Asphaltene Solvation and Stability Analyses of Heavy Crude Oil Emulsions

Emmanuel J. Ekott

Abstract— **Stability analyses of heavy crude oil emulsions have been studied and the relationship between asphaltene solvation and emulsion stability was evaluated. Asphaltene was separated from the sample by precipitating the sample with n-heptane and then vacuum filtered and dried. The amount of water resolved in the different heptol composition reduced as the toluene concentration in heptol increased and also the viscosity of the sample increased as the toluene concentration in heptol increased. The study clearly shows that tuning the composition of heptol allows fine control of colloidal forces between asphaltene surfaces in an organic solvent and therefore determines the stability state of the emulsion. This study reveals that the crude aromaticity is definitely a primary factor in determining the stability of asphaltene-stabilized emulsions while the asphaltene type plays at least a secondary role in determining the resultant emulsion stability.**

Index Terms— **Asphaltene, solvency, crude oil, emulsion, demulsifier.**

I. INTRODUCTION

Crude oil is a naturally occurring flammable dense dark fluid containing many varieties of complex saturates and aromatic hydrocarbon molecules, along with organic impurities containing napthenic acid, sulphur, nitrogen, polycyclic aromatic, resins and asphaltenes, heavy metals and metal salts.

Crude oil is found in reservoirs along with water or brine and during oil production, water is often co-produced. Sometimes, water is also injected into the crude to remove salts or as steam to improve fractionation. Under the production conditions like the highly turbulent nozzles and pipes, a proportion of this water can become intimately dispersed throughout the crude oil as small droplets forming emulsion. An emulsion is a colloidal dispersion of one liquid (disperse phase) in another (continuous phase). Sometimes the emulsions may be very thick and termed heavy crude oil emulsions.

Crude oil emulsions also pose serious challenges to refining operations, provoke corrosions, increase heat capacity and reduce the handling capacity of refining equipment and pipelines (Selvarajan et al., 2001). Emulsion resolution is therefore an important element in handling crude oil, from the time it is produced until it enters the refining process. Most heavy crude oil comes as emulsions and must be properly resolved so that the problems associated with transportation, refining, and environment can be solve. Ekott and Akpabio (2010) reviewed the current state of research in water-in-crude oil emulsion stability, destabilization and interfacial rheology. They reported a research gap in fully understanding the chemistry of emulsion stability. Ekott and Akpabio (2011) also reported on the influence of asphaltene

Emmanuel J. Ekott, Department of Chemistry, Heritage Polytechnic, Nigeria.

content on demulsifiers performance and showed that the destabilization of crude oil emulsion does not necessarily depend on the amount of asphaltene in the emulsion alone. They suggested that the degree of asphaltene solvation may be a more important factor than the quantity of asphaltene present in the crude. Akpabio and Ekott (2010); Ekott and Etukudo (2014) carried out performance evaluation of commercial demulsifiers and reported success of some of the chemicals on heavy crude oil emulsions. They identified QIT 007 demulsifier as best performing demulsifier for the samples of Niger Delta crudes they studied. Akpabio and Ekott (2013) blended gasoline with heavy crude oil and investigated the impact on demulsification. Viscosity was found to be reduced and quantity of demulsifier required was small thereby reducing the purchase cost of demulsifiers. Ekott (2020) studied the relationship between asphaltene solvation and emulsion stability using scaling equations and deduced that such equations are useful tools in their correlations. Further studies by Lakkimsetty et al (2023) on dissolution of asphaltene using heptol solvent and optimization of process parameters using response surface methodology (RSM) elaborated on the behaviour of asphaltenes in hoptol solvents.

To help improve the conversion of crude oil into useful products by reducing losses to sludge and emulsions, it is necessary to better understand the factors that affect their formation. Paramount to this understanding is an in-depth knowledge of the structures and interactions of the asphaltenic components responsible. Asphaltene deposition within reservoir rocks has been blamed for pronounced reductions in well productivity (Cimino et al, 1995). According to Siffert, Bourgeois and Papirer (1984) asphaltenes have been found to facilitate the formation of extremely stable water-in-crude oil emulsions. Understanding asphaltene chemistry and the fundamental mechanisms of colloid formation has been the driving force behind much petroleum researches in recent years. While the study of asphaltene containing oil-water systems has been a fruitful area of research lately, there are just a handful of investigations on asphaltene solvency and even fewer relating emulsion behavior to asphaltene chemistry. Ostlund and co-workers have fractionated asphaltenes in mixtures of aliphatic and aromatic solvents by solubility and characterized their different chemistries (Ostlund et al, 2001). They also used ion exchange chromatography to separate asphaltenes into acidic, basic and neutral groups for subsequent determination of chemical properties. However, none of these studies involved studying emulsion forming properties of asphaltenes. The study of asphaltene colloidal properties has been motivated by their propensity to aggregate, flocculate, precipitate, and to adsorb onto interfaces (Espinat et al, 1993). Clearly, the scientific community lacks an in-depth understanding of asphaltene solvation, chemistry and behavior at the oil-water interface.

