Influence of the Formulated Surfactant on the Characterization of the Base Oil

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Abstract. An emulsion is defined as a phase containing two immiscible liquids consisting of water and oil. In the oil and gas industry, the presence of emulsions results in high costs for pumping equipment, reduced performance and increased corrosion rates in pipelines and other equipment. Numerous studies have been conducted for crude oil emulsions, but are still lacking for emulsions present in base oil. Therefore, the research focuses on characterising the emulsified base oil by comparing the physical and thermophysical properties of the emulsified base oil with and without a formulated surfactant and using the base oil as a control sample to observe the stabilisation of the samples. Physical properties include material composition, particle size and distribution, density, viscosity and shear stress; thermophysical properties include thermal stability. Samples were prepared using a homogeniser (2 hours) followed by ultrasonic treatment (2 hours) with 10 mL of water and 190 mL of base oil at room temperature. About 10 mL of the formulated surfactant was added to characterise the emulsified base oil with surfactant. The samples were further analysed for molecular compounds, particle distribution, physical properties (density and viscosity) and thermal stability using DSC and TGA. The results showed that the emulsified base oil with formulated surfactant has higher viscosity and lower density than the emulsified base oil without formulated surfactant.

1. Introduction

Base oils and lubricants mainly contribute to transport, e.g. in car engines and other applications for smooth rotation and movement of the equipment. Lubricant comprises of base oil and additive, in which ~85% of the base oil in lubricating oil [1]. In addition, the composition of base oil consists of paraffin, isoparaffin, aromatic, and cycloparaffin molecules [2]. Furthermore, base oil can be divided into five different groups. According to the American Petroleum Institute (API), the first three groups of base oils (Group I, Group II, and Group III) are mostly refined from petroleum, while Group IV can be classified as fully synthetic oil and Group V as other types of base oils (silicones, polyesters, etc.)[3]. An emulsion is defined as a phase containing two immiscible liquids consisting of water and oil. Furthermore, an emulsion is the presence of two immiscible mixtures that exhibit unstable thermodynamic properties due to the difference in density between the oil and aqueous phases and the unfavourable contact between oil and water molecules [4]. In addition, the emulsion causes one of the liquids to disperse into the other and form tiny droplets [5]. The

stability of the index emulsion is determined by some properties such as density, resin content and viscosity [5].

The major challenges faced by the oil and gas industry in recent years are in the production process where more than 80% water is present [6]. The presence of water usually has two main causes: the reservoir and hydrocarbon production [6]. The presence of water in the base oil causes emulsification, resulting in an emulsified base oil. The emulsion often forms during transportation and storage of the base oil due to the presence of water vapour in the pipelines and tanks. The presence of an emulsion resulting in emulsified base oil has several disadvantages, such as accelerating the corrosion of transportation and storage equipment due to the presence of water vapour. Water vapour is a compound that contains a small amount of dissolved oxygen, which leads to acceleration of corrosion, high viscosity, high friction losses and also high pressure drop [7]. Due to the above factors, the production cost increases to solve the problem of emulsified base oil as the emulsified base oil affects the quality of the base oil [6].

In this study, the characterisation of the base oil was investigated. A patented formulated surfactant was added to the emulsified base oil as the surfactant acts as a stabiliser in the oil phase solution. To reduce the water-in-oil tension, the formulated surfactant was added. The formulated surfactant is a non-ionic surfactant consisting of natural sunflower and rapeseed oil and polyol (D-sorbitol). Furthermore, the study is based on the preparation of a stable emulsion and the base oil serves as a control sample. Previously, it was shown that the formulated surfactant is an effective stabiliser in emulsified crude oil and this research aims to determine the effectiveness of stability in the base oil [7].

Currently, many studies are being conducted on emulsified crude oil, including characterisation, thermophysical properties and separation methods to remove water or stabilise the emulsion to achieve better quality of emulsified crude oil instead of emulsified base oil [7]. Therefore, this work focused on the preparation of a stable emulsion to mimic the industry's problem in handling stable emulsions. The stable emulsion was prepared by adding the formulated surfactant before characterising the prepared emulsion for further analysis. A comparison between the addition and the addition without the formulated surfactant was investigated to determine the stabilisation and quality of the base oil.

