocarbon composed of a benzene ring which is linked to a methyl group.

A blend of the surfactants, including Gilsonite and Span 83, was used in the experiments. Sorbitan sesquioleate (Span 83) from the Span non-ionic surfactant family is widely used as an emulsifier to formulate creams and ointments for cosmetic use and pharmaceuticals [30-32]. Span 83 has a low hydrophilic-lipophilic balance (HLB) value that is indicative of higher solubility of the surfactant in the oil phase. According to Bancroft's rule, this facilitates the formation of the W/O emulsion. **Figure 1** illustrates the chemical structure of Span 83 with a 2:3 attachment ratio of sorbitan (dehydrated sorbitol molecule) with the unsaturated oleic acid. **Table 1** summarizes the properties of this non-ionic surfactant. Utah Gilsonite 200 mesh powder was used as the naturally occurring solid hydrocarbon, which is a rich source of asphaltenes. Elemental analysis and Saturate, Aromatic, Resin, and Asphaltene (SARA) fractions of the Gilsonite are shown in **Table 2**. Deionized water (DI water) was used in the preparation of the emulsion samples. 1 ppm Total

dissolved solids (TDS) was measured for the DI water using a Conductivity/TDS meter. pH of all emulsion samples was between 7.5-8.

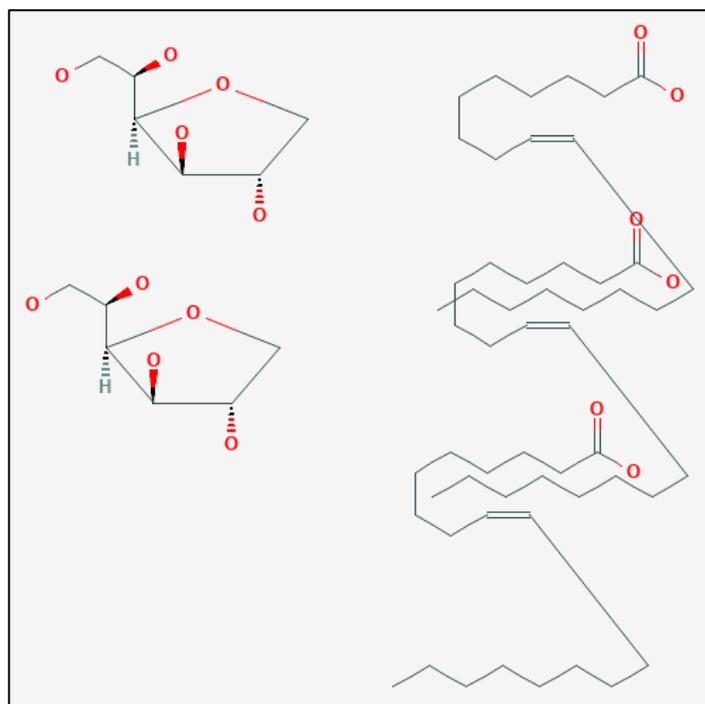


Figure 1- 2D depiction Sorbitan sesquioleate (Span 83) [33]

Table 1- Sorbitan sesquioleate (Span 83) properties

Property	Value
HLB	3 [34]
Cc	4-5 [35]
CMC*	0.024 (%wt/v) [30]
Mwt	560
IFT @ CMC*	13.18 dyne/cm [30]
Viscosity @ room temp	1500 mPa.s
Density	0.989 g/ml

*CMC was determined for light mineral oil and water

Table 2- Properties of Gilsonite

Property	Value	Components	Value [5]
Carbon, wt%	85-86	Saturates, wt%	1.6
Hydrogen, wt%	8.5-10	Aromatics, wt%	0
Nitrogen, wt%	2.25-3.29	Resins, wt%	18.7
Sulfur, wt%	0.22-0.53%	Asphaltenes, wt%	79.7
Oxygen, wt%	1.5%	Colloidal instability index, CII	4.34

A magnetic stirrer was used for the initial mixing of the surfactants and the oil phase. A lab rotor/stator homogenizer with a 12 mm working head diameter and shearing rate capacity of 1,000-28,000 rpm was employed to prepare the emulsions at an ambient temperature of 22 °C and atmospheric pressure. A cone and plate viscometer was used to measure the viscosity, and bottle tests were carried out to monitor the phase separation in the sample emulsions. 12-ml emulsion samples were poured into 14 ml graduated cylinders, and the containers were placed and kept on a flat surface for the specified storage time. The water phase separation was tracked and reported for three days.

This study employs the optical microscopy technique to determine the size distribution of the asphaltene aggregates and the emulsion droplets. For this purpose, a compound microscope (1,000X magnification, Omano OM-139) equipped with a high-resolution 10 MP camera was used to capture the samples' images. The Kohler illumination method in the microscope provides even illumination of the sample and ensures the illumination source is not visible in the micrography.

The captured images were processed using ImageJ opensource software. The images were adjusted using enhancing contrast techniques, and the backgrounds were removed. The aggregates and droplets were recognized using the binary method, and the holes were filled. Minimum Feret diameter and area occupied by the aggregates were extracted, and length (diameter) and area were obtained for the droplets in emulsion samples. In-house codes in Matlab were developed to find the representative sizes of the aggregates/droplets. **Figure 2** displays the workflow of the particle size analysis adopted and **Figure 3** shows the sequence of the work on a sample oil with asphaltene aggregates.

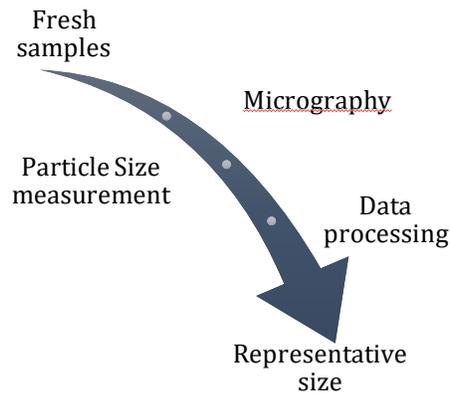


Figure 2- Workflow of image processing

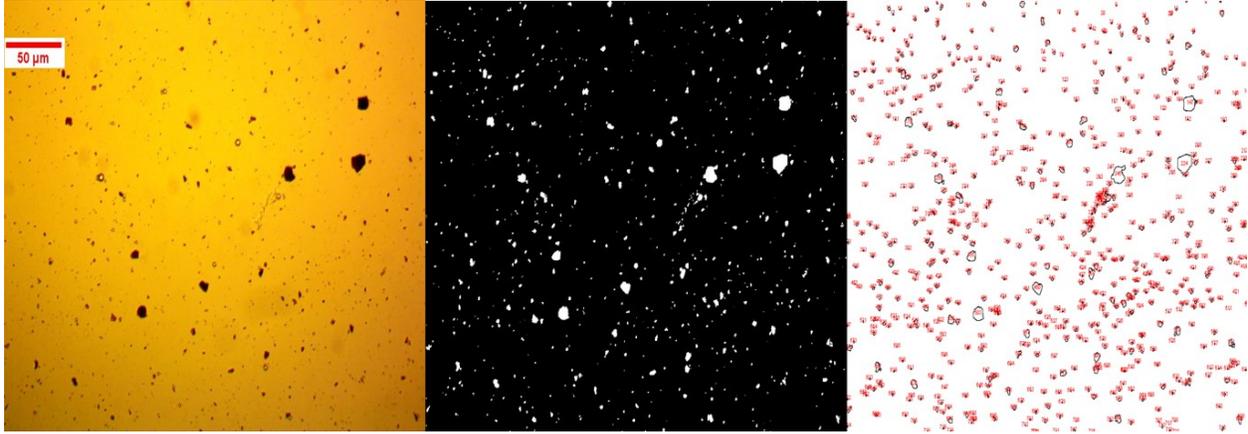


Figure 3- Sequence of image processing using ImageJ on the oil samples containing asphaltene: Micrography (Left), Particle detection (Middle), Particle outlines (Right)

Using the obtained data from ImageJ software such as min Feret diameter, length, and area, the representative sizes were calculated. Such includes the Equivalent Projected Circle (EQPC) diameter, maximum Feret diameter, maximum EQPC, and representative diameters. The size of the aggregates and droplets can be presented in several ways, namely D10 (arithmetic mean diameter), D32 (Sauter diameter), D43 (De Broukere, or Herdan diameter), number-based distribution, and volumetric-based distributions [1-4]. These representative sizes yield different values, and each one describes a specific aspect of the size of particles in the system. **Equation 1** shows the general form of the representative sizes equation [36]:

$$\bar{D}_{pq}^{(p-q)} = \frac{\sum_i D_i^p}{\sum_i D_i^q} \quad (1)$$

where \bar{D} is the averaged representative size, p and q are integers ranging from 1 to 4, and D_i is the *i*th drop's diameter. It is informative to express particle size analysis with more than one representative size to understand the distribution as well as the mean size.

The characterization of the asphaltenes' size and precipitation was performed in mineral oil and the oil mixture containing mineral oil and Toluene in the first stage of the research. Gilsonite in different concentrations was added to the oil to prepare a 12-ml sample. The sample was first stirred gently using a magnetic stirrer then mixed at 1,000 rpm for 1 min by a lab homogenizer. Fresh samples were analyzed using optical microscopy, and the size of the aggregates was determined using particle detection and image processing techniques. **Table 3** demonstrates the testing matrix for this testing phase. Moreover, asphaltene deposition was determined by the SARA method proposed by Gaestel et al. [37]. **Equation 2** is used to analyze the asphaltene deposition potential by the Colloidal Instability Index (CII) [37].

$$CII = \frac{W_{saturates} + W_{asphaltenes}}{W_{resins} + W_{aromatics}} \quad (2)$$

where W is the mass fraction of the crude fractions (saturates, asphaltenes, resins, aromatics), and CII is the colloidal instability index. If CII is higher than 0.9, asphaltene deposition will likely take place in bitumen.

