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EXPERIMENTAL STUDY OF VISCOSITY AS A CRITERION FOR DETERMINATION OF ONSET OF ASPHALTENE FLOCCULATION IN NIGERIA'S CRUDE

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Abstract

Asphaltene are heavy hydrocarbon molecules that exist naturally in petroleum reservoir fluids. Asphaltene precipitation may occur during pressure depletion or during gas injection process for Improved Oil Recovery (IOR). It is an important problem during oil production because it can result in formation damage and plugging of wellbore and surface facilities. In this experimental study, the rheological behaviors of Nigeria's crude oil sample were reported. This research used a typical Nigeria's oil sample to generate information on the asphaltene deposition tendency of a heavy crude oil sample using the standardized test as described by American Society for Testing and Material Method (ASTM) D-3279-90. The results obtained show that the amount of asphaltene precipitated out of a crude sample is dependent upon the type of solvent used. Generally, the lower the number of carbon atoms in the solvent, the greater the amount of asphaltene precipitated. Also contrary to the general belief, that since Nigeria's crude is known for its low asphaltene content, the nation's oil industry needs not to take the asphaltene precipitation effect into consideration, it was observed that asphaltene concentration as low as 1% (percentage weight) is enough to change the rheological behavior of crude samples from Newtonian to Non-newtonian flow. It was also observed that the flocculation and not precipitation of asphaltene was responsible for the change in the rheological behavior. These changes in rheological properties can lead to reduction in the rate of crude oil flow in a petroleum reservoir, and hence reduced productivity.

Keywords: Asphaltene Flocculation; Newtonian Flow; Gas Injection Process; Residual Oil.

1. Introduction

Asphaltenes are defined by the ASTM D-3279-90 (American Society for Testing and Materials) test as the solid that precipitates when an excess of n-heptane or n-pentane is added to a crude oil. The precipitation of asphaltenes is a complex phenomenon that involves asphaltenes and resins since resins have a strong tendency to associate with asphaltenes and such association is what determines to a large extent, asphaltene solubility in crude oil. Both asphaltenes and resin are aromatic hetero-compounds with aliphatic substitutions and they form the most polar fraction of crude oil [1-3].

Nigeria is consistently Africa's largest producer of crude oil with more than two million barrels per day being produced and with hydrocarbons playing a leading role in Nigeria's socio-economic development over the years. More than 85% of Nigeria's hydrocarbon reserves are in the deep offshore hence, there is a strong industrial interest in deep subsea exploration and production. The cost of remediation and lost production resulting from organic deposition in these operations increases almost exponentially hence a lot of money and manpower is sunk into potential remedial work so that any effort to better understand the precipitation phenomena and forecast possible problems is very important.

Although the exact value of the total asphaltene content of a crude oil can not be measured by any precipitation procedure because of the fact that it will not completely precipitate by the existing precipitation procedures, the asphaltene which precipitates using different normal paraffin hydrocarbon solvents can be measured. Using such data in an appropriate poly-disperse deposition model for asphaltene one may be able to estimate the true value of the total asphaltene content of a crude oil [4-8].

The measurement of the asphaltene content of n-C_5 insoluble can be a challenging task since it is well known that some amount of resins will precipitate along with the asphaltene fraction and insoluble material. It is also known that high-molecular-weight solid paraffin/ wax will precipitate out of solution once the asphaltene starts to flocculate[9].

This research thus aims to obtain data using dead oil to generate information on rheology of asphaltene deposition in a crude oil sample. This is a priority due to the high cost and rarity of bottom-hole samples as well as the difficulty in handling them properly during transit from the platform to the laboratory. Also, as Nigeria delves further into deep water crude oil exploration, there is a need to predict the potential of asphaltene deposition in order to alleviate the risks associated with asphaltene flocculation in crude oil production. The development of asphaltene precipitation models has so far generally been anchored on two different descriptions of asphaltene solutions. While one concept considers asphalttenes and resins as molecular entities dissolved in crude oil, the other conceptualizes that asphaltene and resin molecules form asphaltene-asphaltene and asphaltene-resin aggregates that are dispersed in the oil matrix [10-12].

