Effects of Demulsifiers on the Droplet Size and Ashphaltene Content of an Oil Tight Emulsion

Okereke, U; Ohia, N.; Obah, B

Federal University of Technology, Owerri, Nigeria

Abstract—Typically, water in oil emulsion presence in a production facility always gives rise to an increased flow assurance issues such as corrosion, increased cost of managing surface equipment such as pumps, tanks etc, overloading of surface equipment, increased cost of pumping wet crude, on so on. This can ultimately affect oil production rate from the wellbore to surface facility.

Chemical de-emulsifiers (amine group) wereadded in varied proportions to crude oil emulsionsin a virtual production flow station modelled to replicate an improved oil recovery project in the Niger Delta area. In order to enhance the demulsification process of the crude oil emulsion, simulation tests were run to determine the effects of the demulsifiers on droplet size and aspaltene content of electrically stable emulsions. The factors influencing stability and results on how theycan enhance emulsificationof tight crude emulsion werediscussed. The droplet size of the tight crude oil emulsion was observed to have increasedby one percent in value after de-emulsifier injection at a constant temperature and flow rate.

A proportional reduction in asphaltene content was also observed when the concentration and flow rate of the demulsifiers were increased at a constant temperature.When matched against established electrical stability trendline,it showed a decrease in the electrical stability of the emulsion formed as a result of these activities as described above.

Keywords— Emulsion, demulsifiers; demulsification; stability; virtual modelling;asphaltenes; amine; simulation; viscosity; water content, droplets; sensitivity.

I. INTRODUCTION

Water-in-oil crude oil emulsions may be encountered at all stages in the petroleum production and in processing industry. With presence of water, they are typically undesirable and can result in high pumping costs and pipeline corrosions and increase the cost of transportation (M. Hanapi, S. Ariffin, A. Aizan, and I. R. Siti, 2006). Reduced throughput is needed to introduce special handling equipment, contribute to plugging of gravel pack at the sand phase, (R. Espinoza and W. Kleinitz, 2003) and affect oil spill cleanup (F. Merv and F. Ben,2003).

Despite the success of enhanced oil recovery (EOR) process, one of the problems associated with the process is emulsion problem. Efeovbokhan et al. observed that physical factors that enhance oil recovery can also greatly contribute to the formation of very stable emulsions because EOR-induced emulsions are established by surfactant/polymer (SP) and alkaline/surfactant/polymer (ASP) processes which makes breaking of emulsion different from naturally occurring emulsions which are stabilized by asphaltenes and resins (Efeovbokhan et al., 2010). Traditional demulsifiers are often not effective on emulsions created by chemical floods; therefore, the performance of demulsifier in surfactant/polymer–flooding-induced emulsion depends on the selection of the best demulsifier with respect to the system under consideration (Nguyen et al., 2011). In breaking of surfactant/polymer-flooding-induced emulsion with the use of surfactant, Oseghale et al. worked on separation of oil-water emulsions expected during chemical enhanced recovery operations using crude oil from a field in Niger delta during surfactant/polymer flooding operation. Surfactant N-octyltrimethyammonium bromide (C8TAB) was used as the demulsifier and a dosage between 200 and 300ppm was the optimum dose that yielded oil and water phases with oil content reduction from 550 to 70 ppm after 4 hrs. Microscopy test confirmed that addition of N-octyltrimethyammonium bromide (C8TAB) produced significant coalescence shortly after it was added to the emulsion, which is in agreement with an increase of the oil droplet size in the presence of the demulsifier. Their findings show that this investigation worked with the principles of using cationic surfactants as demulsifier [Oseghale et al., 2012].

