IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 9, Issue 5 Ver. I (May. 2016), PP 82-86
www.iosrjournals.org

Comparative Evaluation of Asphaltene Precipitation from Nigerian Crude Oil Residue Using Intermediate and Long Chain Single and Binary N-Alkane Solvent Mixtures

Tobrise, O.O[1];Ofodile, S.E[1];Osu, C.[1] and Achugasim, O[1]*.
[1]*Department of Pure and Industrial Chemistry, University of Port Harcourt, Nigeria.*

Abstract: *Ability of intermediate and long chain n-alkane solvents to precipitate asphaltenes (heavy organics) from crude oil residue was investigated. Precipitation by single n-alkane solvents: normal pentane, octane,dodecane and hexadecane(*nC_5*,* nC_8*,* nC_{12}*, and* nC_{16}*respectively)was studied vis-à-vis that by their combinations (binary solvent mixtures). The solvent combinations studied were* nC_8/nC_{12}*,* nC_8/nC_{16} *and* nC_{12}/nC_{16}*. The results obtained showed that under the same conditions,* nC_8*,* nC_{12}*, and* nC_{16} *solvents precipitated 3.24, 1.28, and 15.27 wt % of Organic solids respectively from crude oil. Also 1:1 v/v ratio of binary combinations of* nC_8/nC_{12}*,* nC_8/nC_{16} *and* nC_{12}/nC_{16} *yielded 2.31, 5.58 and 6.63 wt %of solids respectively. The amount of solids precipitated by* nC_{16} *was a serious departure from the norm, and binary combinations involving* nC_{16} *all gave high solid precipitation. Given that crude oil is a mixture of many hydrocarbons, a study of the chemical environment where solid precipitation occurs, for example during pressure depletions in reservoirs is better done using combination of solvents instead of the usual single solvents. Also, the observed anomalous behavior of* nC_{16} *in the precipitation experiment suggests that studies on the heavy organic precipitation are better carried out in the laboratory using combinations of low and high molecular weight solvents than simulated with extrapolations.*

Keywords*: Asphaltenes, Binary mixtures, Hexadecane, Heavy organics, Dodecane, Octane.*

I. Introduction

The economics of heavy organic precipitation during crude oil production and eventual transportation makes an interesting discuss and has received heightened attention in recent times.Inside the reservoir, crude oil exists as a liquid in which the components (solid/liquid) solubilize in each other forming a single phase. Three parameters have been identified to be responsible for the stability or otherwise of the crude oil: temperature, pressure and the chemical composition of the crude oil [1-6]. A slight variation in any of these parameters could lead to the formation or precipitation of one or more of the solid component out of the crude oil; a phenomenon that is undesirable in crude oil production and transportation. This is because solid precipitation may result in formation damage, well plugging and arterial blockage. These could lead to increased production cost occasioned by costly well work overs and other production treatments. It is then not surprising to see a number of researchers recently peering into the complex and a times intriguing area of solid precipitation in crude oils. Yes complex, because crude oil is the most complex naturally occurring liquid on earth with a whole gamut of compound types [7]. The precipitated solids called heavy organics are composed of mainly waxes, asphaltenes and resins [5,6]. The most complex among these are the asphaltenes which are insoluble in low boiling hydrocarbons. Their presence or absence in crude oil determine to a large extent the stability or otherwise of crude oil in reservoirs and in pipelines. A number of researchers on solid/heavy organics precipitation from crude oil have taken different methods/ approaches: solid precipitation using solvents of different polarities was investigated byOkoye et al [8]. They found that polarity and chain length affected the amount and type of heavy organics precipitated from crude oil. Leontaristis and Mansoori [9] found that increase in temperature and pressure affected the onset of asphaltene deposition. Their work was corroborated by Anderson[10] and Hirschberg [11]. Hammami et al[12] did a number of pressure depletion experiments to determine asphaltene precipitation envelope for a number of live oils from the Gulf of Mexico. Kokal et al[13] used single n-alkane precipitants from nC_5 to nC_{10} to study precipitation from Canadian heavy oils. These works studied the precipitation of asphaltenes from crude oil using single n-alkane solvents while monitoring changes in temperature and/or pressure. The researchers are all in agreement that the amount of asphaltene precipitated by n-alkane solvents decreases with increase in carbon number. The results obtained by single organic solvents were at best academic and does not explain in reality what obtains in the field during asphaltene precipitation in reservoirs or production lines where changes in temperature, pressure and most importantly oil composition occurs. The trend established by the researchers above, does it hold for binary mixtures of alkanes?(considering the summation of their individual carbon numbers). Does the trend also hold for long chain n-alkane solvents?These underscore the need for further work/research involving changes in the chemical environment in which asphaltenes are dispersed(solvents).This work attempts to delve into these gray areas.

