Journal of Petroleum and Gas Exploration Research (ISSN 2276-6510) Vol. 4(4) pp. 53-59, September, 2014
DOI: http:/dx.doi.org/10.14303/jpger.2014.020
Available online http://www.interesjournals.org/JPGER

Full length research paper

Comparative investigation of heavy organics precipitation from crude oil using binary mixtures and single N-alkane organic solvents

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Abstract

Binary mixtures and single n-alkane organic solvents were used to precipitate heavy organics from a solution of crude oil residue to investigate the comparative effects of compositional changes. The results obtained show that under the same condition, single C_5, C_6 and C_7 n-alkane solvent yielded 11.19±0.90, 5.24±0.32 and 0.97±0.05 weight percent precipitate whereas 1:1 v/v ratio binary mixture of C_5:C_6, C_5:C_7 and C_6:C_7 yielded 8.53±0.80, 4.51±0.65 and 3.39±0.59 respectively. Single n-alkane solvents show a decrease in the quantity of precipitate as the carbon number of the precipitant increases. Binary mixtures solvent also show a decrease in the quantity of precipitate with increase quantity of the higher carbon number in the mixtures. Single n-alkane solvents recorded maximum precipitation at 30ml/g precipitant volume and beyond this volume, the percentage precipitate remained constant. Maximum precipitation for 1:1 v/v ratio binary mixture was recorded at 30ml total solvent per gram of oil, after which the percentage precipitate reduced and reached a minimum value at 70ml/g, beyond this volume, the quantity of precipitate remained constant. Binary mixture precipitation has recorded an average minimal quantity of precipitate. It has apparently demonstrated real life precipitation problem since crude oil is a complex mixture of hydrocarbon which contains different n-alkanes at varied ratios. It is therefore, important to approach heavy organic precipitation and deposition problems by laboratory precipitation of heavy organics with mixtures of n-alkane solvents.

Keywords: Heavy Organics, Binary mixtures, Precipitates, Crude oil, N-alkane.

INTRODUCTION

Precipitation is the formation of solid in a solution or another solid during a chemical reaction or by diffusion in a solid. The solid formed during precipitation is called the precipitate while the substance that causes the solid to form is called the precipitant. The solids may remain in suspension if there is no sufficient force of gravity to bring them together. The high molecular weight complex molecules present in crude oil heavy fractions or petroleum residuum are called heavy organics. These consist of asphaltenes, asphaltogenic acids/compounds, diamondoids and derivative, heavy aromatic hydrocarbons, mercaptans, metal carbenes/organometallic, petroleum resins and wax. Heavy organics (HOs) precipitation and deposition on petroleum pipelines, reservoirs, pumps and other refining equipment is a major problem in the oil industries. It has caused blockage in the oil reservoirs, pipelines and other tubular production and processing facilities. Some of the adverse consequences include: reservoir damage, reduction of well productivity which in most cases has led to complete shutdown of oil wells.

There is a wealth of information and database available for the light and intermediate components of petroleum fluids (Mansoori, 1993; Pires et al., 2001; Pedersen and Christensen, 2006). The investigation of the accurate chemical constitution of petroleum heavy fractions is hindered by their complex nature. In petroleum fluids, pressure depletion, variation in temperature and change in composition of the medium in which asphaltenes and other heavy organics are dispersed in solution, as colloid, etc, cause instability of asphaltene/medium equilibrium leading to aggregation and precipitation (Mansoori, 2007b). The broad classes of compounds and compound groups namely, precipitants and solvents exist. N-alkanes belong to the precipitants while the aromatics belong to the solvents. The interactions of these classes define the properties of the medium in which Heavy organics (asphaltenes, resins aromatics and waxes) are dispersed.

Over the last six decades, a number of investigators have researched the nature of heavy organics and mechanisms of organics deposition as a step to solving heavy organic precipitation and deposition problems. But due to its complexity in nature as well as limitations of analytical instruments, the nature of heavy organics is still yet to be fully understood (Eduado et al., 2004; Chukwu et al., 2011). The precipitation of asphaltene in the laboratory using individual n-alkane solvents (Eduardo et al., 2004; Mansoori et al., 2007b) has yielded results that do not completely lend themselves to use in the understanding of the mechanism of deposition and prediction of the precipitation tendency of HO for various reasons. One of which is that the heavy organics precipitated in the field are significantly different in composition from laboratory generated asphaltenes (Eduardo et al., 2004; Chapman et al., 2007; Goual et al.,2011, Mullins et al., 2012). Secondly, crude oil is a complex mixture of hydrocarbon which contains different n-alkanes in varied ratios. Single n-alkane precipitation may not represent exactly what happens in the field. The presence of dissolved gases C_1- C_4 in the liquid medium in a reservoir leads to a significant change in the volume ratios of the individual precipitants, total volume of the precipitants and the volume ratio of the total precipitants to the medium, as a result of pressure reduction. These changes result in variations in the stability of the components of crude oil in solution colloidal dispersion or micelles.

