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Effect of hydrocarbon type in a ternary n-alkane mixture on heavy organics precipitation from crude oil at constant volume ratio and total volume

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Abstract
Different hydrocarbon type mixtures at a fixed volume ratio and for any fixed total volume of the n-alkanes/g of oil were used to generate heavy organic solid precipitates from crude oil residue. The effect of n-alkane types in a precipitant mixture needed to be known. For 15mls/g oil, C_5:C_7:C_8 gave the maximum precipitate value of 1.9% wt while C_5:C_6:C_7 gave the least – 0.6% wt, for 30mls/g oil, C_5:C_6:C_7 gave the maxima (2.4% wt) while C_5:C_6:C_8 gave the minima (1.3% wt), for 45mls/g oil, C_5:C_6:C_7 gave the maxima (1.7% wt) while C_6:C_7:C_8 gave the minima (0.8% wt), for 60mls/g oil, C_5:C_6:C_7 gave the maxima (1.2% wt) while C_5:C_6:C_8 gave the minima (0.7% wt), for 75mls/g oil, C_5:C_6:C_7 gave the maxima (1.2% wt) while C_5:C_6:C_8 gave the minima (0.7% wt). Varying hydrocarbon type mixture at a fixed volume ratio and for any fixed total volume of the n-alkanes/g of oil affects precipitate yield differently. And it can be deduced here that susceptibility of oil to precipitation is a function of the n-alkane types present in the oil.

Keywords: Heavy organic solids (HOS), precipitates, ternary solvent mixtures, n-alkanes, crude oil

1. Introduction

Petroleum which has a complex nature contains hydrocarbon or substituted hydrocarbons in which two major elements – carbon(83-87%) and hydrogen (10-14%) combined with three minor elements: nitrogen (mostly less than 0.1%, occasionally as high as 2%); sulphur (0.1-3%, rarely up to 7%); and oxygen (up to 1.5%) and traces of metals such as vanadium and nickel [1].

Various control and process problems occur during the well production and processing of crude oil as a result of the presence of heavy organics (HO) in crude oil. The economic implications of these problems are tremendous. One main problem here involve the asphaltene (heavy organic) precipitation which can lead to plugging of the tubing and production facilities, even reservoir damage and reduction of well productivity. The asphaltenes are the most pronounced of the heavy organics in crude oil.

Monsoori (2007) argued that the heavy organics is one of the important fractions of petroleum fluids, but because of its complexity it is the least understood [2]. Pressure, temperature and makeup of the surrounding fluid and are among the factors that determine asphaltene stability [3-8].

Rassamdana and Sahimi (1996), Buenrostro-Gonzalez *et al.* (2004) and Mansoori*et al.* (2007) have looked at asphaltene precipitation with single n-alkane solvent in the laboratory [9-11]. However SARA analysis knowledge and single n-alkane precipitation does not easily offer help to the forecasting of the readiness of a crude oil streams to precipitate and deposit heavy organic. Probably this is due to the fact that the n-alkanes are present in the petroleum in different quantities for different oils.

In this study, varying hydrocarbon type ternary 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 a fixed volume ratio and fixed total volume of the n-alkanes/g of oil are used for the precipitation of heavy organic solids from petroleum to find out how different hydrocarbon types in the ternary mixtures will affect the precipitation of heavy organics.

2. Materials and Methods

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

The heavy organics precipitation was done by the same methods of Buenrostro-Gonzalez *et al*. (2004) and Kokal*et al.* (1992) and ASTM/IP (modified) procedures [10, 12]. Different hydrocarbon type ternary 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 a fixed volume ratio of 1:1:1 and each at a fixed total volume (of 15ml, 30ml, 45ml, 60ml and 75ml) respectively were poured into about one gram of crude oil each in a conical flask of 50ml. The mixture was agitated half an hour with the mechanical shaker. After allowing the mixture stand for 48hours, filtration was done with the help of a vacuum pump through a membrane filter of 0.45μm. The conical flask and filter membrane were washed by adding little quantities of the (corresponding) ternary solvent mixture of the n-alkanes to remove any leftover oil (residual). The filter paper (membrane) containing the precipitate was dried with the help of an oven and weighed finally to get the weight of the heavy organic solid precipitate.

Percentage weights of heavy organic solids (HOS) or heavy organics (HO) at each corresponding mixture were calculated thus:

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

Table 1: Precipitated heavy organic solid by varied n-alkane combination mixture at 1:1:1 Volume ratios.15mls/g oil.

Test S/N	Hydrocarbon Type mixture	Wt(g) of Crude oil residue	Wt(g) of HO ppt	Wt% of HO ppt
1	C_5:C_6:C_7	1.0022	0.0061	0.6087
2	C_5:C_6:C_8	1.0111	0.0160	1.5824
3	C_5:C_7:C_8	1.0090	0.0196	1.9425
4	C_6:C_7:C_8	1.0089	0.0132	1.3084

Table 2: Precipitated heavy organic solid by varied n-alkane combination mixture at 1:1:1 Volume ratios.30mls/g oil.