.Crude oil emulsions are complex and should be characterized as completely as possible. Droplet-size distribution, interfacial phenomena, and the nature of organic and inorganic components are important. The viscosity of the emulsion is affected by both the water content and droplet size distribution (Taylor, 1988; Thompson et al., 1987). The increase in aqueous phase of the emulsion leads to an increase in viscosity of emulsion which in turn aggravates flow of emulsion in conduct either at the sand phase or through the surface facilities (Espinoza et al., 2003; Jones et al., 1978). Stable water-in-oil emulsions have been generally found to exhibit high interfacial viscosity and/or elasticity modulus. Viscosity of crude oil emulsion was found to increase with increase in water and decreased with increase in speed of rotation of spindle when demulsifier is added (Abdurahman et al., 2012). The increase of the interfacial rheological parameters has been attributed to non-Newtonian nature of emulsion (Abdurahman et al., 2012) and physical cross-links between the asphaltene particles adsorbed at the water-oil interface (McLean et al., 1997). Demulsification of tight emulsion proved to be a tough method of breaking emulsions with an influence of improper selection of chemicals still unaccounted for in most of the researches.

1.1 Objective of Study

This paper will investigate the effect of selecting and using proper chemicals on tight emulsion samples treated with chemical for two different water in oil tight crude emulsions (electrically stable) collected from different EOR fields from

152

different operators in Niger delta. The aim is to demonstrate the effectiveness of readily available chemical demulsifiers as mentioned above on tight water in oil emulsions as experienced in EOR operations via virtual modelling techniques.

1.2 Background of Study

Produced oilfield emulsions generally have droplets diameter that exceed 0.1µm and may be larger than 100µm. emulsion normally have a droplet size that can be represented by a distribution. Fig. 1.0 show the photomicrograph of water in oil emulsion and the drop-size distribution of typical petroleum emulsion respectively. The drop-size distribution in an emulsion depends on several factors including the:

a) Interfacial tension (ITF)
b) Shear
c) Nature and amount of emulsifying agents
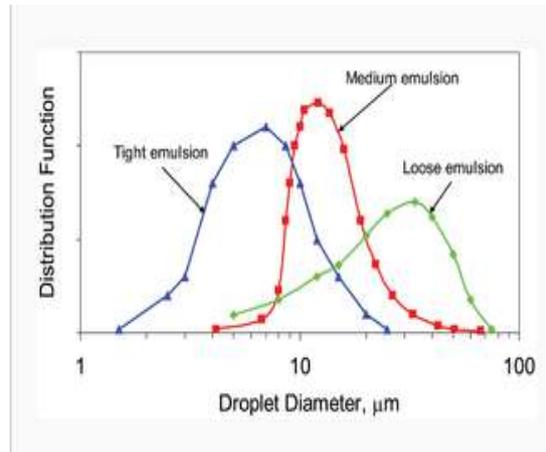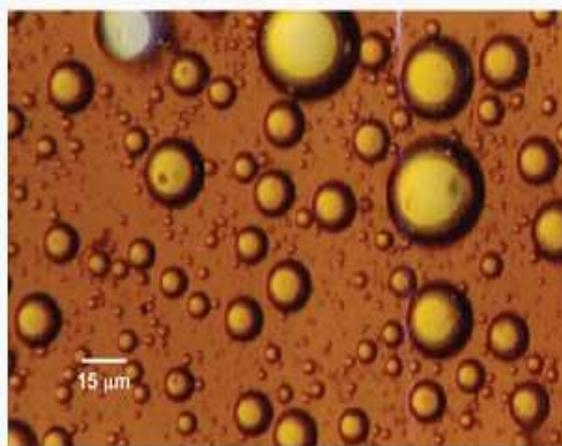d) Presence of solid
e) Bulk properties of oil and water

Fig. 1. Photomicrograph H2O-in-oil emulsion b. Droplet size distribution of petroleum emulsions respectively. (http://petrowiki.org/Oil_emulsions).

II. MATERIALS AND METHODS – VIRTUAL EXPERIMENTAL METHOD

A virtual experiment approach was unutilized for this study. A commercialprocess simulation software; with compositional analysis of default crude oil properties relevant to the Niger Delta production scenario which describesa tight emulsion prone crude oil. Closely related materials that were also utilized include the polymer (decylamine) de-emulsifier reaction set, C7+ and de-emulsifier characterization set.

