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Viscosity-Temperature Dependence Study of Crude Oil Emulsions from Some Oilfields in Niger Delta Region

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Abstract

Crude oil emulsion samples labelled W001, W002, W003, W004 W005 and W006 obtained directly from well-heads of two different oilfields in Niger Delta were characterized with respect to density, SG, BS&W, water cut and sulphur content. Viscosity-temperature dependence study was equally carried out at different temperatures (25ºC to 90ºC) using OFITE 900 Digital Rotational Viscometer at 300 rpm and shear rate of 510.69 s^{-1}. Results obtained revealed that the crude samples were all sweet crude thus having low sulfur contents (0.120 to 0.316%wt) - a typical property of Niger Delta crude oil. Based on API categorization, one of the samples is heavy (W002 – 19.56), three are medium (W/003 – 23.36, W/004 – 23.36 & W/006 – 23.63) and the other two are Light (W001- 33.23 & W005 – 36.93). The BS&W values showed that sample W/003 had little amount of water molecules trapped in the crude (0.5%) while sample W/001 had high water molecules trappled in the crude sample (72%). The viscosity-temperature dependence study carried out at different temperatures (25^0C to 90^0C) established that the viscosity of the emulsions changes with increasing temperature as molecules in the liquid phase gain energy to move faster. Also, the activation energy and the pre-exponential factor (entropic factor) of the samples were determined using the modeling of Arrhenius theory equation.

***Keywords**: Viscosity; Temperature; Crude oil emulsion; Oilfields; Niger Delta.*

1. Introduction

Crude oil is formed alongside gas and saline water known as formation water from the reservoir [1-2]. As the reservoir is being produced, it becomes depleted overtime with a corresponding decrease in the reservoir pressure, producing water alongside. The production of water alongside crude oil creates several problems during production [3]. The water may be produced either as free water which will later settle out of the mixture over-time or could form an emulsion (this could be a tight or loose emulsion).

These immiscible fluids are emulsified and the emulsification process is easily facilitated by the corresponding effect of shear and pressure drop at the wellhead, chokes, valves and any other restrictions along the flow path [4]. When this occurs, an emulsion is formed.

An emulsion is a combination of a two-phase system that is not homogenous when mixed and one is a disperse phase while the other is in the continuous phase [5]. In oil in water emulsion (O/W emulsion), the disperse phase is crude oil while the continuous phase is water. For a water in oil emulsion (W/O emulsion), the disperse phase is water while the crude oil is the continuous phase. According to report [6], various types of emulsions are seen in different fields of technology such as the food industry, pharmaceuticals, and biological systems.

The formation of emulsion is possible during the transportation of crude oil. Hence, it is imperative to check the percentage of water (Base Sediment & Water – BS &W) in the crude oil before transportation. The conditions that support the formation and stability of emulsions include the presence of surfactants (surface acting agents), ionic compositions and pH of the water [4]. The stability of crude oil emulsions has become a major concern among researchers and this has led to formulating different methods of breaking it [4]. The formation of oilfield emulsions which occurs from the reservoir has become complex and a herculean task to resolve in the oil and gas industries. If not properly and adequately resolved, emulsion formation could affect oilfield installations and processes in several ways which include: A high pressure drops in oilfield pipelines and flowlines, an upsurge in the cost of pumping and transportation of the emulsion (water/oil mixture) through the pumps and pipes. Also, damage of pipelines and other oilfield installations as a result of a di-phasic flow and the existence of chloride ions in the water phase. An increase in the rate of corrosion and scaling tendencies as a result of the presence of salts in the formation water thus the lowering of the API gravity of the crude oil [4, 7].

Crude oils can be classified by categorizing them into four primary components which are: saturates (including waxes), aromatics, resins and asphaltenes. This classification of crude oils is commonly referred to as SARA fractionation and it is dependent on its polarity and solubility in a solvent [4].

Viscosity is a property of fluid that indicates the resistance to flow. It is one of the physicochemical properties of fluids that is key to optimizing and designing industrial processes [8]. Viscosity is a property that is affected by temperature and pressure [9]. It thins with an increase in temperature and thickens as temperature decreases. The temperature–viscosity relationship of fluids plays an important role in many fields of technology [10]. The knowledge of viscosity is useful in fluids transport and petroleum industry [11-12]. In the manufacturing companies such as chemical, cosmetic, pharmaceutical etc., viscosity is critical for hydraulic calculations used for fluid transport and energy calculations [9]. Liquid viscosity needs to be measured because it affects several operational areas such as handling, transportation, injection, and combustion efficiency [9].