The relative quantities of the different compound types composition of heavy organics precipitated from crude oil have been studied using analytical methods referred to as SARA (Saturates, Aromatics, Resins and Asphaltenes) analysis (Chukwu, et al., 2011). Information from these analyses 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. Hence, there is the need for a better understanding of the phenomena through the use of binary mixtures and thus make comparison with results from single n-alkane solvents.

In specific terms, this work therefore investigates the effects of mixing two n-alkane solvents containing different number of carbon atoms, on the quantity of heavy organics precipitated, investigates the effects of varying ratios of two n-alkane solvents on the quantity and precipitation pattern of HOs in crude oil, compare the quantities of heavy organics precipitate obtained using single individual n-alkane organic solvents and those of their binary mixtures and thus relate the finding (results) to how changes in the composition of the petroleum fluids could lead to precipitation of heavy organics in petroleum production.

MATERIALS AND METHODS

Materials

The following materials were used: Nigerian Antan crude oil residue of 550^{o}C AET (Atmospheric equivalent temperature), Tetrachloroethylene, n-pentane, n-hexane, n-heptane, Analytical balance model AB54 Metter with accuracy of 0.0001g, Mechanical shaker (staurt flask shaker), Vacuum pump (leybold - heraeus pump), Membrane filter (0.45µm pore size, 47mm diameter as specified by ASTM method), conical flasks, Buchner flasks, Buchner funnels, beakers, measuring cylinder, thermo-stated oven, stop clock, corks, heating mantle and stirring rods.

Methods

Nigerian Antan crude oil residue 550^{o}C AET was collected from the Research and Development Division of Nigerian National Petroleum Corporation (NNPC), Port Harcourt, Nigeria. The solid residue was dissolved in tetrachloroethylene at 29^{o}C and the tetrachloroethylene was evaporated by heating up to its boiling point at 121^{o}C. Aliquots were collected from the bulk residue when necessary.

Precipitation using single n-pentane, n-hexane and n-heptanes (C_5, C_6 and C_7)

The precipitation of heavy organics was carried out by precipitation experiments similar to those implemented by Kokal et al. (1992) and Eduardo et al., (2004) and modified ASTM/IP (American Standard Test Method/Institute of Petroleum) methods. 30ml of the single n-alkane solvents at different ratios were added to approximately 1g of oil each in an appropriate flask. The mixtures were shaken for 30mins using mechanical shaker. It was allowed to stand for 48hrs. After which the solution was filtered using a vacuum pump system with a 0.45µm membrane filter fitted in a Buchner funnel/Buchner flask and connected to the vacuum pump. The flask and the membrane filter were rinsed with small volumes of the corresponding n-alkane single solvents to eliminate the residual oil. The membrane filter with the precipitated material was dried in an oven for 2hrs. It was finally weighed to determine the heavy organic mass precipitate.

Table 1. Heavy organics precipitated using single n-alkanes solvents of different carbon numbers (C_5, C_6 and C_7) at 30ml/g of oil

	C_5		C_6		C_7	
Test S/N	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**
1	0.1162	11.19	0.0558	5.37	0.0098	0.95
2	0.1103	10.83	0.0540	5.24	0.0104	0.99
3	0.1224	11.55	0.0521	5.11	0.0101	0.97
mean	0.1162	11.19±0.90	0.0540	5.24±0.32	0.0101	0.97±0.05

Table 2. Heavy organics precipitated using 1:1 (v/v) ratio of binary mixtures at 30ml/g of oil

	1:1 (v/v) ratio C_5:C_6		1:1 (v/v) ratio C_5:C_7		1:1 (v/v) ratio of C_6:C_7	
Test S/N	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**
1	0.0918	8.85	0.0429	4.25	0.0326	3.15
2	0.0877	8.53	0.0457	4.51	0.0358	3.39
3	0.0836	8.21	0.0485	4.77	0.0390	3.62
mean	0.0877	8.53±0.80	0.0457	4.51±0.65	0.0358	3.39±0.59

