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Original Research Article

Effect of Varying Total Volume of Ternary N-alkane Solvent Mixtures at Constant Volume Ratio of Individual N-Alkanes on the Yield of Heavy Organics from Crude Oil Residues

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Abstract: Heavy organic precipitates were generated from crude oil residue using varying total volumes of ternary n-alkane solvent mixtures: C_5:C_6:C_7, C_5:C_6:C_8, C_5:C_7:C_8 and C_6:C_7:C_8 combinations, respectively, at a constant volume ratio of 1:1:1 of the individual n-alkanes. C_5:C_6:C_7 combination showed precipitation of heavy organics (HOS), which rose to a maximum at 30ml/g of the oil, after which re-dissolution started and stretched to 60ml. An equilibrium yield was observed from 60ml/g oil. At 15ml/g oil, the C_5:C_6:C_8, C_5:C_7:C_8, and C_6:C_7:C_8 curves showed that the HOS are already on the path of re-dissolution stretching between 15-60mls range. Equilibrium yield was also observed for the curves, all from 60mls/g oil. The analysis of variance shows that the effect of varying the volume for the different combinations was significant (P-value=0.047<5%). The results showed that the total volume of n-alkane mixture/g of oil, which gives the maximum precipitate, varies with the n-alkane combination. The experiment also defined the total volume/g of oil for maximum yield and hence the start of redissolution, which was not shown in the single solvent experiments. In pressure depletion in the field, precipitation of heavy organics starts during the expansion of the oil before the bubble point. At the bubble point pressure, the volume of the oil is a maximum. Beyond the bubble point, the volume of the oil contracts to the critical volume where dissolved asphaltene begins to precipitate again. This study can lead to a better understanding of the phase behavior of heavy organics under compositional changes and, hence, the prediction of heavy organic precipitation.

Keywords: Heavy Organics, Ternary mixtures, Precipitates, Crude oil, N-alkanes.

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1. INTRODUCTION

A crude oil at atmospheric pressure and ambient temperature has three main constituents: (i) oils (saturates and aromatics), (ii) resins, and (iii) asphaltenes. Asphaltenes and resins moved from the oil source rock during oil catagenesis and are soluble, chemically altered fragments of kerogen (Goual, 2012). However, unlike resins, asphaltenes contain highly polar species that tend to associate. The interactions of asphaltenes with their chemical environment are very complex. Goual (2012) argued that Asphaltene precipitation/deposition is undesirable, reducing production and oil movement occurring in pipes and equipment.

Constituents of crude oil can precipitate out of solution at any slight change in temperature, pressure and most importantly, chemical environment. These precipitates can be mercaptans, metal carbenes, resins, waxes, diamondoids and their derivatives, asphaltenes, etc. Since all of them have been found to be complex organic compounds, they are usually referred to as heavy organics (HO) or heavy organic solids (HOS). The molecules of these high molecular weight compounds are found to be polydispersed in petroleum fluids (Vasquez *et al.*, 1998; Vasquez & Mansoori, 2000; Mansoori *et al.,* 2007b; Achugasim & Ekpo, 2015).

Over the years, several studies have been conducted in an attempt to proffer a lasting solution to the heavy organic deposition problems in oil field facilities.

Mansoori (1997) and Branco *et al.* (2001) stated that the main condition that triggers heavy organics precipitation and deposition involves the variation in the composition of the medium in which the asphaltene and other heavy organics are dispersed. Dubey and Waxman (1995) argued that alkanes are solvents for resins but not for asphaltenes and as the volume of the solvents increases both the interaction between resins and asphaltenes and the ability of the resins to stabilize the asphaltenes in the system goes feable, resulting in the precipitation of asphaltenes.

In recent years, efforts have been directed towards precipitation of heavy organics in crude oil in the laboratory using single n-alkanes with the belief that results obtained would give a better understanding of the deposition phenomena, predict the onset of organic deposition region and hence help to avoid getting to the region.