2. Methodology

2.1. Materials and methods

The base oil was supplied by a local company in Klang, Selangor. The formulated surfactant consists of sunflower oil, canola oil, and D-sorbitol. In this study, the formulated surfactant was considered as a finished product without going to focus on the details of the formulation.

2.2. Preparation of emulsified base oil

The preparation of emulsified base oil consisted of emulsified base oil with formulated surfactant (EBF) and without formulated surfactant (EB). The EBF was prepared by adding 195 mL of base oil with 10 mL of formulated surfactant. The solution was mixed using ultrasonic (Elmasonic P) for 2 hours with default settings. Then, about 5 mL of water was added and proceeded using a homogenizer (IKA T18 basic ULTRA-TURRAX) for 2 hours. In the meantime, the solution for EB consisted only of base oil and water. The same preparation method was carried out, using an ultrasonic device to break up the particles by cavitation and to ensure the uniformity of the solution with a homogeniser.

2.3. Samples characterization

The physical properties (density, viscosity, volatility, and particle size distribution) and thermophysical properties (thermal stability) were tested through a series of experiments as explained in the following subsections. All the samples were tested, including control samples (pure base oil) and emulsified base oil with and without formulated surfactant.

2.3.1. Physical properties
The physical properties included the identification of the chemical bonding, particle distribution, viscosity, and density size in terms of using FTIR, microscopic test, viscosity test, and density test, respectively. All of the analysis has been conducted at room temperature (25ºC). All the analysis has been conducted thrice to ensure accuracy.

2.3.1.1. Fourier Transformed Infrared (FTIR)
FTIR is a test used to identify unknown materials such as compounds in the solution. The compounds in each sample were tested by using an FTIR spectrometer (PerkinElmer Spectrum 100, USA). 2 drops of the sample was placed in a cuvette and analysed within the resolution range of 450 to 4500 cm^{-1} with a total of 18 scans. The results were collected and processed on the computer (Spectrum software).

2.3.1.2. Particle distribution
The particle size and distribution of the samples had been identified by using a microscope (SWIFT 3004648, Malaysia). A drop of sample had been put on the slide and observed under the microscope with the size of the objective lens of x 40. The size distribution of the solution particles had been observed through a computer that is connected to the microscope.

2.3.1.3. Viscosity
The viscosity of each sample was determined using a viscometer (Brookfield DV-II+ Pro, USA). About 16 mL of each sample had been inserted into the U.L. adapter (which is made up of a water jacket, chamber tube, collar with the thumbwheel, and tube end cap). The spindle used for the viscosity test was type S00 with a speed of 2 rpm. The measurement for the viscosity of base oil is based on the torque percentage (the acceptance results need to be more than 10% or else the results will be invalid).

2.3.1.4. Density
The density of each sample was measured using a density meter (Anton Pear DMA 35 Basic). Approximately 2 mL of samples had been inserted into the equipment into the analyzer and waited for a minute before the reading density could be recorded. For more accuracy, a triple analysis had been conducted at room temperature (25℃).

2.3.1.5. Rheometer
The shear stress over shear rate can be obtained by using a rheometer (Thermo Scientific, USA). Approximately 10 mL of samples were inserted into the becher and cup (CCB26) and locked by the rotor (CC26 Ti). The samples had been waited for a minute and were analysed using a computer.

2.3.2. Thermophysical properties
Thermophysical properties have been conducted to investigate the characterization of the samples based on the thermal effects. Firstly, the degradation of the sample was identified by using TGA prior to further analysed on the thermal physical properties followed by using DSC to identify the crystallization of the samples. The thermophysical properties (thermal stability) had been tested through a series of experiments and had been explained in the subsections below.