II. Materials And Methods

The precipitation experiment was carried out using vacuum distilled Anthan crude oil (500^{o}C). About 1g of the crude was dissolved in about 30ml of the different solvents(between pentane and hexadecane) for the single solvent experiment. The same was done for the binary solvent experiment at different ratios. The crude oil/n-alkane mixtures in conical flasks were stoppered and shaked mechanically with a shaker for 30 minutes and allowed to stand for 48hours. The resultant solution was filtered using a vacuum pump/Buckner funnel system with 0.45micrometer membrane filter. The precipitates on the membrane filter were rinsed with the corresponding n-alkane solvent to eliminate any residual oil. Subsequently the weight of the heavy organics precipitates on the membrane filters were obtained with an analytical balance after drying.

III. Results And Discussion

The result of precipitation with single n-alkane solvents is given in table 1 and fig. 1. It is clear from the result that the rule that the amount of precipitate decreases with increase in carbon number of the precipitant is only true/correct up to one or two carbon numbers after decane. At higher or long chain n-alkanes, the rule collapses as nC_{16} gave higher amount of precipitate than nC_{10} or even nC_5 alkanes. This suggests that the often cited work by Branco et al [14], Eduardo et al [15] and Speight [16] may require reconsideration. For example Eduardo et al [15] in their work, claimed that the amount of heavy organic precipitated formed from crude oil decreases with increase in carbon number of the precipitant(solvent). Given their results, they extrapolated/predicted what the precipitate will be for other n-alkanes not covered in their work. This is not supported by our work. Our results showed that the trend mentioned by Branco et al[14] stopped at nC_{11} or nC_{12} n-alkanes as nC_{16} recorded an even greater precipitate than nC_5 n-alkane.

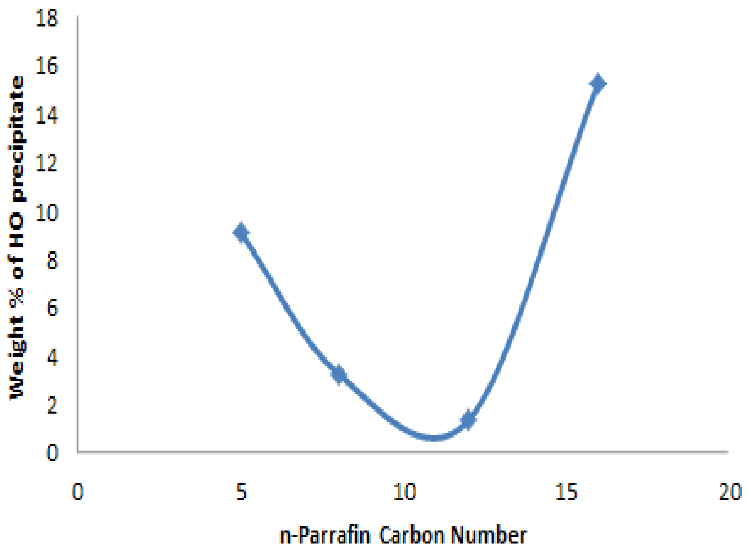

Fig.1 Variation of quantity of precipitate with carbon number of the precipitating n-alkane solvent

Table 1: Amount of heavy organics (HO) precipitated using single c_5, c_8, c_{12} and c_{16} n-alkane solvents.

n-Alkane solvent	Wt. of crude oil residue (g)	Wt. of HO. (g)	Wt. % of HO
C_5	1.0185	0.0928	9.11
C_8	1.0109	0.0327	3.24
C_{12}	1.0293	0.0132	1.28
C_{16}	1.0222	0.1561	15.27

Experiments performed with the binary mixtures of the medium and long chain n-alkane solvents showed that the highest precipitation of asphaltenes were obtained at a total volume of about 30ml to 40ml of the solvent in 1g of the oil [17]. For C8/C12 combination at total volume ratio of 30ml/gram of the oil, the plot showed two maximas at 1:1 solvent ratio and at 30ml of C12. It also showed two minimas at about 10mi C12 and 20ml C8. With regards to the C8/C16 combinations, there were also two minima at 1: 1 solvent mixture and at 30ml C8 (contrast with C8/C12 combination) and maximas at about10ml C16 and 20ml C8 and at about 20ml C16 and 10ml C10. This indicates a sort of similarity in behavior between C8 and C16 solvents. The C12/C16 cobinations also showed two maxima and two minima but with little or no precipitation at 30ml C12 showing that C12 solvent may be a poor precipitant for asphaltenes.This is also indicated in the parabola for the single n-alkane precipitation shown in fig. 1.