However, information from previous asphaltene precipitation works involving mostly the use of a single solvent is not easily applicable to the understanding and possible prediction of the tendency of a crude oil or a mixture of petroleum streams to precipitate heavy organic solids. Probably this is because different crude oils contain many liquid n-alkanes at different ratios, each of which could contribute to the precipitation of HOS in the field or in the mixture of petroleum streams, hence the need to try mixtures of n-alkanes in the precipitation of HOS from crude oil.

This position is reinforced by the fact that heavy organics precipitated in the field are significantly different in composition from laboratory-generated asphaltenes using

single n-alkanes (Buenrostro-Gonzalez *et al.*, 2004; Chapman *et al.*, 2007; Goual *et al.*, 2011; Mullins *et al.*, 2012).

This work therefore investigates heavy organics precipitation from crude oil using ternary mixtures of low molecular weight n-alkane organic solvents (C_5,C_6,C_7,C_8) and studies the effects of varying the total volume of solvent mixture at constant volume ratio of 1:1:1 of the individual n-alkanes, on heavy organics precipitation.

2. MATERIALS AND METHODS

Nigerian crude oil sample (Bonny Light) was collected from the Research and Development Division of Nigerian National Petroleum Corporation (NNPC), Port Harcourt, Nigeria. The crude sample was distilled to a constant volume at a steady temperature of 260^0C.

The precipitation of heavy organics were carried out by precipitation experiments similar to those implemented by Kokal *et al.* (1992) and Buenrostro-Gonzalez *et al.* (2004) and modified ASTM/IP methods. Total volumes of 15ml, 30ml, 45ml, 60ml and 75ml respectively of the different ternary solvent mixtures (C_5:C_6:C_7, C_5:C_6:C_8, C_5:C_7:C_8 and C_6:C_7:C_8), at constant volume ratio of 1:1:1 of the individual n-alkanes, were added to about 1g of oil each in a 50ml conical flask. The mixture was agitated for half an hour using mechanical shaker. It was allowed to stand for 48hrs. After which the solution was filtered using a vacuum pump system through a 0.45μm membrane filter. The flask and the membrane filter were rinsed with small volumes of the corresponding ternary mixtures of n-alkane solvents to eliminate the residual oil. The membrane filter with the precipitated material was dried in an oven and finally weighed to determine the heavy organic mass precipitate.

The weight percentages of the heavy organics at each corresponding mixture were determined using the relationship:

$$\text{Weight \%} = \frac{\text{Weight of HO precipitate in mg}}{\text{Weight of Residue in mg}} \times \frac{100}{1}$$

Table 1: Heavy organics precipitated by 1:1:1 Volume ratios of C_5:C_6:C_7 ternary mixtures for varying total volumes solvent mixture per gram of oil.

Test S/N	Total Volume (m/s)	Wt of crude oil residue (g)	Wt of HO ppt (g)	Wt % of HO ppt
1	15	1.0022	0.0061	0.6087
2	30	1.0188	0.0241	2.3655
3	45	1.0297	0.0170	1.6510
4	60	1.0354	0.0123	1.1879
5	75	1.0124	0.0126	1.2446

Table 2: Heavy organics precipitated by 1:1:1 volume ratios of C_5:C_6:C_8 ternary mixtures for varying total volumes of solvent mixture per gram of oil.

Test S/N	Total Volume (m/s)	Wt of crude oil residue(g)	Wt of HO ppt(g)	Wt % of HO ppt
1	15	1.0111	0.0160	1.5824
2	30	1.0117	0.0133	1.3146
3	45	1.0071	0.0111	1.1022
4	60	1.0049	0.0075	0.7463
5	75	1.0171	0.0069	0.6784

Table 3: Heavy organics precipitated by 1:1:1 volume ratios of C_5:C_7:C_8 ternary mixtures for varying total volumes of solvent mixture per gram of oil.

Test (s/n)	Total Volume(m/s)	Wt of crude oil residue(g)	Wt of HO ppt (g)	Wt % of HO ppt
1	15	1.0090	0.0196	1.9425
2	30	1.0218	0.0180	1.7616
3	45	1.177	0.0110	1.0809
4	60	1.0309	0.0092	0.8924
5	75	1.0250	0.0074	0.7220

Table 4: Heavy organics precipitated by 1:1:1 volume ratios of C_6:C_7:C_8 ternary mixtures for varying total volumes of solvent mixture per gram of oil.