2.3.2.1. Thermogravimetric analysis (TGA)
The TGA was conducted by using a thermogravimetric analyzer (PerkinElmer TGA 8000). The measurements have been performed using nitrogen gas with a flow rate of 20 ml/min. Around 5 mg of samples have been inserted into the ceramic crucible. The temperature measurements started from 30℃ and ended at 500℃ with the heat rate of 5.5℃/min. All the results were analyzed on the computer via software embedded with the TGA to depict the weight of the samples that changed before and after the heating

processes. In addition, the thermal stability and volatile fraction for each sample have been obtained from this analysis.

2.3.2.2. Differential scanning calorimeter (DSC)
Differential Scanning Calorimeter is a thermal analysis apparatus used to measure how the physical properties of a sample change along with the temperature against time by using a Differential Scanning Calorimeter (PerkinElmer DSC 8500, USA). Around 5 mg of samples have been inserted into the aluminum crucible using a micropipette and covered with an aluminum cover. The measurements have been performed by using nitrogen gas with a flow rate of 20 ml/min. The temperature started from -90℃ to 30℃ and ended at -90℃ with a heat rate of 5.5℃/min. Hence, the samples were inserted into the DSC equipment and further analyzed in the DSC software.

3. Results and discussion

3.1. Physical properties
The properties of the control sample (BO) emulsified base oil with (EBF) and without (EB) the formulated surfactant were investigated by FTIR, microscopy, viscosity test, density test and rheometer test to observe the chemical bond, size of distribution, viscosity, density, shear stress and shear rate.

3.1.1. Fourier transformed infrared (FTIR)
Figure 1 shows the comparison of the compound structures in base oil as a control sample, EBF, and EB. Both the control sample and EBF show almost similar functional groups in the sample, except for a small amount of water (hydrogen bonding) in EBF at 3403.89 cm^{-1}. The peaks at ~2921 cm^{-1} and ~2852 cm^{-1} correspond to the symmetric and asymmetric CH_2, both present in EBF and base oil [8]. However, a small peak at 2922.77 cm^{-1} is observed for EB due to the absence of the formulated surfactant. The oscillation of N=O bending was observed at 1376.80 cm^{-1} for both base oil and EBF. The function of nitrogen compounds in the base oil shows that they increase the oxidation rate and decrease the lifetime of the base oil [9]. The presence of nitrogen compounds in the base oil shortens the life of the base oil. Therefore, the period of the base oil including the collection of the base oil for analysis should also be considered before analysing the properties of the base oil. Moreover, the peaks at 1458.61 cm^{-1} and 1459.44 cm^{-1} correspond to aromatic rings and the type of vibration is asymmetric C-C=C stretching. The presence of aromatic rings, especially asphaltenes, has the advantage that they can stabilise the water-in-oil emulsion by forming a thick layer on the water droplets [10]. The absorption peaks at ~2852.39 cm^{-1} and ~2920.88 cm^{-1} are due to the presence of alkanes, which are asymmetric and symmetric H-C-H stretches, respectively. The presence of alkanes in base oil is due to the fact that base oil is derived from heavy saturated hydrocarbons [11].

Moreover, a broad peak at 3339.65 cm^{-1} for EB corresponded to the group OH. Moreover, comparison with the presence of water shows that EB has broader peaks compared to emulsified base oil with formulated surfactant. The presence of the sharper peaks indicates that the compound in these samples is purer and has stronger bonds [12]. The broad peak at about 3339.65 cm^{-1} indicates the presence of the OH stretching for the emulsified base oil without the addition of emulsifier to the base oil. However, compared to the added emulsifier, a weak intermolecular interaction is observed for the bond OH, which is attributed to the stability of the emulsion and the strong attraction between the emulsifier and the base oil. FTIR characterisation thus shows that the presence of a formulated surfactant produces a stable EB.