The experimental methods had the following key approaches:

Virtual modelling of the tight emulsion crude oil properties, compositional analysis, the physical and chemical properties of crude oil used for the experiment such as molar concentrations, API gravity, viscosity, the asphaltene content etc. were obtained and used to build the model.

2.1 Simulation Set-up.

Data used for the simulation study was sourced from a specific flow station as built drawings, flow station equipment data sheet, PVT reports, production chemistry laboratory data and surveillance data from site visit. A quality assurance and quality control analysis were performed on the PVT data gathered to further validate the data and determine the degree of accuracy using the mole balance plot.

This describes the approach taken to model the crude oil stabilization station as it is on the field, this however allows the Engineer to run different de-emulsification scenarios and make optimum decisions.

Basic equipment's used for the simulation includes separator, surge vessel, mixer and valve.

To enable the demulsifier to be effective, it must contact the emulsion and the oil/water interface. Agitation and mixing is required to provide an opportunity for the chemical to mix well with the emulsion. This agitation paves the way for droplet coalescence; which is the point at which the demulsifier is added to the mixture – this is an important phase of the process. The first operation installed in the model is a mixer used to combine the reservoir fluid stream and the de-emulsifier stream. As in most commercial tools installing a mixer can be accomplished by a number of ways. Also separators where installed in the model to separate the gas and liquid phases. Surge Vessels were added to the model to further define the direction of the gas and liquid streams and to control the flow of the two phases. Then pressure valves were added to the model to control the pressure of the inlet and outlet streams in the model.

2.2 Asphaltenes Characterization

Asphaltenes characterization was carried out in the compositional analysis. This characterization is important to determine the fraction of Asphaltenes in the reservoir fluid. Asphaltenes compositions are arranged in ascending order in w/w % from the component of highest abundance to that of lowest abundance ranging from carbon, hydrogen, oxygen, nitrogen and sulfur. Characterization was carried out in all these compositions of Asphaltenes which includes oxygen, sulfur, carbon, nitrogen, hydrogen, traces of vanadium and nickel in ascending order. In this context, the asphaltenes

characterization is defined as the determination of the critical temperatures, critical pressure, acentric factor and interaction parameters of the asphaltenes component. Also performed in the compositional analysis is the C7+ characterization. In order to have a truly representative model, one must characterize the C7+ fraction of the reservoir fluid. Characterization can be defined here as the determination of the critical temperatures, critical pressure, acentric factor and interaction parameters. In this study, C7+ was characterized in the petroleum fraction sub-section using the boiling point, molecular weight and specific gravity as input parameter. The composition is then added to the main composition and an amount entered before calculating the critical properties and acentric factor

2.3 De-emulsifier Characterization

De-emulsifier characterization was also performed in the compositional analysis. De-emulsifier characterization can be defined as the determination of the critical temperatures, critical pressure, acentric factor and interaction parameters. In this study, de-emulsifier was characterized in the petroleum fraction sub-section using the boiling point, molecular weight and specific gravity as input parameter. The composition is then added to the main composition and an amount entered before calculating the critical properties and acentric factor. Amine group de-emulsifier (decyl-amine) was used for this process model

III. SIMULATION TEST AND RESULTS ON EFFECT ON DROPLET SIZE AND ASPHALTENE CONTENT

3.1 Test #1: Droplet Size before Injection.

The Droplet Size was calculated before the injection of the de-emulsifier. Calculation of the Droplet Size of the reservoir fluid can be done using the formula stated below;
Droplet Size = r_d = $0.063 * D [p (N/60)2 * D3/Yow]^{-0.6}$
(Processing)