Test (s/n)	Total Volumes(m/s)	Wt of crude oil(m/s)	Wt of HO Ppt(g)	Wt % of HO ppt
1	15	1.0089	0.0132	1.3084
2	30	1.0144	0.0144	1.3743
3	45	1.0188	0.0079	0.7754
4	60	1.0025	0.0083	0.8279
5	75	1.0071	0.0071	0.7050

3. RESULTS AND DISCUSSION

Experimental results of total yield of HO precipitate for varying total volumes of solvents/g oil for 1:1:1 n-alkane combinations at room temperature and atmospheric pressure are presented in Tables 1 – 4, and their curves are given in Figures 1 – 5.

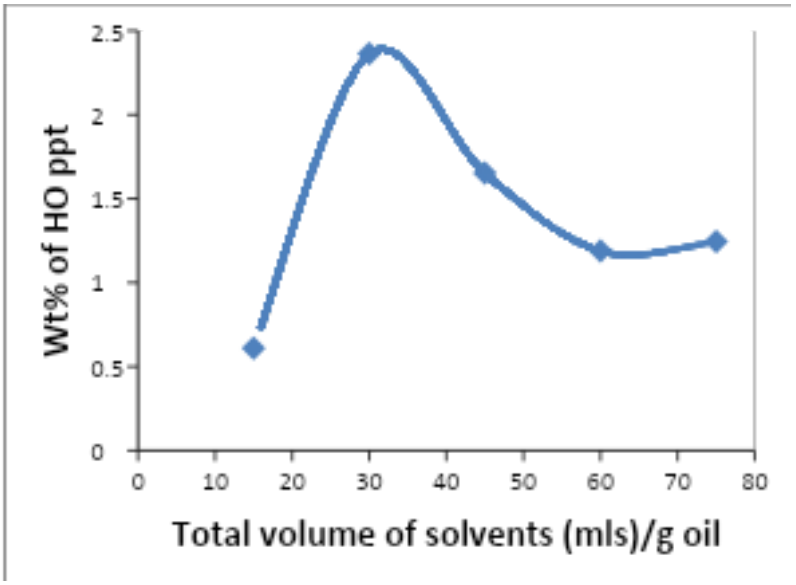

Figure 1: Weight % of Heavy organics precipitate vs varying total volumes of 1:1:1 volume ratios of C_5:C_6:C_7.

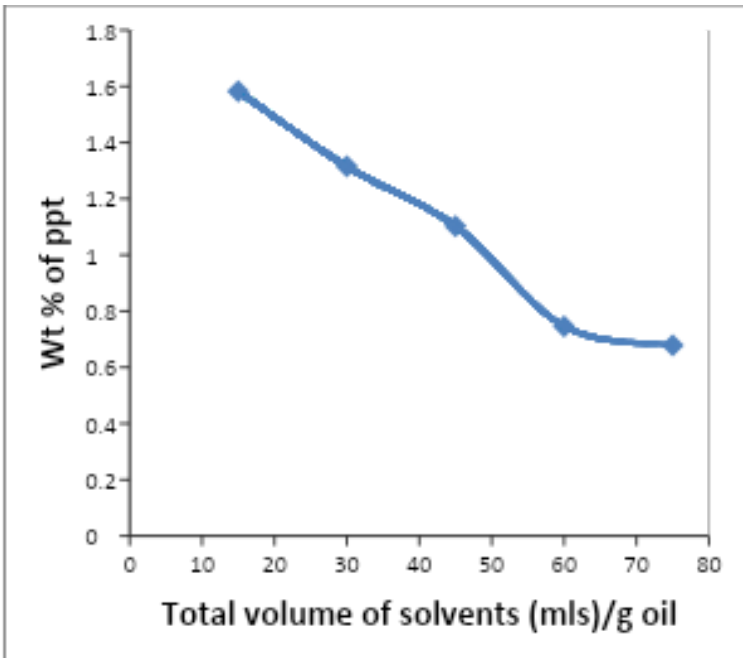

Figure 2: Weight % of Heavy organics precipitate vs varying total volumes of 1:1:1 volume ratios of C_5:C_6:C_8.