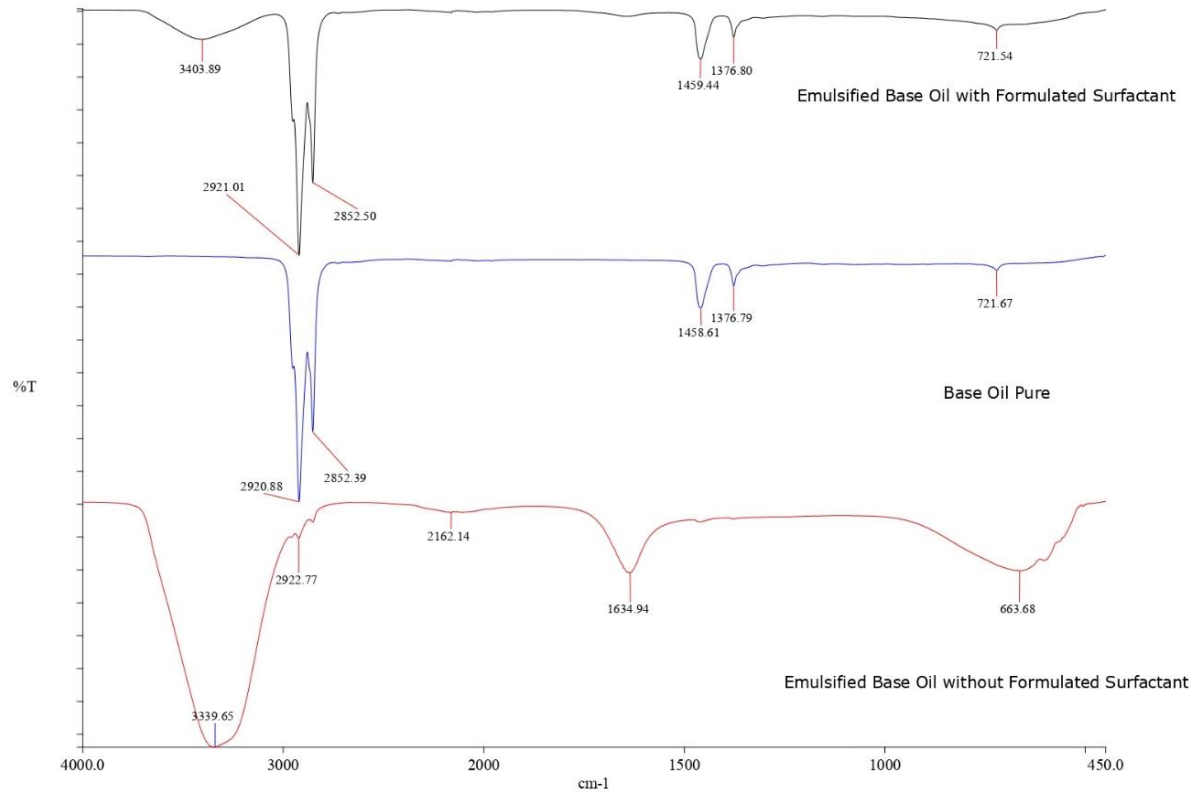


Figure 1. A comparison of FTIR spectrum for the base oil emulsified base oil with and without adding formulated surfactant.

3.1.2. Particle distribution

Figure 2 compares the size distribution for base oil, emulsified base oil without formulated surfactant (EF), and with formulated surfactant (EBF). The purpose of this characteristic is to observe the distribution between water and base oil in three different samples.

(a) (b) (c)

Figure 2. Droplet distribution in (a) base oil, (b) emulsified base oil without formulated surfactant, and (c) emulsified base oil with formulated surfactant

Figure 2(b) showed the drop of water in the base oil, but the oil and water molecules were not connected. Figure 2(c) shows that the water droplet was bound to the base oil after the addition of the formulated surfactant. The presence of the formulated surfactant acts as a 'bond" linking two molecules together and

maintaining the stability of the emulsified base oil. The hydrophilic head of the surfactant adheres to the surface of the water droplet. In contrast, the hydrophobic tail of the formulated surfactant adheres to the surface of the base oil [12]. Moreover, formulated surfactants are active molecules that absorb the interface between oil and water and form a membrane-like layer that can prevent the coalescence of the droplets, thus maintaining the stability of the emulsion. Indeed, the surfactant changes the interfacial state of the solution [13]. Therefore, this analysis showed that the emulsified base oil (EBF) in the presence of formulated surfactants is much more stable than the emulsified base oil without formulated surfactants (EB).

