Ratio Effect of Binary Mixtures of N-Alkane Solvents (NC5, NC6, NC7) on Heavy Organics Precipitation from Afiesere Oil Field Crude

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ABSTRACT

Heavy organics (HOs) precipitation was investigated from a Niger Delta crude by using varying ratios of binary mixtures of normal alkanes precipitating solvents (NC5, NC6 and NC7) to determine the significant effect of changes in composition of the crude oil. The different ratios of the binary mixtures of normal alkane precipitants produced different quantities of heavy organics precipitate showing different phase transitions. These transitions in the phase changes of the varying ratios of the binary mixtures may be attributed to colloidal formations and the different chemical species in different ratios of the binary mixtures of normal alkanes in the crude oil medium.

Keywords: *Heavy Organics, Precipitation, Crude oil, Binary Mixtures, Solubility*

INTRODUCTION

Crude oil (or petroleum) is a multicomponent mixture consisting of naturally occurring hydrocarbons, together with organic compounds of sulphur, nitrogen and oxygen, as well as trace amounts of metallic constituents, such as vanadium, nickel and iron. [(1)] The high molecular weight complex molecules present in the crude oil heavy fractions or petroleum residuum are heavy organics.[(2)] Crude oil can be divided into several fractions such as Saturates, Aromatics, Resins and Asphaltene compounds (SARA).

Solid precipitation during production, transportation, and storage of petroleum fluids is a common problem faced by the oil industry throughout the world. Solids can be precipitated when the oil undergoes phase transitions due to changes in pressure, temperature and composition. Through complex phase transformations, dissolved and suspended solids (asphaltenes, resins, paraffin/wax, diamondoids, formation solids, etc) precipitate out of solution. Such phase segregations are sometimes followed by flocculation of the resulting precipitates. In many instances these deposition phenomena render in complete clogging of flow lines and serious damages to storage vessels and processing equipment. Deposition may occur in reservoir formations, wellbores, production tubing, submersible pumps, surface equipment, pipelines, storage tanks, and refining process equipment. Organic deposition in tubing and production facilities will cause operational difficulties and necessitate costly treatments to remove the deposits. This problem is particularly serious in offshore oil production. The organic deposition problem has confronted the petroleum industry for many decades. The solution or alleviation of the many technological problems posed by such depositions lies on a good understanding of the multi-phase behavior of the species which precipitate. It is also necessary to understand the interactions amongst these various species in the local environment where phase segregation and flocculation takes place. [3,4]

It is important to producers that any potential organic deposition problems can be predicted so that a production strategy can be designed to prevent or mitigate, if possible.

Therefore, it is crucial to know *'when' and 'how much'* heavy organics will separate out of solution in the form of a heavier phase under a given set of operating conditions.[5] The heavy organics precipitated in the field are significantly different in composition from laboratory generated asphaltenes. [6;7;8;9] Laboratory tests may be necessary to blend the most appropriate aromatic solvent and / or dispersant for a given oil field from the points of view of effectiveness, economy, and environmental friendliness. Then special formulas may be blended to achieve the goal of preventing or cleaning the heavy organics deposits which can be used by the field engineers [10]

In this study, the heavy organics precipitation from a particular crude oil in the Niger Delta Region by varying ratio binary mixtures of normal alkane solvent precipitants (Pentane, hexane and heptane) has been investigated.

MATERIALS AND METHODS

The following materials were used: Afiesere oil Field Crude was collected from the Research & Development Division of the Nigerian National Petroleum Corporation (NNPC), n-pentane, n-hexane, n-heptane, Electronic Analytical balance Model-Shimadzu Libror AEG-220, Mechanical Shaker, Drying oven model-Advantec FS 605/Memmert oven, Vacuum(water jet) filter pump-DOA-V130-BN Date code-1196;volts 220/240;Amp 1.9/2.2;Hz 50; Filtration apparatus(micro filtration unit 250ml) with reservoir and coarse (40-60µm) fitted disk as support; Buchner flask/funnel model-Schott DURAN 1000ml; Whatman glass microfiber filter GF/C™, diameter-55mm; graduated measuring cylinder 10ml capacity; beakers 250ml; corks; stirring rods and stop watch.