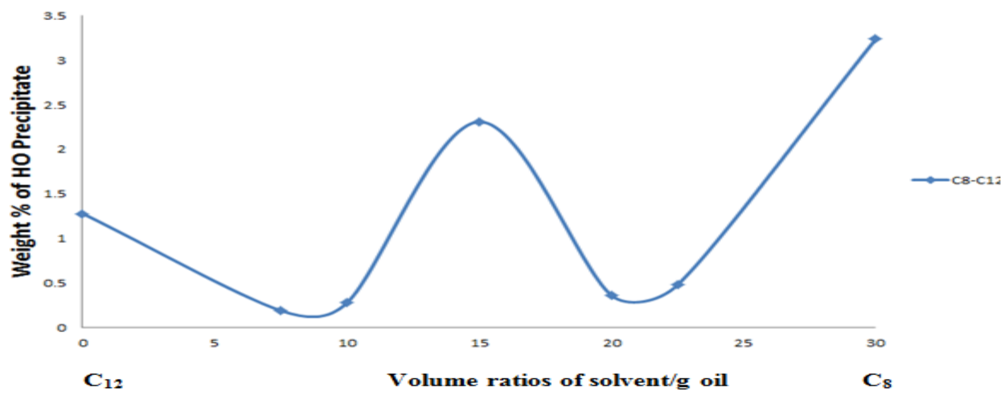

Fig.2 Weight percentage of HO precipitatevs solvent (v/v) ratios of n-C_8 and n-C_{12} binary mixtures at 30ml total solvent per gram of oil

Table 2: Heavy Organics precipitated by varied (v/v) ratios of n-C_8 and n-C_{12} binary mixtures at 30ml/g of crude oil.

Test S/N	Solvent ratio C_8:C_{12}	v/v ratio (ml) C_8:C_{12}	Wt. of crude oil residue (g)	Wt. of HO precipitate (g)	Wt. % of HO precipitate
1	0:1	0:30	1.0293	0.0132	1.28
2	1:3	7.5:22.5	1.0178	0.0019	0.19
3	1:2	10:20	1.0109	0.0028	0.28
4	1:1	15:15	1.0149	0.0234	2.31
5	2:1	20:10	1.0076	0.0036	0.36
6	3:1	22.5:7.5	1.0310	0.0050	0.48
7	1:0	30:0	1.0109	0.0327	3.24

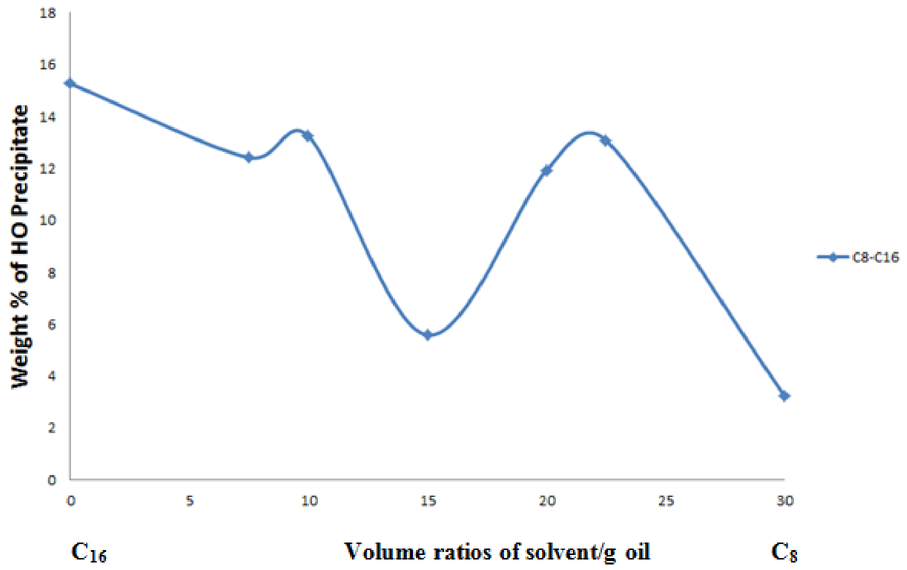

Fig.3 Weight percentage of HO precipitatevs solvent (v/v) ratios of n-C_8 and n-C_{16} binary mixtures at 30ml total solvent per gram of oil

Table 3: Heavy Organics precipitated by varied (v/v) ratios of n-C_8 and n-C_{16} binary mixtures at 30ml/g of crude oil