2. Methodology

Generally, there are two main types of laboratory tests used to determine the possibility of asphaltene flocculation and appraise the conditions for asphaltene deposition, thus providing input into asphaltene models. However, none of these tests are standardized but instead vary from laboratory to laboratory. The only standardized test for determining the asphaltene content of a crude oil is described by ASTM D-3279-90 [17].

In this test, the asphaltenes are precipitated using an excess of a normal alkane solvent (i.e. n-heptane) and the viscosity of the resulting mixture using a calibrated programmable Rheometer. This test is also the standard definition of asphaltenes, although it is highly possible that compounds such as very high molecular weight n-paraffins will also be found in the solids. General literature suggests that crudes with low asphaltene content (<0.5%) which is the characteristic of crude oil from a typical Nigeria's reservoir are more likely to have asphaltene deposition problems than crudes with higher asphaltene contents. The asphaltene flocculation point is the pressure at which asphaltenes first begin to precipitate at a given fixed temperature ([13-16].

This standardized test method may use one of a number of techniques for detecting the asphaltene flocculation such as visual observation, light scattering, filter plugging, etc.

If a number of these precipitated asphaltene measurements are made over a range of temperatures, then an asphaltene flocculation phase envelope can be generated.

3. Asphaltene Precipitation by Composition Changes

Dead oil samples obtained from surface equipment were used in the titration experiments with *n*-alkanes. Titration experiments are to be performed to determine the amount of asphaltene that will be precipitated when a sample of the oil is titrated with four *n*-alkanes samples: n-pentane, n-heptane, n-nonane, and n-dodecane (C_5, C_7, C_9, and C_{12}) with their properties given as shown in table 1.

Normal alkane solvents are used because an excess of them in a crude oil-alkane mixture precipitates asphaltene. Four hydrocarbon solvents are to be used in order to relate/compare the amount of asphaltene precipitated by each.

The oil sample is filtered using a 0.45-μm Teflon membrane to remove any suspended material. A 0.45-μm Teflon membrane is required because the pore space or its porosity is sufficiently small to obstruct the asphaltene particles from passing through. If a filter of greater porosity is used, the precipitated asphaltene would pass through alongside the solvent.

Table 1 n-alkanes properties

	Molecular weight (kg/kmol)	Density (kg/m3)	Dielectric constant	Refractive index
n-Pentane (nC_5)	72.00	626.00	1.873	1.357
n-Heptane (nC_7)	100	638.00	1.921	1.388
n-Nonane (nC_9)	128	717.00	1.972	1.405
n-Dodecane (nC_{12})	170	748.00	2.012	1.422

Next, a volume of n-alkane corresponding to a specific titrant-oil ratio is added to 5g of dead oil in an appropriate flask. The mixture undergoes ultrasonic shaking for 10 minutes and the viscosities of the resulting mixture were determined using a programmable rheometer, then it's left overnight.

Using a vacuum system, the solution of n-alkane and de-asphalted oil is filtered with a previously weighed 0.45-μm filtration Teflon membrane. To eliminate the residual oil, the flask and the filtration membrane are rinsed with small volumes of the corresponding n-alkane and the membrane with the precipitated material is dried in a vacuum oven at atmospheric pressure and room temperature for over 6 hours before being weighed to determine the asphaltene mass precipitated [17-25].

4. Asphaltene Titration Experiment

Objective: To determine the asphaltene content of a Nigeria's light crude oil (API>30) and thus determine the amount of asphaltene that would precipitate on titration with different hydrocarbon solvents, and also the viscosities of the crude system during asphaltene fluocculations.

Apparatus: **-** crude oil of API 30^{o} whose asphaltene flocculation tendency is to be investigated.