According to published report [13], it was established that temperature has a strong influence on the viscosity of fluid products with viscosity generally decreasing with increase in temperature. The relationship between the viscosity of a fluid and temperature has been established to be in the form of Arrhenius equation. The Arrhenius equation was first written in 1913 and the developed by Eyring in 1936 [8]. The Arrhenius equation is expressed as presented in equations 1 and 2.

$$K = Ae^{-Ea/RT} \tag{1}$$

$$ln\, n = \frac{Ea}{RT} + ln\, A \tag{2}$$

where R the gas constant (8.31 $JK^{-1}mol^{-1}$); Ea, is the Arrhenius activation energy; A is the pre-exponential/Entropic factor. This can sometimes be called Arrhenius constant.

When the natural logarithm of viscosity (*ln ŋ*) is plotted against the reciprocal of absolute temperature in Kelvin (1/T) for a liquid system, the graph is basically linear; while -Ea/R is the slope and ln A is the intercept.

2. Materials and method

Six crude oil emulsion samples were obtained from different oilfields located within the Niger delta region of Rivers state, Nigeria. The samples were collected directly from the wellhead at their flow line pressures and labeled W/001, W/002, W/003, W/004, W/005 and W/006. Thereafter, they were shipped to the laboratory for preservation and further analysis.

All reagents used are of analytical grade and obtained from BDH. Basic characterizations were done on the samples. Density and specific gravity were done based on ASTM D1289 using hydrometer (HB-Instruments co.). Water cut (%vol/vol) by "Dean and Stark" distillation using ASTM D4007 method. The BS&W was done by ASTM D4006 with a centrifuge machine (Damon/IEC) and the sample pre-heated to 60^{0}C in a thermostatic water bath (Mermmert). The sulphur content was determined according to ASTM D4294 using X-ray Fluorescence sulphur analyser (Horiba SLFA-2800). The sulphur analyser was previously calibrated before sample analysis with a standard oil of known sulphur content.

Rotational rheometry is a vital and powerful mechanism used for the measurement of complex shear rheology [3, 14]. In this study, the OFITE 900 Digital Rotational viscometer was used. The rheology test was carried out at 300 rpm and at various temperatures from 25^{0}C to 90^{0}C. The emulsion samples were later heated in a thermostatic bath (Memmert) and centrifuged in a centrifuge machine (Damon/IEC) at 600 rcf (relative centrifugal force) to separate the water in the emulsions from the crude oil and the recovered crude oil was characterized based on SG, density, API (ASTM D1289) and kinematic viscosity (using Stanhope-Seta KV-8 viscometer bath by ASTM D445).

3. Results and discussion

3.1. Characterization

Characterizations of the emulsion samples were measured, and the results listed in Table 1. The SG and density of the studied emulsion samples as shown in Table 1 obviously depict W/004 as the heaviest while W/005 is the lightest. W/005 and W/001 have very close densities. This observation is similar to the values obtained for W/003 and W/006. The sample W/004 has the highest BS&W value. This is indicative of the fact that the sample has a high percentage of water dispersed in a continuous phase of the crude oil than observed for other samples.

Table 1. Values of specific gravity, density, BS&W and water cut of the crude oil emulsion samples

S/N	Sample ID	SG @ 60°F	Density @ 15°C (g/cm^3)	BS&W (%)	Water cut (%vol/vol)
1	W/001	0.8596	0.8570	7	72
2	W/002	0.9397	0.9388	20	30
3	W/003	0.9117	0.9108	0.5	6
4	W/004	0.9627	0.9618	40	50
5	W/005	0.8551	0.8542	17	60
6	W/006	0.9189	0.9161	22	59

The water cut for the samples W/001, W/002, W/003, W/004, W/005 and W/006 are: 72%, 30%, 6%, 50%, 60% and 59% respectively. Sample W/001 has the highest water cut with 72%, while sample W/003 has the lowest with 6%. The implication of the high water cut is that the well where the sample was taken is producing more water than crude oil. Hence, for every 100 barrels of produced crude oil emulsion that flows out from the well-head, 72 barrels is water while 28 barrels is crude oil. It is understood that the viscosity of emulsion is affected by increasing the amount of water cut fractions [15].

According to previous report [16], any crude sample with sulfur content less than 0.5% is sweet crude. Samples with total sulfur content more than 0.5% are sour crude. Table 2 presents the weight % of sulfur content in the crude oil samples. All the samples measured have low sulfur content ranging from 0.12 to 0.31 which implies that all the samples fell under the classification of sweet crude. Sulfur and its compounds are very poisonous and dangerous to people, environment and assets (oilfield installations). It can lead to rust and could be the cause of corrosion of metals on oilfield installations. The presence of sulfur and its compounds have a very foul and offensive odour. Sulfur is a cause of worry to gas producers and refineries [16]. However, all six samples are sweet crude a characteristic of Niger Delta crude.

