

De-emulsification of Nigerian light crude oil using heavy Alkylbenzene Sulfonate and its rheological verification

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Abstract: This technical paper evaluates de-emulsification and rheological verification of Nigerian light crude oil emulsion viscosity using statistic model. The light crude oil which is paraffin base, of low wax content was emulsified with brine solution to obtain stable emulsion before de-emulsification with heavy alkylbenzene sulfonate. The measurements of the viscosity of the emulsion before and after water separation were carried out using rotational viscometer. Model prediction coefficients of emulsion viscosity, using shear stress and concentrations relationship was established by application of statistical analysis of statistic software version (6). The graphs of observed data versus predicted, shear stress and shear rate data, measured values and predicted values were plotted respectively and 99.954% was obtained as correlation co-efficient. Also, from statistical analysis modeling, the flow behavior index of light crude oil emulsion viscosity is 0.99701, which is approximately 1, which shows the Newtonian fluid behavior.

Keywords: Nigerian Light crude oil, De-emulsification, Emulsion viscosity, Statistical analysis, Rheological Verification, Newtonian fluid.

1. Introduction

Light crude oil is due to the presence of a high number of paraffin, which are straight and branched chain hydrocarbons that has high hydrogen to carbon ratio. The least light crude oil contain roughly 60% paraffin [1]. It generally has low wax content. The tendency to form stable or unstable emulsions of different kinds varies greatly among different oils[2]. The natural petroleum emulsion resulting from the secondary production consists of crude oil as dispersion medium and brine as dispersed phase, normally stabilized by natural chemicals such as asphaltenes, resins, and solids[3]. Emulsion stability is the ability of the dispersed phase of the emulsion to resist coalescence or sticking together of droplets. Emulsions are stabilized by the presence of a film between dispersed droplets and the continuous phase. According to Macbain [4] in 1950, showed that the film is of many thick molecules, while on the other hand, Fischer [5] in 1966 showed that this film is only mono-molecular.

1.1 Emulsion Rheology

The viscous water in oil emulsions formed are undesirable because they do not only cause serious processing problem but also lead to significant cost increase for pumping and transportation [6]. Six factors which may affect the rheological properties of emulsion are [7]:

1. Viscosity of the external (continuous) phase.
2. Volume concentration of the dispersed phase.
3. Viscosity of the internal (dispersed) phase.
4. Nature of the emulsifying agent and the interfacial film formed at the Interface.
5. Droplet size distribution in the continuous phase.
6. Shear rate.

Rheology is usually defined as the science of deformation and flow properties. One of the important rheological parameters characterizing the properties of emulsion is the viscosity. Most emulsions show more non-Newtonian flow behavior. In non-Newtonian systems, viscosity is a function of the shear rate. Thus, it is most inaccurate to refer to these measurements as liquid viscosity; the very useful designation "apparent viscosity" is widely used. The other most important factor on the viscosity of emulsion is the presence of surface-active materials which also influence other mechanical properties of the water-oil interface [7]. Emulsions exhibit various types of flow properties depending on fluid type, they are, [8]:

- Newtonian fluids : If the viscous shear stress and the shear rate are linearly related by

$$\tau = - \mu \, du/dr \quad (1)$$

Where: τ = Shear stress(mPa)

du/dr = Shear rate(sec⁻¹)

μ = Viscosity(mPa.sec)

- Bingham Plastic fluids: Bingham plastics satisfy a slightly modified constitutive relationship, usually written in the form

$$\tau = \tau_y + \mu(- du/dr) \quad (2)$$

Where:

τ_y represents the yield stress of the fluid (lbs/100ft²)

- Power law fluids: These fluids, without yield stress, satisfy the power law model in the following Equation

$$\tau = k (- du/dr)^n \quad (3)$$

Where:

k = Consistency index (Eq-centipoise)

n = Flow behavior index (Dimensionless)

- Herschel-Bulkley fluids: This is a modified power law with yield stress characteristics.

