Scientia Africana, Vol. 11 (No.2), December 2012. Pp 108-114
© Faculty of Science, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

AN INVESTIGATION OF THE ROLE OF CARBON-CHAIN LENGTH OF PRECIPITATING SOLVENT IN THE PRECIPITATION/DISSOLUTION OF HEAVY ORGANICS

[1]S. E. Ofodile and [2]O. R. Johnson-Ajinwo

[1]Department of Pure and Industrial Chemistry
Faculty of Science
University of Port Harcourt
Port Harcourt
Nigeria.

[2]Department of Pharmaceutical & Medicinal Chemistry
Faculty of Pharmaceutical Sciences
University of Port Harcourt
Port Harcourt
Nigeria

Received: 24-03-10
Accepted: 06-08-10

ABSTRACT

An investigation of the role of carbon-chain length of precipitating solvent in the precipitation/dissolution of heavy organics (HO) has been carried out.

The heavy organics-rich residue was generated from a medium crude called Qua Iboe blend having an API gravity < 40. The precipitates were obtained from the n-pentane (n-C_5), n-hexane (n-C_6) and n-heptane (n-C_7) solvents using a modified ASTM D6560 method. Precipitation of heavy organics, Dissolution of heavy organics precipitates of lower molecular weight n-alkane solvents by higher molecular weight n-alkane solvents and Stirring in of precipitates of the higher molecular weight n-alkane solvents in lower molecular weight n-alkane solvents (i.e. reprecipitation) were the experimental determinations carried out using the named solvents. The following results were obtained from these experiments: Precipitated heavy organics from n-pentane, n-hexane and n-heptane were 8.68%, 7.46% and 6.25% respectively. The dissolution showed that 95% of n-C_5 ppt. and 96% of n-C_6 ppt. dissolved in n-C_6 and n-C_7 solvents respectively. The re-precipitation results demonstrated that 93% of n-C_6 ppt. and 96% of n-C_7 ppt. were insoluble in n-C_5 and n-C_6 solvents respectively. These findings further reiterate the observation that heavy organics precipitation increases with decrease in carbon-chain-length of the precipitating solvent. It is also shown that HO precipitation from solutions does occur. This same trend is also observed in the precipitation and dissolution.

INTRODUCTION

Crude oil is a complex mixture of hydrocarbons and heteroatomic organic compounds of varying molecular weight and polarity (Speight, 1991). In the petroleum industry it is the practice to separate crude oil into four chemically distinct fractions, namely; Saturates, Aromatics, Asphaltenes and Resins (SARA Analysis). Asphaltene and resins together with compounds such as paraffin/wax, diamondoid (adamante), mercaptans and organometallic compounds (which are usually of less consequence) are referred to as heavy organics (HO).

Asphaltenes are defined operationally as the non-volatile and polar fraction of petroleum that is insoluble in n-alkanes (i.e. pentane). While Resins are defined as the non-polar fraction of crude oil that is soluble in n-alkane (i.e. pentane) and aromatic solvents (i.e. toluene) and insoluble in ethyl acetate (NTNU, 2000). Asphaltene and resins usually co-precipitate in crude oil. The presence of asphaltene in HO precipitate (ppt), is of serious consequence as it is responsible for the hardening of the ppt which ultimately creates some of the following problems encountered in oil production and processing.

(i) Well bore plugging and pipeline deposition during recovery and transportation.
(ii) Water contamination during well head storage and in pipelines can lead to the formation of emulsions because the asphaltene constituent is highly polar and surface active.
(iii) Sedimentation and plugging during Crude oil storage (and during product storage) can occur due to oxidation of the asphaltene constituents and the increased polarity of the oxidized products. (Mansoori, 1996, Speight, 2004). This is a global issue and the economic implication of this problem is devastating, as it could require as much as a quarter of a million dollars to clean-up a problematic oil wells, (SPE, 2010)

Several factors, like changes in reservoir pressure, temperature, compositions and high gas oil ratio (GOR) may cause asphaltene to precipitate from the crude oil as solid, resulting in decreased yield of petroleum distillates (Mansoori. 1996, Kokal et al., 2008).

