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STABILIZATION OF MODEL CRUDE OIL EMULSION BY ASPHALTENE

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ABSTRACT
As part of an ongoing research into the stability of oil-field emulsions, model oils have been utilized to probe the effects of asphaltene interactions on crude oil/water emulsion stability. Asphaltenes were precipitated from treated Ondo State oil sand bitumen with n-hexane in a 40:1 solvent to bitumen ratio which was allowed to stand for 24 hours and then filtered. Model oils were prepared from n-hexane and toluene with varying masses of asphaltene dissolved in them (0.05-0.1%). Emulsions were prepared from mixtures of model oil with 5ml of de-ionized water. Results showed that the stability of the prepared emulsions increased with asphaltene concentration of the model oil; with the model oil containing 0.1% of asphaltene forming the most stable emulsion. Therefore, the higher the concentration of asphaltene in the model oil, the more stable the model oil/water emulsions formed. This is similar to literature reports on oil-field emulsion therefore the interaction of asphaltene with the prepared model oils can be used as a model to study crude oil emulsion stabilization processes.

Keywords: Asphaltene, Bitumen, Crude oil, Emulsion, Model oil, Stabilization.

INTRODUCTION

Petroleum, in one form or another has been used since ancient times and is now important across society including in economy, politics and technology. The rise in importance was mostly due to the invention of the internal combustion engine, the rise in commercial aviation and the increasing use of plastic. More than 4000 years ago, according to Herodotus and Diodorus Siculus, asphalt was used in the construction of the walls and towers of Babylon; there were oil pits near Ardericca (near Babylon), and a pitch spring on Zacynthus (Chisholm et al, 1911). Great quantities of it were found on the banks of the river Issus, one of the tributaries of the Euphrates. Ancient Persian tablets indicate the medicinal and lighting uses of petroleum in the upper levels of their society.

In the 1850s, the process to distil kerosene from petroleum was invented by Ignacy Łukasiewicz, providing a cheaper alternative to whale oil. The demand for the petroleum as a fuel for lighting in North America and around the world quickly grew. The world's first commercial oil well was drilled in Poland in 1853. Oil exploration developed in many parts of the world with the Russian Empire, particularly the Branobel Company in Azerbaijan; taking the lead in production by the end of the 19th century (Akiner et al, 2004). Oil exploration in North America during the early 20th century later led to the United State of America becoming the leading producer by the mid 1900s. As petroleum production in the United State of America peaked during the 1960s, however, Saudi Arabia and Russia surpassed the United State of America

The process of recovering crude oil from beneath the earth begins by forcing a blend of oil and water through a vertical casing to the surface. The resulting shear energy and pressure decline produces a" tight" oil/water emulsion once at the surface. En route to the production equipment, where primary separation and dehydration take place, many emulsions are heated, pressurized, pumped, and pushed through pipelines. Once at the production facility, the emulsion is generally a homogenized blend of oil, water, gas and contaminants. The understanding of this production history can provide the expert with some valuable insight into the nature of the crude oil and water emulsion.

Crude oil is seldom produced alone. It is generally comingled with water, which creates a number of problems during oil production. Produced water occurs in two ways; some of the water may be produced as free water (i.e. water that will settle out fairly rapidly), and some of the water may be produced in the form of emulsions (Becher et al, 1983). Emulsions are difficult to treat and cause a number of operational problems, such as tripping of separation equipment in gas/oil separating plants (GOSPs), production of off-specification crude-oil, and creating high pressure drops in flowliness. Emulsions have to be treated to remove the dispersed water and associated inorganic salts to meet crude specification for transportation, storage and export and to reduce corrosion and catalyst poisoning in downstream-processing facilities. Emulsion can be encountered in almost all phases of oil production and processing; inside the reservoirs, wellbores, well heads, and wet crude-handling facilities; transportation through pipelines and crude storage; and during petroleum processing (Schramm et al, 1992).