$$\tau = \tau_y + k (- du/dr)^n \quad (4)$$

They heavy crude oil exhibits a non-Newtonian shear thinning behavior over examined shear rate range of 0.1 – 750s – 1[9]. He therefore concluded that the viscosity of heavy crude oil decreases considerably with temperature over the range of 25 - 65⁰C. Chenwei [10] in 2015 studied the Rheology of water-in-oil emulsion with different drop sizes. In his study, he prepared three sets of emulsions with different average drop sizes and their corresponding viscometer data were determined using a concentric viscometer. Results indicated that the flow behavior of concentrated emulsions changes qualitatively from Newtonian flow with shear rates. He also discovered that in Newtonian flow regime, a smaller drop size leads to a higher viscosity, and the increments are more pronounced at higher dispersed phase volume fractions.

1.1 De-emulsifiers Characteristics

De-emulsifiers are molecules that aid the separation of oil from water usually at low concentrations. They prevent formation of water in oil mixture. The structures of de-emulsifiers are not easily categorized as emulsifiers. Some de-emulsifiers are polymers; others have structures similar to non-ionic emulsifiers. De-emulsifiers are surfactants that are important in breaking the emulsion system [11].

The best de-emulsifiers are one that can reduce the interfacial shear viscosity increases the interfacial mobility and destabilizing the water-oil emulsion. To ensure the high quality performance, a de-emulsifier should possess the following characteristics [12]:

- The de-emulsifier should be able to partition into the water phase and oil phase.
- Dissolved in the oil phase. The concentration of de-emulsifier in the droplet must be sufficient enough to ensure a high diffusion flux to the interface.
- The de-emulsifier must be high enough to suppress the interfacial tension gradient, thus accelerating the rate of film drainage therefore promoting coalescence.

Since de-emulsifiers are surfactants, understanding the role of de-emulsifiers as surface active agents is very important. Basically, there are two groups in the

de-emulsifier molecule; hydrophobic (water disliking) group and a hydrophilic group (water liking group) [13]: (a) The hydrophilic effect is referred to the water-preferring nature of species. Hydrophilic usually means that a species prefers the aqueous phase rather than the oil phase,(b)The hydrophobic effect is referred to the water-avoiding nature of a species. Hydrophobic usually means that a species prefers the oil phase to the aqueous phase [14]. Igwilo et al [15] in 2017 carried out work on an experimental analysis of chemical de-emulsification using polymerization and sulfonation methods in Niger Delta crude oil to know the effect of salt concentrations and P^H on water separation efficiency. They concluded that water separation increases with decrease in salt concentration. Separation efficiency of water from Niger Delta crude oil was evaluated using five different de-emulsifiers: two commercial ones, that is, RP6000 and Chimec 2439, PPA prepared by polymerization, LAS and HAS both prepared by sulfonation [16]. They concluded that LAS and HAS prepared by sulfonation gave 90% and 88.3% of water separation efficiency respectively. PPA prepared by polymerization gave 75%, while commercial LP6000 and Chimec 2439 produced the same value of 87.5%.

2. Methodology

Laboratory measurements were carried out on emulsified Nigerian light crude with brine, which was followed by de-emulsification process after obtaining stable emulsion using heavy Akyl Benzene Sulfonation (HAS) de-emulsifier on the crude oil of the following composition: specific gravity 0.86 at 15.6⁰ C, 33⁰ API, 0.0005% by wt. salt content, 0.05% by vol. water and sediment content, 2.10% by wt. asphaltene, 0.0153% by wt. ash content, 2.08% by wt. sulfur content, 44cP viscosity at 20⁰ C were carried out. The de-emulsification tests were performed on emulsion and the de-emulsifier were then tested using bottle test method [17]. The water was pumped from the reservoir tank at 65 °C into condensers. At the same time, the contents of the beakers were added to the condensers to separate water from crude oil emulsion for 120 minutes. After the formation of the water in crude oil emulsion and emulsion breaking, the dynamic viscosity of the emulsion before and after water separation using rotational viscometer (model NDJ-4) were measured at room temperature. Before taking the measurement, the calibration of viscometer was checked with laboratory standard viscosity oil. The