Table 3- Colloidal characterization of asphaltene in oil testing plan

	Objectives	Gilsonite concentration (%wt/v oil)	Type of oil
Colloidal characterization of asphaltene aggregates in oil	-Number of aggregates (implication of precipitation)	0.1,0.5,1,10	Mineral oil
	-Size of the aggregates	0.1, 1	Mineral oil + Toluene (Toluene Volume fraction: 0.125,0.25,0.5)

The second phase of the research involved preparing emulsions using two surfactants (Gilsonite and Span 83) only after evaluating the base emulsion with Span 83 and testing the possibility of formulating W/O emulsions using Gilsonite. A classical approach was adopted for the preparation of the emulsions [1]. Firstly, the surfactant(s) were mixed with the oil (oil mixture) using the magnetic stirrer. Then water (and NaCl solution) was added to prepare 12-ml emulsion samples by homogenizing the fluid mixtures at 1,000 rpm for 1 min. Fresh emulsion samples were used for micrography. Emulsion samples were poured into the 14-ml graduated cylinders, and the phase separation was monitored for three days in the bottle tests. The objective was to compare the kinetic stability in emulsions with different oil compositions and Gilsonite concentrations to investigate Gilsonite's role (asphaltene/resin micelles) in stabilizing the emulsion samples. **Table 4** shows the testing plan for this phase of the research.

Table 4- Testing plan for the model emulsion and base emulsion

	Objectives	Water fraction	Span 83 (%wt/v)	Type of oil	NaCl (M)
Base emulsion characterization	-Kinetic stability analysis	0.1,0.2,0.3,0.4	5	Mineral oil	0, 0.51M
	-Size of the droplets				
		Water fraction	Type of oil	Gilsonite concentration (%wt/v)	NaCl (M)
Model emulsion with Gilsonite and 5 % wt/v Span 83	-Kinetic stability analysis	0.1	Mineral oil	0.25,1	0.51M
	-Size of the droplets	0.1	Mineral oil + Toluene (Volume fraction: 0.125,0.25,0.5)	0.25,1	0.51M
		0.4	Mineral oil + Toluene (Volume fraction: 0.125,0.25)	1	0.51M

2.1. Surfactant(s) Selection

Several criteria are commonly used for the selection of suitable surfactants to formulate emulsions. Such includes the surfactant Critical Micelle Concentration (CMC) and Hydrophilic Lipophilic Balance (HLB), among others [1-3]. The issue with such criteria is that they only account for the surfactant-related properties and neglect other important aspects of emulsification such as the

temperature, salinity, and oil composition and properties. Hydrophilic Lipophilic Deviation (HLD) concept attempts to address this issue by accounting for other conditions in the emulsification process [38].

This work adopts the HLD concept to select suitable surfactants and assess the Gilsonite performance as the emulsifier. HLD has several components, including a surfactant-specific term, oil-specific term, temperature, and salinity. HLD is a function of the entire system under which the emulsion is prepared. **Equation 3** shows the HLD components and equation [38]:

$$HLD = Cc - k.EACN - a\Delta T + f(s) \quad (3)$$

where Cc is the characteristic curvature value that represents the surfactant solubility, EACN stands for equivalent alkane carbon number and describes the oiliness, k and a are constants, ΔT is the temperature difference from 25° Celsius, $f(s)$ is the salinity term where s is the salinity in g/100ml. $f(s)$ equates $\ln(s)$ for ionic surfactants and $0.13s$ for non-ionic surfactants.

HLD value of zero indicates an ideal and balanced system in which the interfacial tension is minimum. Negative HLD values suggest an O/W emulsion will take shape while positive HLD values indicate the formation of W/O emulsion [38]. In this study, emulsions were prepared at room temperature and ambient pressure, and EACN of Paraffinic mineral oil is reported 18 elsewhere [38]. Therefore, a Cc larger than 3.06 is required in a non-saline system to formulate a W/O emulsion. Span family of non-ionic surfactants such as Span 83 (Cc : 4-5) can meet this requirement. However, asphaltene alone as the surfactant with a low Cc value (Cc :0.8-2.3 [39]) cannot stabilize a W/O emulsion when mineral oil is present in the system. Though, a blend of the surfactants can lead to W/O emulsions' formation if the mixture Cc value exceeds 3.06. Cc of a blend of surfactants can be determined by **Equation 4** in which x is the molar weight of the surfactant i [39]:

$$Cc = \sum x_i.Cc_i \quad (4)$$

3. Results and Discussions

3.1. Colloidal Behavior and Precipitation of Asphaltene in Oil

Colloidal instability index (CII) is 4.34 for Gilsonite, indicating very unstable conditions for the asphaltenes. When Gilsonite is added to mineral oil, mainly composed of saturates, CII will only increase, signifying the deposition severity of the asphaltenes in the mineral oil. A visual assessment of this deposition was performed by adding 1% wt/v Gilsonite to the mineral oil, and severe deposition of asphaltene was observed in the sample after only 5 minutes. **Figure 4** displays the asphaltene deposits on the bottom surface of the beaker.

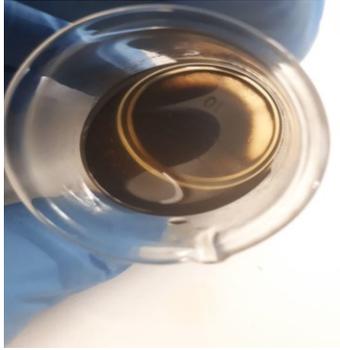


Figure 4- Asphaltene deposition in the mineral oil

The size of the aggregates in the mineral oil was determined for four levels of Gilsonite concentration according to the testing plan presented in **Table 3**. Experimental values are the average of three samples. **Figure 5** displays the variation in the representative sizes with Gilsonite concentration in mineral oil, and **Figure 6** shows both number-based and volumetric-based size distributions. Minimum Feret diameter was used to calculate the representative sizes following a comparison study, which showed minimum Feret diameter and EQPC are fairly similar in the description of the aggregate sizes, especially for the aggregate sizes larger than 2 micrometers, with the maximum 10% variability for the aggregates smaller than 0.5 micrometers.

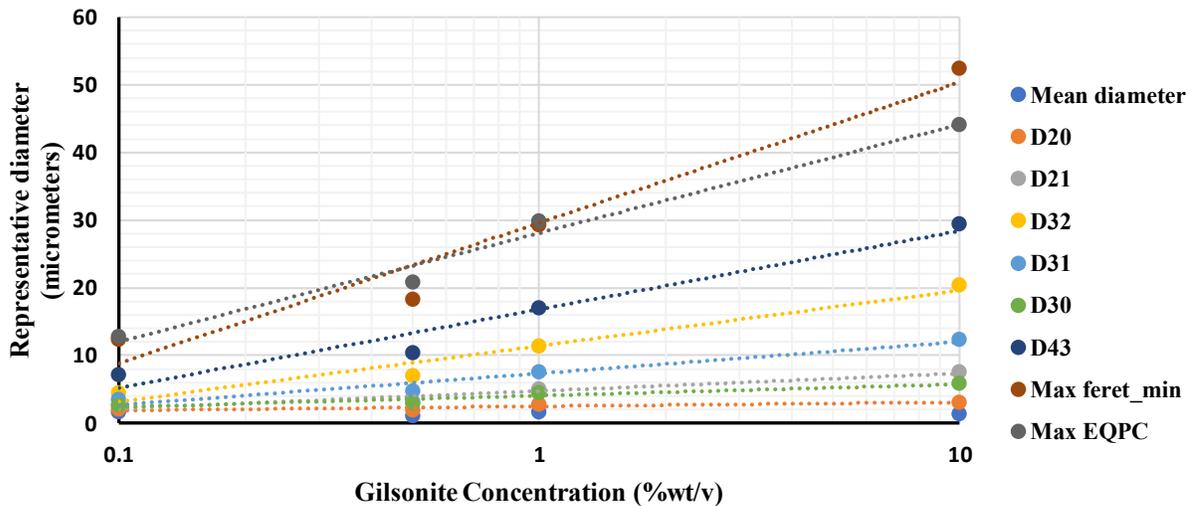


Figure 5- Representative sizes of the asphaltene aggregates for different concentrations of Gilsonite in mineral oil

