Available online at www.elixirpublishers.com (Elixir International Journal)

Applied Chemistry

Elixir Appl. Chem. 125 (2018) 52311-52315

ISSN: 2229-712X

Determination of Onset of Heavy Organic Precipitation from a Nigerian Crude Oil using *n*-Alkane Solvents

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ARTICLE INFO

Article history:
Received: 10 September 2018;
Received in revised form:
3 December 2018;
Accepted: 13 December 2018;

Keywords
Onset,
Heavy organics,
Precipitation,
Crude oil,
n-alkanes.

ABSTRACT

Heavy organic deposition in the production and processing of crude oil has been a problem in the oil and gas sector. Although, some efforts have been made to minimise it such as changes in composition, pressure and/or temperature; this study attempts to address the Nigerian situation. The article investigated the onset of heavy organic precipitation by transmitting microscopy study of the precipitant volumes reported for single nC_5; nC_6; nC_7 and nC_8 alkane precipitants as 5.02ml, 5.05ml, 6.00ml and 7.10ml respectively to start precipitation in 1:1 (v/v) precipitant: toluene solution to 2±0.5g crude oil. Their varied binary mixtures nC_5:nC_6; nC_5: nC_7; nC_5: nC_8; nC_6: nC_7; nC_7: nC_8 showed onset of HO precipitation with ratios of 7:3, 1:1, 4:1, 3:2 and 9:1 respectively with no onset volume detected for nC_6: nC_8 within the ratio range being investigated. Hence, the outcome of these results of the precipitant volumes at onset of HO precipitation for single *n*-alkanes and volume ratios of binary mixture *n*-alkane solvents should not be altered or exceeded during injection of fluids for enhanced oil recovery or as diluents into Afiesere heavy crude oil to improve flow properties.

Introduction

Crude oil is a complex mixture of hydrocarbons and other compounds of varying molecular weight and polarity [1, 2] which can be divided into several fractions such as saturates, aromatics, resins and asphaltenes (SARA). Asphaltenes which are heavier polar fraction of oil are insoluble in normal alkanes [3] but are soluble in aromatic solvents. A major issue in flow assurance is the precipitation of organic and inorganic solids from crude oil which is caused by any change in temperature, pressure and composition (such as addition of a miscible solvent to oil) that may destabilize the crude oil solution, and then the heavy and/or polar fraction separates from the oil mixture into steric colloids, micelles, and another liquid phase or into a solid precipitate. Smaller-size heavy organic particles may be dissolved in petroleum fluid, whereas relatively large heavy organic particles may precipitate out of the solution due to addition of a certain amount of a paraffin hydrocarbon. Further addition of paraffin hydrocarbons to the crude oil mixture will flocculate heavy organics out of the solution to form random aggregates [4]. In other words, if the crude oil is not monitored carefully and the heavy organics being maintained in the crude oil solution, it will come out of the solution as precipitate, flocculates, agglomerates and finally deposits [4].

Onset of precipitation also known as the onset volume is the minimum volume of precipitant required to start flocculation/agglomeration. In other words, it is that known precipitant volume when precipitation occurs. Onset volumes for precipitants/dispersants dosage ought to be known for a particular crude oil to prevent precipitation/agglomeration /flocculation/deposition in order to reduce incessant shutdown for pipeline/turn around maintenance of facilities/reservoirs as well as cost reduction.

There have been a number of cases of shutdown of petroleum industries due to the deposition of heavy organics. For example, the Hassi Messaould field, Algeria experienced heavy organics (HO) deposition in tubings which posed some serious production problems. [5]. In 1977, Venezuela oil field resulted in complete shutdown of wells due to the formation of heavy organics (HO) deposition [6]. Five years on, Ventura Avenue field, California, USA gave an account in which heavy organics (HO) played a significant role in production and economics of the deep horizon [7]. Thereafter, Prinos field, North Aegean Sea also experienced well production ceasure after a few days of start-up and a quarter million dollars were used to remedy it [8]. Also, heavy organic (HO) materials deposited on the production installations of Mexico oil fields were reported [9, 10]. The United States of America had their own loss of production/income to the industry; it was estimated that each remediation event cost about US $ 500,000 (onshore) and $3,000,000 (offshore) [11]. Bonga oil field, Nigeria, experienced four times shut down for maintenance from 2015 to 2017 due to deposition problem. [12].