Where:
p = density of continuous phase (oil) = 0.88 g/cm3
D = diameter of mixer impeller = 31.5 cm
N = speed of agitation = 382 rpm (revolution per minute).
Yow = specific gravity of o/w (oil-in-water) mixer = 0.9
$r_d = 0.063 * 31.5 [0.88(382/60)2 * (31.53)/0.9]^{-0.6}$
$r_d = 1.98[35.67 * 34728.75]^{-0.6}$
$r_d = 1.98[1238774.51]^{-0.6}$
$r_d = 4.37e^{-4} \mu m$

3.2 Test #1: Droplet Size after injection.

Droplet size was also calculated after de-emulsifier was injected. An increase in the droplet size of the continuing phase shows effect of the de-emulsifier in emulsion breaking.
Parameters:
P = density of continuous phase (oil) after injection
   $= 0.87$ g/cm^3
D = diameter of mixer impeller (D) = 31.5 cm
N_s = speed of agitation = 382 rpm
Yow = specific gravity of o/w mixer = 0.9
Substituting into droplet size formula
$r_d = 0.063 * 31.5 [0.87(382/60)^2 * (31.5^3)/0.9]^{-0.6}$

$r_d = 1.98 (35.26 * 34728.75)^{-0.6}$
$r_d = 1.98 (1224535.725)^{-0.6}$
$r_d = 4.40e^{-4}$
The droplet size (r_d) = $4.40e^{-4}$

The result simulation interface above shows that there was a 1% increment in the water droplet size after de-emulsifier injection at constant temperature and flow rate. This when matched against the electrical stability trend line delineates that there was a decrease in the stability of the emulsion formed as increase in water droplet size leads to a decrease in electrical stability

3.3 Test #2: Droplet Size before Injection.

The Droplet Size was calculated before the injection of the de-emulsifier. Calculation of the Droplet Size of the reservoir fluid can be done using the formula stated below;
Droplet Size = r_d = $0.063 * D [p (N/60)^2 * D^3/Yow]^{-0.6}$
(Droplet diameter, μm)
Where:
p = density of continuous phase (oil) = 0.88 g/cm^3
D = diameter of mixer impeller = 31.5 cm
N = speed of agitation = 382 rpm (revolution per minute).
Yow = specific gravity of o/w (oil-in-water) mixer = 0.9
$r_d = 0.063 * 31.5 [0.88(382/60)^2 * (31.5^3)/0.9]^{-0.6}$
$r_d = 1.98[35.67 * 34728.75]^{-0.6}$
$r_d = 1.98[1238774.51]^{-0.6}$
$r_d = 4.37e-4 \mu m$

3.4 Test #2: Droplet Size after Injection.

Droplet size was also calculated after de-emulsifier was injected. An increase in the droplet size of the continuing phase shows effect of the de-emulsifier in emulsion breaking.
Parameters:
P = density of continuous phase (oil) after injection
   $= 0.87$ g/cm^3
D = diameter of mixer impeller (D) = 31.5 cm
N_s = speed of agitation = 382 rpm
Yow = specific gravity of o/w mixer = 0.9
Substituting into droplet size formula
$r_d = 0.063 * 31.5 [0.87(382/60)^2 * (31.5^3)/0.9]^{-0.6}$
$r_d = 1.98 (35.26 * 34728.75)^{-0.6}$
$r_d = 1.98 (1224535.725)^{-0.6}$
$r_d = 4.40e-4$
The droplet size (r_d) = $4.40e-4 \mu m$

The result simulation interface above shows that there was a 1% increment in the water droplet size after de-emulsifier injection at constant temperature and flow rate. This when matched against the electrical stability trend line delineates that there was a decrease in the stability of the emulsion formed as increase in water droplet size leads to a decrease in electrical stability.

Small changes like these make a huge difference in the droplet weight. When droplets are heavier they tend to drop off and less likely to support movement, hence the reduction of electrical stability. Smaller droplet sizes are known to have higher electrical stability with higher emulsion viscosities. U. Okereke, N. Ohia, B. Obah, Sensitivity Analysis on factors

Okereke, U; Ohia, N.; and Obah, B, "Effects of demulsifiers on the droplet size and ashphaltene content of an oil tight emulsion," *International Research Journal of Advanced Engineering and Science*, Volume 3, Issue 3, pp. 152-156, 2018.

affecting crude oil emulsion stability. Petroleum and Coal January, 2017.