- Alkane anti-solvents (n-alkanes: C_5, C_7, C_9, C_{12}).
- 0.4μm Teflon material filter
- 250ml beakers
- 1000ml cylinders
- Electronic shaker,
- Electronic mass balance
- Vacuum oven
- -Programmable Rheometer.

Procedure:

1. The 0.45μm is weighed using the electronic mass balance
2. The crude oil sample is filtered using a 0.45μm Teflon material to remove any suspended particles in the sample.
3. The sample is poured into beakers.
4. A volume of n-alkane is added to the flasks to meet a fixed corresponding titrant-oil ratio.
5. The titrant-oil mixture is placed on the electronic shaker for about 15 minutes for thorough mixing, the viscosity of the resulting mixture was determined with the programmable rheometer and then left overnight.
6. The mixture is filtered though the Teflon material
7. The precipitated asphaltene is dried in a vacuum oven.
8. The amount of precipitated material (asphaltene) is measured.

The experiment is repeated with different titrant/oil ratios and complete precipitation is obtained above a certain solvent/oil ratio (typically between 10 and 30cm^3/g).

6. Discussion of results

Analyzing the resulting plots from the generated data obtained from the experiments, From figure 1, it was noticed that initially at low solvent/crude oil ratios, the weight fraction of asphaltene precipitated increases steeply as the solvent/crude oil ratio increases. However, at higher ratios, the increase in fraction precipitated is less pronounced and in fact almost seems to be constant, thus indicating that there is an optimum solvent/crude oil ratio range at which precipitation occurs. Typically, according to Hirschberg [23], this range is between 10cm^3/g to 30cm^3/g, a range which figure 1 is in accordance with.

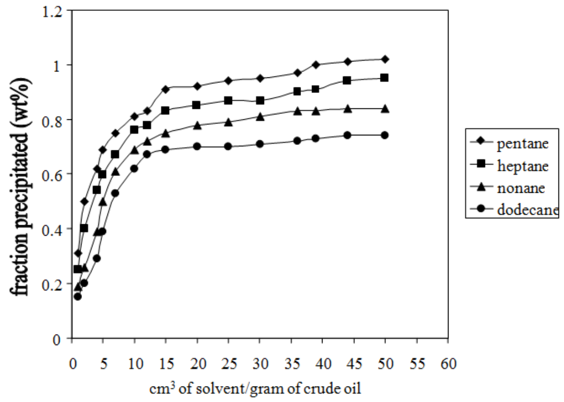

Fig 1 Fraction weight percentage of precipitated asphaltene of volume of different solvents per mass of crude oil

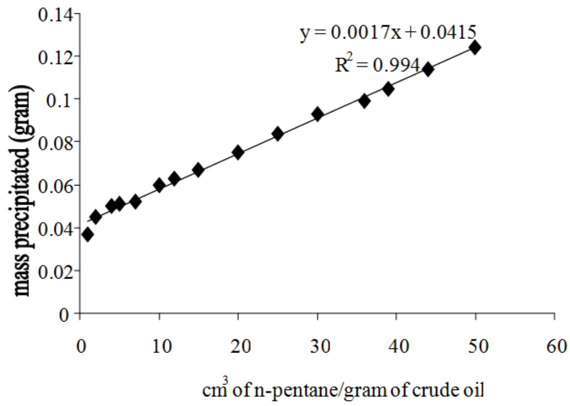

Fig 2 Mass of precipitated asphaltene at different volume of n-pentane per mass of crude oil

This constant value of the precipitated asphaltene at higher solvent/crude oil ratios can be explained by the fact that the initially precipitated asphaltenes are dispersed upon precipitation and trap some of the unreacted crude oil, thus shielding them from reacting with the solvent. Therefore, once the crude oil that is in contact with the solvent has been fully deasphalted, there is no further reaction. Also, this constant value of the precipitated asphaltene at higher solvent/crude oil ratios can be explained by the equilibrium in the rate of precipitation and consequent rate of dissolution of asphaltene in the crude oil.