A major contribution was made by Spiecker and Kilpatrick (2004) when they studied asphaltene chemistry and their propensity to aggregate in solution and correlated it to the stability of water-in-oil emulsions for California and Argentina oils. It is now well recognized that asphaltenes from different crude oil sources can have vastly different properties and hence the need to study asphaltenes from different crude oils including those of Niger Delta region of Nigeria and their impact in the stability of crude oil emulsions.

II. MATERIALS AND METHODS

Five crude oil emulsion samples from Niger Delta region of Nigeria were used for this study. Samples were collected from both onshore and offshore oil well sources for balanced investigation. The onshore samples were SPDC Yokri, SPDC Otumara, and Seplat Oben emulsions. Chevron VRMT and Mobil QIT emulsions were from offshore locations. The samples were collected into labelled plastic containers from flow stations by opening of flow valves.

   100ml of crude oil emulsion sample was measured and weighed. 25ml of n-heptane was added, and shaken to dissolve for 10 minutes. It was then vacuum filtered. The precipitate was rinsed with excess n-heptane until the effluent runs were clear. The precipitate was then dried in an oven at $25^{o}C$ for an hour. 3g portion each was measured into 5 different flasks and 1ml each of 5 different heptol mixtures was added. The heptol mixtures were prepared by mixing heptane and toluene in the following proportion by volume respectively: 90:10, 80:20, 70:30, 60:40, and 50:50. To each flask, a fresh crude oil emulsion sample was added to make a volume 300ml (this was the viscometer instrument required volume for measurement of viscosity). It was stirred and allowed to stand for 1 hour. The viscosity of each of the mixture was then measured with viscometer and recorded after thorough stirring. 10ml of each of the mixtures was thereafter taken into 5 test tubes and 1ml of QIT 007 demulsifier was added to each test tube and allowed to stand for 10 minutes. The percentage water separated was recorded as an index for stability of emulsion based on the contribution of soluble asphaltene. The entire process was repeated for the other four crude oil emulsion samples.

III. RESULTS AND DISCUSSIONS

Asphaltene solvency tests were carried out to investigate the impact of asphaltene solvation on stability of crude oil emulsions. Higher amounts of water separation indicate weaker emulsions because of increased droplet coalescence. Lower values indicate reduced droplet coalescence and more stable emulsions. Viscosity and amount of water separated were determined for the five samples asphaltenes in a set of five heptol mixtures. Results for viscosity and amount of water separation for the asphaltene solvency tests are presented on tables 1 and 2 respectively. Viscosity results show that the viscosity of SPDC Yokri increased from 40 to 50 centistokes (38.88%), while 34.14% was recorded for SPDC Otumara, 23.07% for Chevron VRMT, 48.14% for Seplat Oben and 30% for Mobil QIT emulsion. These clearly demonstrate the asphaltene solvency impact on viscosities of the emulsions and hence the emulsions

stability. It shows that the stability of the emulsions increases as the amount of soluble asphaltene increases as depicted by the increases in viscosity.

The impact of increasing the viscosity of the emulsion in the asphaltene solvency test was highly revealing. The water resolved curves were generally of similar shape and they all indicated maximum emulsion stability at 50:50 heptane/toluene ratios. The curves were not however the same in terms of gentleness of the slopes. It is suspected that emulsion stability was dominated by two primary factors: asphaltene source and solubility in heptol. The asphaltene source must have been responsible for the dissimilarities in the slope of the plots which indicates the intensity of impact on water resolution and hence emulsion stability. Asphaltenes from SPDC Otumara and Mobil QIT emulsions seem to have stronger emulsion stabilization tendencies as compared to asphaltenes from SPDC Yokri and Chevron VRMT emulsions. Effect of solvent solvency on viscosity and stability of the samples are shown in figures 1 – 5. Figures 2 and 5 for SPDC Otumara and Mobil QIT have more gentle slopes indicating that their asphaltenes have stronger emulsion forming and stability properties than those from the other samples. The percentage water resolved between heptol mixtures of 90:10 to 50:50 further confirmed this. While asphaltene solubility in the different heptol mixtures was able to resolve only 70.0% and 66.66% for SPDC Otumara and Mobil QIT respectively, a larger amount of water of 77.14% and 84.61% was resolved for SPDC Yokri and Chevron VRMT asphaltenes. These show that asphaltenes from SPDC Otumara and Mobil QIT samples were able to stabilize their emulsions much more than those from the other three samples.