The precipitation of heavy organics was carried out by precipitation experiments similar to those implemented by Kokal et al (1992)[13] and Eduardo et al (2004)[6] and modified ASTM/IP methods. 30ml of binary mixtures of normal alkane solvents in varying ratios were added to approximately 1g of crude oil in an appropriate flask. The mixtures were shaken for 30 minutes using Mechanical shaker and allowed to stand for 2 days (48 hours). After which the solution was filtered with a 55mm diameter Whatman glass microfiber 40-60µm membrane filter (**W_1**) using vacuum pump fitted in a Buchner flask/funnel. The filter paper with the precipitated material (**W_2**) was dried in an oven for 2 hours at 333K (60°C) and weighed to determine the heavy organics mass precipitate.

RESULTS AND DISCUSSION

The percentage weights of the heavy organic precipitated using varying ratios of binary mixtures of n-alkane solvents are presented in the Tables below:

Table 1: Heavy Organics precipitated using varying ratios of binary mixture of n-Pentane (nC5) & n-Hexane (nC6) @ 30ml/g oil

Test S/No	NC5: NC6 Solvent ratios (ml)	wt. HO precipitated	wt. % HO precipitated
1	30:0	0.0193	1.88
2	27.5:2.5	0.0118	1.16
3	25:5	0.0124	1.20
4	22.5:7.5	0.0195	1.90
5	20:10	0.0136	1.31
6	17.5:12.5	0.0135	1.31
7	15:15	0.0129	1.26
8	12.5:17.5	0.0120	1.17
9	10:20	0.0104	1.02
10	7.5:22.5	0.0178	1.74
11	5:25	0.0117	1.14
12	2.5:27.5	0.0251	2.42
13	0:30	0.0121	1.19

Table 2: Heavy Organics precipitated using varying ratios of binary mixture of n-Pentane (nC5) & n-Heptane (nC7) @ 30ml/g oil

Test S/No	NC5: NC7 Solvent ratios (ml)	wt. HO precipitated	wt. % HO precipitated
1	30:0	0.0192	1.88
2	27.5:2.5	0.0086	0.83
3	25:5	0.0025	0.24
4	22.5:7.5	0.0015	0.15
5	20:10	0.0036	0.35
6	17.5:12.5	0.0055	0.54
7	15:15	0.0027	0.26
8	12.5:17.5	0.0045	0.44
9	10:20	0.0038	0.37
10	7.5:22.5	0.0063	0.61
11	5:25	0.0040	0.39
12	2.5:27.5	0.0064	0.63
13	0:30	0.0096	0.93

Table 3: Heavy Organics precipitated using varying ratios of binary mixture of n-Hexane (nC6) & n-Heptane (nC7) @ 30ml/g oil

Test S/No	NC6: NC7 Solvent ratios (ml)	wt. HO precipitated	wt. % HO precipitated
1	30:0	0.0123	1.19

2	27.5:2.5	0.0104	1.02
3	25:5	0.0095	0.91
4	22.5:7.5	0.0096	0.94
5	20:10	0.0099	0.96
6	17.5:12.5	0.0101	0.98
7	15:15	0.0094	0.93
8	12.5:17.5	0.0090	0.88
9	10:20	0.0091	0.90
10	7.5:22.5	0.0086	0.85
11	5:25	0.0091	0.89
12	2.5:27.5	0.0098	0.95
13	0:30	0.0095	0.93

Fig. 1: Effect of medium properties on heavy organics precipitation for varied solvent (v/v) ratios of C5:C6 binary mixture.