Investigating the effect of different volumes of n-alkanes of different carbon number on the mass of asphaltene deposited in order to determine which of the n-alkane will precipitate the biggest amount of asphaltene. Figs 2-5 show the plots of the mass of precipitated asphaltene using different volume of n-alkane per mass of crude oil.

From figures 2-5, it can be deduced that the mass of asphaltene precipitation increases as the ratio of the n-alkane to the mass of crude oil increases. The corresponding figures also show that there is a direct linear relationship between the alkane/crude oil ratio and the mass/amount of asphaltene precipitated from this mixture.

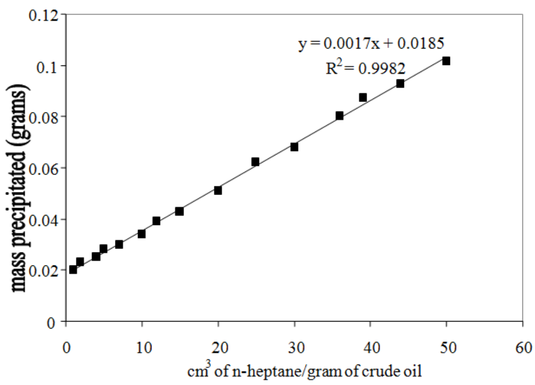

Fig 3 Mass of precipitated asphaltene at different volume of n-heptane per mass of crude oil

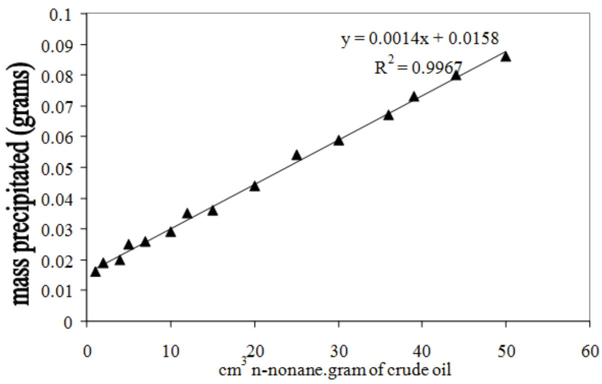

Fig 4 Mass of precipitated asphaltene at different volume of n-nonane per mass of crude oil

Comparing the figures and values for the four different types of solvents used, pentane precipitates the largest amount of asphaltene. Also, from fig. 6, it can be seen that the number of carbon atoms in a solvent affects the total fraction of asphaltene precipitated. This follows the typical trend of asphaltene precipitation experiments whereby increase in the carbon number of the solvents generally leads to a decrease in total asphaltene precipitation.

It is also noticed that the colour of the asphaltene precipitated differs slightly solvent to solvent.

Generally, it can be seen that for a given crude oil sample, the asphaltene precipitation follows a typical trend from left to right, regardless of the carbon content of alkane being used as a precipitation agent, i.e. there is an initial high precipitation rate at low solvent/crude oil ratios after which the precipitation becomes or tends to become constant at higher solvent/oil ratios.

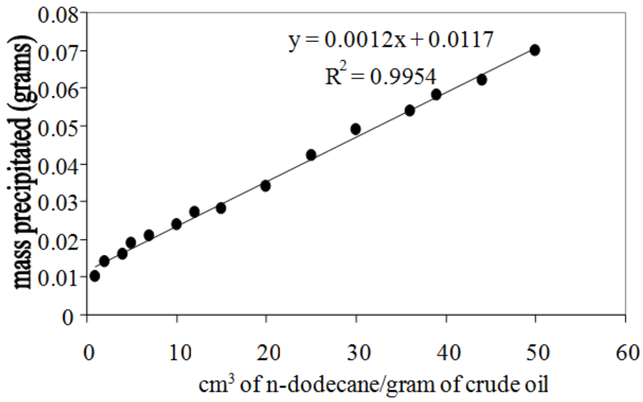

Fig 5 Mass of precipitated asphaltene at different volume of n-dodecane per mass of crude oil