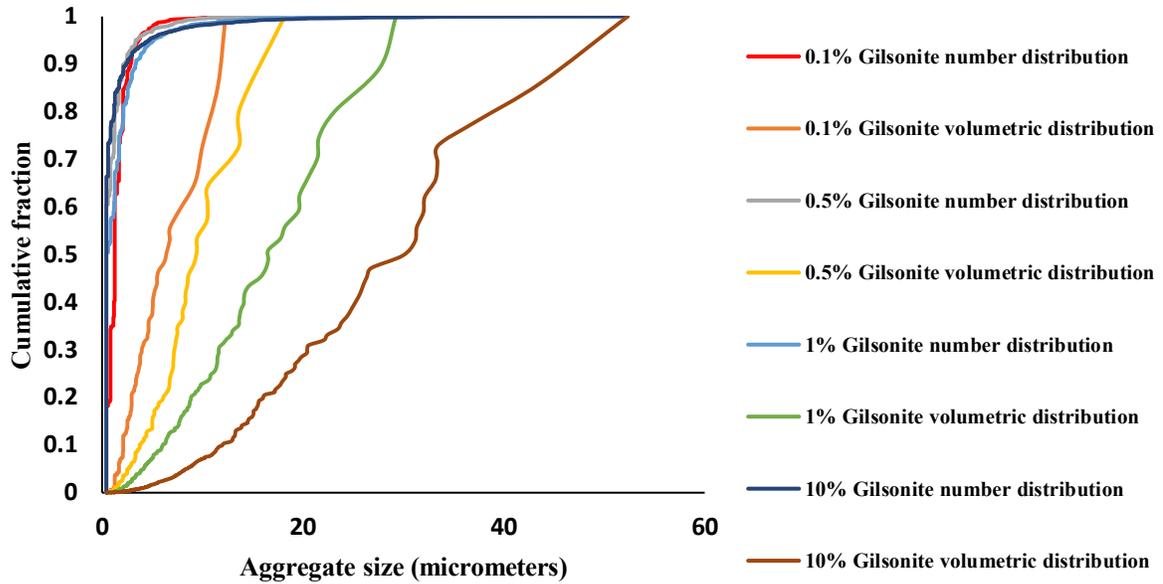


Figure 6- Number and volumetric-based size distribution of the asphaltene aggregates for different concentrations of the Gilsonite in mineral oil

According to the results presented in **Figure 5** and **Figure 6**, number-based representative sizes such as the arithmetic mean diameter of the aggregates and number-based size distribution do not exhibit meaningful differences with Gilsonite concentration. However, area and volumetric representative sizes and volumetric size distribution of the aggregates increase with the added Gilsonite dosage in the mineral oil. This implies a higher fraction of the sample's actual volume is occupied by larger aggregates, while the frequency fraction of the aggregates does not change substantially. The following equation form can describe the mathematical trend of increase in aerial and volumetric representative sizes:

$$D_{pq} = p_1 \ln(C) + p_2 \quad (7)$$

where D_{pq} is the representative size in micrometers, C is the concentration of the Gilsonite (~asphaltene) in the oil phase (%wt/v), and $P_{1,2}$ are calibration constants that are functions of the aggregate size.

Literature supports these results and indicates the aggregates' size increases with higher asphaltene concentration in the system [26]. **Figure 7** displays the micrographs of the mineral oil samples containing different Gilsonite concentrations that explicitly show that the maximum size and number of the aggregates increase with more asphaltene in the mineral oil. However, the fraction of smaller-sized aggregates increases simultaneously, suggesting only small differences in the frequency-based cumulative fraction of the aggregate size distribution are expected. This fraction corresponds to the new size range forming due to a higher concentration of the asphaltene in the mineral oil. Added Gilsonite concentration corresponds to an increase in the precipitation level in the mineral oil due to insolubility of asphaltene in saturates which in turn results in clumping of the asphaltene aggregates and formation of larger flocs [40].

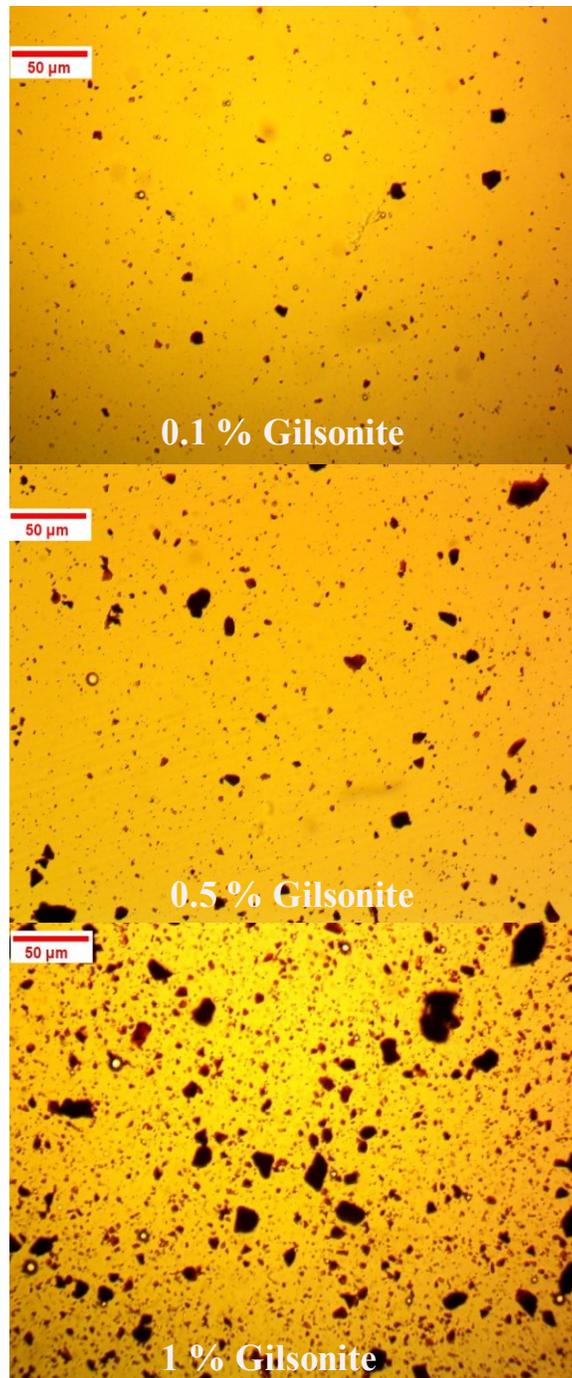


Figure 7- Micrography of the mineral oil with different concentrations of Gilsonite

In the next phase, Gilsonite was added in two concentrations to the blended oil containing mineral oil and three volumetric fractions of Toluene. This was done under the testing matrix shown in **Table 3** to perform a full factorial experimental design. The number of aggregates and changes in the aggregates' size were determined for each oil blend sample. The total number of aggregates detected by microscopy is a measure of asphaltene solubility or precipitation rate. A lower number of aggregates counted corresponds to less asphaltene precipitation in the oil sample. The

hypothesis is that less precipitation is expected when the fraction of Toluene increases in the oil blend because of the high asphaltene solubility in the aromatics.

Figure 8 shows the number of aggregates detected in the micrography of oil blend samples in a Gilsonite concentration range. The largest number of detected asphaltene aggregates is observed in the mineral oil with Gilsonite's highest concentration. As expected, adding Toluene to the oil blend resulted in a decrease in the number of detected precipitates due to asphaltene's solubility in the aromatics. However, the rate of change in the number of precipitates is sharper when the concentration of asphaltene is higher in the oil blend up to a point where the fraction of Toluene is high enough that overcomes the effect of asphaltene concentration in the oil blend (50% Toluene in the oil blend). At that critical point, the precipitation intensity is very small and independent from the concentration of asphaltene in the system (for the range of asphaltene concentration examined here).

Figure 9 displays the change in the aggregates' size for the oil blends with 1 %wt/v Gilsonite. Again, the trend shows that the aggregates' mean size does not change, indicating an equal decrease in the size of all the aggregates. This interpretation can be verified by the witnessed decreasing trend of Sauter diameter and De Broukere diameter with a larger fraction of Toluene in the oil blend. These representative diameters suggest that the aggregates' volume is decreasing. For the mean aggregate size to remain somewhat constant, such a decrease should apply to all aggregates in the oil sample.

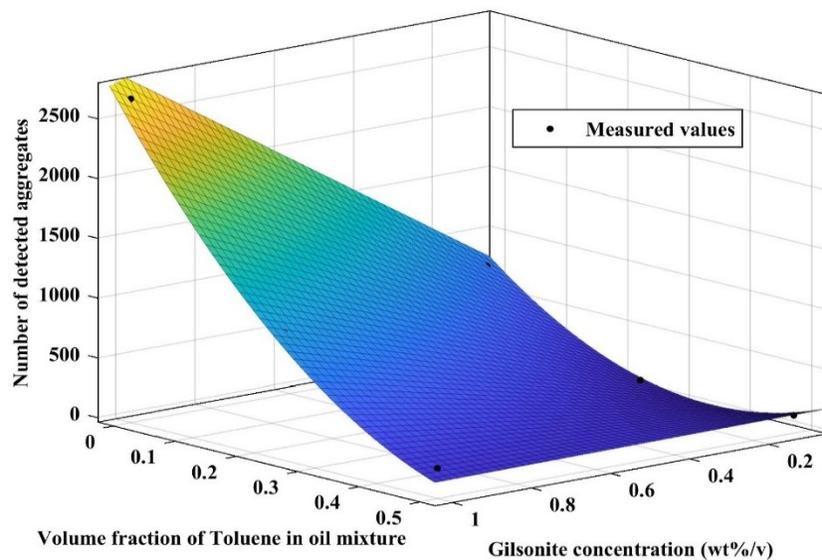


Figure 8- Number of asphaltene aggregates detected in the micrograph for a range of Gilsonite concentration and Toluene fraction in the oil blend