viscometer was thoroughly cleaned in between the measurements of the samples. This apparatus has four rotational low speeds (0.3, 0.6, 1.5 and 3) rpm and four rotational high speeds (6, 12, 30 and 60) rpm. The viscosity measurement was therefore determined from the rotational speed [18]. Using the laboratory measurements generated, figure 1 was obtained from table 1. Also, figure 2 was obtained from measured data from table 1 and the predicted data from figure 2. Finally, using the rotational viscometer data and the formulas in the supplementary data, table2 and table3 in appendix were then generated that gave rise to figure 4. Figure 5 was also obtained from figure 2 and table 3. The accuracy and comparison of the model predictions were correlated, and quantified using statistical model of statistical software version 6.

3. Results and discussions

Figure 1 was obtained from table1 that showed the effect of shear stress on emulsion viscosity before and after water separation. From this figure, it can be seen that the emulsion viscosity decreases rapidly with increase in shear stress until it tends to 200 dyne/cm². At this zone, the velocity is very low, so the emulsion has a non-Newtonian behavior. After that, the viscosity becomes almost constant with shear stress, the emulsion behave like Newtonian fluid. It can be observe that, at 80 ppm of heavy alkybenzene sulfonate, the viscosity has the smallest value of 49mPa.sec. This is because heavy alkybenzene sulfonate has a great ability to remove water from emulsion, hence the viscosity decreases when large amount of water was removed.

Table 1: Shear stress and Emulsion viscosity data before and after water separation of different concentrations of de-emulsifier (HAS) =0, 20, 40, 60 and 80 ppm at time (120min), Temperature =65° C

Shear Stress (dynes/cm ²)					Viscosity (mPa.sec)				
8.4	5	4.6	4.1	3.6	211	125	116	104	91.5
15.8	9.8	8.8	7.1	6.6	197	123	110	89.5	83
31.8	26	20.9	18	14	144.6	119	95.3	82	64
52.5	48.7	36.1	28.7	23.1	125	116	86.1	68.5	55.2
92.7	96.3	73.3	55	44.8	116	112	85.2	64	52.1
173	185	147	107.6	89.9	109	107	85	62.2	52
587	460	360.3	266.4	212.3	108	107	84	62.1	49
987	909.1	721.5	532.5	420.9	106	107	84	42	49

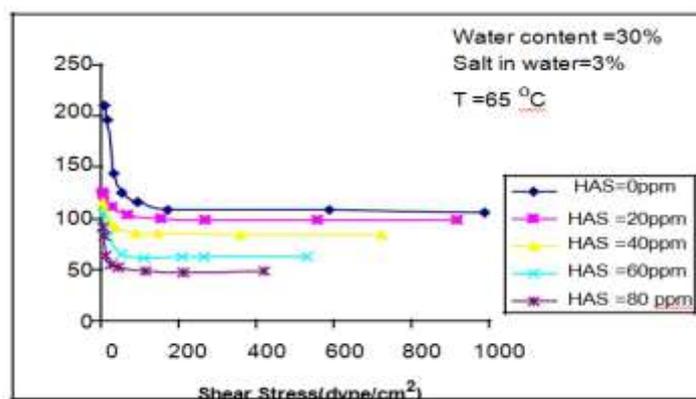


Figure 1: Effect of Shear Stress on Viscosity Using Different Concentrations of De-emulsifier (HAS)

3.1 Viscosity Correlation

Viscosity of emulsion after water separation has been correlated with concentrations of heavy alkybenzene sulfonate and shear stress as shown in equation 5. The correlation coefficient and predicted – observed values has been plotted. As was expected, viscosity of emulsion is inverse proportionality to each de-emulsifier concentration and shear stress, and therefore, enhanced the results obtained in figure 1. The correlation obtained is:

$$\mu = a (\tau^b) D^c \quad (5)$$

Where the coefficients a, b and c are constants

The coefficients of equation (5) were estimated by statistical analysis using statistic software version (6).

$$\mu = 522.801(\tau^{-0.0548}) D^{-0.42411} \quad (6)$$

Figure 2 shows the three dimensional graph, where the concentration and shear stress has inverse proportionality to emulsion viscosity. The correlation coefficient, R was 93.2177%. Figure 3 shows the observed – predicted value of viscosity.

