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Stabilization of Model Crude Oil Emulsion using Different Concentrations of Asphaltene

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ABSTRACT

As part of an ongoing research into the stability of oil-field emulsions, model oil samples 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 before it was filtered. Model oil samples 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 5 cm^3 of de-ionized water. Results showed that the stability of the prepared emulsions increased with asphaltene concentration of the model oil sample, 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 or crude oil is any naturally-occurring flammable mixture of hydrocarbons found in geologic formations, such as rock strata. Most petroleum is a fossil fuel, formed from the action of intense pressure and heat on buried dead zooplankton and algae. Petroleum, in one form or the other has been used since ancient times and is now important across society including in economy, politics and technology (Chisholm *et al*, 1911). 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 (Chisholm *et al*, 1911). 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 (Chisholm *et al*, 1911). Ancient Persian tablets indicate the medicinal and lighting uses of petroleum in the upper levels of their society.

In the 1850s, the process of separating 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

Emulsification is the process whereby there is a formation of the mixture of water and crudeoil during exploration (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) spectroscopy, 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.

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

MATERIALS AND METHODS

Sample Collection and Preparation

Bitumen sample was collected from Agbabu Bitumen Deposit, Agbabu in Okitipupa L.G.A of Ondo State on the 6^{th} of April 2010. It was kept in a cool place to prevent melting.

Tar sand was collected at Ore –Irele in Irele L.G.A of Ondo State on the 6^{th} 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 using 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 using mechanical shaker for five minutes and then left to stand for a period of 24 hours in a dark cupboard. It 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 weight 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

Exactly 60 cm^3 of n-hexane was mixed with 40 cm^3 of toluene in a 250 cm^3 conical flask. Before mixing, 0.05-0.1 g of asphaltene was dissolved in 40 cm^3 toluene. To prepare 0.05 % concentration of asphaltenes, 0.05 g of asphaltenes was dissolved in 40 cm^3 of toluene and was made up to 100 cm^3 with hexane, since asphaltene are soluble in toluene. This procedure was repeated using 0.06, 0.07, 0.08, 0.09 and 0.1 g of asphaltene respectively. The mixture of n-hexane and toluene is referred to as hextol model oil (McLean *et al*, 1997).

Preparation of emulsions

Crude oil emulsions were prepared by dispersing 5 cm^3 of deionized water in 20cm^3 model oil sample 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 cm^3 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.

Determination of the emulsion stability

The stability of emulsions was assessed by monitoring the increase with time the position of clear water-emulsion interface. The emulsion collected in 10 cm^3 measuring cylinder was allowed to stand that is under gravity and the volume of water resolved was recorded with time as a measure of the stability of the emulsion.

RESULTS AND 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 in oil fields.

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

Time (hr)	Emulsion volume (cm^3)	Resolved water volume (cm^3)
0	7.0	0.0
30	7.0	0.0
60	6.0	1.0
120	3.0	4.0
180	1.0	6.0
240	0.9	6.1
1440	0.2	6.8

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 Figs. 1 and 2 there was a sudden rise in the degree of stabilization from 0.06 to 0.07 % asphaltene concentration (Fig. 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).

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

Time (min)	Emulsion volume (cm^3)	Resolved water volume (cm^3)
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 (cm^3)	Resolved water volume (cm^3l)
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

It was observed that at 0.08 % asphaltene (Table 4), 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 Figs. 1 and 2 respectively (Tables 5 and 6), 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 (Table 7).

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 (Table 8). 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 Fig. 3.