Precipitation using Binary Mixtures of n-pentane: n-hexane (C_5:C_6), n-pentane: n-heptane (C_5:C_7) and n-hexane: n-heptane (C_6:C_7)

Similar method as in single solvent was used. 30mls of the binary mixtures at different ratios were added to approximately 1g of oil each in an appropriate flask. The mixtures were shaken for 30mins using mechanical shaker. It was allowed to stand for 48hrs. After which the solution was filtered using a vacuum pump system with a 0.45µm membrane filter fitted in a Buchner funnel/Buchner flask and connected to the vacuum pump. The flask and the membrane filter were rinsed with small volumes of the corresponding binary mixtures of n-alkane solvents to eliminate the residual oil. The membrane filter with the precipitated material was dried in an oven for 2hrs. It was finally weighed to determine the heavy organic mass precipitate. The weight percents of the heavy organics at each corresponding ratio were determined using the relationship:

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

Precipitation at 1:1 (v/v) Ratios for C_6:C_7 and C_5:C_7 for Varying Total Volumes of Solvent Mixtures

This was carried out to determine the lower limiting value of total volume of precipitating solvent mixture for maximum heavy organic precipitate yield with binary mixtures of n-alkanes. 1:1 (v/v) ratio of n-hexane vs n-heptane (C_6:C_7) and n-pentane vs n-heptane (C_5:C_7) binary mixtures were measured, starting from 5:5mls (v/v) ($V_{T=}$10mls) per gram of oil to 65:65mls (v/v) (V_T =130mls). The procedure as applied on C_6:C_7 binary mixture stated above was judiciously followed and the final weights of precipitate at each corresponding total volume were taken. The quantities of precipitate weight percent of heavy organics were determined and the results recorded. In all cases, the graphs relating the weight percents of HO to the solvent ratios (v/v) were plotted.

RESULTS AND DISCUSSION

The results of the experiments for single n-alkanes and 1:1 v/v ratios of n-alkane binary mixtures at room temperature and atmospheric equivalent pressure are presented on tables 1 and 2. Tables 3, 4, and 5 show the comparison of the weight percent precipitates while tables 6, 7and 8 present the result for different ratios of C_6:C_7 binary mixture and 1:1 v/v ratios of binary mixtures for varying total volumes of solvents respectively.

DISCUSSION

The weight percent values of heavy organic precipitate for single n-pentane, n-hexane and n-heptane at 29^oC are presented in table 1.For a given volume of precipitant, the amount of heavy organic precipitate decreases as the carbon number of n-alkane precipitant increases (fig. 1a). This present study with nC_5, nC_6 and nC_7 records a general trend similar to those observed by

Table 3. Comparison of Heavy organics precipitated using single C_5, single C_6 and 1:1 (v/v) ratio C_5:C_6 binary mixtures at 30ml/g of oil

	C_5		C_6		1:1 (v/v) ratio C_5:C_6	
Test S/N	**Wt.of HO ppt. (g)**	**Wt.% of HO ppt.**	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**
1	0.1162	11.19	0.0558	5.37	0.0918	8.85
2	0.1103	10.83	0.0540	5.24	0.0877	8.53
3	0.1224	11.55	0.0521	5.11	0.0836	8.21
mean	0.1162	11.19±0.90	0.0540	5.24±0.32	0.0877	8.53±0.80

Table 4. Comparison of Heavy organics precipitated using single C_5, single C_7 and 1:1 (v/v) ratio C_5:C_7 binary mixtures at 30ml/g of oil

	C_5		C_7		1:1 (v/v) ratio C_5:C_7	
Test S/N	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**
1	0.1162	11.19	0.0098	0.95	0.0429	4.25
2	0.1103	10.83	0.0104	0.99	0.0457	4.51
3	0.1224	11.55	0.0101	0.97	0.0485	4.77
mean	0.1162	11.19±0.90	0.0101	0.97±0.05	0.0457	4.51±0.65

Table 5. Comparison of Heavy organics precipitated using single C_6, single C_7 and 1:1 (v/v) ratio C_6:C_7 binary mixtures at 30ml/g of oil