Laboratory analyses (tests) and field intervention help producers of crude oil to minimise or remediate HO deposition by the use of chemically induced-solvent (solvent treatment). It is interesting to note that, heavy organics precipitated in the field are significantly different in composition from laboratory generated heavy organic compounds [13,14,15,16]. Moreso, the fact that the field samples are richer in n-heptane components than the laboratory produced heavy organic compounds using single individual solvents has been reported [14,17]. Hence, the need for binary *n*-alkane solvent mixture studies in predicting heavy organics precipitation.

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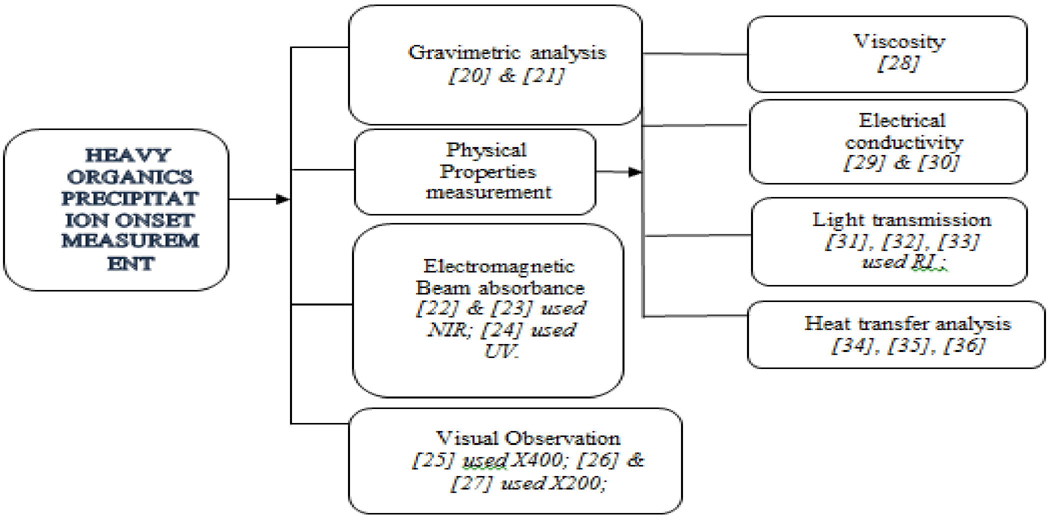

Fig. 1. Categories of HO precipitation onset measurement methods.

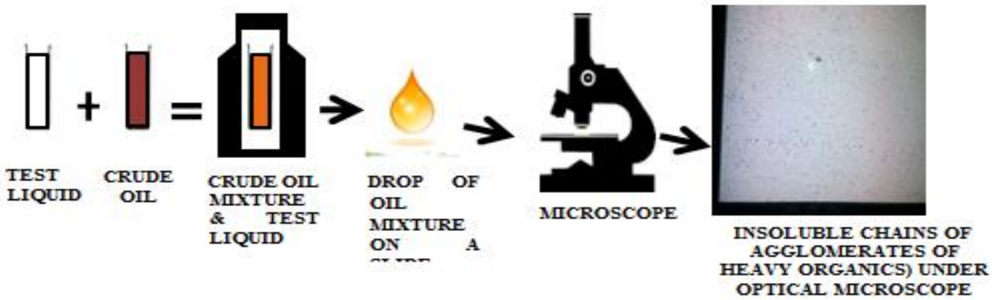

Figure 3. Procedure for Light transmission method for Onset of heavy organic precipitation.

Also, the measurement of heavy organic onset of precipitation for single *n*-alkane solvents using Alaska crude oil by light transmissionvia refractive index [18] and North western Colorado crude oil by electromagnetic beam absorbance via near-infrared absorbance [19] had been reported, but the effect of mixture of *n*-alkane solvents on the heavy organics onset of precipitation are not well understood. Nigerian crude oil (Afiesere) using single and binary mixture ratios of *n*-alkanes by light transmission via microscope to know the required dosage of precipitants (diluent) mixture ratios in terms of volume/volume for optimization that enables the well/reservoir to operate for several years without heavy organics precipitating out of the crude oil solution especially asphaltene deposition problems was considered. Heavy organic deposition can be minimised significantly if the onset volume is known. From the fore going, predicting the onset of precipitation volumes (onset solvent ratios) at which precipitation of heavy organic occurs is crucial in understanding the fluid property and the remedial work to be carried out in ensuring improved oil recovery from the subsurface to the surface facilities.