Test S/N	Hydrocarbon Type mixture	Wt(g) of Crude oil residue	Wt(g) of HO ppt	Wt% of HO ppt
1	C_5:C_6:C_7	1.0188	0.0241	2.3655
2	C_5:C_6:C_8	1.0117	0.0133	1.3146
3	C_5:C_7:C_8	1.0218	0.0180	1.7616
4	C_6:C_7:C_8	1.0144	0.0144	1.3743

Table 3: Precipitated heavy organic solid by varied n-alkane combination mixture at 1:1:1 Volume ratios. 45mls/g oil.

Test S/N	Hydrocarbon Type mixture	Wt(g) of Crude oil residue	Wt(g) of HO ppt	Wt% of HO ppt
1	C_5:C_6:C_7	1.0297	0.0170	1.6510
2	C_5:C_6:C_8	1.0071	0.0111	1.1022
3	C_5:C_7:C_8	1.177	0.0110	1.0809
4	C_6:C_7:C_8	1.0188	0.0079	0.7754

Table 4: Precipitated heavy organic solid by varied n-alkane combination mixture at 1:1:1 Volume ratios. 60mls/g oil.

Test S/N	Hydrocarbon Type mixture	Wt(g) of Crude oil residue	Wt(g) of HO ppt	Wt% of HO ppt
1	C_5:C_6:C_7	1.0354	0.0123	1.1879
2	C_5:C_6:C_8	1.0049	0.0075	0.7463
3	C_5:C_7:C_8	1.0309	0.0092	0.8924
4	C_6:C_7:C_8	1.0025	0.0083	0.8279

Table 5: Precipitated heavy organic solid by varied n-alkane combination mixture at 1:1:1 Volume ratios. 75mls/g oil.

Test S/N	Hydrocarbon Type mixture	Wt(g) of crude oil residue	Wt(g) of HO ppt	Wt% of HO ppt
1	C_5:C_6:C_7	1.0124	0.0126	1.2446
2	C_5:C_6:C_8	1.0171	0.0069	0.6784
3	C_5:C_7:C_8	1.0250	0.0074	0.7220
4	C_6:C_7:C_8	1.0071	0.0071	0.7050

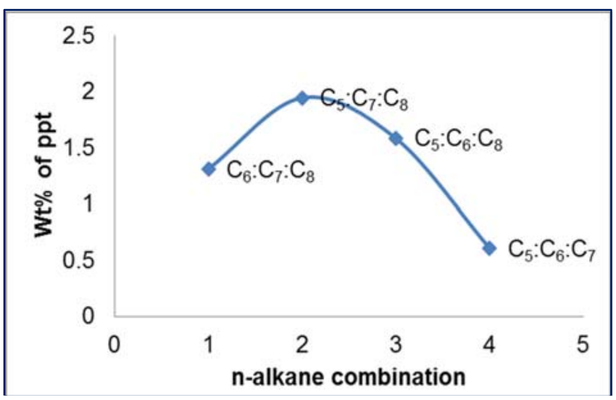

Fig 1: Wt% of HO pptvs hydrocarbon combination mixture at constant volume of 15mls and constant ratio of 1:1:1 of mixture.

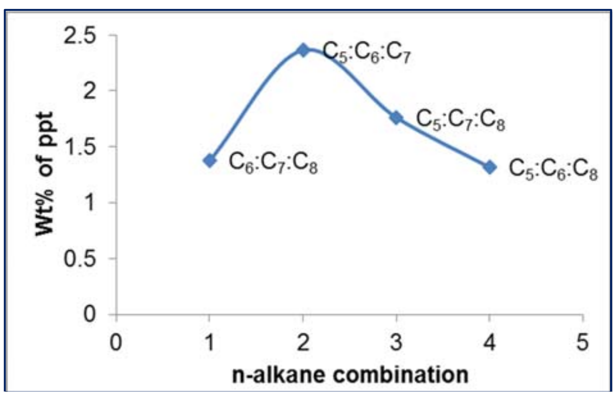

Fig 2: Wt% of HO pptvs hydrocarbon combination mixture at constant volume of 30mls and constant ratio of 1:1:1 of mixture.

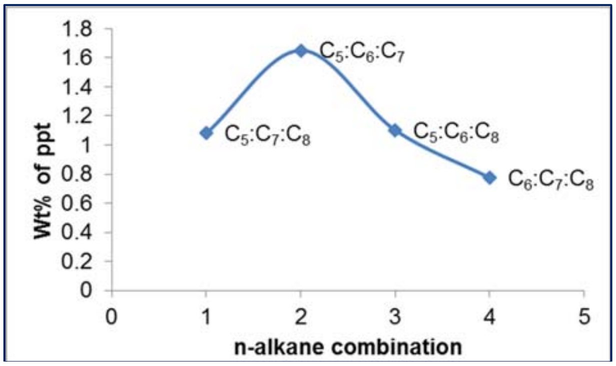

Fig 3: Wt% of HO pptvs hydrocarbon combination mixture at constant volume of 45mls and constant ratio of 1:1:1 of mixture.