Test S/N	Solvent ratio C_8:C_{16}	v/v ratio (ml) C_8:C_{16}	Wt. of crude oil residue (g)	Wt. of HO precipitate (g)	Wt. % of HO precipitate
1	0:1	0:30	1.0222	0.1561	15.27
2	1:3	7.5:22.5	1.0374	0.1288	12.42
3	1:2	10:20	1.0047	0.1331	13.25
4	1:1	15:15	1.0013	0.0559	5.58
5	2:1	20:10	1.0122	0.1207	11.92
6	3:1	22.5:7.5	1.0074	0.1318	13.08
7	1:0	30:0	1.0109	0.0327	3.24

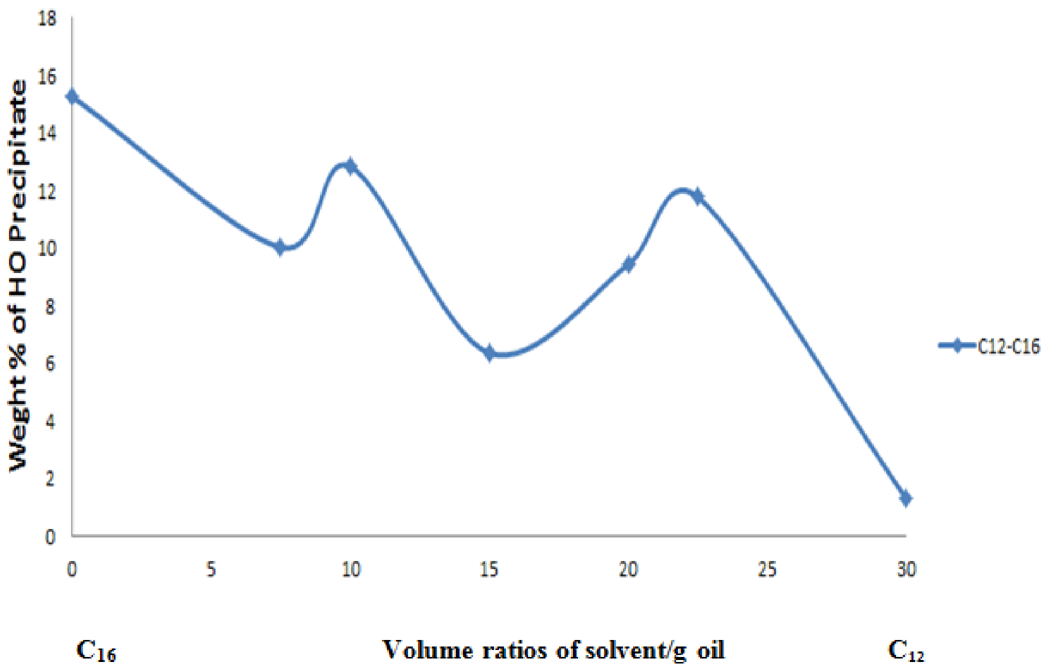

Fig.4: Weight percentage of HO precipitatevs solvent (v/v) ratios of n-C_{12} and n-C_{16} binary mixtures at 30ml total solvent per gram of oil

Table 4: Heavy Organics precipitated by varied (v/v) ratios of n-C_{12} and n-C_{16} binary mixtures at 30ml/g of crude oi

Test S/N	Solvent ratio C_{12}:C_{16}	v/v ratio (ml) C_{12}:C_{16}	Wt. of crude oil residue (g)	Wt. of HO precipitate (g)	Wt. % of HO precipitate
1	0:1	0:30	1.0222	0.1561	15.27
2	1:3	7.5:22.5	1.0260	0.1029	10.03
3	1:2	10:20	1.0320	0.1325	12.84
4	1:1	15:15	1.0019	0.0637	6.36
5	2:1	20:10	1.0286	0.0971	9.44
6	3:1	22.5:7.5	1.0283	0.1213	11.77
7	1:0	30:0	1.0293	0.0132	1.28

The results also demonstrated three stages in the transitions from liquid to solid and vice versa at different ratios of the n-alkane mixtures. These are shown in fig. (2-4). The stages are (1) the first solid –liquid transition where the heavy organics which were insoluble begins to dissolve at the addition of more solvents. (2) The liquid-solid phase transition where colloidal formations and growth of colloidal particles occur leading to agglomeration and precipitation. (3).The last solublization of the colloids as the next longer n-alkane solvent is added.These multi-phase process is observed in line with the conclusions of Escobedo and Mansoori [18] and Osuji [19], that asphaltene deposition is a multi-phase phenomena. What this shows is that the study of heavy organic precipitation using combinations of only low molecular weight n-alkanes does not tell the whole story, that precipitation with intermediate and long chain alkanes has a completely different story to tell.