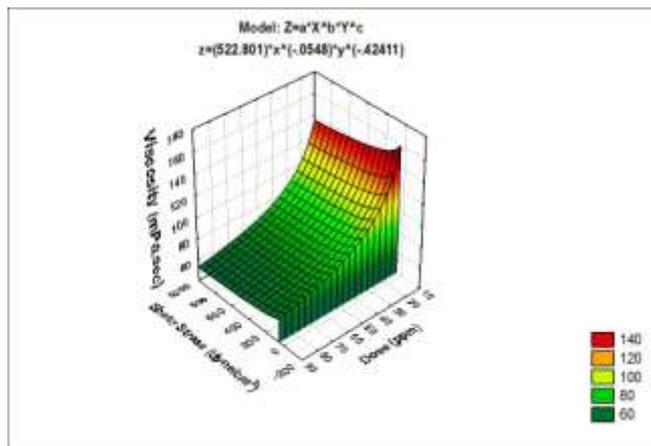


Figure 2: 3D – Shear Stress and Emulsion Viscosity Correlation

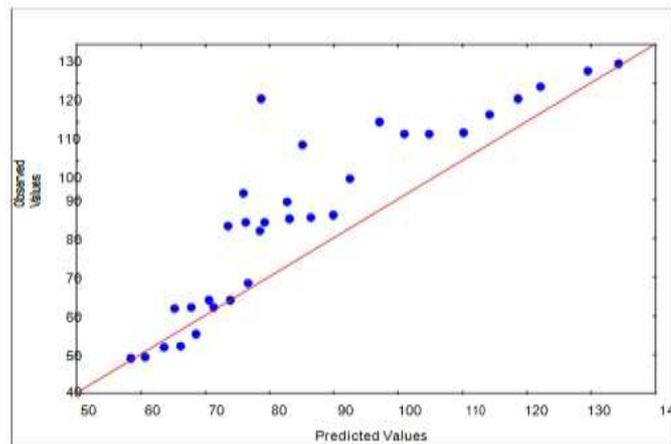


Figure 3: Predicted – Observed Values for Emulsion Viscosity Correlation

3.2 Relationship between Shear Stress and Shear Rate

To prove that the relationship between shear stress and shear rate obeys the Newtonian law, a mathematical correlation has been evaluated equation 7, where the correlation of coefficient is R= 99.954% as shown in figures 4 and 5. The correlation obtained is:

$$\tau = m \cdot \gamma^n \quad (7)$$

Where the coefficients m, n are constants

The coefficients of equation (7) were estimated by statistically analysis, using statistic software version 6.

$$\tau = 59.0318 \cdot \gamma^{0.99701} \quad (8)$$

From the above correlation it can be seen that the power of shear rate (γ) is close to one. That means the emulsion behave like Newtonian fluid.

