

Influence of Asphaltene Content on Demulsifiers Performance in Crude Oil Emulsions

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Abstract: Chemical demulsification process is the most widely applied method of treating water-in-crude oil emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. Crude oil emulsions are stabilized by asphaltenes which are colloiddally dispersed in the crude oil. Asphaltenes consist mainly of polar heterocompounds and is known that they decrease the interfacial tension between oil and water and form stable interfacial films. This research investigates the performance of demulsifiers in relation to whole asphaltene contents of crude oil emulsions. The performances of ten chemical demulsifiers on destabilization of five crude oil emulsions of different asphaltene contents from different oil wells were studied. Results showed that the viscosity of the emulsions increases as the water content increased. One of the emulsions, Seplat Oben flow station emulsion, however behaved differently. The difference in behavior was accounted for by phase inversion of the emulsion from water-in-oil emulsion to oil-in-water emulsion due to its high water content. There was no significant influence of whole asphaltene content on demulsifier performance for the studied emulsions. It is therefore, recommended that the resin content of the crude and the solvency of the asphaltene in each emulsion be studied and correlated with emulsion stability so as to shed more understanding on the influence of asphaltene on demulsifiers performances and stability of crude oil emulsions. The findings suggest that demulsifier screening be performed on each well and the best performing demulsifier adopted for that well.

Key words: Chemical demulsification, demulsifier, emulsion, asphaltene, solvency, crude oil

INTRODUCTION

Petroleum emulsions is known to be formed in the highly turbulent nozzles and piping used for oil production and transportation. Some oil wells in the Niger Delta region of Nigeria, also have very tight crude oil emulsion in the oil reservoir. These emulsions can increase pumping and transportation expenses, corrosion of pipes, pumps, production equipment and distillation columns and the poisoning of downstream refining catalysts. Sometimes, the oil well may be abandoned if flow is extremely difficult and the emulsions difficult to separate, especially in wells regarded as having marginal crude.

Despite years of research, there is a lack of a fundamental understanding of the mechanisms governing, the stability of oil-continuous emulsions. With crude oil emulsions, the importance in long-term stability of a rigid and protective film surrounding, the water droplets is clear. The detailed properties of this film together with a fundamental knowledge of the chemistry of the interfacially active components in the crude oil are far

from being fully understood. However, studies have established the significance of components such as asphaltenes and resins (McLean and Kilpatrick, 1997).

The focus of this study is on the influence of percentage asphaltene content of crude oil emulsion on the demulsifier performance.

The destabilization of crude oil emulsions forms an integral part of crude oil production. Ekott and Akpabio (2010) reported that stable emulsions are typically broken using gravity or centrifugal settling, application of high electric fields and addition of destabilizing chemicals (demulsifiers). Other methods such as pH adjustment, filtration, membrane separation and heat treatment techniques may also be used. The use of condensed CO₂ has also been suggested and studied by Zaki *et al.* (2003). Methods currently available for demulsification of water-in-crude oil emulsions can be broadly classified as chemical, electrical and mechanical.

In chemical demulsification, chemical substance known as demulsifier is added to the water-in-crude oil emulsion. These demulsifiers are surface active agents (surfactants) and develop high surface pressure at crude

oil-water interface (Abdurahman and Yunus, 2009). It results in replacement of rigid film of natural crude oil surfactants by a film which is conducive to coalescence of water droplets. Abdurahman *et al.* (2007a-c) reported that the percentage of water separated is the best indicator of emulsion stability because it is a measure of the degree of aggregation or flocculation of individual emulsion water droplets and coalescence of aggregated water droplets. They reported that water phase pH has a strong influence on emulsion stability. Specker (2001) discussed asphaltenes and resin as large polyaromatic and polycyclic condensed ring compounds containing heteroatoms. Anderson and Birdi (1990, 1991) stated that chemically, asphaltenes and resins represent the pentane or hexane insoluble portion of the oil. Anklam (1997) reported that in the oil industry water comes into contact with crude oil on many occasions, creating emulsions stabilized by various components in the oil including asphaltenes and resins. Understanding and controlling demulsification is of primary importance for breaking emulsions and for using emulsions in industrial processes that require emulsion destabilization as a main step. At drilling site, the recovered oil will contain some water and hydrophilic impurities which need to be removed before shipping and processing. The water concentration may vary but a target specification for water and sediments removal may be $\leq 1\%$ (Rowan, 1992).

It has been reported that emulsion aging tends to increase its stability and that emulsion breaking must be carried out as soon as possible in the production facility close to the well.