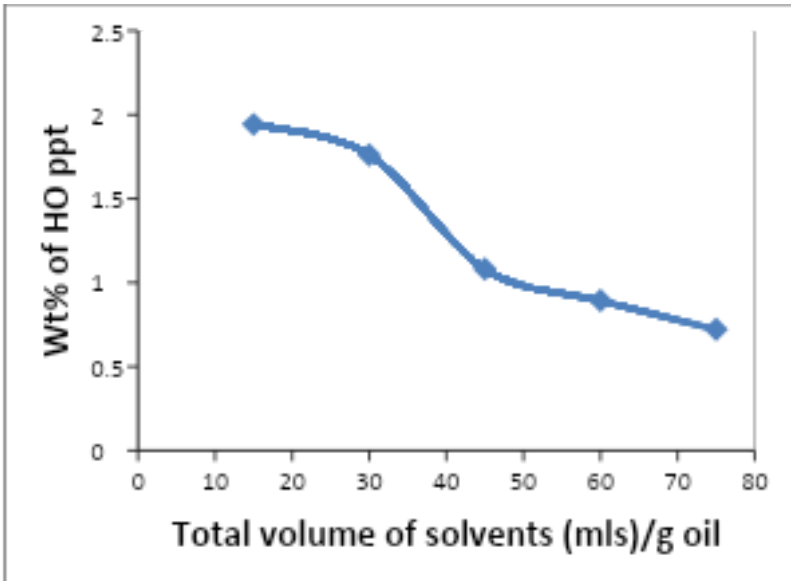

Figure 3: Weight % of Heavy organics precipitate vs varying total volumes of 1:1:1 volume ratios of C_5:C_7:C_8.

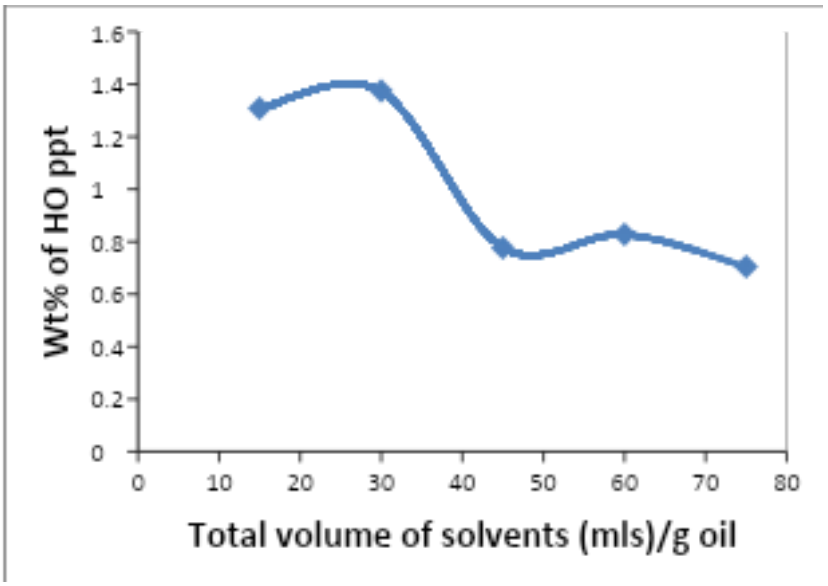

Figure 4: Weight % of Heavy organics precipitate vs varying total volumes of 1:1:1 volume ratios of C_6:C_7:C_8.