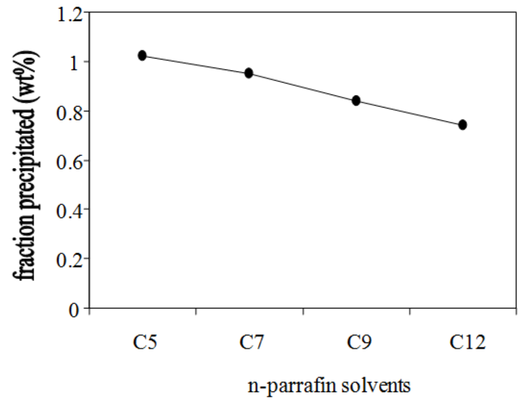

Fig 6 Total weight fraction percentage of precipitated asphaltene for different n-parrafin solvents

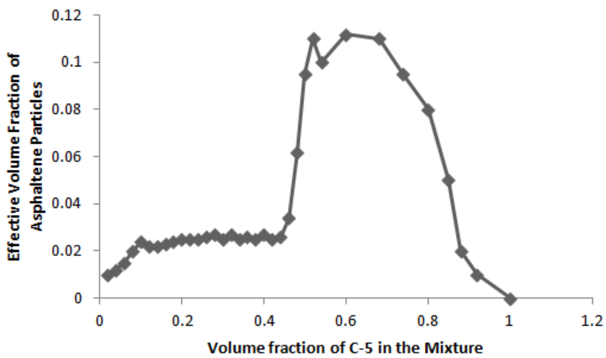

Fig 7 Effective Volume Fraction against Volume Fraction of n-Pentane in the Mixture

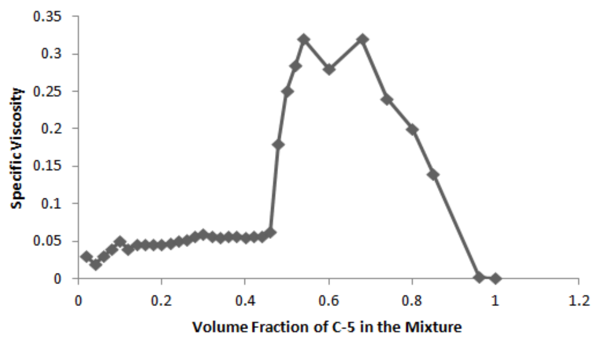

Fig 8 Specific Viscosity against the Volume fraction of n-Pentane in the Mixture

Fig.7 shows the effective volume fraction as a function of n-pentane in the mixture for the crude oil sample. It is interesting to note that even before the onset of flocculation the volume fraction of the suspended particles increases with increasing precipitating solvent concentration. This suggests that at low solvent concentrations, aggregation takes place although at a slower rate. Whereas after the onset the aggregation mechanism is very rapid. This is shown by a point after which the effective volume fraction increases more rapid with solvent concentration. This point is obviously the onset of asphaltene flocculation. This behavior can be explained considering that the onset marks the beginning of solid separation. Therefore, as concentration of n-pentane increases the amount of asphaltene precipitation increases as well. We also notice that there is a maximum in effective volume fraction followed by a decrease. We have seen in figure 1 that the amount of asphaltene increases very rapidly after the onset of deposition to finally approach a constant value. This explains the maximum observed in the effective volume fraction.