Water-in-crude oil emulsions are mostly stabilized by naturally occurring surfactants (asphaltenes and resins) which adsorb at interfaces and tend to inhibit or delay the interdrop film drainage, hence preventing drop-drop coalescence and water separation. Several approaches have been reported to study the associated phenomena and some trends and correlations have been found between properties. However, the general phenomenology is not completely understood, certainly because there are too many concomitant effects in extremely complex systems from the chemical point of view so that direct and clear-cut analysis is essentially impossible. In this research, the influence of percentage asphaltene content on the ability of a demulsifier to optimally perform has been studied with five water-in-crude oil emulsions and ten demulsifiers.

MATERIALS AND METHODS

Crude oils from different wells, exhibit a wide range of physical and chemical properties. To predict the behavior

of any crude oil with regard to for instance, emulsion stability, knowledge of these properties is of utmost importance. For this study, the properties of the five crude oil emulsions were determined for API, viscosity, whole asphaltene (%), water content (%) and pH of water phase. API gravity was determined with the expression:

$$\text{API} = \frac{141.5}{\text{Specific gravity at } 60/60^{\circ}\text{F}} - 131.5 \quad (1)$$

The specific gravity of the emulsion was measured with hydrometer at temperature of 80°F and then converted to $60/60^{\circ}\text{F}$ using specific gravity reduction table for API determination.

A Fan viscometer model 34A, manufactured by Expotech USA Inc. was used for viscosity measurement. The viscometer cup was cleaned and filled to the graduation level with one sample. The equipment was then switched on and allowed to run at 300 rpm and the viscosity value was read. This was repeated for the other four samples.

To measure asphaltene content, 100 mL of an emulsion sample was measured and weighed and 20 mL of heptane (analytical grade manufactured by Fisher Scientific UK Ltd.) was added to it, shaken and allowed to dissolve for 10 min before it was vacuum filtered. The precipitate was rinsed with excess heptane and filtered again until the effluents ran clear. The weight of the precipitate (asphaltene) was measured and percentage fraction present in the crude oil emulsion calculated as:

$$\text{Whole asphaltene (\%)} = \frac{\text{Weight of precipitate}}{\text{Weight of emulsion sample}} \times 100 \quad (2)$$

To determine the water content of the emulsions, a distillation unit was set up. The 100 mL of emulsion sample was measured into a round bottom flask and 100 mL of xylene was added and the flask was placed in an electrical heating mantle with temperature set at 100°C .

The distillation was allowed to run for 1 h. The quantity of water distilled out was measured in a measuring cylinder and recorded. The process was repeated for the other four samples. The percentage water content of the emulsion was calculated as:

$$\text{Water content (\%)} = \frac{\text{Vol. of water distilled (mL)}}{\text{Vol. of emulsion (mL)}} \times 100 \quad (3)$$

The pH of the water phase of the emulsion was measured using pH meter.

Demulsification of crude oil emulsions: To determine the demulsifiers performances with respect to asphaltene contents of the emulsion, ten graduated centrifuge tubes were filled to 10 mL mark each with SPDC Yokri flow station crude oil emulsion. The 1 mL of each of the ten demulsifiers was then added to each of the test tubes. The demulsifiers used for this study were Baker BASF V13-312, demulsifier PD 42, Lechem Keccroh EB 42, Demulsifier LECHEM-PD 42, WAMCO II, demulsifier 202 B, Demulsifier 14/08, Nalco-Exxon 006-1442, QIT 007 and BE 027. The tubes were hand shaken before being centrifuged for 5 min. The tubes were then allowed to stand for 10 min and the volume of water separated was read off from the tubes and recorded as volume of water separated. The experiment was repeated for SPDC Otumara flow station crude oil emulsion, Chevron VRMT emulsion, Seplat Oben flow station emulsion and Mobil QIT emulsion. The percentage water separated was calculated thus:

$$\text{Water separated(\%)} = \frac{\text{Vol. of water separated(mL)}}{\text{Vol. of total water in emulsion(mL)}} \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Results for temperature show that all the crude oil emulsions assumed the temperature of the room which was 82°F. Result for the API gravity varied from 15.42 for SPDC Yokri flow station crude emulsion to 38.33 for mobil QIT emulsion. Viscosity was high for SPDC Yokri flow station emulsion, SPDC Otumara flow station crude

emulsion, Chevron VRMT crude emulsion with values of 39, 38 and 37 cst, respectively while Seplat Oben flow station emulsion and Mobil QIT emulsion have values of 25 and 10 cst respectively. Highest asphaltene content of 24.7% was recorded for SPDC Yokri flow station crude emulsion and only 8.03% was recorded for mobil QIT emulsion. The highest water content of 62.0% was recorded for Seplat Oben flow station emulsion.