IV. Conclusion

This research work has supported the already established trend that for low molecular weight n-alkanes, thequantity of heavy organics precipitated from crude oil withalkanes as solvents, decreases with increase in the carbon number of the alkanes. However, it went further to report and establish that the trend mentioned above does not hold for long chain n-alkanes where C_{16} n-alkane precipitated more solids than C_5 .

Acknowledgements

The authors are grateful to the Nigerian National Petroleum Cooperation (NNPC) for the provision of Crude oil samples used for this research.

References

[1] D. Vazquez, and G.A.Mansoori,*Analysis of heavy organic deposits. Journal of petroleum Science and Engineering 26*,2000, 49-56.

[2] J.A. Koots, and J.G. Speight,*Relation of petroleum Resin to Asphaltenes. Fuel. 54, July*. 1975.

[3] O. Achugasim,C.M. OjinnakaandL.C. Osuji, *Management of petroporphyrins in a crude oil polluted environment . Europian Chemical Bulletin. 2 (10)*,2013, 794-796.

[4] M.A. Anismov,I.A. Dmitrieva,A.A. Krupina,A.S. Kurlyandskii,andI.K. Yudin,*Association and phase formation of solution of asphaltenes.Chemical Technology of Fuel and Oils 8*1998, 34-36.

[5] H.D. Runninsen,B. Bjorndal,A,B. Hanson, and W.B Pederson,*Wax Precipitation from North sea crude oils. Energy and Fuels. 5*.1991, 895-908.

[6] T.F. Yen,W.H. Wu, and G.V. Chilingar, *A study of the structure of petroleum asphaltenes and related substances by proton magnetic resonance. Energy Sources7(3,)* 1984, 34-44.

[7] C.M. Ojinnaka,L.C. Osuji,L.andO. Achugasim,Remediation of hydrocarbons in crude oil contaminated soil using Fenton's reagent. Environmental Monitoring and Assessment 184(1), *2012*, 6527-6540.

[8] I.P.Okoye, S.E. Ofodile,andO.C. Chukwu,*The effect of different solvent polarity on the precipitation of heavy organics from a crude oil deposit in the Niger Delta. Sciencia Africana 10(2), 2011*, 9-15.

[9] K.J. Leontaritis,andG.A. Mansoori,*Asphaltenedeposition,Asurvey of Field experience and research Approaches. Journal of Petroleum Science ane Technology. 1 1998, 229.*

[10] *S.I. Anderson, Dissolution of solid BoscanAsphaltenes in Mixed solvents. Fuel Science and Technology 12, 1994*, 51.

[11] A. Hirschberg, N.J. Delong,B.A. Schiper, and J.G. Mayers, *Influence of temperature and pressure on asphaltene flocculation. Soc. Pat .En.gJ.June 283*, 1984 121-129

[12] A. Hammami,C.H. Phelps,Monger-McClure and T.M. Little,*Asphaltene precipitation from live oil: An Experimental investigation of onset conditions and reversibility. Energy and Fuels. 14, 2000,* 14.

[13] S.L. Kokal, J. Najaman,S.G. Sayegh, and A.E.George,*Measurement and correlation of asphaltene precipitation from heavy oils by Gas Injection. J, Can. Petrol. Technol 31*,1992, 24.

[14] V.A. Branco,G.A.Mansoori,L.C. De AlmeiderXavier,S.J. Park, and H. Manafi,*Asphaltene flocculation and collapse from petroleum fluids. J. Pet Sci . Eng. 32*,2001, 217-230.

[15] B.G. Eduardo,L.G. Carlos, G.V. Aljandro, and W. Jianzhong,*Asphaltene Precipitation in crude oils: Theory and experiments. Journal of Alche 50(10), 2004*, 2552-2570.

[16] J.G. Speight,*The chemistry and technology of petroleum(3rd edition. p110-120 Marcel Dekker Inc. New York.1999)*

[17] O. Achugasim, and I.E. Ekpo,*Precipitation of heavy organics (asphaltenes) from crude oil residue using Binary mixtures of n-alkanes. Advances in Chemical Engineering and Science. 5*, 2015, 96-101.

[18] J. Escobedo,andG.A. Mansoori,*Viscometric principles of onset of colloidal asphaltenes flocculation in paraffinic oils and asphaltenemicellization in aromatics. SPE prod facil. May*.1992, 116-122.

[19] L.C. Osuji, *Petroleum Chemistry and Toxicology in Theory and Practice(p501-514Jesso International. Owerri.2011)*