Generally, heavy organic precipitation onset measurement methods can be grouped into four categories namely: (i) gravimetric analysis (ii) physical properties (iii) electromagnetic beam absorbance and (iv) visual observation as shown in Figure 1. Gravimetric analysis describes a set of methods in analytical chemistry for the quantitative determination of an analyte based on the mass of a solid precipitation. Visual observation by microscope with different magnifications is always used to determine the onset of HO (asphaltene) precipitation directly. Electromagnetic beam absorbance methods (Near Infrared and Ultraviolet/visible spectrophotometers) are also widely used to detect the onset of heavy organics precipitation. The physical properties measurement methods, such as viscosity, particle size analysis, electrical conductivity, light transmission (refractive index), acoustic techniques and heat transfer analysis are good indications for the condition of heavy organics precipitation [37].

Materials and Method

Sample location and collection

Afiesere Oil Field (Fig. 2) is located at Afiesere community in Ethiope Local Government Area of Delta State, Nigeria on OML 30 of the NPDC FIELD. The crude oil sample was collected from the Research & Development Division of the Nigerian National Petroleum Corporation (NNPC).

The onset of heavy organic precipitation was carried out by the Light transmission method [27]. 2 ± 0.5g of crude oil was weighed into glass vials of 25ml capacity and 10ml of 1:1 mixture of Toluene/*n*-alkane was added to form the crude oil mixture. Different volumes of the *n*-alkane precipitating solvents were added to the crude oil mixture.

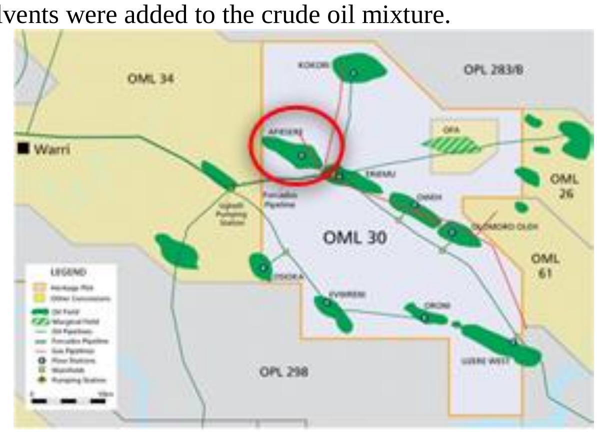

Figure 2. Map of OML 30 Afiesere oil field (in red) Courtesy: SPDC website.

The vials were sealed immediately and waited for five (5) minutes at room temperature. Thereafter, 0.5ml was taken from each vial with the aid of syringe/needle and placed on a microscopic glass slide, covered with a slip and observed quickly through a microscope at 100X magnification installed with AMCAP software. The pictures were viewed and captured on a Television screen.

Results and Discussion

Effects of single *n*-alkane solvents on the onset of heavy organic precipitation in Afiesere crude oil

The effects of single nC_5 *n*-alkane solvent on the onset of heavy organic precipitation at different volumes are presented in Plate 1. There were no precipitates observed when 5.00ml nC_5 was added to the crude oil mixture (Plate 1.01) but precipitation of the heavy organics (HOs) occurred when 5.02ml nC_5 was introduced into the crude oil mixture and the precipitates were visible on the slide (Plate 1.02). As 5.04ml nC_5 precipitant was added, globules of floating liquid indicated the absence of precipitates (Plate 1.03).

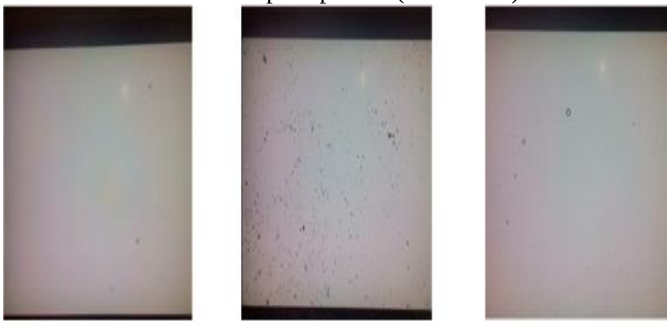

Plate 1.01: 5.00ml Plate 1.02: 5.02ml nC_5 Plate 1.03: 5.04ml

Plate 1. Microscopic slides for single nC_5 precipitant.

The effects of single nC_6 *n*-alkane solvent on the onset of heavy organic precipitation at different volumes are presented in Plate 2. There were no precipitates observed when 5.00ml nC_6 was added to the crude oil mixture (Plate 2.01) but precipitation of the heavy organics (HOs) occurred when

5.05ml nC_6 was introduced into the crude oil mixture and the precipitates were visible on the slide (Plate 2.02). As 5.10ml nC_6 precipitant was added, agglomeration of the precipitates (aggregates) was observed (Plate 2.03).