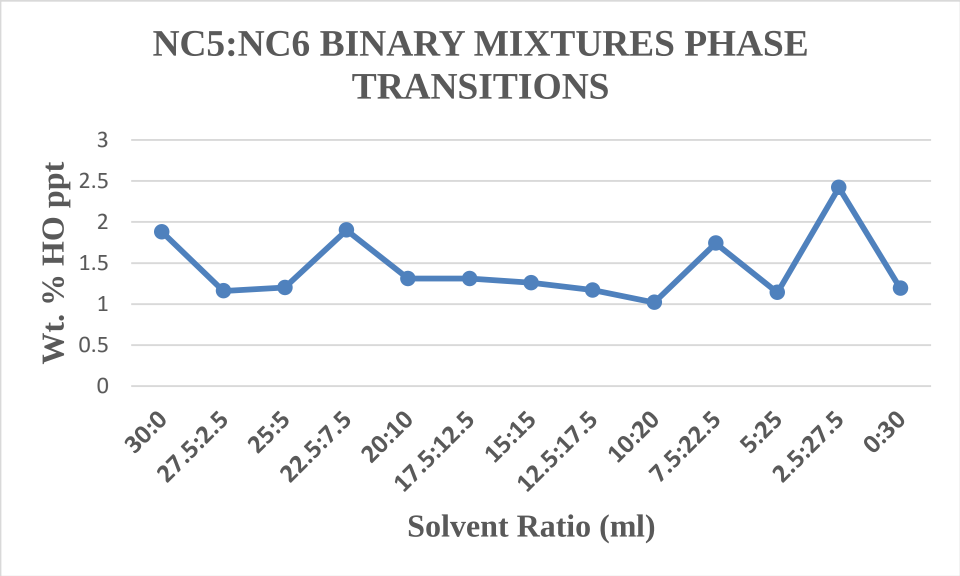


Fig. 2: Effect of medium properties on heavy organics precipitation for varied solvent (v/v) ratios of C5:C7 binary mixture.

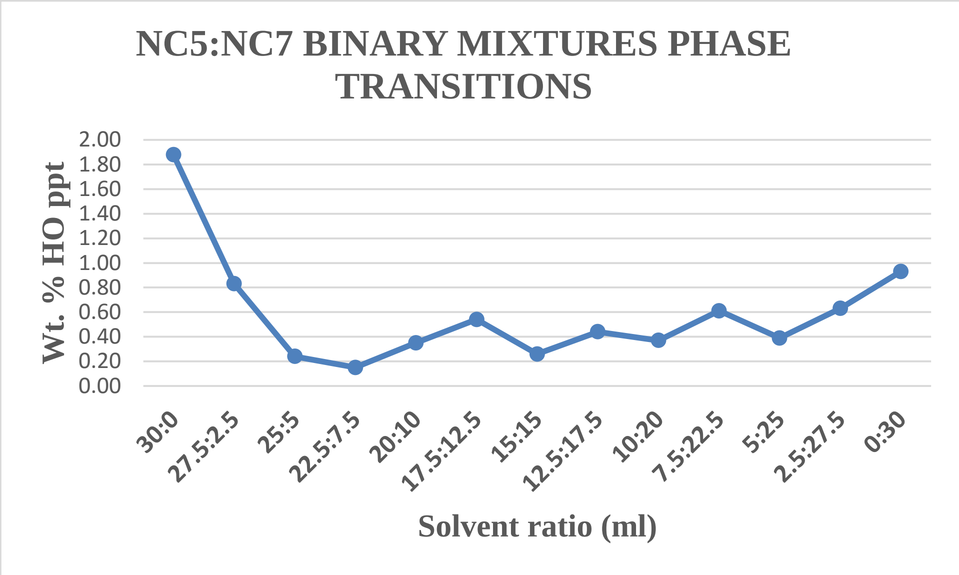
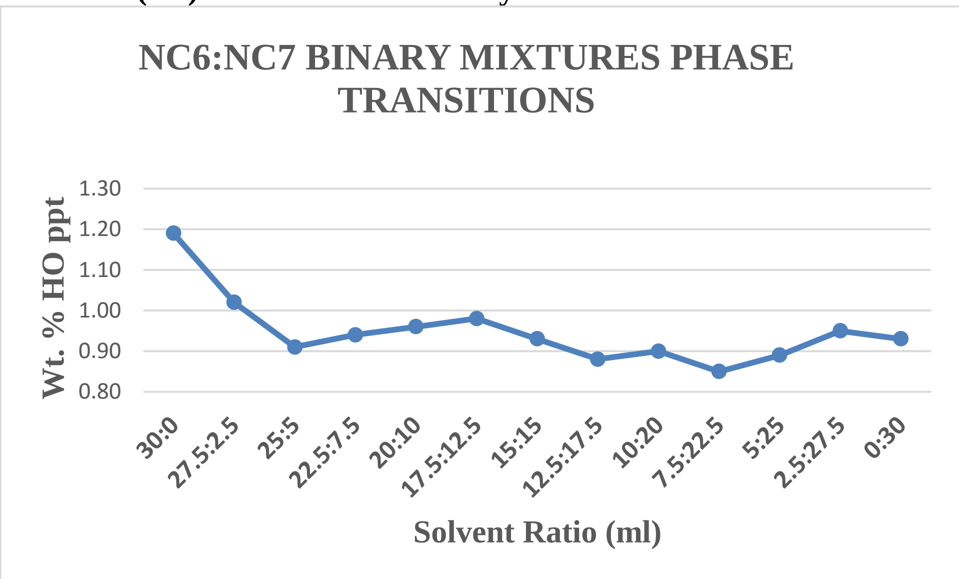