Table 2. Sulfur content in the samples

S/N	Sample ID	Sulphur content (wt. %)
1	W/001	0.23137
2	W/002	0.31625
3	W/003	0.21529
4	W/004	0.12000
5	W/005	0.1316
6	W/006	0.23452

Table 3 shows the density, SG and API values of the crude oil samples from the emulsion samples. Crude oil can be classified as light, medium or heavy, based on its measured API gravity. Light crude is any crude oil having an API value greater than 31.1°. Medium crude oil is defined as any crude that is having API gravity between 22.3° and 31.1°, while heavy crude oil is defined as one that has API gravity below 22.3^0 [17-18]. Based on API categorization, one of the samples is heavy (W002), three are medium (W/003, W/004& W/006) and the other two are Light (W001 & W005). The density and API gravity of the samples ranged from 0.8376 to 0.9339 (g/cm^3) and 19.56 to 36.93 respectively.

Table 3. Density, SG and API values of crude oil samples

S/N	Sample ID	Density @ 15oC	SG @ 15^{o}C	API (°)
1	W/001	0.8564	0.859	33.23
2	W/002	0.9339	0.9367	19.56
3	W/003	0.9110	0.9137	23.36
4	W/004	0.9110	0.9137	23.36
5	W/005	0.8376	0.8401	36.93
6	W/006	0.9094	0.9121	23.63

Figure 1. shows the distribution of the density values of crude oil and the emulsion samples for all samples measured. The density of emulsion for all samples were higher than that of the crude oil. This is expected as the density of emulsion is a function of a number of factors such as the BS&W (amount of water present), nature of the oil (API categorization) and temperature.

Figure 1. Variation in the densities of crude oil and emulsion

Figure 2 shows the variation in the viscosities of the crude oil samples at different temperatures. Sample W/004 has the highest viscosity at all temperatures of measurement and this translates to high specific gravity as seen in Table 1. While, sample W/005 has the lowest viscosity and this also resulted in its low specific gravity. From the chart (Fig. 2 and 5), it is observed that the viscosity of the sample reduces with increase in temperature. As the temperature increases there is an increase in the kinetics of the sample as the molecules in the sample gains energy and therefore moves faster. As temperature increases, the molecular interchange that occurs in the liquid samples is comparable to what exists in a gas stream, with the exception that there are significant cohesive forces that take place between the molecules of a liquid unlike in gases [8]. The effect of the temperature is to relax the forces holding the molecules together hence increasing the intermolecular interactions. Solids have more cohesive forces than liquids because the molecules of the solid material are well compacted and would require a stronger energy to free the molecules. So, in order of cohesiveness of their molecules, we have solid>liquid>gas.

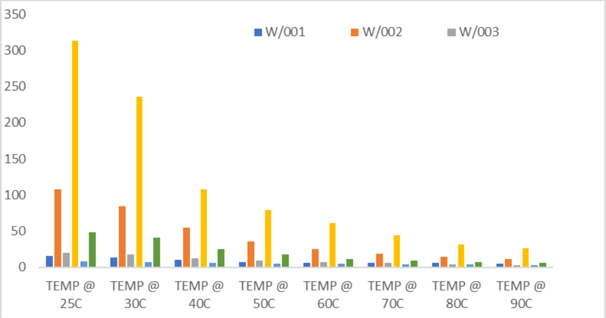

Figure 2. Variation in viscosity at different temperatures

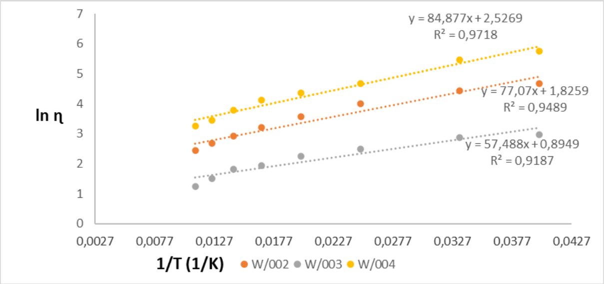

Figure 3. ln ŋ against 1/T for samples W/002, W/003 & W/004

Figures 3 and 4 explain the plot of natural logarithm of viscosity (ln ŋ) against the inverse of the absolute temperatures (1/T) in Kelvin. Modeling the Arrhenius equation and comparing it with the Viscosity temperature study, the natural logarithm of viscosity against the reciprocal of absolute temperature in Kelvin was found to be linear.