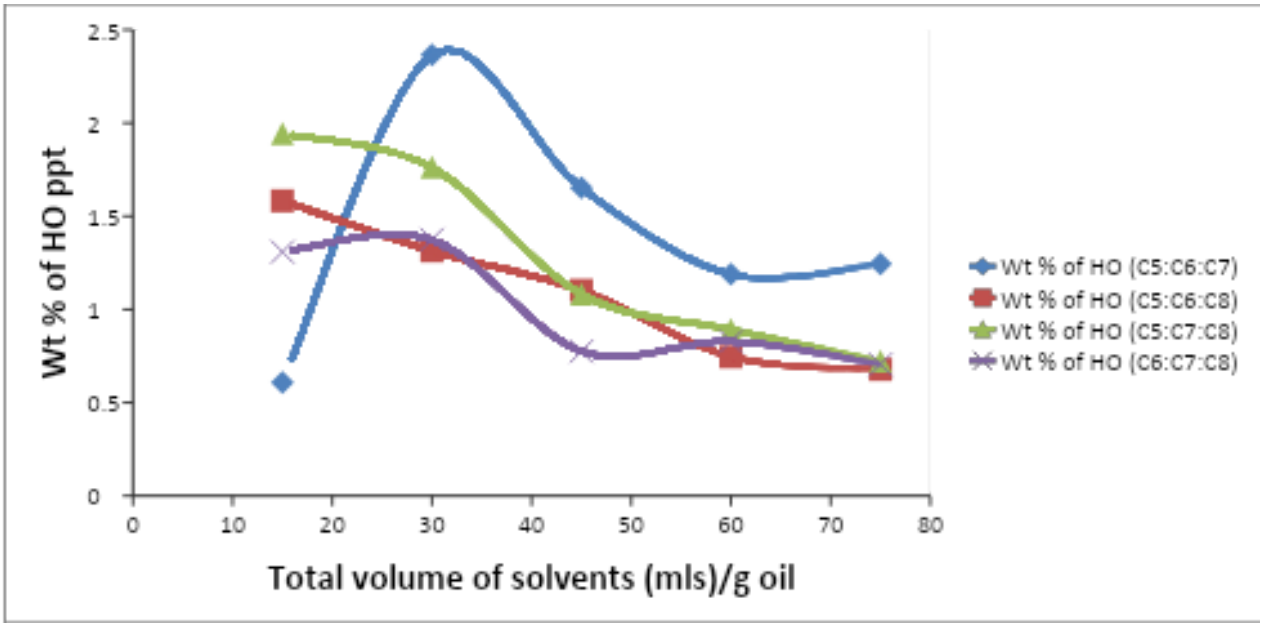

Figure 5: Weight % of Heavy organics precipitate vs varying total volumes of 1:1:1 volume ratios of C_5:C_6:C_7, C_5:C_6:C_8, C_5:C_7:C_8 & C_6:C_7:C_8.

The curve in fig 1 involves the C_5:C_6:C_7 n-alkane solvent mixture at 1:1:1 volume ratio. At varying total volume of n-alkane mixture per g of the oil, optimum yield of HOS (heavy organics) was observed at 30mls, after which re-dissolution started till a total volume of mixture/g oil of 60mls was reached. A constant value was attained from 60mls and thereafter a steady (equilibrium) yield despite volume rise was observed.

A comparison of fig 1 with fig 2, 3 and 4 shows that the HOS appear to be more soluble in the C_5:C_6:C_7 combinations (0.6% yield) in a smaller total volume (15mls) than the C_5:C_6:C_8 (1.6% yield), C_5:C_7:C_8 (1.9% yield) and C_6:C_7:C_8 (1.3% yield) combinations which appear to have high HOS values at the lowest total volume used. Anova shows that the effect of varying the volume for the different combinations were significant (P-value=0.047<5%). The high precipitation at low volume and redissolution at high volume could be as a result of resin solubility. At low quantity of the solvent /g of oil, there is low solubility of resin, thus co-precipitation with asphaltenes, at high/higher quantity of solvent, increased solubility leads to less precipitate and hence redissolution.

A steady drop in the curve occurred in C_5:C_6:C_8 plot, which showed a downward yield in the HOS as the total volume of solvent increased. A steady yield was also observed from 60mls.