3.4 Test #3: Results on Asphaltene Content.

Asphaltenes are well known for their tendency to aggregate or flocculate and by this nature it also tends to stabilize oil emulsions. This phenomenon and nature of asphaltenes is also coalescence. Depending on the type of crude oil asphaltene can be a real menace and can clog pipeline and tubings. Any reduction in asphaltene composition can be very beneficial in the entire oil production process.

TABLE 1. Changes in asphaltene compositions with respect to flow rate and concentration of de-emulsifier.

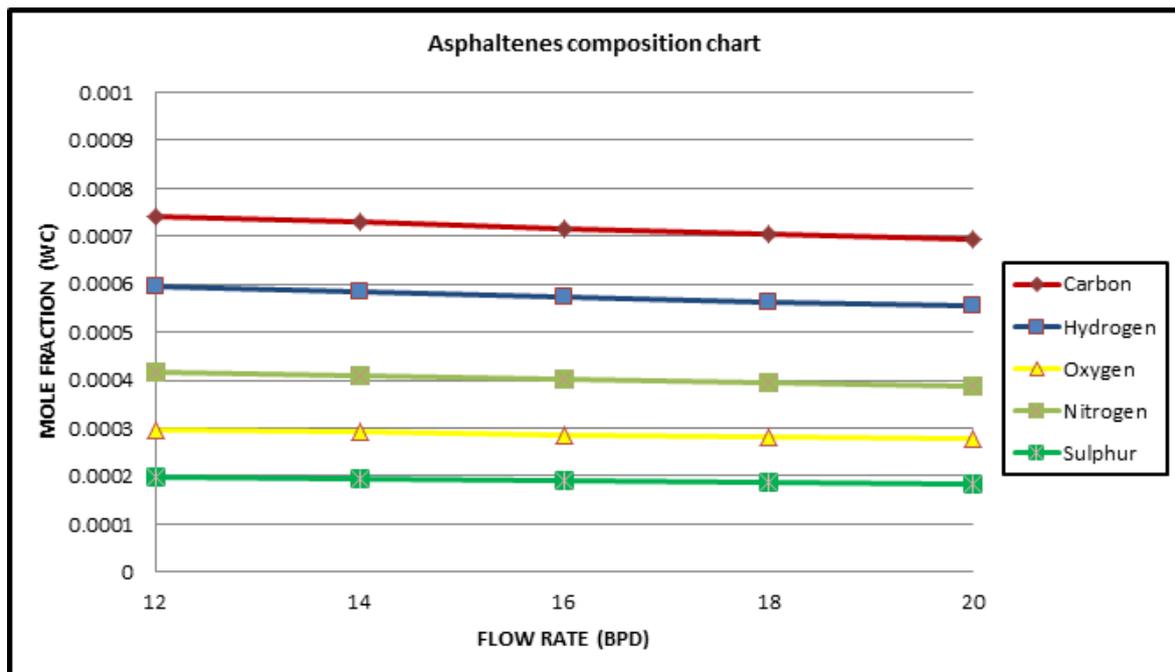| CONCENTRATION (PPM)	ASPHALTENE COMPOSITION (MOLE %)				
	CARBON	HYDROGEN	OXYGEN	NITROGEN	SULPHUR
12	0.000742	0.000594	0.000297	0.000416	0.000198
14	0.000729	0.000583	0.000292	0.000408	0.000194
16	0.000717	0.000573	0.000287	0.000401	0.000191
18	0.000705	0.000564	0.000282	0.000395	0.000188
20	0.000693	0.000555	0.000277	0.000388	0.000185

Fig. 2. Mole fractions of asphaltene composition.