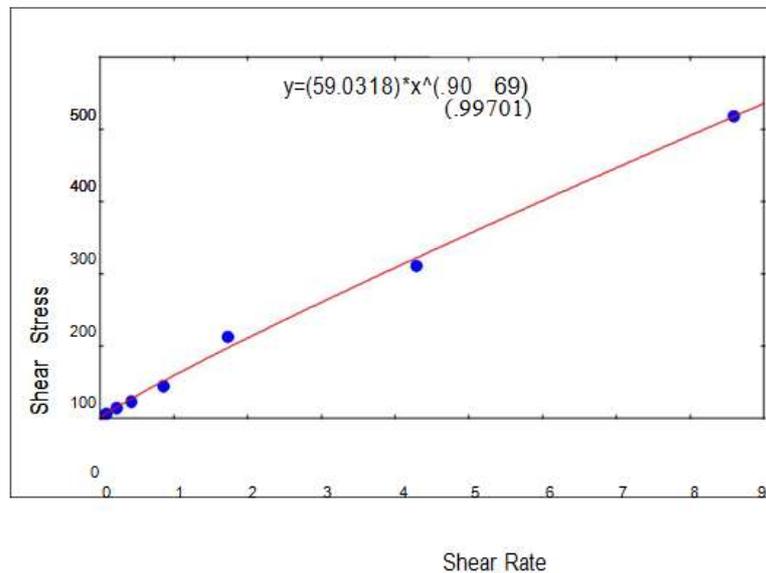


Figure 4: Relationship between Shear Rate and Shear Stress

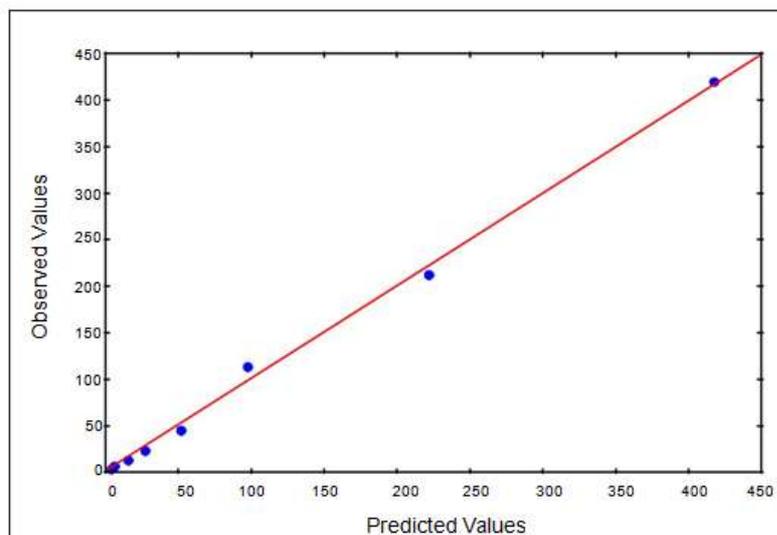


Figure 5: Predicted – Observed Value of Shear Stress Correlation

3. Conclusions

The following conclusions could be obtained: Emulsion Viscosity after water separation is inversely proportional to shear stress and concentration of de-emulsifier. The emulsion behavior after water separation is like a Newtonian fluid. The power of shear rate was (0.99701), which is approximately equal to one.

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References

- [1] Petroleum.co.uk(2015) API Gravity Classification of Crude Oil.
- [2] Schramm, L. L.(1992) Emulsions Fundamentals and Applications in the Petroleum Industry. American Chemical Society, Washington DC, pp. 1-45.
- [3] Bhardwaj, A. and Hartland, S.(1998) Studies on Build up of Interfacial Film at the Crude Oil/Water Interface. J. Dis. Sci. Tech., 19(4):465-473, (1998).
- [4] MacBain, J. W.(1950) Colloid Science, Reinhold Publishing Corp., New York, USA.
- [5] Fischer, E.K. and Harkins, W.D., J.(1966) Phys. Chem., 36, 98, (1932), P. (1966).
- [6] Pekdemir, T., Akay, G., Dorgu, M., Merrills, R.E., Schleicher, B.(2003) De-emulsification of highly stable water in oil emulsions. Separation Science and Technology 38 (5), 1161-1183.
- [7] Becker, J. R.(2005) Crude Oil Waxes, Emulsions, and Asphaltenes. Penn Well Publishing Company. Oklahoma. 126-129.
- [8] Wilson C.(2001) Computational Rheology for pipeline and annular flow, by Butter Worth – Heineman.
- [9] Mamdouh, T. G., Shadi, W.H., Basim, A., Nabil, E.(2012) Rheological properties of heavy crude oil mixtures for improving flowability. Journal of Petroleum Science and Engineering, Vol.81, pp. 122 – 128.
- [10] Chinwei, L., Mingzhong, L., Rui, H., Jibin, L., Chunting, L.(2015) Rheology of water-in-oil Emulsions with different drop sizes. Journal of Petroleum Science and Engineering, Vol.64, pp. 82 – 88.
- [11] Aske, N.(2002) Characterization of Crude Oil Components, Asphaltene Aggregation and Emulsion Stability by means of Near Infrared Spectroscopy and Multivariate Analysis, Norwegian University of Science and Technology, Ph.D Thesis .
- [12] Krawczyk, M.A.(1990) Mechanisms of De-emulsification. Institute of Technology, Ph.D Thesis.