Differential asphaltene solubility in different heptol mixtures was responsible for the observed increased in viscosities of the emulsions. All the emulsions showed significant increase in viscosity as the asphaltene concentration increased. This resulted in formation of more stable emulsion. For all the plots (figures 1 - 5), as the viscosity of the emulsion increases, the amount of water resolved reduces indicating more stable emulsion. With exception of figure 4, all the other plots have the upper line being the viscosity plot line and the lower line being the water plot and the two lines do not intercept. However, figure 4 plot for Seplat Oben emulsion presents an interesting case of the viscosity plot intercepting the water plot. Figure4 also have the water plot line being on top while the viscosity plot line is below; a reverse of the other plots. At toluene volume fraction of about 0.27, the water plot line intercepts the viscosity plot line and crosses over to assume the shape of plots of the other emulsions. A possible interpretation to this emulsion behavior as shown in the graph is that the emulsion must have contained very weak surface active agents. The surface active agents have been highly precipitated and very weakly solvated. It is believed that the extent of solvation of asphaltenes for this emulsion type is higher than those of the other four emulsions. Moreover, the amount of water present in this emulsion was very large and near phase inversion water level in emulsions.

Another possible explanation to this interesting Seplat Oben emulsion behavior is through phase inversion. At first it

seems to show oil-in-water emulsion behavior for mixtures of 90:10 and 80:20 heptane/toluene when compared with the shapes of the other plots. As the heptane fraction reduces to 70%, the sample seem to show a water-in-oil emulsion behavior. Figure 4 presented the Seplat Oben behavior of phase inversion from oil-in-water emulsion to water-in-oil emulsion. In figure 4, the point where the plot of percentage water resolved of the Seplat Oben emulsion sample crosses the plot of viscosity is a possible point of phase inversion. It is suspected that Seplat Oben emulsion with water content of 62% was just at the point of phase inversion and any critical factor can reverse the emulsion type. Increasing the viscosity of the emulsion by increasing the asphaltene content without corresponding increase in water content might cause inversion. For this sample, the viscosity increased from 27 to 40 centistokes by reducing the heptane fraction from 90% to 50%. While 50% water was resolved with 90:10 heptane/toluene ratios, only 10% water was resolved with 50:50 heptane/toluene ratios. All these changes in behavior point to a possible phase inversion. From the results we can see an emerging picture of the role of asphaltene chemistry and solvency behavior in governing emulsion stability and also its possible influence in establishing point of emulsion phase inversion.

Estimation of emulsion inversion point is important to improve viscosity correlations. Therefore, many attempts to develop mathematical models for phase inversion in emulsions have been made. Some of these models are based on experiments carried out in a stirred vessel, where phase inversion was detected by a jump in emulsion conductivity, while others were based on experiments carried out in horizontal pipes to simulate two-phase flow of oil water (Jing, 2006). This study has provided a possible graphical method of estimating inversion point of emulsion as the intercept of viscosity and amount of water resolved under various heptanes/toluene ratios. However, this requires further investigation.

Table 1. Viscosities (cst) for Asphaltene Solvation Tests

Heptol Mixture (% Toluene v/v)	SPDC Yokri	SPDC Otumara	Chevron VRMT	Seplat Oben	Mobil QIT
0.1	40	41	39	27	10
0.2	41	45	40	32	10
0.3	44	49	43	34	12
0.4	46	53	46	38	12
0.5	50	55	48	40	13

Table 2. Percentage Water Separation for Asphaltene Solvation Tests

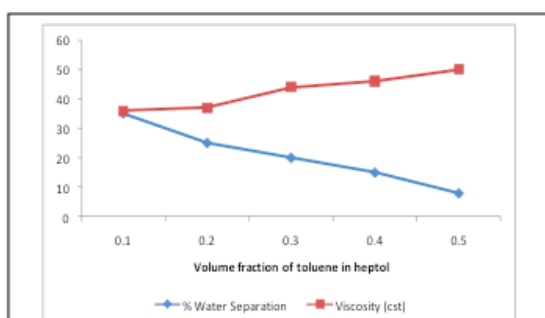| Heptol Mixture (% Toluene v/v)	SPDC Yokri	SPDC Otumara	Chevron VRMT	Seplat Oben	Mobil QIT
0.1	35	20	26	50	6
0.2	25	16	18	40	4
0.3	20	12	10	25	4
0.4	15	10	6	20	3
0.5	8	6	4	10	2