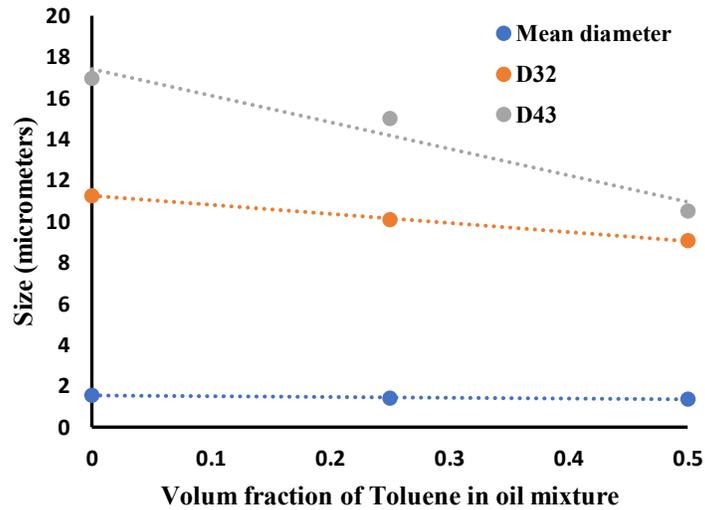


Figure 9- Change in the size of the aggregates with the addition of Toluene in different fraction to the oil blend containing mineral oil and Toluene

To summarize, the precipitation severity is the highest in the mineral oil with greater concentrations of Gilsonite. Adding Toluene to the oil causes more solubility of the asphaltenes and less precipitation. Precipitation severity is a function of oil composition and concentration of asphaltene. When the volume fraction of Toluene is large enough, the effect of oil composition dominates the asphaltene concentration parameter. In other words, the solubility of asphaltene in the fluid mixture increases. Larger aggregates form when more Gilsonite is added to the system, and smaller flocs form when Toluene fraction increases in the blended oil. Asphaltene precipitates clump together, forming larger particles (flocs). These larger asphaltene flocs tend to deposit and adsorb on the surfaces [19].

3.2. Base W/O Emulsion

A base W/O emulsion composed of 5 %wt/v Span 83 was prepared at ambient temperature and pressure. The emulsion samples were prepared with 1000 rpm and 1 min mixing time homogenization settings. The effects of phase ratio and salinity on the kinetic stability and droplet size of the emulsion samples were investigated.

Figure 10 illustrates the effect of salinity (NaCl) and phase ratio on emulsions' mean droplet diameter. The data points are the average of three experimental values for each case. A statistically significant interaction between salinity, water content, and the mean droplet size is visible in **Figure 10**. The mean droplet diameter is magnified with salinity in 10% emulsion, whereas the change in the droplet diameter with water salinity is statistically insignificant in the 40% emulsion.

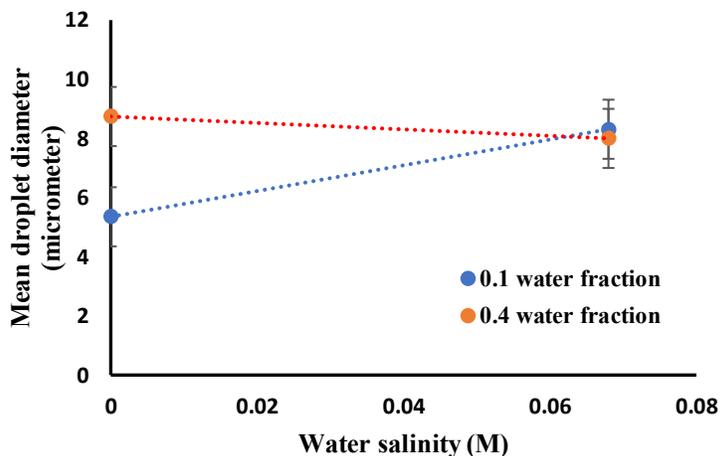


Figure 10- Effect of NaCl and phase ratio on the mean droplet diameter (Reproduced with permission from[41])

The increase in the droplet size for the dilute emulsion is most likely a result of the salting-out phenomenon, which leads to partitioning of the surfactant towards the oil phase and misorientation of the surfactant molecules. Salting-out is the reduction in the solubility of the aqueous phase when high concentrations of electrolyte in the water phase leads to the more frequent interactions between the solvent molecules and salt ions, leaving fewer solvent molecules available for interaction with the solute molecules (in this case surfactant molecules) [41].

The viscosity of the W/O emulsion increases in higher water content, which in turn reduces the rate of approach among the droplets. This can prevent the coalescence between the water droplets in the emulsion, causing further stability and preventing the emulsion droplets' enlargement. Kinetic stability results and the viscosity values demonstrated in **Figure 11** validates this hypothesis by showing that the concentrated emulsions are tighter than the dilute emulsion. Additionally, larger water droplets in the concentrated emulsions have a smaller interfacial area which requires a reduced amount of surfactant concentration for interfacial film coverage. This factor would also positively affect the kinetic stability of emulsions as observed in the case of concentrated emulsion which resists droplets coalescence in the presence of an electrolyte.

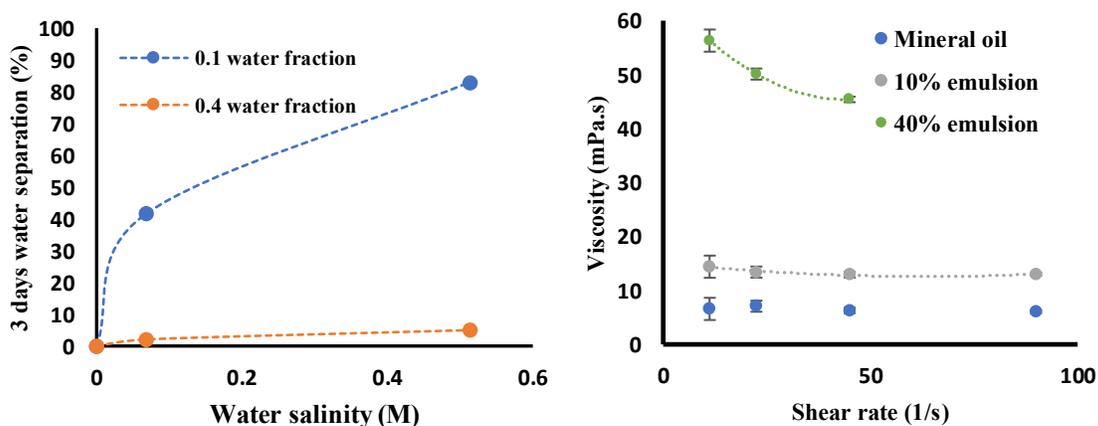


Figure 11- Left: Effect of water content and salinity on water separation in emulsion samples; Right: Change in the viscosity of emulsion with the phase ratio (Reproduced with permission from[41])

Statistical analysis of the results verifies the strong interaction between the mean droplet diameter, salinity, and phase ratio. P-value is smaller than 0.05 in the two-way ANOVA test that indicates the interaction effect is statistically significant. P-Value is 0.02 in the two-tail t-test in 10% emulsion between the mean droplet diameter for different salinity levels indicating a significant change in the mean droplet diameter with added salt concentration. However, a P-value of 0.16 in the two-tail t-test means the difference in the mean droplet diameter of the droplets with different levels of NaCl concentration in the 40% emulsion is statistically insignificant. In other words, the phase ratio's effect is dominant in the 40% emulsion, overriding the effect of salt in the system.

Finally, the mean droplet diameter increased with larger water content in the emulsions prepared without NaCl in the water phase. The difference is statistically significant and is caused by the elevation of viscosity in the 40% emulsion that requires higher mixing energy to form smaller droplets.

3.3. Model Emulsions

As discussed in Section 2.1, negative HLD values for the emulsions prepared at room temperature, with mineral oil as the continuous phase and Gilsonite as the stabilizer, indicate unlikeliness of forming the W/O emulsion. This was examined by preparing the emulsions in different Gilsonite concentrations (0.1 %wt/v and 1%wt/v). Emulsions exhibited immediate water separation after homogenization, which supports the premise presented. Therefore, a blend of surfactants was used to prepare model emulsion samples that yield a higher Cc value, guaranteeing the formation of W/O emulsion.

5% Span 83 was mixed with different dosages of Gilsonite, and the kinetic stability of the emulsion samples was put to the test. Moreover, the effect of oil composition on the stability of emulsions was assessed. **Figure 12** displays the emulsion sample prepared with Gilsonite only and the emulsion sample prepared with a blend of surfactants. Water phase separation is apparent in the bottom part of the samples prepared with Gilsonite in **Figure 12**. In contrast, the emulsions with a blend of surfactants show stability in terms of water phase separation upon preparation.

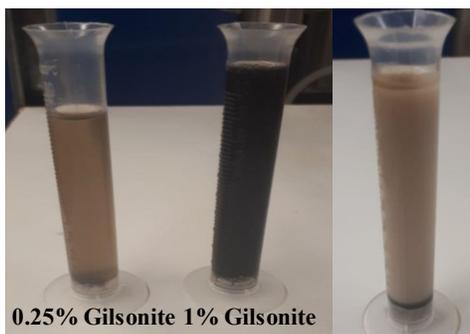


Figure 12- Left: Emulsions prepared with Gilsonite; Right: emulsion prepared with a blend of surfactants (0.25% Gilsonite and 5% Span 83)

Figure 11 implies that the base emulsion (5% Span 83) is stable during the three-day storage time when no electrolyte is present in the system. Water phase separation occurs when NaCl is added to the water and is magnified with higher electrolyte concentration. To examine the kinetic stability

of the emulsion samples prepared with Gilsonite and Span 83 surfactant blend, the salt's highest concentration in the water phase (0.51 M) from the previous round of experiments on the base emulsion was selected. The dilute emulsion shows intense water separation in this salinity level, as shown in **Figure 11**.