In Figure 1-4, the total yield of HOS for varying total volumes of solvent mixture/g of oil showed the following:

- C_5:C_6:C_7 combination yielded HOS that showed more solubility in smaller total volumes of solvent.
- C_5:C_6:C_7 curve showed maxima at 30mls, 2.4% wt, after which re-dissolution started. Finally, an equilibrium yield was observed from 60mls.

In general, it can be concluded that the quantity of HOS yields for any of the other combinations (C_5:C_6:C_8, C_5:C_7:C_8 & C_6:C_7:C_8) appears high at the lowest total volume of solvent used and then decreases as total solvent volume increases (re-dissolution) until an equilibrium/steady yield is obtained for subsequent solvent rise.

Comparing the single, binary & ternary solvent systems for HOS precipitation for varying total volume of solvent, the following deductions can be made:

For the **single** system, fig 6, Buenrostro-Gonzalez *et al.* (2004) in their work looked at the effects of composition and pressure on asphaltene precipitation in two Mexican crude oils using titration experiments. The amount of asphaltenes precipitated decreases as the carbon number of the *n*-alkane diluent increases.

They also observed that the amount of HOS yield rose steadily as the volume of precipitant to oil ratio increased to 10ml, then plateaus to 50ml/g oil.

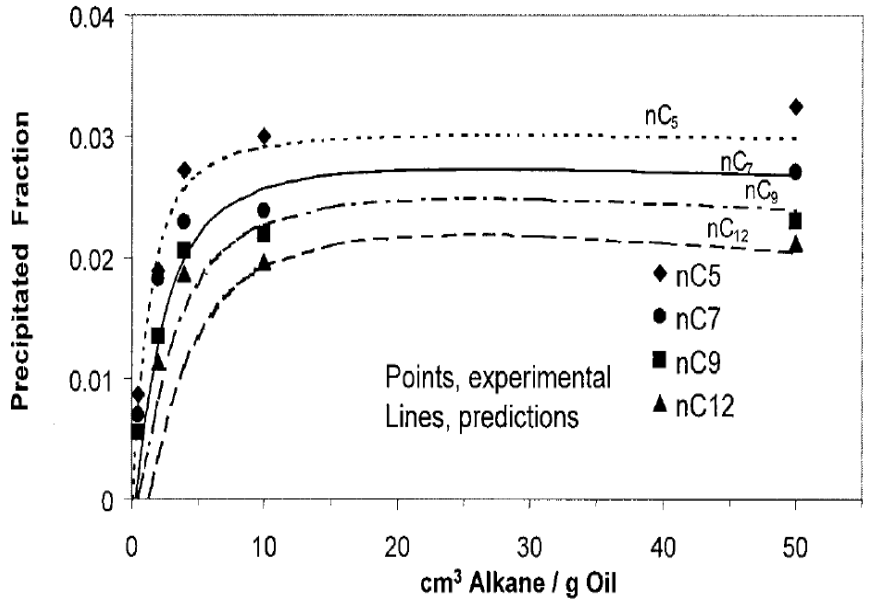

Figure 6. Asphaltene precipitation prediction for Y3 tank oil sample with n-alkane (Buenrostro-Gonzalez *et al.*, 2004).

For the **binary** system, Udourioh *et al.* (2014) in their work carried out the precipitation of heavy organics with binary solvents by experiments similar to those implemented by Kokal *et al.* (1992) and Buenrostro-Gonzalez *et al.* (2004).

Analysis of their results in terms of variation of the total volume precipitant/g of oil shows that precipitation of HOS here increased steadily and continued to give a maximum yield at 30mls of solvent mixture/g oil. Then re-dissolution started and stretched between 30-50mls solvent range. Beyond 50mls/g oil, an equilibrium/steady yield was observed.