SPDC Yokri flow station emulsion had water content of 47.2%, SPDC Otumara flow station crude emulsion 26.4%, Chevron VRMT crude emulsion had 32.0% while Mobil QIT emulsion had the least water content of 8.3%. The pH of the water phase of the emulsions did not vary much. The values were between 8.23 for SPDC Yokri flow station crude emulsion and 8.60 for Mobil QIT emulsion. Detail results of the emulsions properties are shown in Table 1. Table 2 shows the results of ten demulsifiers performances on the five crude oil emulsions through percentage water separation.

The viscosity of the emulsions increases with increasing water content, except for Seplat Oben flow station emulsion as shown in Table 1. The viscosity increases from 10 cst for Mobil QIT emulsion to 39 cst for SPDC Yokri flow station emulsion. The low viscosity value of 25 cst for Seplat Oben flow station emulsion is worthy of note. It is therefore suspected that there might have been emulsion phase inversion for Seplat Oben flow station emulsion with water content of 62.0%.

Ting (2003) reported that the viscosity of water-in-oil emulsion increases with increasing the water cut before reaching what is called inversion point beyond which the continuous phase changes to water. He reported that the

Table 1: Properties of crude oil emulsions

Crude oil emulsion samples	SPDC Yokri F/S	SPDC Otumara F/S	Chevron VRMT	Seplat Oben F/S	Mobil QIT emulsion
API gravity	15.42	20.19	30.60	21.01	38.33
Viscosity (cst)	39.00	37.00	38.00	25.00	10.00
Asphaltene (%)	24.70	16.84	14.09	12.83	8.03
Water content (%)	47.20	26.40	32.00	62.00	8.30
pH of water	8.23	8.26	8.40	8.25	8.60
Temperature °F	82.00	82.00	82.00	82.00	82.00

Table 2: Demulsifiers performance on crude oil emulsions

Crude oil samples	Water separated by demulsifiers (%)									
	Baker BASF V 13-312	Demulsifier PD 42	Lechem Keccroh EB 42	Demulsifier Lechem PD 42	WAMCO II	Demulsifier 202 B	Demulsifier 14/08	Nalco-Exxon 006-1442	QIT 007	BE 027
SPDC Yokri F/S crude emulsion	53.19	63.83	42.55	42.55	21.27	53.19	53.19	63.83	75.00	63.83
SPDC Otumara F/S crude emulsion	57.69	76.92	76.92	57.69	38.46	38.46	57.69	76.92	38.46	57.69
Chevron VRMT crude emulsion	87.50	87.50	78.13	75.00	78.13	62.50	93.75	87.50	78.13	87.50
Seplat Oben F/S crude emulsion	64.62	80.65	32.26	64.62	32.26	64.62	64.62	80.65	80.65	80.65
Mobil QIT emulsion	50.00	75.00	62.50	62.50	50.00	50.00	75.00	62.50	85.00	75.00