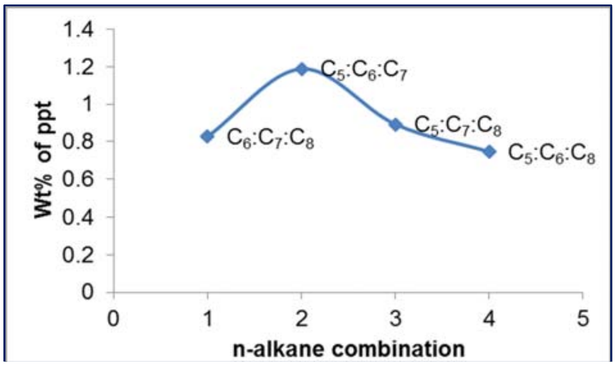

Fig 4: Wt% of HO pptvs hydrocarbon combination mixture at constant volume of 60mls and constant ratio of 1:1:1 of mixture.

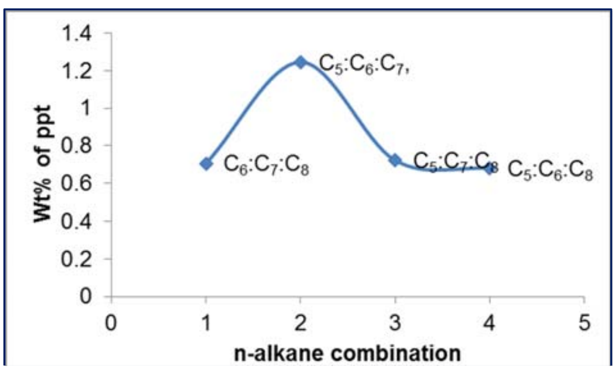

Fig 5: Wt% of HO pptvs hydrocarbon combination mixture at constant volume of 75mls and constant ratio of 1:1:1 of mixture.

The curves in fig 1 – 5, involve total HOS yield for varying hydrocarbon type mixture at a fixed volume ratio and fixed total volume of the n-alkanes/g of oil.

The different n-alkane combination gave maxima & minima HO values as follows; for 15mls/g oil, C_5:C_7:C_8 gave the maximum HOS value of 1.9% wt while C_5:C_6:C_7 gave the least – 0.6% wt, for 30mls/g oil, C_5:C_6:C_7 gave the maxima (2.4% wt) while C_5:C_6:C_8 gave the minima (1.3% wt), for 45mls/g oil, C_5:C_6:C_7 gave the maxima (1.7% wt) while C_6:C_7:C_8 gave the minima (0.8% wt), for 60mls/g oil, C_5:C_6:C_7 gave the maxima (1.2% wt) while C_5:C_6:C_8 gave the minima (0.7% wt), for 75mls/g oil, C_5:C_6:C_7 gave the maxima (1.2% wt) while C_5:C_6:C_8 gave the minima (0.7% wt).

A comparison of fig 1 with fig 2, 3 and 4 show 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.

It was observed that for most of the fixed total volumes of n-alkane used, C_5:C_6:C_7 gave a maxima. This could be attributed to effect of the contribution of low carbon numbers (in this combination) factor on solubility of HOS. This is in line with the common feature of single solvent precipitations in which Buenrostro-Gonzalez *et al.* (2004) in their work stated that HOS precipitated increases as carbon number of the n-alkane decreases [10]. However, for 15mls/g oil, C_5:C_7:C_8 produced a maxima which we could attribute to smaller total volume effect that does not favor the C_5:C_6:C_7combination as observed from the experimental results.

The higher carbon number n-alkane hydrocarbons appear to have precipitation lowering effect - probably due to higher solubility of the components with increasing carbon number up to C_8.

As the fixed total volume increased there was no further marked change in the results obtained as the curve for fixed 60mls/g is same for fixed 70mls/g oil, indicating a state of equilibrium being approached.

3. Conclusion
In summary, since P_i (assumed as precipitation factor) for each n-alkane is different and if it is additive and V_i additive, then P_iV_i is additive. $\sum P_iV_i$ = contribution of each n-alkane type into the HO precipitate. Hence it can be deduced here that varying hydrocarbon type mixture at a fixed volume ratio and for any fixed total volume of the n-alkanes/g of oil affects HOS yield differently.

A significant finding here is that susceptibility of an oil to precipitation is a function of the n-alkane types present in the oil.

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