3.1.3. Viscosity and density

Table 1 shows the physical properties (viscosity and density) of three different samples, namely the control, the emulsified base oil without (EB), and the one with formulated surfactant (EBF). The results show that the EBF has the highest viscosity, followed by pure base oil and EB. The viscosity is significantly related to the interactions between the water and oil droplets. The higher interaction is due to the presence of the formulated surfactant, which enhances the interaction between water and oil. In addition, the formulated surfactant reduces the interfacial tension by adsorbing at the interface and shielding the unfavourable interactions between the water and oil molecules. The molecules of the surfactant have the ability to form a strong interfacial film to reduce the surface tension between the water and oil molecules. In addition, the emulsified base oil is more stable and water separation is lower when a formulated surfactant is adsorbed on the droplet surface [14]. Therefore, the samples with higher viscosity are more stable. The results were significant for the size of the distribution, as mentioned earlier. The higher viscosity of the sample indicates less coalescence of the droplets, resulting in less separation of the emulsion [15]. As for the FTIR spectrum results, EBF showed a weak OH, indicating a more stable emulsion than without the addition of the formulated surfactant.

The reason EBF is more stable is due to its high density, where the droplets of the emulsion are better distributed and more densely packed [16]. In addition, the size of the droplets in the base oil emulsion with formulated surfactant is smaller compared to the other two samples. A smaller droplet size indicates greater stability and thus contributes to higher viscosity. Furthermore, a stronger interaction between the formulated surfactant and the emulsified base oil leads to a more stable emulsion.

Table 1. Viscosity of base oil, emulsified base oil without formulated surfactant (EB), and emulsified base oil with formulated surfactant (EBF)

Samples	Viscosity (cP)	Density (g/cm^3)
Base oil (control)	235.7±1.0	0.868 ± 0.03
Emulsified base oil without formulated surfactant (EB)	220.2±1.0	0.876 ± 0.03
Emulsified base oil with formulated surfactant (EBF)	258.5±1.0	0.879 ± 0.03

3.1.4. Rheometer

Figure 3 shows a linear proportion of shear stress to the shear rate. All samples had a similar trend. The highest shear stress is pure base oil, followed by EBF and EB. The increase of the shear stress is significantly and gradually with the shear rate due to the increase in hydrodynamic effect which causes the increase in shear rate and shear stress [17]. Furthermore, with the presence of formulated surfactant increased the shear stress and led to higher viscosity hence causing a reduction in the interfacial tension by adsorbing the interface and screening the unfavourable interactions between the water and oil molecules. Hence, with higher shear stress, the emulsified base oil with formulated surfactant will be more stable [18-19].