Emulsification is the process whereby water-in-oil emulsions are formed (Fingas, et al, 2002). The availability of methodologies to study emulsions is very important. In the past ten years, both dielectric methods and rheological methods have been exploited to study formation mechanisms and stability of emulsions made from many different types of oils (Fingas et al, 1993), (Sjöblom et al, 1994). Standard chemical techniques, including Nuclear Magnetic Resonance (NMR), chemical analysis techniques, microscopy, interfacial pressure, and interfacial tension, are also being applied to emulsions. These techniques have largely confirmed findings noted in the dielectric and rheological mechanisms. The mechanism and dynamics of emulsification were poorly understood until the 1990s.

It was not recognized until recently that the basics of water-in-oil emulsification were understood in the surfactant industry, but not in the oil industry. In the late 60s, Berridge and coworkers were the first to describe emulsification in detail and measured several physical properties of emulsions (Berridge et al, 1968). Berridge described the emulsions as forming because of the asphaltene content of the oil. The oil's composition was not felt to be a major factor in emulsion formation. Some workers speculated that particulate matter in the oil may be a factor and others suggested it was viscosity. Evidence could be found for and against all these hypotheses.

A study was conducted on emulsions revealed that emulsion formation might be correlated with oil composition (Twardus et al, 1980). It was suggested that asphaltene and metal porphyrins contributed to emulsion stability. In the same year another study on emulsion revealed that the asphaltene and waxes in the oil stabilized water-in-oil emulsions (Bridie et al, 1980). The wax and asphaltene content of two test oils correlated with the formation of emulsions in a laboratory test.

Mackay and coworkers hypothesized that emulsion stability was due to the formation of a film in oil that resisted water droplet coalescence (Mackay et al, 1981 and 1982). The nature of these thin films was not described, but it was proposed that they were caused by the accumulation of certain types of compounds. Later work led to the conclusion that these compounds were asphaltene and waxes. A standard procedure was devised for making emulsions and measuring stability. This work formed the basis of much of the emulsion formation theory over the past two decades.

Much of the information on emulsions available in the oil industry has been obtained by practical studies in the laboratory or in the field. In the early 90s, Jenkins and coworkers studied emulsions formed in the laboratory and concluded that the formation did not correlate with previously established codes of properties, or with pour point, asphaltene, and wax contents of the fresh oils (Jenkins et al, 1991). They suggest that, in the absence of any correlation, every oil should be characterized using a standardized procedure in the laboratory.

Other examples of empirical studies include a two-year study conducted on emulsions (Walker et al, 1995) at Warren Spring Laboratory in Britain in which approximately 40 North Sea crude oils were prepared and characterized in the laboratory. Some of these oils were subsequently spilled at sea and some of their properties measured. It was concluded that the laboratory procedures did not result in emulsions similar to those found at sea, but also noted that there was a marked lack of characterization techniques to study emulsions.

The same group participated in another field trial conducted (Walker et al, 1995). The correlation between parallel experiments, physical properties, and emulsion characteristics was poor. It was concluded that delays in sampling and analyses were partially responsible for the poor results as well as the lack of standard measurement and characterization techniques. It was also noted that slight differences in release conditions resulted in major differences in slick behaviour. It was found that there must be a high level of energy for emulsions to form and that the oil must be weathered to a degree before release. Stability could not be characterized, but appeared to be a continuum through the process.

This study is therefore to investigate the effect of asphaltene as one of the major components of crude oil in stability of emulsions using a model crude oil.

Sample Collection and Preparation

Bitumen

Bitumen sample was collected from Agbabu Bitumen Deposit, Agbabu in Ondo State on the 6th of April 2010. It was kept in a cool place to prevent melting.

Tar sand

Tar sand was collected at Ore –Irele in Ondo State on the 6th of April, 2010. It was stored in a bag-co sac and kept in a cool place.