Figure 8 shows plots of the specific viscosity against the volume fraction of precipitating n-Pentane or the crude sample. As can be seen from the figure, there is a point at which the effect of the suspended particles increases more rapidly. This point coincides with the previously determined onsets of asphaltene flocculation for this crude oil. The rapid increase in the specific viscosity may be explained considering the fact that at the onset there is no solid-phase separation at all. Whereas after this point, the amount of asphaltenes flocculated out of solution increases very rapidly with increasing solvent concentration reaching the limiting value as shown in figure 1. Furthermore, as the concentration of the precipitating solvent in the mixture increases the diameter of asphaltene aggregates increases as well.

Figure 9 shows the kinematic viscosity curve of the crude oil sample the onset of flocculation is detected as a point when the kinematic viscosity remain constant even with increase in percentage of solvent in the mixture, after which the kinematic viscosity decreeses further with increase in percentage volume of solvent.

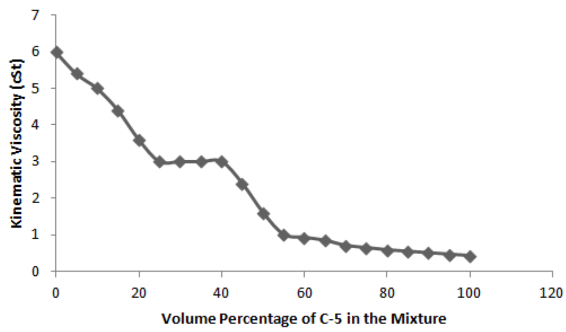

Fig 9 Kinematic Viscosity against Volume Percentage of n-Pentane in the Mixture

7. Conclusion and recommendation

On comparison of the values for precipitated asphaltene with that from the Mexican and Caspian sea, Nigerian crude is seen to have a relatively low asphaltene content and as such the problems associated with asphaltene deposition such as reduction in production rate, near wellbore formation damage, the need for pigging and other mechanical and chemical remediation methods might not required.

However, a lackadaisical approach should not be taken and generalizations should not be made because the factors that induce asphaltene precipitation and consequent deposition vary over wide operational range, leading to increase in viscosity of petroleum reservoir fluids and subsequently decrease in rates of fluid flow in the petroleum reservoirs. Therefore, for every crude being produced, asphaltene precipitation tests should be carried out to determine the likelihood of asphaltene deposition.

With more than 85% of Nigeria's hydrocarbon reserves in the deep offshore, there is a strong industrial interest in deep sub-sea exploration and production. Because of the conditions encountered in deep water, factors that are not generally considered risky in land operations are multiplied by almost a factor of 12 and become very unsafe .i.e. an asphaltene precipitation of 1.5g on land operations might be considered as safe whereas in the deep offshore, could plug pipelines and conduits.

The cost of remediation and lost production resulting from asphaltene deposition in these deep water operations increases almost exponentially hence a lot of money and manpower is sunk into potential remedial work. Thus, any effort to better understand the precipitation phenomena and forecast possible problems is very important.

Asphaltene deposition also plays a very important role in flow assurance since asphaltene molecules can interact with each other and cause catastrophic blockage formations in pipelines thus resulting in flow assurance failure, thus the probability of it should be assessed and monitored very closely.

From the experiments performed using n-pentane, n-heptane, n-nonane and n-dodecane, it was observed that for the same solvent/crude oil ratios, the fraction of asphaltene precipitated increases with a decrease in the carbon number of the solvent. Thus, higher molecular weight alkanes precipitate a smaller fraction of asphaltene and so, the use of low molecular weight n-alkanes during miscible recovery should be discouraged in tertiary oil recovery processes. Since asphaltenes also flocculate during gas lifting, the use of rich gases (i.e. ethane, propane, butane) should also be avoided as they are more likely to precipitate asphaltenes.

It should also be noted that the crude oil used in this experiment is dead crude and as such does not take into cognisance, the role of gas in asphaltene deposition. Thus, it is recommended that an asphaltene precipitation model be developed using the values obtained from this work in order to characterise the crude. This model may then be further developed to duplicate the conditions encountered in the reservoir and thus study the change in asphaltene precipitation that would occur if the effects of gases are added.

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