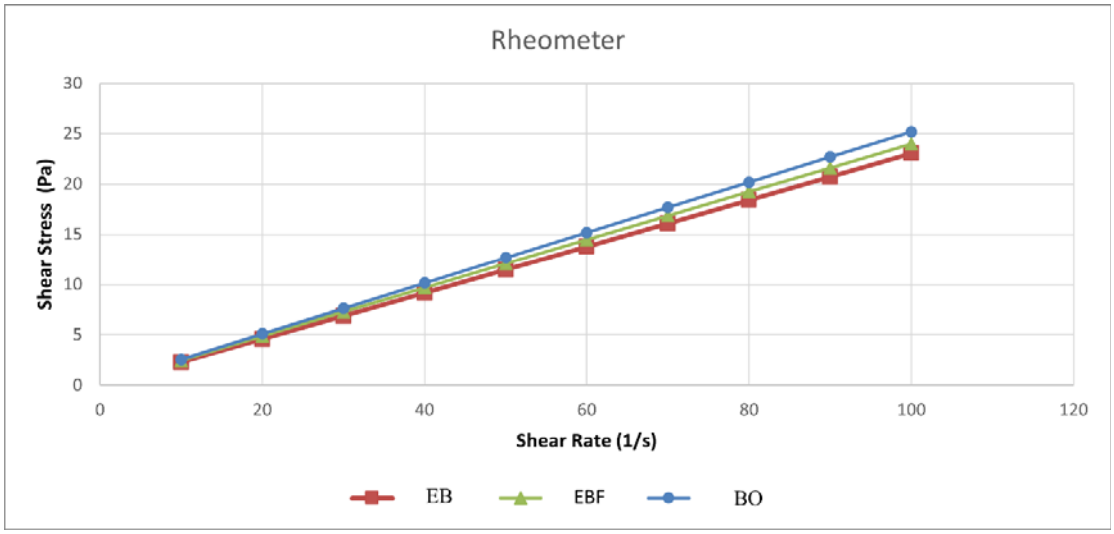


Figure 3. Rheometer analysis for base oil as a control sample, emulsified base oil without formulated surfactant (EB), and emulsified base oil with formulated surfactant (EBF)

3.2. Thermophysical properties

3.2.1. Thermogravimetric analysis (TGA)

Figure 4 shows the curves of weight loss (%) at different temperature derivatives for base oil (as a control sample), emulsified base with the formulated surfactant, EBF, and emulsified base without the formulated surfactant, EB. A fluctuation of the decomposition step is observed from 30°C to 100°C. This is due to the unstable emulsion, where the solution tends to separate and the weight loss was about 2%. The initial degradation temperature, T_{onset}, at the 1st decomposition step for EBF and base oil is 230°C and 210°C, respectively. The final degradation temperature, T_{offset}, is 360°C (EBF) and 320°C (base oil). The weight loss of EBF and base oil is 90% and 92.5%, respectively. The results are consistent with the viscosity of the sample. The higher the viscosity, the more stable the sample. The presence of the surfactant proves that the molecules are more resistant to decomposition at high temperatures. Thus, the presence of surfactant prevents thermal decomposition, hence the emulsified base oil is more stable [20]. T_{offset} at the 2nd decomposition step is observed at 330°C, 360°C and 320°C for EB, EBF and base oil, respectively. Finally, the T_{offset} for all samples is at 500oC with 15% (EB), 8% (EBF), and no change in weight loss for the base oil.