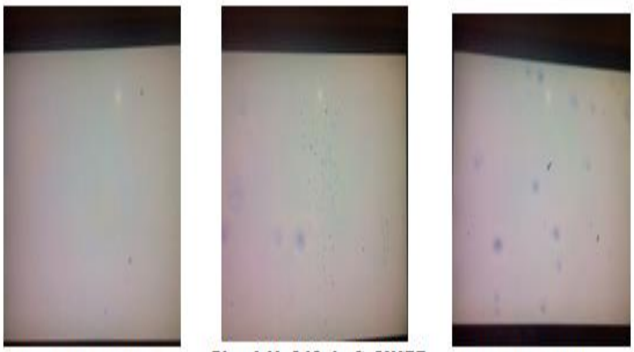

Plate 2.01: 5.00ml nC_6 Plate 2.02: 5.05ml nC_6 ONSET Plate 2.03: 5.10ml nC_6

Plate 2. Microscopic slides for single nC_6 precipitant.

The effects of single nC_7 *n*-alkane solvent on the onset of heavy organic precipitation at different volumes are presented in Plate 3. There were no precipitates observed when 5.50ml nC_7 was added to the crude oil mixture (Plate 3.01) but when 6.00ml nC_7 was added to the crude oil mixture, the heavy organcs (HOs) were precipitated (Plate 3.02) and on continuous introduction of the nC_7 precipitant, it showed reduction of HO precipitate scattered on the slide (Plate 3.03).

Plate 3.01: 5.50ml nC_7 Plate 3.02: 6.00ml nC_7 ONSET Plate 3.03: 6.50ml nC_7

Plate 3. Microscopic slides for single nC_7 precipitant.

The effects of single nC_8 *n*-alkane solvent on the onset of heavy organic precipitation at different volumes are presented in Plate 4. There were no precipitates but a clear background with a light small strand of aggregate seen (Plate 4.01) when 7.0 ml nC_8 precipitant was added to the crude oil mixture. Nevertheless, when 7.10ml nC_8 was added to the crude oil mixture, the heavy organics (HOs) that precipitated spread across the surface of the slide (Plate 4.02). Subsequent addition of nC_8 precipitant to the crude oil mixture showed reduction in precipitation (Plate 4.03).

Plate 4.01: 7.00ml nC_8 Plate 4.02: 7.10ml nC_8 ONSET Plate 4.03: 7.20ml nC_8

Plate 4. Microscopic slides for single nC_8 precipitant.

Effects of varied binary mixture ratios of *n*-alkane solvents on the onset of heavy organic precipitation in Afiesere crude oil

The effects of varied binary mixture ratios of nC_5 and nC_6 *n*-alkane solvents on the onset of heavy organic precipitation are presented in Plate 5. There were no precipitates but light flocculates observed (Plate 5.01) when 6:4ml binary mixture ratios of nC_5 and nC_6 precipitants respectively were added to the crude oil mixture. However, the precipitation of the heavy organics (HOs) occurred when 7:3ml binary mixture ratios of nC_5 and nC_6 precipitants were added to the crude oil (Plate 5.02) which became clearer on the slide due to the solubility of HOs as a result of the addition of 8:2ml binary mixture ratio (Plate 5.03)

Plate 5.01: 6:4 nC_5 & nC_6 Plate 5.02: 7:3 nC_5 & nC_6 Onset Plate 5.02: 8:2 nC_5 & nC_6

Plate 5. Microscopic slides for binary mixture ratios of nC_5 & nC_6 precipitants.

The effects of varied binary mixture ratios of nC_5 and nC_7 *n*-alkane solvents on the onset of heavy organic precipitation are presented in Plate 6. When 4:6ml binary mixture ratio of nC_5 and nC_7 precipitants was added to the crude oil mixture, the slide was clear (Plate 6.01). Upon introduction of 5:5ml binary mixture ratios of nC_5 and nC_7

precipitants, HO precipitation occurred (6.02) and strands of agglomerates noticed when 6:4ml added (Plate 6.03).

Plate 6.01: 4:6 nC_5 & nC_7 Plate 6.02: 5:5 nC_5 & nC_7 ONSET Plate 6.03: 6:4 nC_5 & nC_7

Plate 6. Microscopic slides for binary mixture ratios of nC_5 & nC_7 precipitants.

The effects of varied binary mixture ratios of nC_5 and nC_8 *n*-alkane solvents on the onset of heavy organic precipitation are presented in Plate 7. When 7:3ml binary mixture ratios of nC_5 and nC_8 precipitants were added to the crude oil mixture, dots of agglomerates were seen (Plate 7.01). It was interesting to note that, the precipitation of the heavy organics (HOs) occurred when 8:2ml binary mixture ratio of nC_5 and nC_8 precipitants were added to the crude oil (Plate 7.02) and upon continuous addition of 9:1ml binary mixture ratios, dots of aggregates resurfaced again (Plate 7.03).