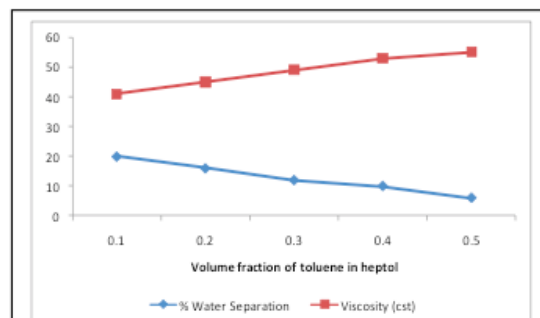Figure 1. Effect of solvent solvency on viscosity and stability of Precipitated Asphaltene SPDC Yokri Crude Emulsion

Figure 2. Effect of solvent solvency on viscosity and stability of Precipitated Asphaltene SPDC Otumara Crude Emulsion
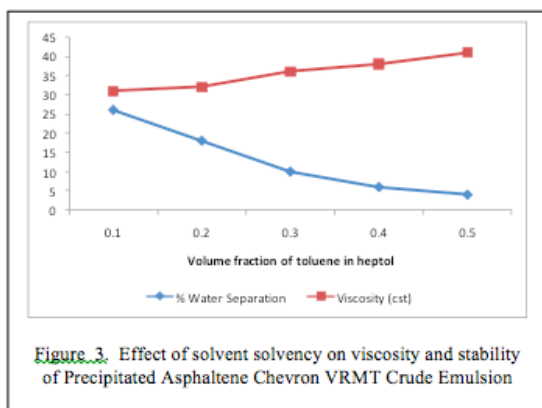
Figure 3. Effect of solvent solvency on viscosity and stability of Precipitated Asphaltene Chevron VRMT Crude Emulsion
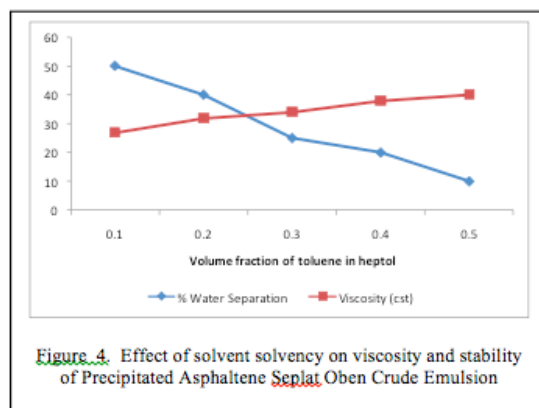

Figure 4. Effect of solvent solvency on viscosity and stability of Precipitated Asphaltene Seplat Oben Crude Emulsion
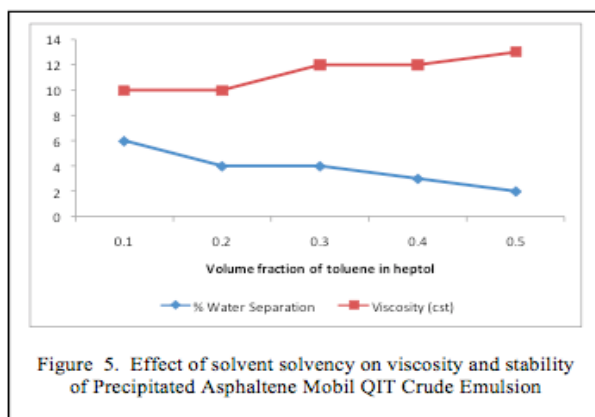

Figure 5. Effect of solvent solvency on viscosity and stability of Precipitated Asphaltene Mobil QIT Crude Emulsion

IV CONCLUSION

Results from this study have shown that the viscosity of the emulsions increases as the degree of asphaltene solvation increases. The amount of water separated from the emulsion also reduced as the extent of asphaltene solvation increased. The emulsion stability as measured by the amount of water separated and the change in viscosity clearly points to the sensitivity of asphaltene solvation to solvent composition. Our study clearly shows that tuning the composition of heptol allows fine control of colloidal forces between asphaltene surfaces in an organic solvent and therefore determines the stability state of the emulsion. This study reveals that the crude aromaticity is definitely a primary factor in determining the stability of asphaltene-stabilized emulsions while the asphaltene type plays at least a secondary role in determining the resultant emulsion stability. It is recommended that the study be extended to toluene volume fraction of 0.9. This will provide a better understanding of the nature of segment interaction between asphaltenes. This interaction in organic solvent such as heptol can be attractive or repulsive, depending on the quality of the solvent. The study in toluene range of 0.1 to 0.9 will provide the points of change from attractive to repulsive force.

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