Fig. 3: Effect of medium properties on heavy organics precipitation for varied solvent (v/v) ratios of C6:C7 binary mixture.



For binary mixtures of n-alkanes, lower carbon number n- alkane binary mixtures also record higher precipitate while higher carbon number binary mixtures record lower precipitate. However, the trend of precipitation as the volume of corresponding precipitant mixture is altered differs completely from those of single n-alkane precipitating solvents.[(2)] Heavy organic precipitation with binary mixtures show a three – stage phase transition as demonstrated in the plot for NC5:NC6; NC5:NC7 and NC6:NC7 binary mixtures (fig. 1, 2 and 3).

Table 1 and fig. 1 show that the quantity of precipitate decreases as the quantity of NC6 in NC5:NC6 ratio increases at 1:0 ratio (100% pure NC5) with a percentage precipitate of 1.88 till it reaches a minimum at 1:2 ratio with a percentage yield of 1.02 and then maximum at 1:11 ratio with percentage precipitate of 2.42 . Further addition of the NC6 shows different phase changes and transitions, and finally to the 0:1 ratio (NC6 100% pure solvent) where the percentage precipitate (1.19) is recorded.

Table 2 and fig. 2 show that the quantity of precipitate decreases sharply as the quantity of NC7 in NC5:NC7 ratio increases from its highest at 1:0 ratio (100% pure NC5) with a percentage precipitate of 1.88 till it reaches a minimum at 3:1 ratio with a percentage yield of 0.15. Further addition of the NC7 shows different phase changes and transitions, and finally to the 0:1 ratio (NC7 100% pure solvent) where the percentage precipitate (0.93) is recorded.

Table 3 and fig. 3 show that the quantity of precipitate decreases slightly as the quantity of NC7 in NC6:NC7 ratio increases from its highest at 1:0 ratio (100% pure NC6) with a percentage precipitate of 1.19 till it reaches a minimum at 1:3 ratio with a percentage yield of 0.85. Further addition of the NC7 shows different phase changes and transitions, and finally to the 0:1 ratio (NC7 100% pure solvent) where the percentage precipitate (0.93) is recorded.

This trend in the phase changes of the varying ratios of the binary mixtures may be attributed to colloidal formations, growth of colloidal formation and eventual collapse of the resulting colloids due to limitations on the size of Brownian particles suspended in the media.[(11)]

Also, the excess n-alkane solvents disrupts the environment in which the heavy organics are dispersed thereby causing instability resulting in precipitation. Since, Crude oil is a supersaturated mixture of long chain alkanes of various length. Light hydrocarbons act as the solvent, whereas heavier hydrocarbons act as solutes. Straight chain hydrocarbons constitute roughly 80 to 90% of the crude oil composition, whereas the balance is compose of branched iso-paraffin or aromatic cycloparaffins.[(12)] The Afiesere crude oil composition may have contributed to the various phase transitions in the binary mixtures.

CONCLUSION

The composition of the heavy organic deposits suggests strong interaction between the asphaltenes, saturates and other materials involved in the deposition process. The investigation however showed that the amount of heavy organics precipitated varies with the number of carbon atom of the solvents used.

The mechanism of deposition of heavy organics from crude oil in the field can better be understood by precipitation of heavy organics from crude oil in the laboratory using binary mixtures of n-alkane precipitating solvents. Precipitation with binary mixtures of n-alkane precipitant shows a three-stage phase transitions: Solid –liquid, Liquid-Solid and Solid-Liquid, as the volume ratios of the precipitants varies. This gives rise to a curve demonstrating the precipitation and deposition phenomena similar to those which occur in the field. Therefore, the use of binary mixture is a better approach to predicting the onset of heavy organic precipitation and thus prevents this problem.

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