3.3.1. Model Emulsion with Mineral Oil

Bottle tests were performed for the 10% emulsions samples according to the testing matrix presented in **Table 4**. Samples were examined in the short term (2 hours) and longer storage time (3-days), and the separation of water from the emulsion with time was monitored. These experiments were initially carried out for the emulsions prepared with mineral oil, with results presented in **Figure 13**.

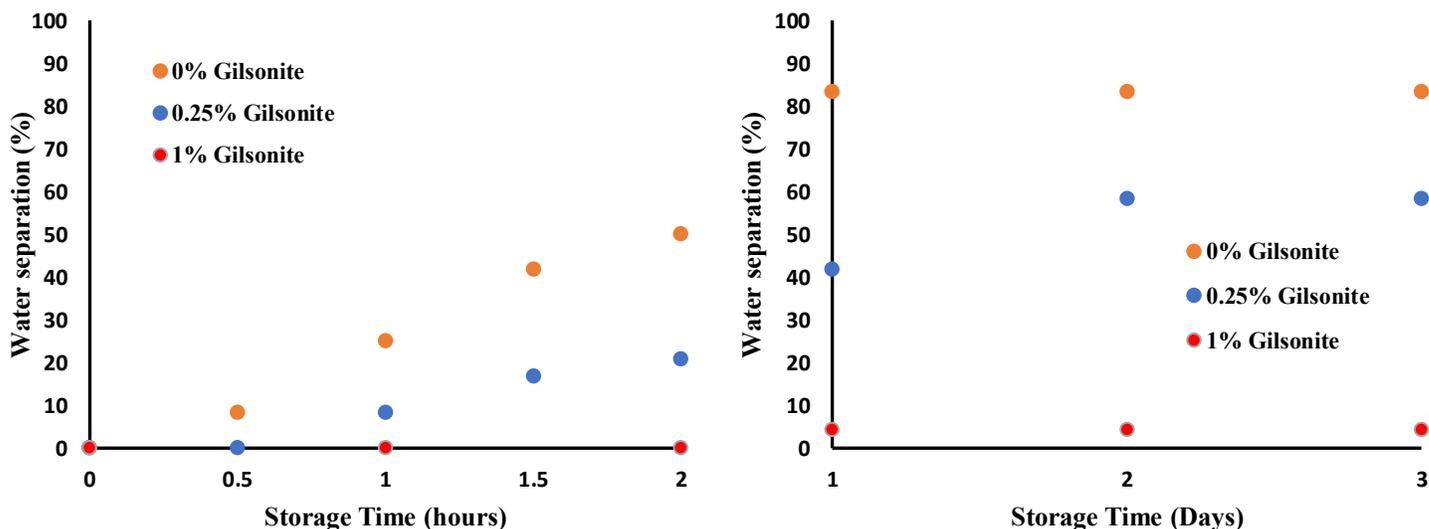


Figure 13- Water phase separation in model emulsions with mineral oil as the primary phase

According to the results depicted in **Figure 13**, emulsions with no Gilsonite (5% Span 83) demonstrated the highest water phase separation. The kinetic stability increased with the addition of Gilsonite to the emulsion and was improved for higher concentrations of Gilsonite. It can be concluded that the Gilsonite contributes to the kinetic stability of emulsions. Asphaltene aggregates cover the droplets' interfacial area during homogenization, establishing rigid films around them and stabilizing the emulsion through steric hindrance. **Figure 14** shows the micrography of the samples with/without Gilsonite and 0.51 M water salinity.

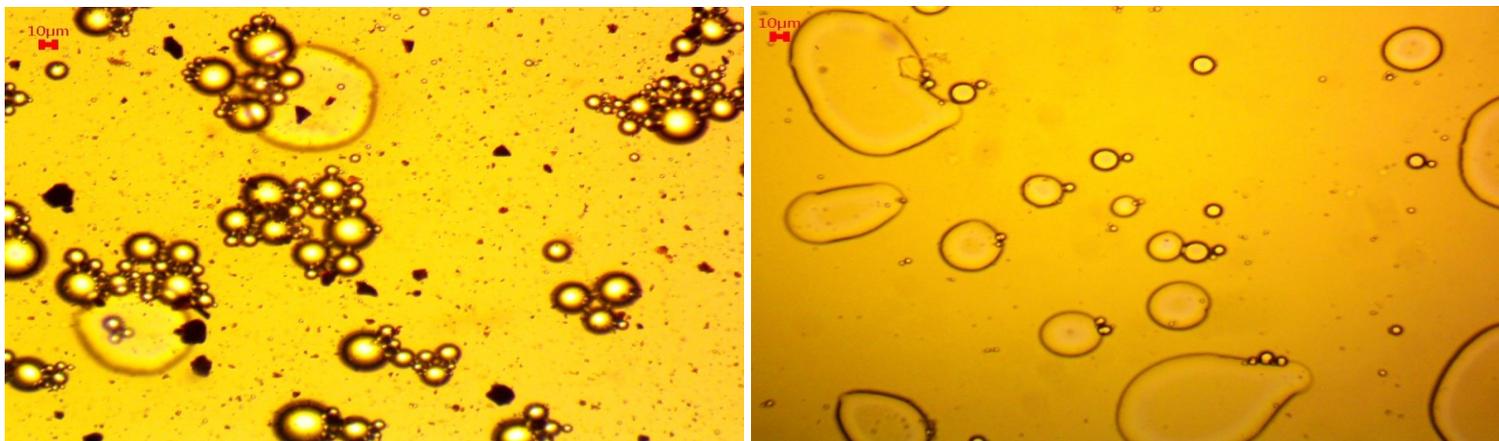


Figure 14- Micrographs of emulsion samples: 0% Gilsonite and 5% Span 83 (Right) and 0.25% Gilsonite and 5% Span 83 (Left) in emulsions prepared with 0.51 M NaCl

Micrographs show that emulsion without Gilsonite (5% Span 83) displays signs of droplet deformation and coalescence upon collision immediately after preparation. These are recognized mechanisms of instability in emulsions. Salting-out is responsible for the partitioning of the surfactant toward the oil phase and weak coverage of the surfactant molecules' interfacial films. On the other hand, emulsions with a blend of Gilsonite and Span 83 were more stable.

Although flocculation is detected in the emulsion samples because of the strong Van der Waals forces caused by electrolytes' presence in the system, droplets resist coalescence. This is due to the formation of rigid interfacial films with asphaltene aggregates contributing to this phenomenon. Micrographs exhibit the difference in the appearance of the interfacial films of base emulsion and model emulsion with Gilsonite. The droplets are protected by thicker and darker surfactant(s)-covered films. This is in agreement with the results in previous studies where the formation of rigid and viscoelastic interfacial films by asphaltene aggregates is reported [27-29,40]. Nano and micro aggregates cover the droplets during homogenization and prevent the coalescence of the droplets upon flocculation. However, larger asphaltene aggregates are mostly dispersed in the oil phase and are unlikely to stabilize the emulsion. Further notes on the importance of the aggregates' size in stabilizing emulsions are included in section 3.3.2.

Finally, a sensitivity analysis was performed on the effect of Gilsonite concentration on the droplets' size and viscosity of the emulsion. **Figure 15** illustrates the change in the mean droplet diameter of the 10% emulsion samples with 5% Span 83 and a range of Gilsonite concentration. The mean droplet diameter increased linearly with the addition of Gilsonite in the emulsion. This is presumably due to the elevated viscosity of the emulsion due to added Gilsonite, which is a well-known viscosifying agent [6].

The effect of Gilsonite on the emulsion's viscosity was characterized for 10% emulsion with 0.1 %wt/v Gilsonite and 5 %wt/v Span 83 and compared to the base emulsion. It should be noted that the attachment of asphaltene aggregates on the cone results in erroneous readings of viscosity. It is generally challenging to measure the viscosity of fluids containing asphaltene, regardless of the type of the viscometer [42]. This is especially the case when higher concentrations of Gilsonite are

added to the fluid. Thus, the emulsion's viscosity was tested only for 0.1 %wt/v Gilsonite, and the results are displayed in **Figure 16**.