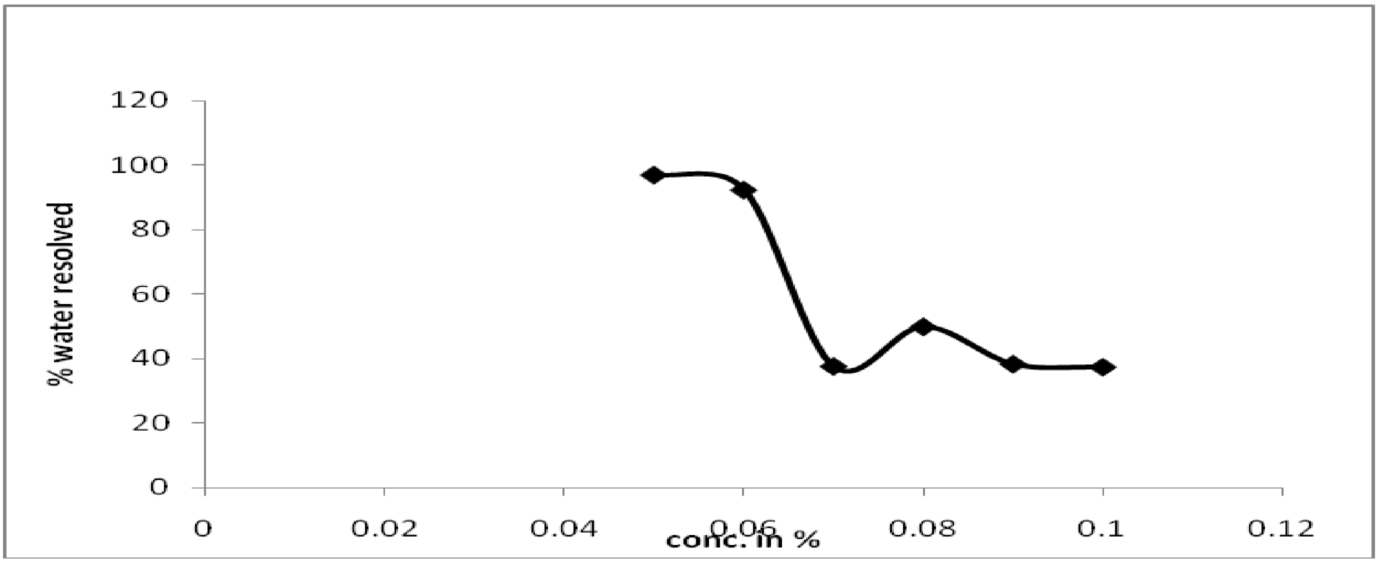

Fig.1: Percent water resolved in an emulsion as a function of asphaltene concentration in model oil after 1440 minutes.

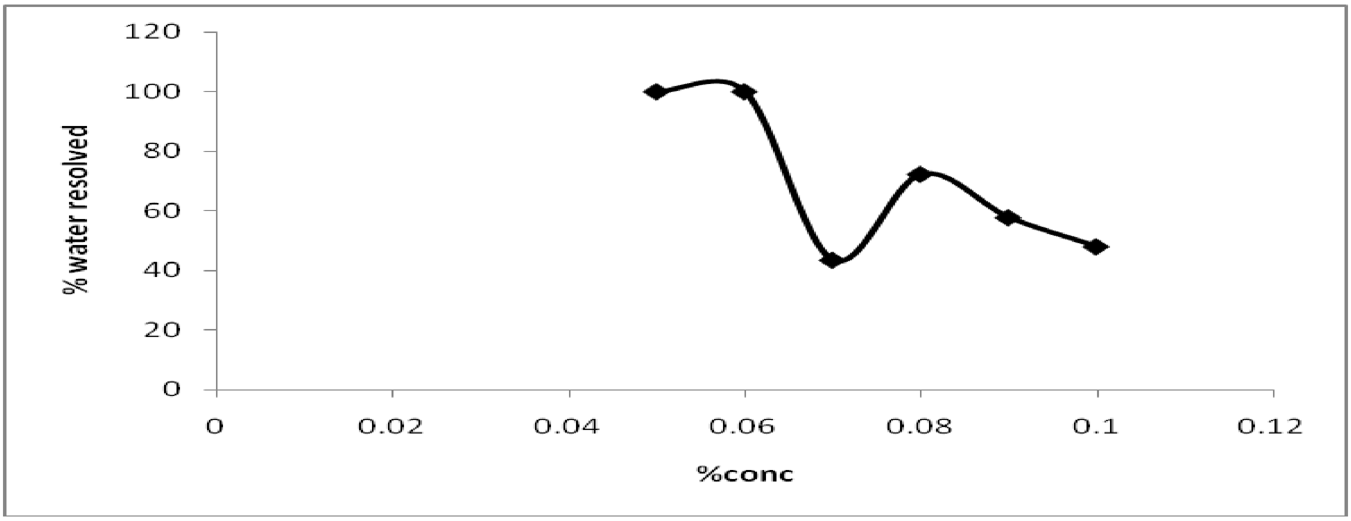

Fig.2: Percent water resolved in an emulsion as a function of asphaltene concentration in model oil after 2880 minutes