From literature, it is known that paraffin/wax and resins, coprecipitate with asphaltene (Mansoori, 1996). It is also established that the quantity of asphaltene precipitated decreases with increasing number of carbon atoms in the molecule of the n-alkane solvent (Shkalikov et al, 2008).

This work further investigates the observations related to chain-length of solvents in the precipitation of HO from crude oil in the n-alkane homologous series.Also, the dissolution and re-precipitation of HO solids from crude oil atmospheric residue using two n-alkane organic solvent were investigated.

MATERIALS AND METHODS

Experimental

The crude oil used for this research work was sourced from the Research and Development Division of the Nigerian National Petroleum Corporation (NNPC), Port Harcourt.

A medium crude named Qua Iboe blend having an API gravity of less than 40 was used.
Other materials used are as follows:
Analytical Balance (AE 240 mettler), Filter papers (whatman grade 4), Filter funnel of borosilicate glass, Oven (ThermoFischer Scientific), centrifuge (Eppendorf), Heating mantle (Optics Tech) DS6 Distillation equipment (Precision Scienctific Group, USA).

Solvents

The following analytical grade (BDH) n-alkane solvents were used: Pentane, Hexane and Heptane. The following methods were employed in this work.

Scientia Africana, Vol. 11 (No.2), December 2012. Pp 108-114
© Faculty of Science, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

Distillation

100cm^3 of the crude was distilled using this D86 distillation equipment (Model No. 747651) at the analytical services laboratory of NNPC, Port Harcourt. The fraction boiling below 260^{0}c was distilled off, leaving 50cm^3 of the HO rich residue.

Precipitation

Precipitation was achieved using a modified ASTM D6560 method (ASTM, 2000). 5cm^3 (i.e. 4.125g) of the crude's residue was added (with stirring) to 120cm^3 of pentane, hexane, heptanes solvents respectively, representing a ratio of approximately 1.0g of sample to 30cm^3 of solvent. The mixture were centrifuged for 30min and allowed to stand for 48hrs before filtration. The HO ppt contained in the filter papers were dried in the oven at 60^{0}c for 30min to prevent excessive oxidation and weighed.

RESULTS

The weight percent of heavy organics precipitated by the various solvents are presented in the tables below.

Table 1: Heavy Organics Precipitated Using Different, N-Alkane Solvents.

Test	n-Pentane (wt.%)	n-Hexane (wt. %)	n-Heptane (wt.)
1	8.45	7.30	6.15
2	8.76	7.40	6.50
3	8.82	7.69	6.11
Mean	8.68±0.1	7.46±0.1	6.25±0.1

Table 2: Reprecipitated n-C_5-HO after Dissolution in n-C_6 solvent.

Test	Wt. of n-C_5 HO in n-C_6 solvent	Wt. of HO Reprecipitated (g)	Wt. % of Reprecipitated HO ppt.
1.	0.3509	0.0256	4.79
2.	.5341	0.0198	5.64
3.	0.4671	0.0301	6.44
Average			**5.62±0.1**

Table 3: Reprecipitated n-C_6 HO (wt.%) after dissolution in n-C_7

Test	Wt of dissolved (g) n-C_6 HO in n—C_7 solvent	Wt of HO Reprecipitated (g)	Wt % of Reprecipitated HO ppt
1.	0.5110	0.0224	4.38
2.	0.4932	0.0254	5.15
3.	0.4056	0.0164	4.04
Average			**4.52±0.1**

Table 4: Reprecipitated n-C_6 HO (wt. %) after Stirring in n - C_5 solvent.