Extraction of Asphaltenes

Asphaltenes were separated from Ondo State oil sand bitumen that has been treated to remove most of the sand and water. The asphaltene were precipitated from the bitumen with n-hexane (Analytical grade) in a 40:1 solvent to bitumen (cm^3/g) ratio. The mixture was vigorously mixed for five minutes and then left to stand for a period of 24 hours in a dark cupboard. The thoroughly mixed mixture was later filtered through a Whatman 40 Ash less filter paper. The asphaltene, which was gotten as residue on the filter paper, were allowed to dry in an oven at 110 °C until a constant mass was achieved. The asphaltene were kept in desiccators. This procedure was repeated severally until the required amount of asphaltene was extracted.

Preparation of Model Oil

60 ml of n-hexane was mixed with 40 ml of toluene in a 250 ml conical flask. Before mixing, certain amount of asphaltene was dissolved in 40 ml toluene, to prepare a model oil of different concentrations of asphaltene, since asphaltene are soluble in toluene. The mixture of n-hexane and toluene is referred to as hextol model oil.

Preparation of emulsions

Crude oil emulsions were prepared by dispersing 5ml of deionized water in model oil using a mechanical shaker at speed range of 300-500 rpm for 10 min (Cavallo et al, 1990 and Omole et al, 2005). The emulsion portion was dispensed into a 10 ml measuring cylinder and its volume was recorded. Also the resolution of the emulsion was also monitored at different time interval to determine the stability of the emulsion. This was repeated for the model oil at different concentrations of asphaltene already prepared.

Stability of emulsions

The stability of emulsions was assessed by monitoring the increase with time the position of clear water-emulsion interface. The emulsion collected in 10 ml measuring cylinder was allowed to stand i.e. under gravity and the volume of water resolved was recorded with time as a measure of the stability of the emulsion.

RESULTS AND DISCUSSION

Table 1 Volume of water resolved for 0.05% asphaltene stabilized emulsion per time

Time (min)	Emulsion Volume (ml)	Resolved water volume (ml)
0	7.0	0.0
30	7.0	0.0
60	6.0	1.0
120	3.0	3.0
180	1.0	6.0
240	0.9	6.1
1440	0.2	6.8

Table 2: Volume of water resolved for 0.06% asphaltene stabilized emulsion per time

Time (min)	Emulsion volume (ml)	Resolved water volume (ml)
0	4.0	0.0
60	3.0	1.0
420	3.0	1.0
1020	0.6	3.4
1440	0.3	3.7
1860	0.1	3.9

Table 3: Volume of water resolved for 0.07% asphaltene stabilized emulsion per time

Time (min)	Emulsion volume (ml)	Resolved water volume (ml)
0	5.3	0.0
60	5.0	0.3
180	4.5	0.8
420	4.5	0.8
1440	3.3	2.0
2280	3.0	2.3
4320	2.3	3.0
5760	0.8	4.5
7200	0.2	5.1

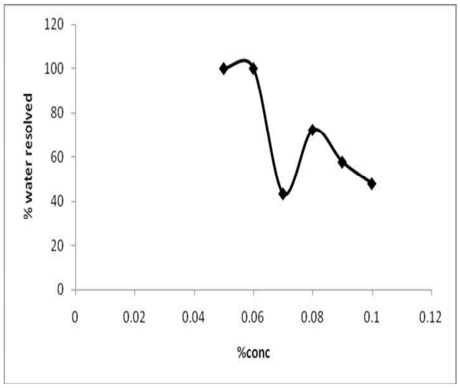

Fig.1: Percent water resolved in an emulsion as a function of asphaltene concentration in model oil after 1440 minutes.

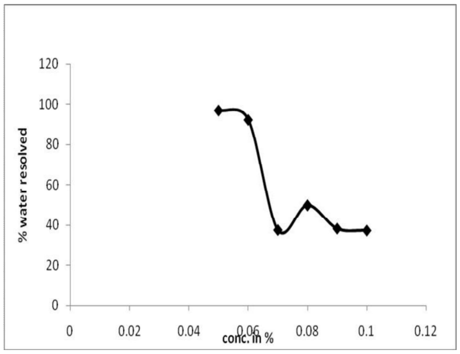

Fig.2: Percent water resolved in an emulsion as a function of asphaltene concentration in model oil after 2880 minutes.