	C_6		C_7		1:1 (v/v) ratio of C_6:C_7	
Test S/N	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**	**Wt. of HO ppt. (g)**	**Wt. % of HO ppt.**
1	0.0558	5.37	0.0098	0.95	0.0326	3.15
2	0.0540	5.24	0.0104	0.99	0.0358	3.39
3	0.0521	5.11	0.0101	0.97	0.0390	3.62
mean	0.0540	5.24±0.32	0.0101	0.97±0.05	0.0358	3.39±0.59

other researchers in their experiments (Branco, et al., 2001; Eduardo, et al., 2004; Kokal, et al., 1992). 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 precipitants. Heavy organic precipitation with binary mixtures show a three – stage phase transition as demonstrated in the plot for C_6:C_7 binary mixture (fig. 1b). Table 6 and fig. 1b show that the quantity of precipitate decreases sharply as the quantity of nC_7 in C_6:C_7 ratio increases from its highest at 11:1 to 3:1 ratio till it reaches a minimum at 2:1 ratio with a percentage yield of 1.94±0.03. The precipitate then increases substantially and reaches a maximum value of 3.39±0.80 at 1:1 ratio. Further addition of the nC_7 precipitant brings the quantity of precipitates down to the second minimum value of 1.48±0.03 at 1:2 C_6:C_7 ratios, and finally to the nC_7 100% pure solvent where the least percentage precipitate (0.97±0.05) is recorded. This trend 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 (Escobedo and Mansoori, 1992). It was observed as shown in tables 3, 4 and 5, that under the same condition, the weight percent of heavy organic precipitated with single nC_5 was 11.19±0.90, nC_6= 5.24±0.32 and nC_7= 0.97±0.05.

However, when 1:1 v/v ratio of C_5:C_6 binary mixture was used the weight percent of heavy organic precipitate reduced to 8.53±0.80. This is attributed in part to the partial re-dissolution of asphaltene in the solvent mixture (Kokal et al., 1992). Similarly, 1:1 v/v ratio of C_5:C_7 binary mixture produced 4.51±0.65, and a value of 3.39±0.59 was obtained for 1:1 v/v ratio of C_6:C_7 binary mixture. This is possible because those components of heavy

Table 6. Heavy Organics Precipitated by varied (v/v) ratios of n-C_6 and n-C_7 Binary Mixtures at 30ml/g of oil

Test S/N	Solvent ratio C_6:C_7	v/v ratio (mls) C_6 : C_7	Wt. of crude oil residue (g)	Wt. of HO precipitate (g)	Wt. % of HO ppt.
1	0:1	0 : 30	1.0423	0.0101	0.97
2	1:11	2.5 : 27.5	1.0468	0.0107	1.02
3	1:5	5 : 25	1.0593	0.0113	1.07
4	1:3	7.5 : 22.5	1.0435	0.0149	1.43
5	1:2	10 : 20	1.0243	0.0152	1.48
6	5:7	12.5 : 17.5	1.0427	0.0170	1.63
7	1:1	15 : 15	1.0555	0.0358	3.39
8	7:5	17.5 : 12.5	1.0025	0.0166	1.66
9	2:1	20 : 10	1.0600	0.0206	1.94
10	3:1	22.5 : 7.5	1.0902	0.0367	3.37
11	5:1	25 : 5	1.0609	0.0424	4.00
12	11:1	27.5 : 2.5	1.0623	0.0433	4.08
13	1:0	30 : 0	1.0301	0.0540	5.24

Table 7. Heavy Organics Precipitated by 1:1 (v/v) ratios of n-C_6 and n-C_7 Binary Mixtures for varying total volumes of solvent mixtures per gram of oil

Test S/N	v/v ratio (mls) C_6 : C_7	Total volume(mls)	Wt. of crude oil residue (g)	Wt. of HO precipitate (g)	Wt. % of HO ppt.
1	5 : 5	10	1.0108	0.0158	1.56
2	10 : 10	20	1.0524	0.0212	2.01
3	15 : 15	30	1.0104	0.0292	2.89
4	20 : 20	40	1.0444	0.0202	1.94
5	25 : 25	50	1.0034	0.0112	1.11
6	30 : 30	60	1.0310	0.0098	0.95
7	35 : 35	70	1.0076	0.0076	0.75
8	40 : 40	80	1.0096	0.0074	0.73
9	45 : 45	90	1.0376	0.0074	0.71
10	50 : 50	100	1.0014	0.0076	0.76
11	55 : 55	110	1.0196	0.0076	0.75
12	60 : 60	120	1.0106	0.0076	0.75
13	65 : 65	130	1.0074	0.0076	0.75

organics insoluble in lower carbon number n-alkane solvent may be soluble in higher carbon number n-alkane solvent (Chukwu et al., 2011).