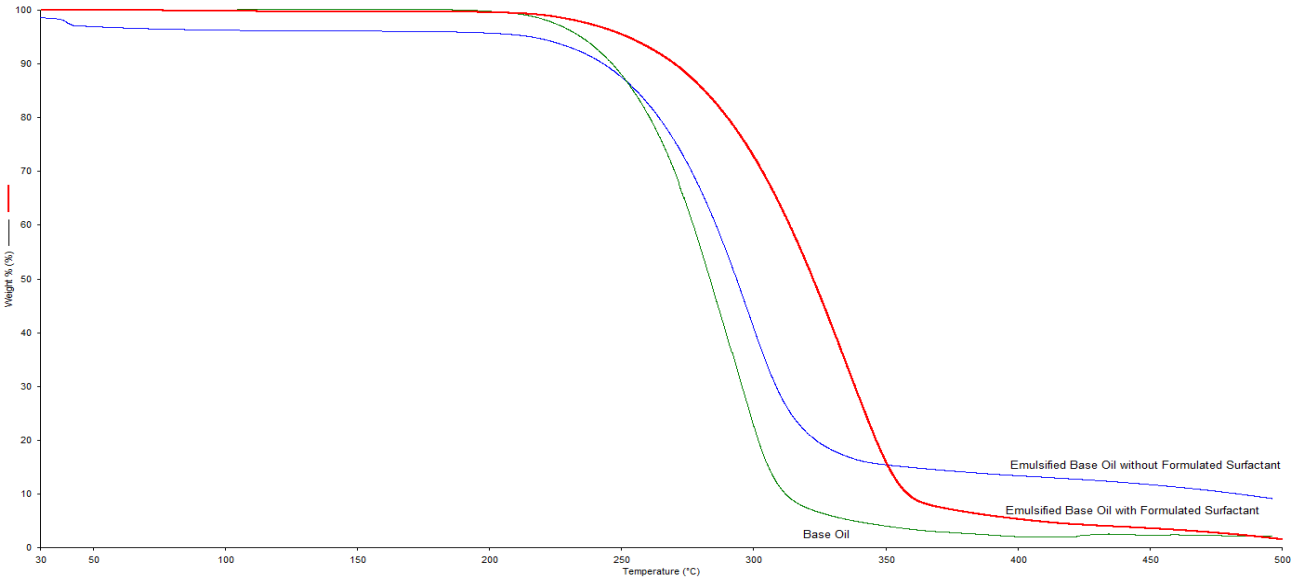
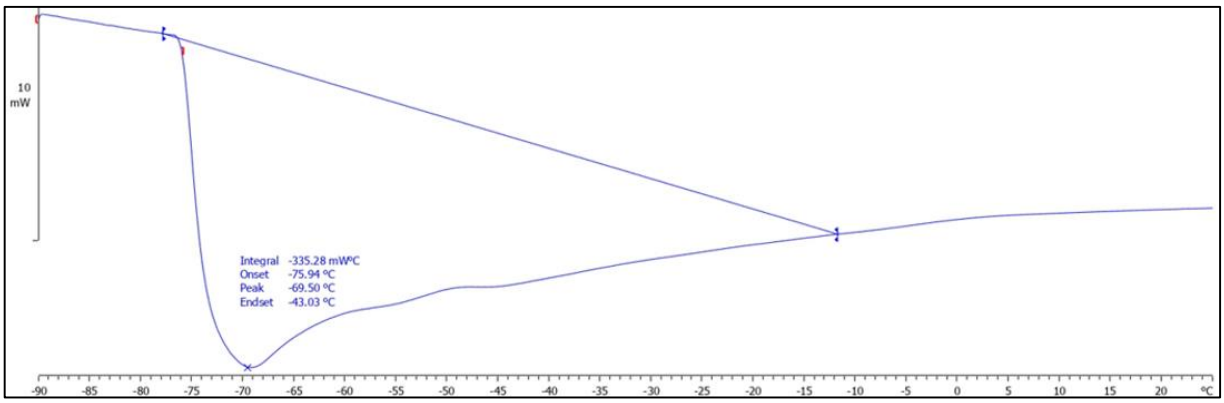


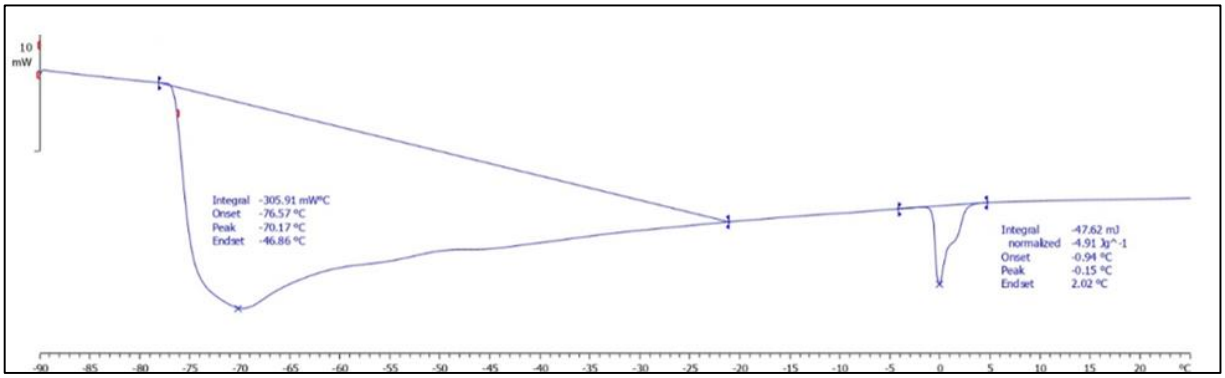
Figure 4. TGA results for pure base oil, emulsified base oil without formulated surfactant (eb), and emulsified base oil with formulated surfactant (EBF)