Test	Wt of n-C_6 HO stirred in n-C_5 solvent (g)	Wt. of un-dissolved HO (g)	Wt. % of un-dissolved HO
1	0.42 19	0.4030	95.52
2	0.3521	0.3251	92.33
3	0.05821	0.5542	95.21

Average **94.35±0.1**

Table 5: Re-precipitated (n-C_7) HO (wt.%) after Stirring in n-C_6 solvent.

Test	Wt of n—C_7 HO stirred in n-C_5 solvent (g)	Wt. of un-dissolved HO in (g)	Wt. % of un-dissolved HO
1	o.2863	0.2750	96.05
2	0.3430	0.3294	96.04
3	0.5125	0.4972	97.02

Average **96.37±0.1**

The error margin of 90% confidence interval of the results was determined using the formula and the values given below:

$$\overline{X} \pm \frac{ts}{\sqrt{n}},$$

where $\bar{X}$ = mean

t = student's test value, which for three measurements is given as

2.920.

s = 0.069 (absolute)

n = 3, i.e. n-i =2

It has been suggested that such properties as compound types present in the ppt, carbon-chain lengths, colour, textures, hardness of ppt, the units (monomers) and their quantities that associate at precipitation will vary (Chandra et al. 2006). Whether the variable that determines the quantity of ppt in different solvents is the solubility of the monomers or their quantities that aggregate in each solvent cannot be ascertained from these experiments.

However, if monomer types and solubilities are responsible for the variation, then a range in the components present in a ppt will be observed as shown in scheme 1 below. The scheme notes a small band where co-precipitation may occur but the results obtained herein shows that this is only a small fraction (about 2-3% of total).

n-C_5 soluble	n-C_5 insoluble
n-C_6 S	n-C_6 insolubles
n-C_7 S	n-C_7 insolubles
n-C_8 S	n-C_8 insolubles

Fig. 1: Range of soluble and insoluble fractions of Crude Oil in liquid n-alkane solvents.

This proposed schematic illustration suggests that this could be used in solvent fractionation of crude oil residue.

Extrapolating the above result to the use of liquefied n-alkane gas, for instance liquid propane, the scheme will be as shown.

n-C_1 S	n-C_1 insolubles
n-C_2 S	n-C_2 insolubles
n-C_3 S	n-C_3 insolubles

Fig. 2: Range of soluble and insoluble fractions of crude oil in liquid n-alkane gases.

Liquefied n-propane and n-butane are currently used in refining for deasphalting vacuum residue to obtain bright stock oil as liquid (soluble) and asphalt as residue, bitumen (insoluble). (Ayer et al. 1959, Bristow et al. 1986). By this scheme, this asphalt residue should yield some fractions soluble in n-pentane, n-hexane, etc. Similar results will be obtained, if liquid methane and ethane are used for fractionation.

The properties of the various fractions will be of interest and suitable for further work. This is likely because some authors who have characterized asphaltenes obtained from different methods inferred that asphaltene composition varies continuously with no dramatic change in the composition from fraction to fraction (Kharrat, 2009, Zhao and Shaw, 2007, Yang et al. 2004, Nalwaya et al. 1999).

DISCUSSION

The results of the weight percent of the heavy organics precipitated by the n-alkane solvents, namely: pentane, hexane and heptane are presented in tabIe 1. It is observed, that the quantity of HO precipitate obtained decreased with increase in the carbon chain-length of the precipitating n-alkane soIvent. This is an already established fact, which has been reported by other investigators. (Gonzales et al. 2004, Galeana et al. 2004, Kokal et al. 1995, Rassamdana,1996).

The results of the dissolution of a lower molecular weight n-alkane, n-C_5 HO ppt by a higher molecular weight n-alkane, n- C_6 solvent are presented in Table 2. It was observed that virtually all the n-C_5 HO were dissolved in the n-C_6 solvent, although 5% of it reprecipitated on standing. This is not unexpected as asphaltene (Ho) precipitation decreases with increase in molecular weight of the precipitating solvent. This implies that most of the HO which precipitated in n-C_5 solvent are soluble and will not precipitate in n-C_6 solvent.