Precipitation of Heavy Organics with 1:1 (v/v) ratio Binary Mixtures of C_6:C_7 and C_5:C_7 at varied total volume of solvent

Tables 7 and 8 show the results for precipitation of heavy organics at 1:1 (v/v) ratios of C_6:C_7 and C_5:C_7 respectively, for varying total volumes of solvent mixtures. It was observed that at 30mls/g total solvent volume (i.e.15:15mls), the highest precipitate was reached. Further increase in the total solvent volume at 1:1 (v/v) ratio brings the quantity of precipitate down substantially (fig.2b). According to the report from previous researchers (Branco et al., 2001; Eduardo, et al., 2004) with single solvent precipitants, the amount of precipitate increases substantially as the volume of the individual precipitant to oil ratio increases up to a point 10ml to 30ml/g oil where apparently complete precipitation is obtained (fig.2a). However, it was observed that the limiting value of total volume of precipitating solvent mixtures for maximum heavy organic precipitate at 1:1 (v/v) ratio binary mixture is 30mls/g; above this volume, there is a substantial decrease in precipitate. At 70mls/g total solvent (i.e.35:35mls), the least precipitate is obtained, and from this volume

Table 8. Heavy Organics Precipitated by 1:1 (v/v) ratios of n-C_5 and n-C_7 Binary Mixtures for varying total volumes of solvent mixtures per gram of oil

Test S/N	v/v ratio(mls) C_5 : C_7	Total volume(mls)	Wt. of crude oil residue (g)	Wt. of HO precipitate (g)	Wt. % of HO ppt.
1	5 : 5	10	1.0062	0.0252	2.51
2	10 : 10	20	1.0024	0.0346	3.45
3	15 : 15	30	1.0122	0.0466	4.61
4	20 : 20	40	1.0142	0.0346	3.42
5	25 : 25	50	1.0046	0.0312	3.10
6	30 : 30	60	1.0080	0.0218	2.17
7	35 : 35	70	1.0122	0.0188	1.85
8	40 : 40	80	1.0142	0.0188	1.86
9	45 : 45	90	1.0084	0.0186	1.85
10	50 : 50	100	1.0180	0.0190	1.87
11	55 : 55	110	1.0022	0.0188	1.87
12	60 : 60	120	1.0128	0.0188	1.85
13	65 : 65	130	1.0142	0.0186	1.85