Using graphical method and the linear least-squares fitting approach (equ 3),

$$Y = mX + C \qquad (3)$$

where: Y is ln ŋ (natural logarithm of the viscosity); m is the slope of the straight line graph (which is Ea/R, from the equ 2); X is the reciprocal of the absolute temperature (1/T); C is the intercept of the straight line graph which is the pre-exponential factor, A (see equ 2).

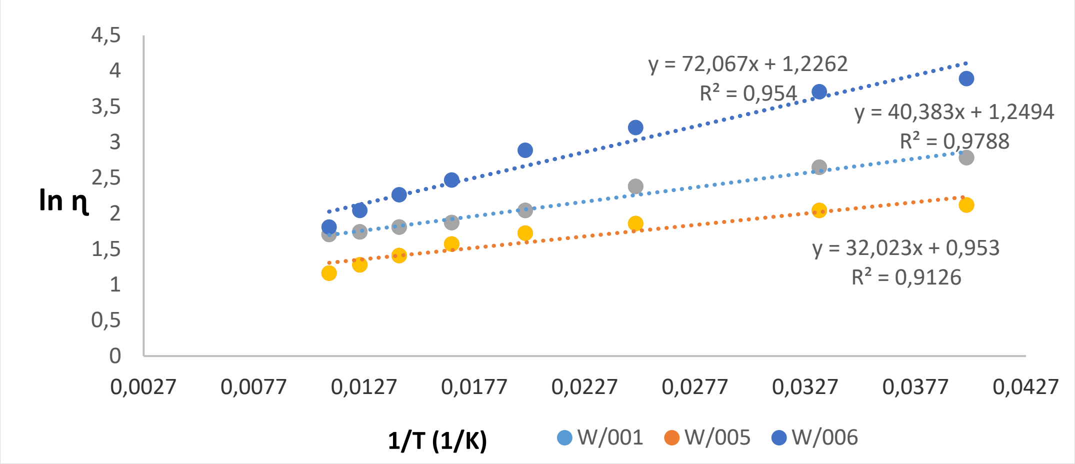

Figure 4. ln ŋ against 1/T for samples W/001, W005 & W/006

Applying equations 2 and 3, the activation energies (Ea) for samples W/001, W002, W003, W004, W005 and W006 were found to be 33.56J/mol, 64.06J/mol, 47.78J/mol, 70.54J/mol, 26.61J/mol and 59.90 J/mol respectively. The Entropic factor/Pre-exponential constant (A) for W/001, W/002, W/003, W/004, W/005 and W/006 were found to be 3.48cP, 6.20cP, 2.44cP, 12.51cP, 2.59cP, 3.40 cP respectively.

According to previous report [8], for most liquid systems, the plot of natural logarithm of viscosity versus the reciprocal of absolute temperature in Kelvin is usually linear. The establishment of a linear/straight line graph culminating into good R^2 (regression coefficient) values, shows the correctness of the results obtained. The results obtained show the validity of the relationship between the Arrhenius equation parameters. Consequently, the results obey the linear Arrhenius behaviour.

Figure 5 shows the plot of the kinematic viscosity at different temperatures ranging from 40^0C to 80^oC of the crude oil samples extracted from the emulsions. The plot followed the same trend as that of the emulsion samples (the viscosity decreases as the temperature increases).

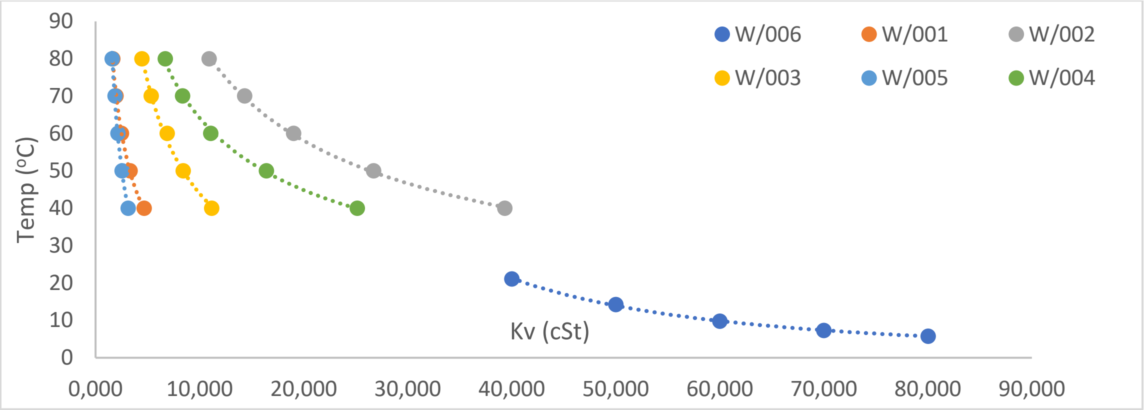

Figure 5. Plot of temperature (°C) against kinematic viscosity (cSt) for the crude oil