Plate 7.01: 7:3 nC_5 & nC_8 Plate 7.02: 8:2 nC_5 & nC_8 ONSET Plate 7.03: 9:1 nC_5 & nC_8

Plate 7. Microscopic slides for binary mixture ratios of nC_5 & nC_8 precipitants.

The effects of varied binary mixture ratios of nC_6 and nC_7 *n*-alkane solvents on the onset of heavy organic precipitation are presented in Plate 8. There were no precipitates but flocculates observed when 5:5ml binary mixture ratio of nC_6 and nC_7 precipitants was added to the crude oil mixture (Plate 8.01). Interestingly, with 6:4ml binary mixture ratio, HO precipitation was detected which indicated the onset (Plate 8.02) and upon continuous mixing of 7:3ml binary mixture ratio, the slide became clearer as a result of the solubility of HOs (Plate 8.03).

Plate 8.01: 5:5 nC_6 & nC_7 Plate 8.02: 6:4 nC_6 & nC_7 ONSET Plate 8.03: 7:3 nC_6 & nC_7

Plate 8. Microscopic slides for binary mixture ratios of nC_6 & nC_7 precipitants.

The effects of varied binary mixture ratios of nC_6 and nC_8 *n*-alkane solvents on the onset of heavy organic precipitation are presented in Plate 9. When 1:9ml binary mixture ratio of nC_6 and nC_8 precipitants was added to the crude oil mixture, globules and droplets of floating liquid were observed indicating that, there were no precipitates (Plate 9.01) but strands of aggregates, thick HO flocculate, dark HO deposit (Plate 9.02) and a clear slide surface observed which indicated complete dissolution of these aggregates. It was observed that, no precipitation was formed with the binary mixture ratios of nC_6 and nC_8 precipitants being investigated.

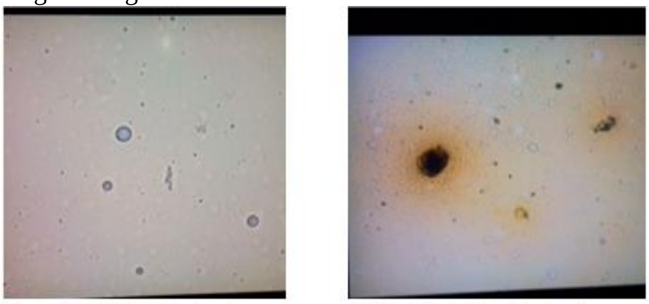

Plate 9.01: 1:9 nC_6 & nC_8 Plate 9.02 9:1 nC_6 & nC_8

Plate 9. Microscopic slides for binary mixture ratios of nC_6 & nC_8 precipitants.

The effects of varied binary mixture ratios of nC_7 and nC_8 *n*-alkane solvents on the onset of heavy organic precipitation are presented in Plate 10. There were strands of HO flocculates seen (Plate 10.1) and their dissolution followed (Plate 10.2) by the addition of 7:3ml and 8:2ml binary mixture ratio of nC_7 and nC_8 precipitants to the crude oil mixture respectively. It was interesting to note that, the precipitation of the heavy organics (HOs) occurred when 9:1ml binary mixture ratio of nC_7 and nC_8 precipitants was introduced into the crude oil mixture (Plate 10.3).

Plate 10.01: 7:3 nC_7 & nC_8 Plate 10.02: 8:2 nC_7 & nC_8 Plate 10.03: 9:1 nC_7 & nC_8 ONSET

Plate 10. Microscopic slides for binary mixture ratios of nC_7 & nC_8 precipitants.

Conclusion

Onsets of Heavy organic precipitations were recorded for volumes of 5.02ml, 5.05ml, 6.0ml and 7.1ml of single nC_5, nC_6, nC_7 and nC_8 respectively. The volume of single solvents used to induce precipitation increased with increasing carbon chain.

At binary mixture ratios of 7:3, 5:5, 8:2, 6:4 and 9:1, the heavy organic onset precipitations were recorded for the binary mixtures of nC_5 & nC_6; nC_5 & nC_7; nC_5 & nC_8; nC_6 & nC_7 and nC_7 & nC_8 respectively with exception to nC_6 & nC_8 that onset was not detected under the mixture ratios being investigated. Hence, these results can be used to predict deposition problem in the production industry during injection of fluids for enhanced oil recovery or as diluents into Afiesere heavy crude oil to improve flow properties.

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