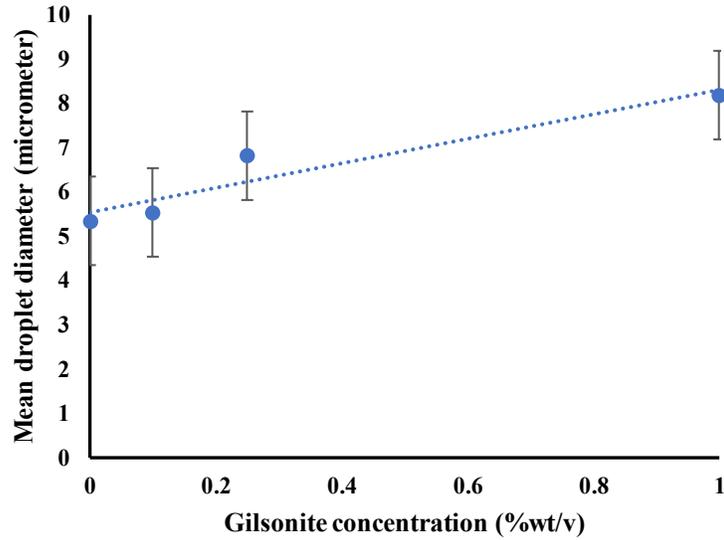


Figure 15- Change in the droplet size with Gilsonite concentration

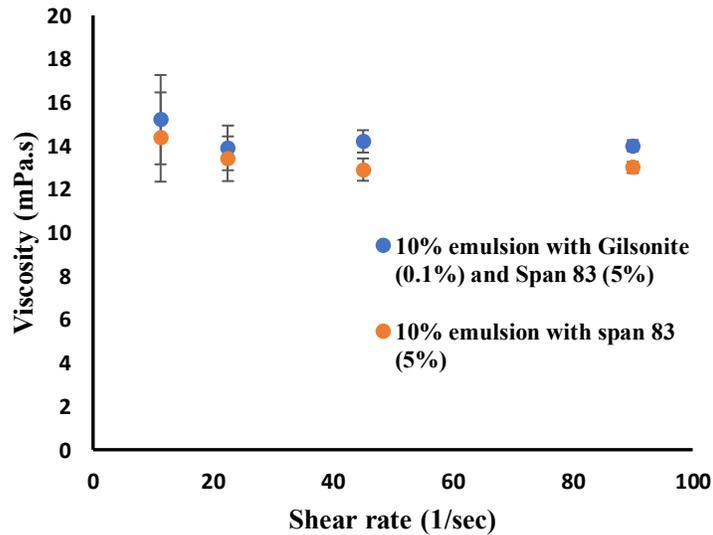


Figure 16- Viscosity of the 10% emulsion with and without Gilsonite

Results presented in **Figure 16** prove the viscosifying effect of Gilsonite in the fluid mixture. The elevated viscosity influences the size of the droplets and stability of the emulsions, as shown in **Figure 13** and **Figure 15**. The emulsion's higher viscosity is thought to be a stabilizing factor by reducing the rate of approach among droplets [43]. Therefore, Gilsonite enhances emulsions' stability by increasing the viscosity and steric hindrance provided by small asphaltene aggregates covering the droplets' interfacial film.

3.3.2. Model Emulsion with the Oil Blend

The testing matrix shown in **Table 4** was followed with 2 levels of Gilsonite concentration and 3 levels of Toluene to mineral oil volumetric ratios to investigate the effects of oil composition and asphaltene concentration on the kinetic stability of the model emulsions. **Figure 17** displays the 3D plot of 3-day water separation in 10% emulsions. **Figure 18** displays the short term (2 hours) and a longer storage time (3 days) water phase separation of the model emulsions in different oil blends and 0.25 %wt/v Gilsonite. **Figure 19** demonstrates similar test results for model emulsions with 1% wt/v Gilsonite.

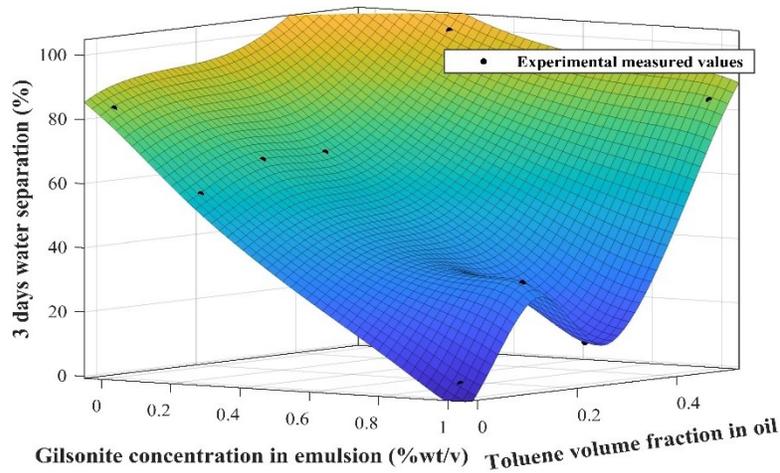


Figure 17- water phase separation (3 days storage time) for the blends of oil and a range of Gilsonite concentration

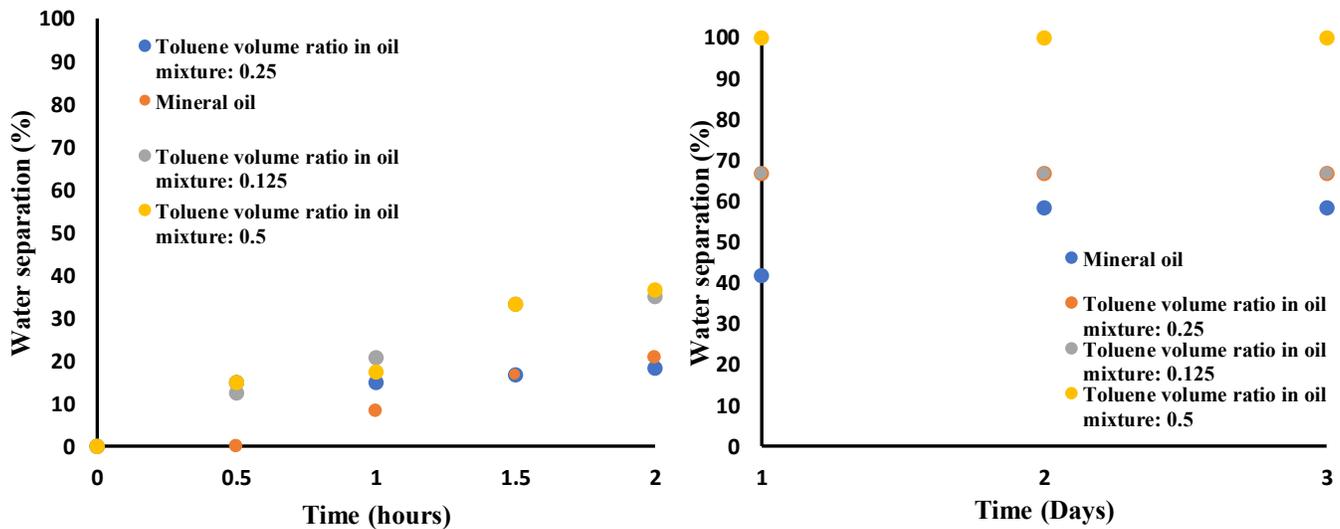


Figure 18- Water separation in emulsions with different oil blends and 0.25 %wt/v Gilsonite

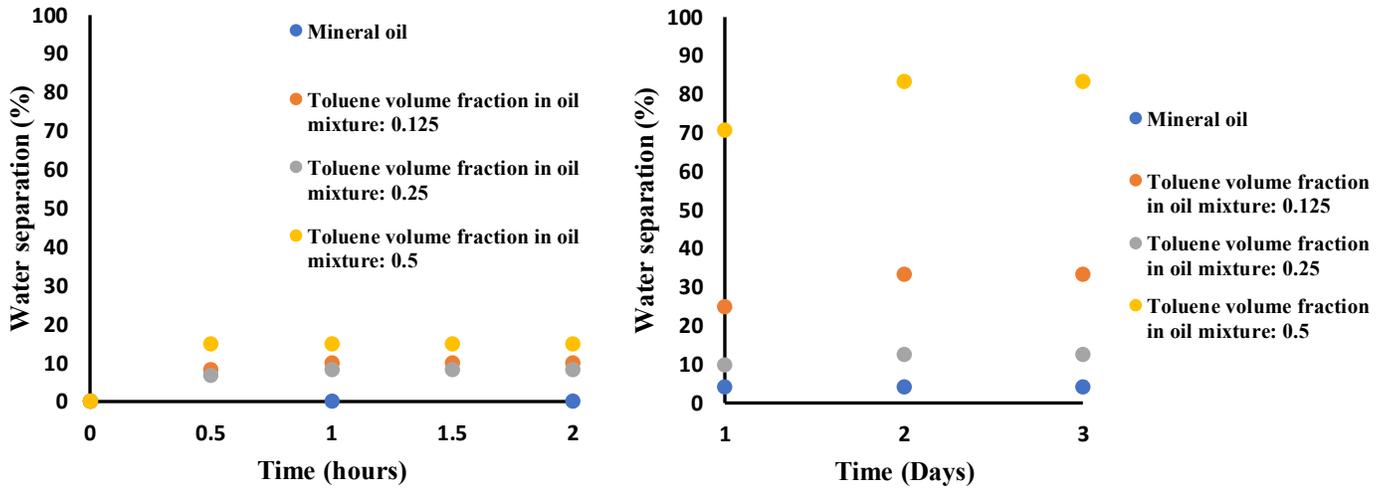


Figure 19- Water separation in emulsions with different oil blends and 1% wt/v Gilsonite

As expected, emulsions prepared with mineral oil exhibit the least water phase separation, representing the most stable emulsions. Literature similarly reports the higher stability of the emulsions when precipitation increases [26]. The highest level of precipitation was observed in mineral oil, as shown in **Figure 8**. The least stable emulsion was the one prepared with 50% Toluene in the oil mixture. In a high fraction of Toluene in the oil blend, the intensity of precipitation is minimized, as shown in **Figure 8**, due to the high solubility of asphaltene in aromatics. Hence, asphaltene precipitation has a crucial role in promoting the stability of emulsions.