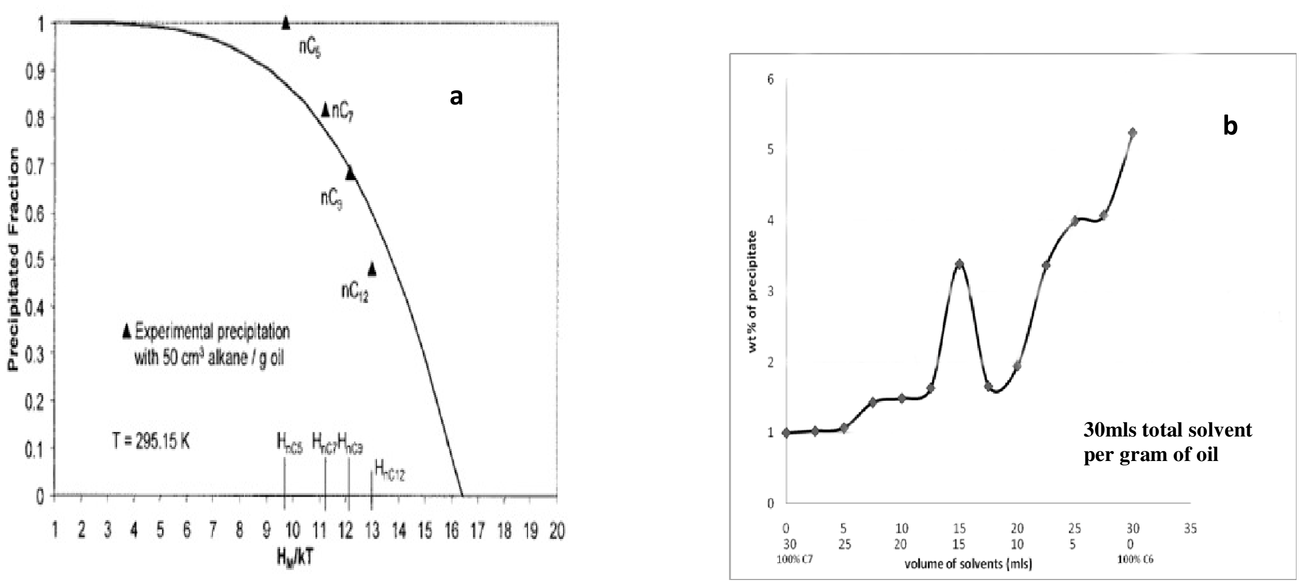

Fig. 1: a) Effect of medium properties on heavy organics precipitation for single n-alkane solvent (carbon number of the precipitant) (Eduardo et al, 2004). **b**) Effect of medium properties on heavy organics precipitation for varied solvent (v/v) ratios of C_6:C_7 binary mixture.

upward, the quantities of precipitate remain constant (Fig. 2b). The change in the volume is attributed to the dilution of the oil with greater quantity of precipitants (binary mixture of n-alkane). As the carbon number of the normal n-alkane increase, its density and dielectric constant increases as well. Considering the precipitant-to-oil ratio from 30ml/g up, the screening effect of the over interactions of solutes becomes stronger, decreasing the energy parameter of the attractive potential, thus leading to a decrease in the amount of the precipitated material. The predicted fractional precipitation by Njiofor (2012) also agrees with the experimental results for the binary mixtures.

CONCLUSION

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 solvents than single solvents. The trend of precipitation in single

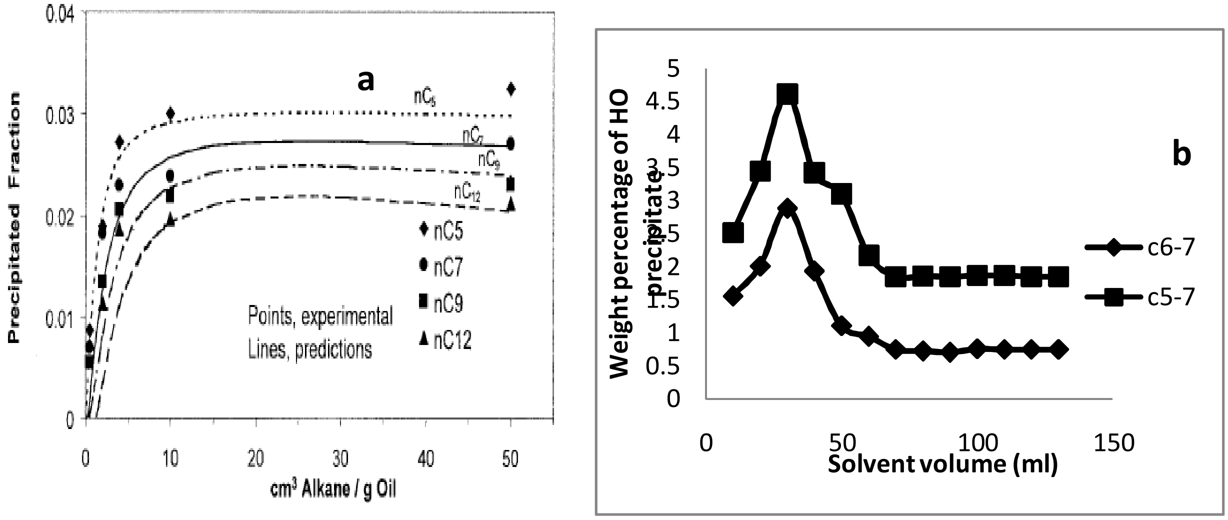

Fig. 2: a) Prediction of the asphaltene precipitation with individual n-alkane for Y3 tank oil sample (Eduardo et al.,2004).
b) Prediction of heavy organic precipitation with 1:1 (v/v) ratio of n-alkane binary mixtures for Nigerian Antan Crude Oil

n-alkane solvent demonstrates a corresponding decrease in the quantity of precipitate as the carbon number of n-alkane organic solvent increases. Precipitation with binary mixtures n-alkane shows a three-stage phase transition: Solid –liquid, Liquid-Solid and Solid-Liquid, as the volume ratios of the precipitants vary. 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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