3.2.2. Differential Scanning Calorimeter (DSC)

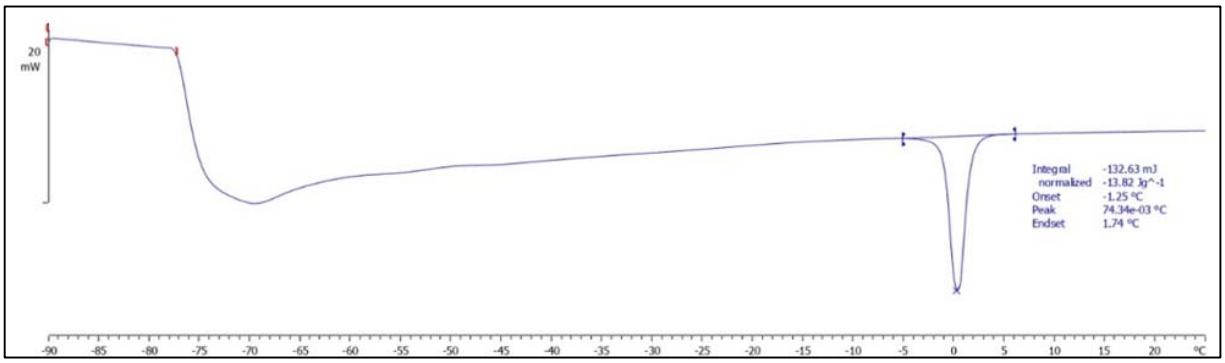
The samples (pure base oil, EB and EBF) were analysed in DSC to determine the thermal behaviour including crystallisation of the respective samples. The peaks in Figure 5 (a), (b) and (c) represent the crystallisation peaks of the samples. Figure 5 (a) and (c) show that there is only one crystallisation peak, while Figure 5 (b) shows two crystallisation peaks. The comparison of the results shows that EBF can withstand higher temperatures compared to the other two samples. This analysis is performed in an exothermic reaction as shown in the DSC equipment. Furthermore, Figure 5 (c) shows that EBF is more stable as it does not crystallise easily at low temperatures [24]. Furthermore, a comparison with the onset value shows that lower onset values (Figure 5 (a) & (b)) result in the emulsified base oil being less stable.



(a)



(b)



(c)

Figure 5. DSC results for (a) pure base oil, (b) emulsified base oil without formulated surfactant (EB), and (c) emulsified base oil with formulated surfactant (EBF)

4. Conclusion

In this study, the characterisation of the base oil was investigated. The difference in physical and thermophysical properties between the base oil and the emulsified base oil with and without a formulated surfactant is significantly related to the stability of the emulsion. The stability of the emulsion was improved by the presence of surfactants in the base oil. The hydrophilic head of the formulated surfactant molecules attaches to the surface of the water droplet, while the hydrophobic tail of the formulated surfactant molecules attaches to the surface of the base oil to create a 'bond' between the water and oil, thus maintaining the stability of the emulsified base oil. In addition, the formulated surfactant can decrease viscosity and increase density by providing more interactions between the droplets and the surface of the surfactant molecules, thereby decreasing surface tension and interfacial tension by forming an interfacial film to maintain the stability of the emulsified base oil. Furthermore, the presence of the formulated surfactant can maintain the thermal stability of the emulsified base oil, thereby reducing the unstable compounds. In summary, the addition of a formulated surfactant can maintain the stability of the base oil and thus improve the quality of the base oil.

5. References

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