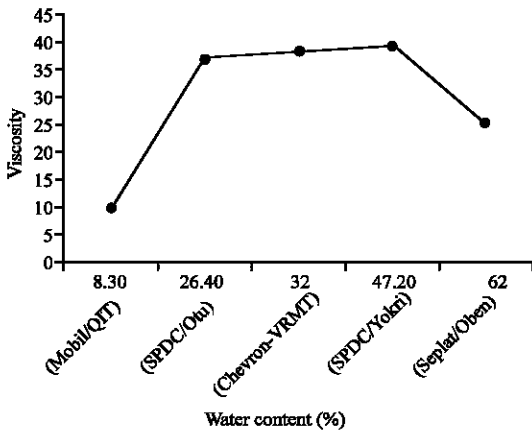


Fig. 1: Effect of water content on viscosity

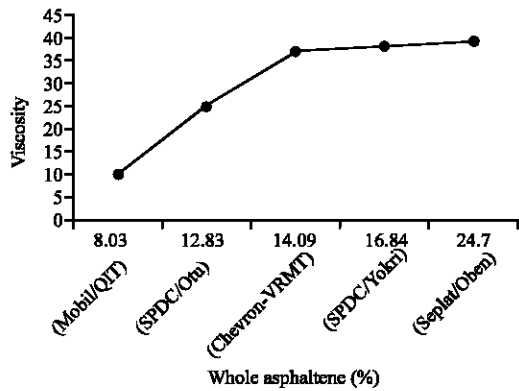


Fig. 2: Effect of asphaltene content on viscosity

viscosity of water-in-oil emulsions increases as much as two orders of magnitude over the viscosity of dry crude. For this study, the sharp increase in viscosity from 10-37 cst for an increase in water cut by 18.1% as shown in Fig. 1. Alwadani (2009) also reported that for water-in-crude oil emulsion at temperature of 25°C, phase inversion takes place when water cut is between 60-70% and may occur at lower water cut when emulsions are at higher temperature. Emulsions for this study were at temperature of 27.8°C. Therefore, the low viscosity of Seplat Oben flow station emulsion is due to phase inversion of the emulsion. A physical examination of the emulsion also confirmed this. The viscosity contents of the emulsions were also closely related to the percentage whole asphaltene content. SPDC Yokri flow station crude emulsion with the highest asphaltene content of 24.7%, also had the highest viscosity value of 39 cst. The results show that the higher the asphaltene content the more viscous the emulsion. Mobil QIT emulsion with 8.03% asphaltene had viscosity of only 10cst. Figure 2 shows that viscosity of the emulsion increases as the asphaltene

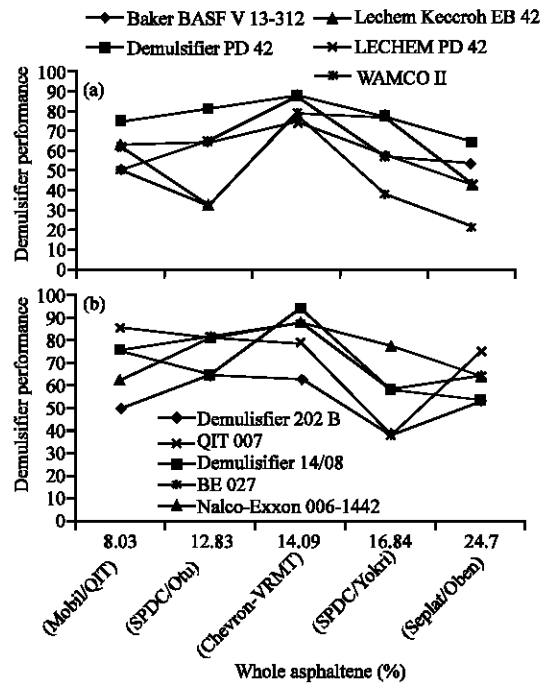


Fig. 3: a) Effect of asphaltene content on demulsifier performance; b) Effect of asphaltene content on demulsifier performance

content increases. This was as expected. Demulsifiers performance tests show that while QIT 007 demulsifier gave the best water separation result of 75.00% for SPDC Yakori crude oil emulsion, it could only separate 38.46% water for SPDC Otumara crude oil emulsion. For this emulsion, the best performing demulsifiers were Demulsifier PD 42, Lechem Keccroh EB 42 and Nalco-Exxon 006-1442 with performance of 76.92% water separation. A different demulsifier, Demulsifier 14/08 performed best for Cheron VRMT emulsion with 93.75% water separation. QIT 007 gave best performance for Seplat Oben and Mobil QIT crude oil emulsions with water separation values of 80.65 and 85.00%, respectively. Table 2 shows that demulsifiers perform differently on different emulsions. For the five emulsions studied, those with high asphaltene content did not separate better than those with low asphaltene content. Figure 3a and b are plots of demulsifier performance (in terms of percentage water separation) against (%) whole asphaltene. The plots were separated due to lines overlaps. At asphaltene content of 14.09% for Chevron VRMT emulsion, all the ten demulsifiers showed the best performance.

CONCLUSION

Results from this study have shown that the viscosity of the emulsions increases as the water content

increase. Seplat Oben flow station emulsion, however behaved differently. The difference in behavior has been accounted for by phase inversion of the emulsion from water-in-oil emulsion to oil-in-water emulsion due to its high water content. Since, the ten demulsifiers performed differently for each of the samples studied, it is proper that demulsifier screening be performed on each well and the best performing demulsifier adopted for that well. The stability of the emulsion might be influenced by the degree of solubility of asphaltene rather than the percentage whole asphaltene present in crude oil emulsion. It is therefore, recommended that the resin content of the crude and the solvency of the asphaltene in each emulsion be studied and correlated with emulsion stability.

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