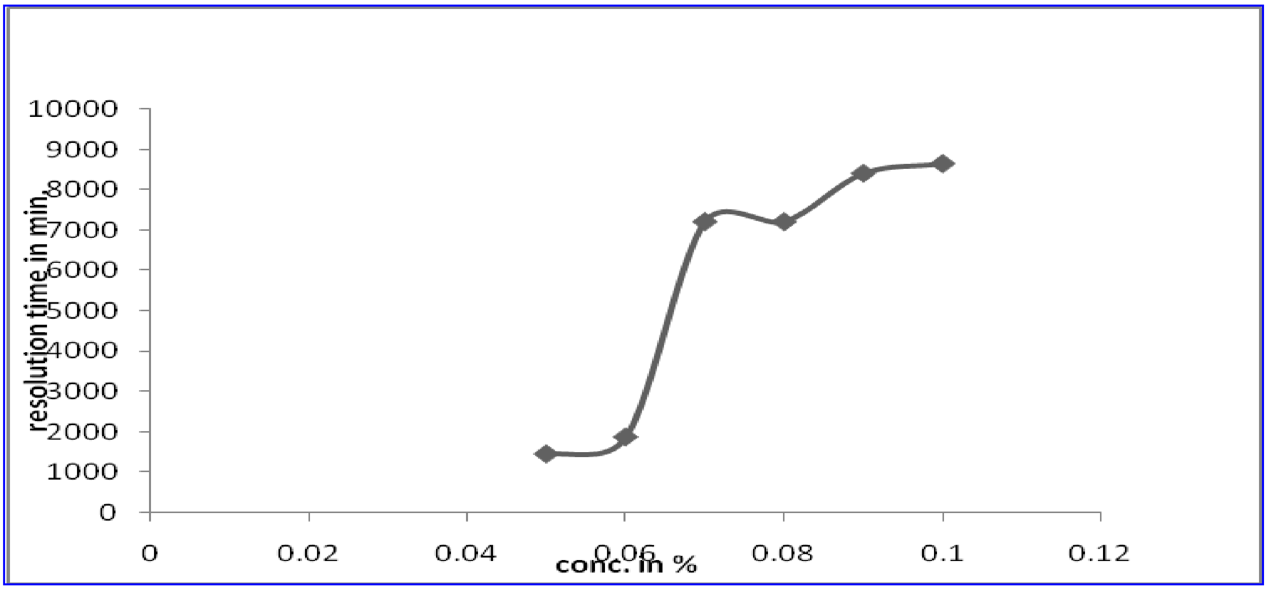

Fig.3: Resolution time for model oil at varying concentration of asphaltene

Table 4: Volume of water resolved for 0.08 % asphaltene stabilized emulsion per time

Time (min)	Emulsion volume (cm^3)	Resolved water volume (cm^3)
0	3.6	0.0
60	3.5	0.1
120	3.0	0.6
1200	2.0	1.6
1440	1.8	1.8
2880	1.0	2.6
4320	0.8	2.8
5760	0.4	3.2
7200	0.1	3.5

Table 5:% water resolved at 1440 minutes per asphaltene concentration

(%)Conc.	% water resolved
0.05	97.14
0.06	92.50
0.07	37.74
0.08	50.00
0.09	38.46
0.10	37.50

Table 6:% water resolved at 2880 minutes per asphaltene concentration

%Conc.	% water resolved
0.05	100
0.06	100
0.07	43.39
0.08	72.22
0.09	57.69
0.10	47.92

Table 7:Volume of water resolved for 0.09 % asphaltene stabilized emulsion per time