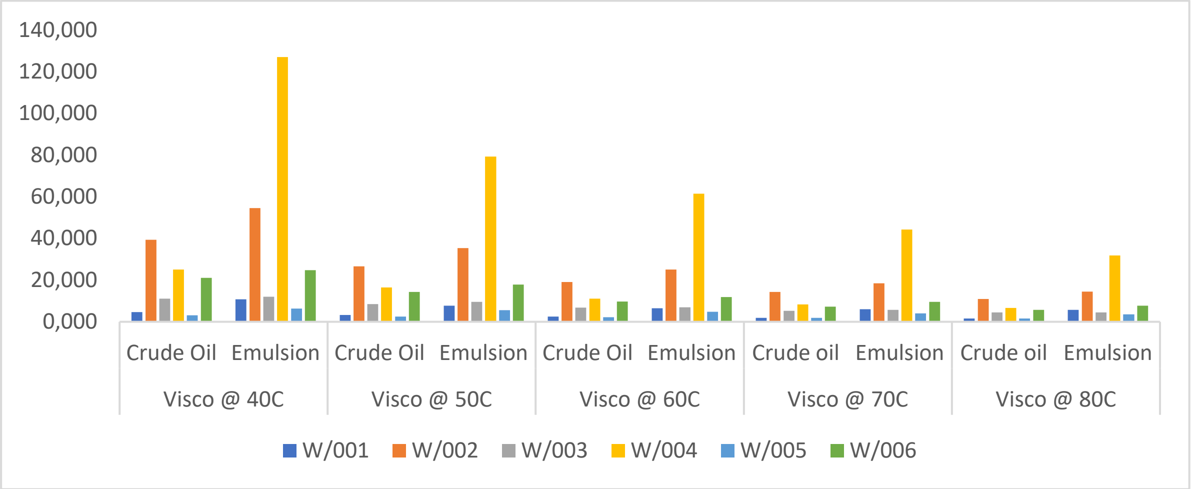

Figure 6. Crude oil–emulsion variation at 40°C–80°C

Figure 6. shows the viscosity distribution of the extracted crude oil and the crude oil emulsions for samples W/001 to W/006. A number of factors accounts for the viscosity of crude oil emulsions. Emulsion viscosity is a function of the viscosity of crude oil, viscosity of water, BS &W (amount of water present), API of the crude oil and temperature of measurement. That is;

$$\mu_e = f(\mu_o, \mu_{w,APIo}, T) \qquad (4)$$

where: μ_e = viscosity of emulsion; μ_o = viscosity of emulsion; μ_w = viscosity of emulsion; API° = API of the crude oil; T= temperature.

The viscosity of emulsion for all samples measured and at all test temperatures should be higher than that of the pure crude oil samples. This is clearly shown in Figure 6. The percent of water present in the emulsion has a strong influence on the viscosity and density of the emulsion as seen in Tables 1 and 3 and Figure 6.

4. Conclusion

It can be concluded from this study that temperature affects the viscosity behaviour of crude oil emulsions. The viscosity of the sample reduces with an increase in temperature. As the temperature (thermal energy) increases there is an increase in the kinetics of the sample as the molecules in the sample gains energy and they move faster thereby leading to chemical reactions.

For the emulsion and extracted pure crude oil samples, at different temperatures of measurement, there is a decrease in the viscosity as temperature increases. This result corroborates the study done on Palm oil and soybean oil [8]. This study shows that viscosities of emulsion were considerably affected by different temperatures as seen in a similar work done[19]. Since, the viscosity of the emulsions is significantly affected by temperature causing an inter-molecular movement and breakage of the cohesive forces/interfacial tension between the oil/water interface. The values of two viscosity-Arrhenius parameters such as the activation energy (Ea) and pre-exponential/entropic factor (A) were also determined and they obey the Arrhenius behaviour. Basically, for all of the samples studied, the plot of natural logarithm of viscosity (ln ŋ) against the reciprocal of the absolute temperature in Kelvin (1/T) followed the Arrhenius linear regime [9] and gave a good regression coefficient. In summary, crude oil emulsions from Niger Delta region also obey the already established behaviours. Also, the viscosity of crude oil emulsions is a function of number of factors such as the viscosity of crude oil, BS &W (amount of water present), API of the crude oil and temperature of measurement.

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