Figure 17 shows that emulsions' stability in 12.5% and 25% Toluene in oil mixture was quite similar in emulsions with 0.25% wt/v Gilsonite. **Figure 19** indicates that emulsion with 25% Toluene in oil mixture is even more stable than the emulsion with 12.5% Toluene and 1% Gilsonite, which contradicts the common assumption that higher precipitation always parallels the formation of a more stable emulsion [23-25]. **Figure 8** shows that the higher the Toluene, the less the asphaltene precipitation, and the expectation was to witness higher emulsion stability with lower Toluene in the oil mixture. The experimental results of the stability tests refute this hypothesis.

A colloidal approach was adopted to investigate the role of asphaltene aggregates in stabilizing emulsions. In this perspective, asphaltene aggregates are considered colloidal particles. They are treated as solid particles that cover the droplets' interfacial area and prevent the coalescence of the droplets through steric hindrance. For this to be true, the size of the solid particles must be smaller than the droplets to contribute to emulsion stability, as is the case for a Pickering emulsion [44].

In this approach, both the aggregate and emulsion droplet sizes are equally important. Moreover, the intensity of precipitation and the number of aggregates are of the utmost importance for emulsions stability. The reason the least stable emulsion has the highest fraction of Toluene and the least concentration of Gilsonite, as depicted in **Figure 17**, can be associated with less precipitation in such conditions. **Figure 8** shows the number of aggregates detected in the oil blends is considerably high for both 12.5% and 25% Toluene especially when Gilsonite

concentration is high (1% wt/v). Besides, there is no significant difference in the number of aggregates between 12.5% and 25% Toluene when Gilsonite concentration is 0.25%. This means that many aggregates can contribute to the droplets' stability in the case of 1% Gilsonite, even for 25% Toluene in oil mixture. Also, the number of aggregates that potentially cover the droplet interfacial area for 25% Toluene is fairly close to the 12.5% Toluene when 0.25% Gilsonite is present in the system. The latter can describe equal stability observed in 12.5% and 25% Toluene emulsion samples with 0.25% Gilsonite. However, the number of aggregates analysis (asphaltene precipitation intensity) cannot justify emulsion's superior stability with 25% Toluene compared to 12.5% Toluene when Gilsonite concentration is 1% wt/v.

Figure 9 displays the size of the asphaltene aggregates decrease with the addition of Toluene to the oil blend. In emulsion with 1% wt/v Gilsonite, the mean aggregate size to mean droplet size ratio of the emulsion with 25% Toluene in oil mixture is 0.06 while this value is 0.14 for the 12.5% Toluene, showing 133% variation between the two emulsions. The smaller this value, the better the potential for the asphaltene aggregates to cover the droplets. Such conditions favor the stability of emulsions with 25% Toluene compared to the 12.5% Toluene.

The mean size of the aggregates/droplets may not be the optimum representative size to describe emulsions' stability. Volumetric-based representative sizes describe the physics more accurately by depicting the sample's actual volume occupied by the particles of a specific size. Therefore, the particle size distributions (aggregates and emulsion droplets) are illustrated in **Figure 20** to understand better where the aggregates and droplets' size lie concerning one another.

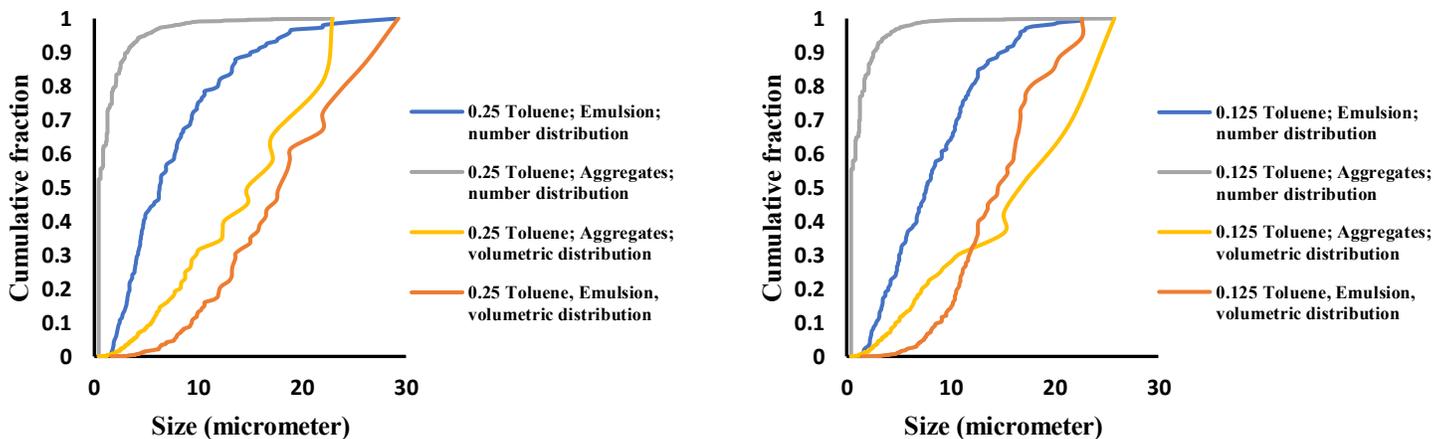


Figure 20- Aggregate and droplet size distribution in 10% emulsions with 1% Gilsonite and Left) 25% Toluene; Right) 12.5% Toluene

The particle size distributions shown in **Figure 20** indicate the aggregates in emulsion with 25% Toluene are generally sorted in a fashion that the smaller asphaltene aggregates could potentially cover all droplets. However, this is not the case for 12.5% Toluene where a significant portion of aggregates is larger than the droplets, which cannot take part in stabilizing the emulsions. This is reflected in the stability experiments and justifies the improved kinetic stability of the 10% emulsion with 1% wt/v Gilsonite and 25% Toluene compared to the 12.5% Toluene.

Finally, the stability of the emulsion can also be influenced by interfacial tension [2]. However, the kinetic stability of W/O emulsions prepared with non-ionic surfactants and even with

asphaltene is thought to be mainly driven by the steric hindrance and through mechanical stability provided by the surfactants [19]. For completeness, the surface tension of different liquid mixtures was calculated in capillary rise experiments and the contact angle was determined using optical microscopy. Contact angle values obtained in surface tension experiments (liquid-air-capillary tube systems) exhibit no significant difference for the mineral oil+Span and mineral oil+Span+Gilsonite. This was also the case for the surface tension of these two liquids.

IFT between the mineral oil containing Span 83 and water at CMC is reported 13.18 dynes/cm elsewhere [30]. There was an insignificant change in the contact angle of the mineral oil containing Gilsonite and Span 83 compared to the mineral oil+Span 83 and one may conclude the change in interfacial tension is not considerable. However, this requires further examination and measurement of interfacial tension for the system that includes both liquids for a more realistic assessment. **Figure 21** and **Figure 22** illustrate the contact angles and measured surface tension for different fluids.

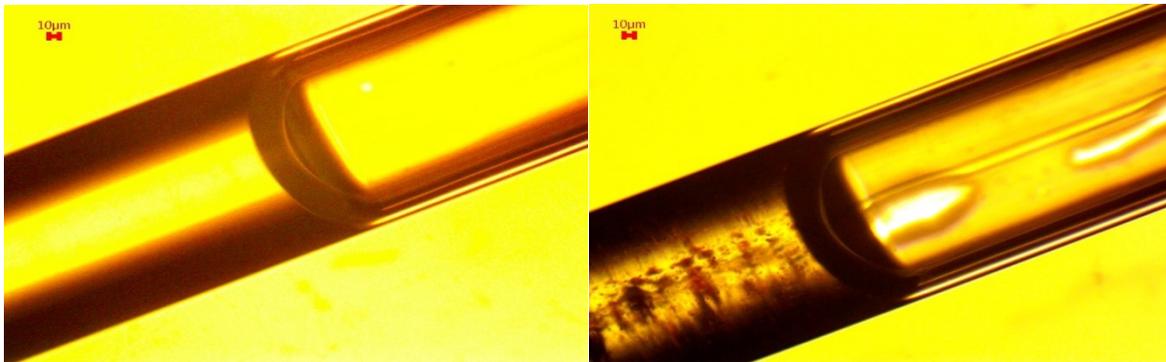


Figure 21- Contact angle between mineral oil+Span 83-air (Left) and mineral oil+Span 83+Gilsonite-air (Right) showing the same value of approximately 30°.

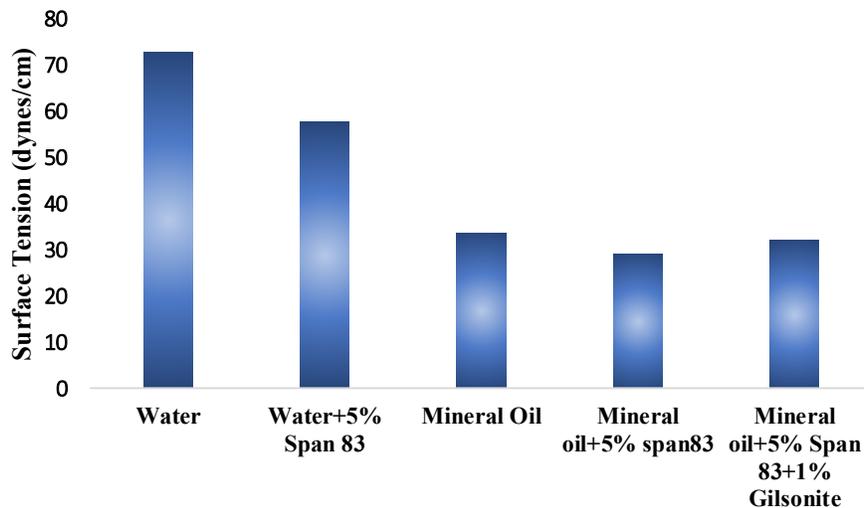


Figure 22- Measured surface tension for different liquids

3.3.2.1. The Effect of Phase Ratio

This trend was reversed for the 40% emulsion with 1% wt/v Gilsonite. The experiments show significantly higher water separation in emulsion with 25% Toluene than 12.5% Toluene in the oil blend when the water content was increased to 40%. Moreover, emulsion stability was improved for the 40% emulsion with 12.5% Toluene than the 10% emulsion containing the same amount of Toluene in the oil blend. **Figure 23** displays the water separation for emulsions with 2 levels of water content. It should be noted that the concentration of Gilsonite was kept constant (1% wt/v) with reference to the oil phase, and the same is true for the salt in the water phase (0.51 M). **Figure 24** illustrates the mean droplet diameter variation with water content and Toluene fraction in the oil blend.