The chart above shows the changes in asphaltene composition in the continuing phase. As the concentration and flowrate of the de-emulsifier increases the composition of the asphaltene reduces. The chart shows the effect of the de-emulsifier on the asphaltene composition in the continuous phase. The chart also shows that the injection de-emulsifier into the header of the flow station lead to the destabilization of the emulsion.

IV. CONCLUSION AND RECOMMENDATION

The effect of de-emulsifier in emulsion breaking has been analyzed from a thermal, physical and mechanical point of view respectively to ensure flow assurance of fluid from the well head to the production system. Selection of the right demulsifiers is crucial to emulsion demulsification. Observation has demonstrated that highe concentration and flowrates of the demulsifiersyield better results as long as they can be efficiently managed.

Knowledge of what to expect from production processes in an EOR project when a change occurs in certain scenarios can be simulated virtually within the plant operating philosophy, ensuring shorter downtime, cost savings and more economic benefit for a given system.

REFERENCES

[1] N. H. Abdurahman and W. K. Mahmood, "Stability of water-incrude oil emulsions: effect of cocamide diethanolamine (DEA) and Span 83," *International Journal of Physical Sciences*, vol. 7, no. 41, pp. 5585–5597, 2012.

[2] D. Christopher, A. David, G. Anne, G. Alain, and B. Patrick, "Stability of water/crude oil emulsions based on interfacial dilatational rheology," *Journal of Colloid and Interface Science*, vol. 297, no. 2, pp. 785–791, 2006.

[3] V. Efeovbokhan, T. Akinola, and F. Hymore, "Performance evaluation of formulated and commercially available de-emulsifiers," in *Nigerian Society of Chemical Engineers Proceedings (NSChE '10)*, vol. 40, pp. 87–99, 2010.

[4] R. Espinoza and W. Kleinitz, "The impact of hidden emulsion on oil producing wells—stimulation concept and field result," in *Proceedings of the SPE European Formation Damage*, The Hague, The Netherlands, SPE paper 00082252, 2003.

[5] M. Fingas, and B. Fieldhouse, "Studies of formation process of water-in-oil emulsions," *Marine Pollution Bulletin*, vol. 47, pp. 9-12, 369-396, 2003.

[6] M. Hanapi, S. Ariffin, A. Aizan, and I. R. Siti, "Study on demulsifier formulation for treating malaysian crude oil emulsion," Tech. Rep., Department of Chemical Engineering, UniversitiTechnologi Malaysia, 2006.

[7] T. J. Jones, E. L. Neustadter, and K. P. Whittingham, "Water in- crude oil emulsion stability and emulsion destabilization by chemical demulsifiers," *Journal of Canadian Petroleum Technology*, vol. 17, no. 2, pp. 100–108, 1978.

[8] D. Langevin, S. Poteau, I. H´enaut, and J. F. Argillier, "Crude oil emulsion properties and their application to heavy oil transportation," *Oil and Gas Science and Technology*, vol. 59, no. 5, pp. 511–521, 2004.

[9] F. Merv and F. Ben, "Studies of the formation process of water-in- oil emulsions," *Marine Pollution Bulletin*, vol. 47, no. 9–12, pp. 369–396, 2003.

[10] K. P. Micheal, C. Shaokum, and C. M. Samuel, "The key to predicting emulsion stability: Solid content," in *Proceedings of the SPE International Symposium on Oil Field Chemistry*, Houston, Tex, USA, SPE paper 93008, 2005.

[11] N. Ohian and R. Raji, "The use of demulsifier in crude oils from Niger Delta marginal fields: A comparative analysis of diethylene glycol and phenol," *Academia Journal of Scientific Research*, vol. 3, issue 5, pp. 075-081, 2015.

[12] S. D. Taylor, "Investigations into the electrical and rheological behaviourof W/O—emulsions in high voltage gradients," *Colloid & Surfaces*, vol. 29, pp. 25–51, 1988.

[13] D. G. Thompson, A. S. Taylor, and D. E. Graham, "Emulsification and demulsification related to crude oil production," *Colloid& Surfaces*, vol. 15, pp. 175–189, 1987.