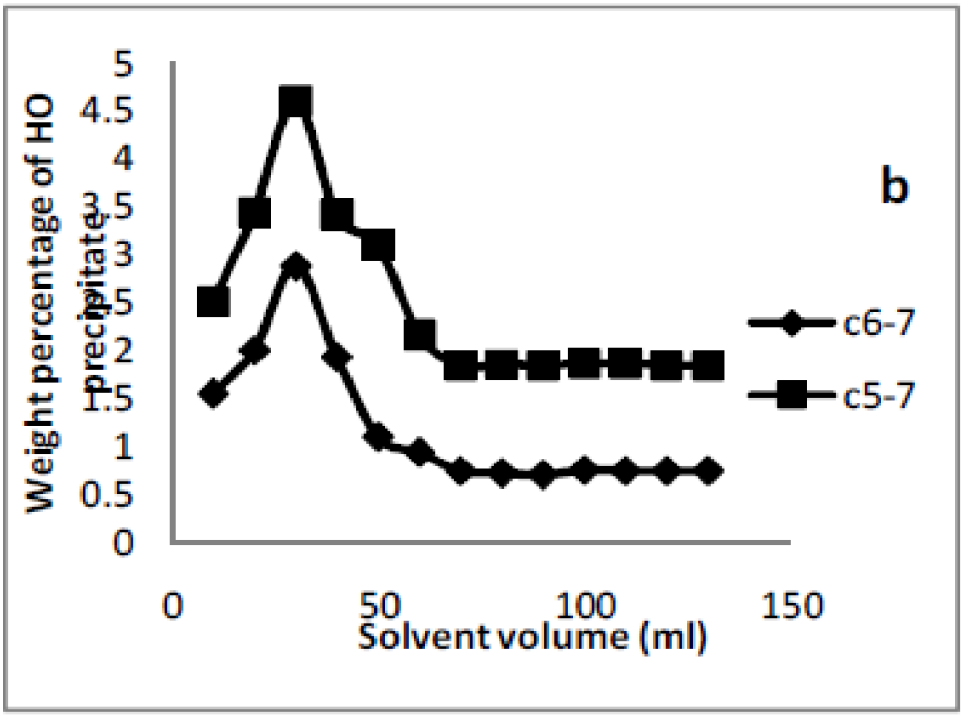

Figure 7: Weight % of HO precipitate vs varied total volumes/g of oil of 1:1 (v/v) ratio of C_5:C_7 and C_6:C_7 binary mixture (Udourioh *et al.*, 2014)

Our **ternary** solvent system, C_5:C_6:C_7 curve showed a precipitation of HOS, which rose till 30mls/g of the oil after which re-dissolution started stretching between 30-60mls (i.e. 30mls) range. An equilibrium yield was observed from 60mls/g oil. At the chosen starting solvent volume of 15mls/g oil, the C_5:C_6:C_8, C_5:C_7:C_8 & C_6:C_7:C_8 results show the HOS are already on the path of re-dissolution, stretching between 15-60mls (i.e. 45mls) range. Equilibrium yield was also observed for the curves, all from 60mls/g oil.

Chapman *et al.* (2007) and Njiofor (2012) discovered that the asphaltene samples from the field are stronger in n-heptane composites than the ones produced using single individual solvents in the laboratory. In the field, when the light ends leave after the bubble point, the oil will be rich in n-hexane C_{6+} components. This could account for the field samples being richer in n-heptane components and for the equilibrium/steady yield obtained at a point after re-dissolution started despite solvent rise.

Escobedo & Mansoori (1992). Vazquez and Mansoori (2000) and Buenrostro-Gonzalez *et al.* (2004) observed that precipitate can take place at pressures above the bubble point in production well tubing. They argued that the lighter ends expand as the fluid rises, increasing their influence on the stabilizing resins and increasing the tendency of asphaltene precipitation.

4. CONCLUSION

The observations from the experimental results show that there is a critical total volume/g of oil at which precipitation starts, and precipitation increases as the volume

increases to a maximum. As the volume increases, further redissolution sets in to a minimum until an equilibrium/steady yield is obtained for subsequent solvent rise.

At saturation pressure/bubble point pressure, the volume of the oil is a maximum. Beyond the bubble point, the volume of the oil contracts to the critical volume where dissolved asphaltene begins to precipitate. The results have shown that the total volume of solvent mixture/g of oil, which gives the maximum precipitate, varies with the n-alkane combination.

It has also defined the total v/g oil for maximum yield and hence the start of redissolution, which was not shown in the single solvent experiments.

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