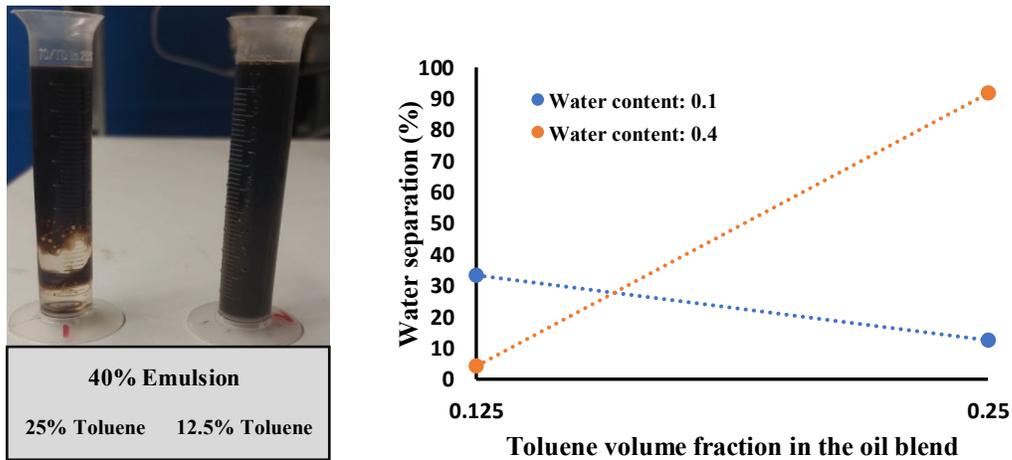


Figure 23- Water separation in emulsion with water content and Toluene fraction in the oil blend

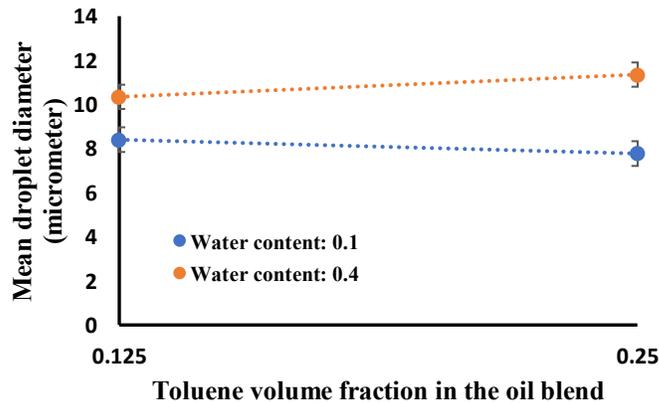


Figure 24- Mean droplet diameter variation in emulsions with Toluene fraction in the oil blend

As previously mentioned, two main conditions must be met for the asphaltene to stabilize the emulsions, including the adequate intensity of asphaltene precipitation and smaller aggregate size in relation to the diameter of internal phase droplets. According to **Figure 24**, the mean droplet diameter of the emulsion increases in higher water contents due to concentrated emulsions' elevated viscosity. Although the second condition is satisfied still, 40% emulsion with 25% Toluene is extremely unstable compared to 10% emulsion of the same Toluene content in oil.

An increase in the water content of emulsion is associated with more frequency of the number of droplets, as observed in the micrography. This condition amplifies the interfacial area that requires more asphaltene aggregates for interfacial film coverage of the droplets. However, Gilsonite concentration in oil remains unchanged for 40% emulsion with 25% Toluene. The precipitation intensity is insufficient to meet the additional requirement of asphaltene precipitates for the droplets' coverage. Hence, the first condition (intensity of asphaltene precipitation) is not satisfied, resulting in a large water separation.

Asphaltene precipitation is high enough for promoting the stability of the 40% emulsion with 12.5% Toluene. The higher stability of the 40% emulsion than 10% emulsion with similar Toluene content in the oil blend can be explained in two ways. Firstly, the droplets' size is larger in 40% emulsion, and the ratio of mean aggregate size to the mean emulsion droplet diameter is even smaller than 10% emulsion (0.11 in 40% emulsion and 0.14 in 10% emulsion). Additionally, the stability of an emulsion can be augmented by higher viscosity, which reduces the rate of approach among droplets. It was shown in **Figure 11** that the base emulsions with higher water content exhibit higher viscosity. It can be concluded that a combination of higher viscosity and smaller aggregate to droplet size ratio provides the means of higher kinetic stability in 40% emulsions with 12.5% Toluene compared to the 10% emulsion of the same oil blend.

To summarize, testing results affirm that increasing the Gilsonite concentration (asphaltene concentration) enhances emulsion stability in all the oil blend samples examined. However, the effect is much more significant in mineral oil, resulting in the most stable emulsions. The least stable emulsions are the ones prepared with very high fractions of Toluene. Nonetheless, the addition of Toluene to the oil blend (mineral oil and Toluene) does not necessarily end in the formation of less stable emulsions.

Incorporating both colloidal and thermodynamical views of asphaltene precipitation indicates high precipitation accompanied by a smaller size of the asphaltene aggregates than the emulsion droplets' size yields higher kinetic stability emulsions. In the case of 10% emulsions with 25% Toluene in oil blend, more resistance to the water separation was recorded because these conditions were met. However, this was not the case for emulsion with 12.5% Toluene due to the significant portion of the asphaltene aggregates larger than the droplets.

The higher water phase ratio increased the emulsion droplets' size, emulsion viscosity, and the frequency of droplets. The lack of high asphaltene precipitation destabilized the 40% emulsion with 25% Toluene. In contrast, the combination of small aggregate to droplet size ratio, the elevated viscosity, and high asphaltene precipitation resulted in excellent stability in 40% emulsion with 12.5% Toluene. These results affirm that both conditions of asphaltene precipitation and smaller aggregates than the droplets must be satisfied to achieve stable emulsions.

The findings of this study have important implications for a better understanding of the crude oil emulsion features. Solvents (n-alkanes) used in the petroleum industry for in-situ upgrading of bitumen could lead to the intense precipitation of asphaltenes and the formation of tight W/O emulsions [45]. Although bitumen upgrading is desirable, the formation of tight emulsions could be costly and requires energy-expensive demulsification processes. It might be beneficial to re-

formulate solvents so that less stable emulsions are produced while sufficient precipitation of asphaltenes from the heavy crudes guarantees an improved recovery.

Conclusions

This paper introduced Gilsonite, mainly composed of asphaltenes, as a surfactant, and investigated the role of Gilsonite in stabilizing W/O model emulsion. Moreover, the effect of Gilsonite concentration and oil composition on the asphaltene precipitation was examined. It was found that the most severe precipitation occurs in the mineral oil with higher concentrations of Gilsonite. The addition of Toluene (aromatics) in the oil blend decreased the precipitation intensity. Also, the size of the asphaltene aggregates decreased by the addition of Toluene to the oil blend. Results indicate that most kinetically stable emulsions are prepared with mineral oil and more asphaltene in the system. Asphaltene precipitates/aggregates stabilize the emulsions through steric hindrance and form rigid interfacial layers around the droplets. The least stable emulsion contains a large fraction of Toluene (50%) in the oil blend. The 10% emulsion containing 25% Toluene in the oil blend exhibited higher stability than the emulsion with 12.5% Toluene. It was observed that the high asphaltene precipitation supported by the smaller aggregates compared to the droplet size causes this improvement in kinetic stability. These results contradict the consensus (thermodynamical models) that simply increasing the aromaticity minimizes the emulsion stability. Integrating colloidal and thermodynamical perspectives of the asphaltene precipitation can explain the results presented. Finally, increasing the water content in emulsion resulted in a change in the droplets' size and the frequency of droplets that require more asphaltene precipitation for stability. Therefore, the 40% emulsion with 12.5% Toluene was more stable than the emulsion with 25% Toluene, mainly due to the higher asphaltene precipitation.

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Nomenclature

Cc: Characteristic curvature
CII: Colloidal instability index
CMC: Critical micelle concentration
D10: Mean droplet diameter (micrometer)
D32: Sauter diameter (micrometer)
D43: De Broukere diameter (micrometer)
EACN: Equivalent alkane carbon number
HLB: Hydrophilic lipophilic balance
HLD: Hydrophilic lipophilic deviation
M: Molarity (mol/lit)
ppm: Parts per million
rpm: Rounds per minute
T: Temperature (°C)
W: mass fraction (%)

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“TOC Graphic”