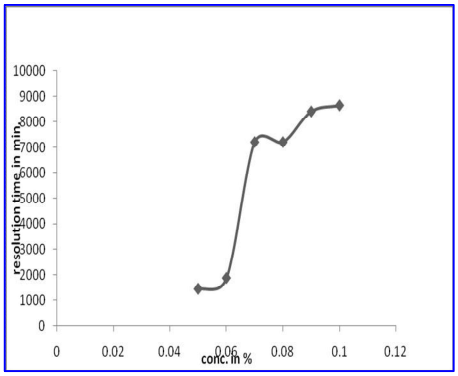

Fig.3: Resolution time for model oil at varying concentration of asphaltene

Discussion

From the results obtained, it was observed that at 0.05% asphaltene concentration, the time required for the maximum resolution of the emulsion was 1440 minutes (Table 1). This indicates that the emulsion formed was not stable at all as the emulsion formed was completely resolved within a day. This may be the kind of concentration level of asphaltene present in the light crude oil, for example Bonny light from Nigerian Oil Field that do not present any oil field emulsion problems and hence in high demand. This time lag should not create any difficulties during the usual exploration/exploitation activities on oil fields.

At 0.06% asphaltene concentration, the time required for complete separation of the water from the model oil was 1860 minutes (Table 2) where the highest volume of water resolved was recorded. This is longer than that of 0.05% asphaltene stabilized emulsion. As shown in both figures 1 and 2 there was a sudden rise in the degree of stabilization from 0.06% to 0.07% asphaltene concentration (Figure 1) this suggests that the emulsion stabilization process is likely to be a two stage process using the inversion method of stabilization. This method is known to lead to an increase in stabilization of any resulting emulsion formed. This is also obvious from the reduction in the amount of water resolved.

When 0.07% asphaltene was used to stabilize the emulsion formed, the time for complete separation of the water from the oil increased to 7200 minutes, higher than what was observed for 0.05% and 0.06% asphaltene respectively (Table 3).

It was observed that at 0.08% asphaltene, there was a drop in the degree of stabilization despite the increase in the concentration of the asphaltene when compared with 0.07% asphaltene concentrations as shown in figures 1 and 2 respectively, this usually occurs when the emulsion is close to the inversion point where the flip in the emulsion type occurs. The emulsion may invert from oil in water to water in oil. Both of these types of emulsions are possible in oil field emulsions due to presence of other solid particles e.g. resins (Mansurov et al, 1987)

At 0.09% asphaltene, there was an increase in the time required for complete resolution of water from the emulsion formed compared with what happened at 0.08% asphaltene, at this concentration the resolution time was 8400 minutes which suggests the emulsion formed was more stable than the one formed from the previous concentrations.

At 0.1% asphaltene, the highest resolution time was recorded at 8640 minutes indicating that the emulsion formed was most stable, since this is the highest concentration used in the study. This effect can be seen virtually in all the figures confirming the significance of asphaltene concentration on water/crude oil emulsion stability where the % water resolved was low.

The emulsion produced at the lowest asphaltene concentration 0.05% was completely resolved after 1440 minutes. The emulsion produced from the next higher asphaltene concentration of 0.06% and the highest concentrations were completely stable to gravity over the same period of time. The resolution time at each concentration also indicates that the stability of emulsion increases as the asphaltene concentration increases because the more the resolution, the more stable the emulsion as shown in figure 3.

Conclusion

Water-in-crude oil emulsions have great importance in the oil industry. Results from this study tend to support the proposed mechanism in which emulsion stability is governed primarily by the concentration of asphaltene in the crude oil. So, the primary contributor to the stability of emulsions produced in this study was not just the asphaltene but the concentration of asphaltene.

In this work, emulsions produced from model oils containing asphaltene exhibited stabilities which can be likened to those produced from crude oils therefore model oils can be used as a model/demo in the study of crude oil emulsions.

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