- [13] Ariany Z.(2003) Characterization of Malaysian Crude Oil Emulsion-Formation and Stability Study. University Teknologi Malaysia, MSc Thesis.
- [14] Ese, M.H., Galet, L., Clause, D. and Sjoblom, J.(2006) Properties of Langmuir Surface and Interfacial Films Built up by Asphaltenes and Resins Influence of Chemical De-emulsifiers, J. Coll. Int. Sci. 220: 293-301.
- [15] Igwilo, K.C., Ogbudu, R.E., Okolie,S.T.A., Ohia, P.N., Okolie, N. (2017) Experimental Analysis of Chemical De-Emulsification Using Polymerization and Sulfonation Methods on Niger Delta Crude Oil. International Journal of Petroleum and Gas Engineering Research vol. 1, No. 1, pp. 1 – 8, Published by European Centre Research Training and Development, UK. Editor e- mail address is editor.ijpger@ea-journals.org.
- [16] Igwilo, K.C., Ogbudu, R.E., Anawe, P.A.L., Orodu, O.D., Okolie, T.A.(2017) De-emulsification Efficiency of the Niger Delta crude oil using Different De-emulsifiers. GE- International Journal of Engineering Research, vol. 5, Issue 3, ISSN (O): 2321 – 1717, ISSN(P):2394 – 420X. Web site: www.aarf.asia.
- [17] Lissant K. J.(1983) De-emulsification Industrial Application. Marcel Dekker Ins., New York, USA.
- [18] Bird, B. R., Stewart, W. E., Lightfoot, E.(2002) Transport Phenomena, 2nd edition. John Wiley co.

Appendix

Sample of viscosity and shear stress calculation:

$$\mu = a \cdot k$$

Where:

μ = Viscosity (mPa.sec).

a= is the reading indicated by indicator, K= Constant

Table 2: Calculated Viscosity values

K	A	μ (mPa.sec)
200	0.62	125
100	1.23	123
40	2.98	119
20	5.8	116
10	11.2	112
5	21.4	107
2	53.5	107
1	107	107

$$\omega = 2\pi N / 60$$

Where: ω = angular frequency (Sec⁻¹)P

N= rotational speed (rpm)

$$\omega \cdot r^2$$

$$\gamma = \frac{\omega \cdot r_o^2 - \omega_i \cdot r_i^2}{r_o - r_i}$$

Where:

γ = Shear rate (Sec⁻¹)P

r_i , r_o = radius of inner cylinder=18.8mm r_o , r_i = radius of outer cylinder=36.2mm

$$\tau = \mu \cdot \gamma$$

Where:

τ = Shear stress (mPa).

Table 1: Calculated Shear stress and Shear rate values

N (rpm)	Ω ⁻¹ (Sec)	μ (mPa.sec)	γ ⁻¹ (Sec)	T (mPa)
0.3	0.031	125	0.04	5
0.6	0.063	123	0.08	9.8
1.5	0.16	119	0.22	26
3	0.31	116	0.42	48.7
6	0.63	112	0.86	96.3
12	1.26	107	1.73	185
30	3.14	107	4.29	460
60	6.28	107	8.5	909.1