Time (min)	Emulsion volume (cm^3)	Resolved water volume (cm^3)
0	5.2	0.0
60	4.8	0.4
1440	3.2	2.0
2880	2.2	3.0
4320	2.0	3.2
5760	1.0	4.2
7200	0.6	4.6
8640	0.2	5.0

Table 8:Volume of water resolved for 0.10% asphaltene stabilized emulsion per time

Time (min)	Emulsion volume (cm^3)	Resolved water volume (cm^3)
0	4.8	0.0
60	4.5	0.3
720	4.0	0.8
1440	3.0	1.8
2880	2.5	2.3
4320	1.4	3.4
5760	1.0	3.8
7200	0.4	4.4
8640	0.1	4.7

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. 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.

REFERENCES

Akiner, S. (2004) the Caspian: Politics, Energy, Security (ed.), London: Routledge Curzon. Allen ... *Scandinavian Journal of Social Theory*, 16: 5–26.

Berridge, S. A., Thew, M. T and Loriston-Clarke, A. G., 1968. "The Formation and Stability of Emulsions of Water in Crude Petroleum and Similar Stocks," *Journal of the Institute of Petroleum*, 54 (539): 333-357.

Bridie, A. L., Wanders, T. H., Zegueld, W and Van Der Heijde, H. B., 1980. “Formation, Prevention and Breaking of Sea Water in Crude oil Emulsions “Chocolate mousse” *Marine Pollution Bulletin*, 11: 343-348.

Cavallo, J. D. and Chang, F., 1990. Emulsion preparation and stability. Chemical Engineering Progress, 86: 54-59.

Chisholm, H, 1911. “Petroleum Encyclopedia Britannica (Eleventh ed.) Cambridge University. 29: 316–322

Fingas, M. F., Fieldhouse B. and Bobra, M., 1993. “The Physics and Chemistry of Emulsion” In Proceedings of the Workshop on Emulsions, Marine Spill Response Corporations, Washington D.C, 80: 237-242.

Fingas, M. F., Fieldhouse, B., Lambert, P., Wang, Z., Noonan, J., Lane, J., Mullin, J.V., 2002. Water-in-oil emulsions formed at sea, in test tanks, and in the laboratory, Environment Canada Manuscript Report EE-170, Ottawa, Ont.

Mackay, D. and Zagorski, W., 1981. “Studies of the Formation of water in oil Emulsions”, in proceedings of the Fourth Annual Arctic Marine Oil spill Program Technical Seminar, Environment Canada, Ottawa, Ontario, 7: 75-86.

Mackay, D. and Zagorski, W., 1982. “Studies of water/oil Emulsions, Environment Canada, Ottawa, Ontario, 8: 93.

Mackay, D. and Zagorski, W., 1982. “water in oil Emulsions; A Stability Hypothesis” in proceedings of the Fifth Annual Arctic Marine Oil spill Program Technical Seminar, Environment Canada, Ottawa, Ontario, 8: 61-74.

Mackay, D. and Zagorski, W., 1984. “water in oil Emulsions; Some Recent Advances” in proceedings of the Seventh Annual Arctic Marine Oil spill Program Technical Seminar, Environment Canada, Ottawa, Ontario, 37-46.

Mansurov, I. R., Il’yasova, E. Z., Vygovskoi, V. P., 1987. Chemical Technology Fuels Oils 23 (1-2), 96.

McLean J. D., and Kilpatrick, P. K., *J. Colloid Interface Sci*. 189, 242 (1997)

Omole, O. and Falode, O. A, 2005,Effects of Mixing Conditions, Oil type and Aqueous Phase Composition on Some Crude Oil Emulsion, Journal of Applied Sciences, 5(5): 873-877.

Sjöblom, J, Skodvin, T., Jakobsen, T. and Dukhin, S. S., 1994. “Dielectric Spectroscopy and Emulsions: A Theoretical and Experimental Approach”, *Journal of Dispersion Science and Technology*, 15: 401-421.

Twardus, E. M., 1980. A study to evaluate the compatibility and other Physical and Chemical Properties of Aged oils and Emulsions, Environment Canada manuscript Report, 159

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