5% of the n-C_5 HO ppt that re-precipitated indicates the presence of n-C_6 and possibly n-C_7

insoluble in the C_5 ppt. It is known that asphaltenes are of variable molecular weights because of the tendency of the asphaltene constituents to associate even in dilute solution in non-polar solvents. (Speight, 2004). Hence the nature and number of component units which associated may be different for different solvents.

The results in table 3, again- reaffirm the established fact that asphaltene precipitation decreases with increase in the molecular weight of the precipitating solvent.(Gonzales et al, 2004). Hence only about 4% of the n-C_6 HO reprecipitated from n-C_7 solvent.

It is therefore possible that the n-C_6 HO ppt contains n-C_7 ppt as well as n-C_8 and n->C_8 precipitates.

From the results presented in table 4, it may be observed that over 93% of the n-C_6 ppt was insoluble in the n-C_5 solvent. This confirms that the components of HO insoluble in a higher carbon number solvent will not dissolve in a lower carbon number solvent.

The results contained in table 5 clearly show that about 96% of the C7 ppt is essentially insoluble in the n-C_6 solvent, a further confirmation of the trend that HO insoluble in higher carbon number solvent will be insoluble in lower carbon number solvent.

While 7% n-C_6 ppt and 4% n-C_7 ppt were un-dissolved. These could be co-precipitated n-C_5 and n-C_6 soluble resins in n-C_6 and n-C_7 precipitates respectively as a result of the tendency of asphaltenes to associate.

CONCLUSION

i. Heavy organic precipitation decreases with increase in carbon-chain length of the precipitating solvent
ii. Reprecipitation of heavy organics does occur
iii. Dissolution, precipitation, and reprecipitation decreases with increase in carbon-chain length of the precipitating solvent. This is in consequence with the already observed trend in the precipitation of n-alkane series of solvents. It may be inferred from these results that each precipitated HO may consist of different compounds or the same compounds in different ratios.

The consequence of these findings is confirmed by differences observed in the precipitation and dissolution of the HO precipitates in the solvents. Also given that the physical properties of asphaltenes are sensitive to the extraction method/solvents used for separation since the amount and exact chemical composition of extracted asphaltene will vary with the different procedures, e.g. n-C7 asphaltene are more aromatic i.e. H/C atomic ratio of n-C7 asphaltene is lower compared to n-C5 asphaltene. (Ancheyta et al. 2002).

REFERNCES

Chandra W.A, Yicheng L., Hassan H.L (2006): Precipitation of Asphaltenes from solvent-diluted heavy oil and thermodynamic properties of solvent-diluted heavy oil solution. *Fuel*, vol. 85, issue 4, pg. 492-506.

NTNU(2000): Investigation of Asphaltene Precipitation, Nowegian University of Science and Technology (NTNU).

Ancheyta J., Centerio G., Trejo F., Marroqun G., Garca J.A, Tenorio E., Torres A. (2002): Extraction and characterization of Asphaltenes from different crude oils and solvent. "*Energy fuels* 16 (5), 1121-1127, 2002.

Ofodile, S. E and Nwachukwu, I. R (2007): Precipitation of Asphaltene from crude oil by non-alkane solvents, unpublished M.Sc.

Scientia Africana, Vol. 11 (No.2), December 2012. Pp 108-114
© Faculty of Science, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

thesis in the Department of Pure and Industrial Chemistry, Uniport, Nigeria.

Kharrat A.M. (2010): DBR Technology Centre, Schlumberger, Edmonton, Canada, Personal communication, 2010.

Yang X., Hamza H., Czarnecki J. (2004): Investigation of sub-fractions of Athabasca Asphaltenes and their role in emulsion stability. *Energy fuels*, 18(3), 770-777.

Yarranton H.W, (2005): Asphaltene Self-association, *J. Disp. Sci Tech.* 26(1), 5-8.

Zhao B. and Shaw J.M. (2007): Composition and size distribution of coherent nanostructures in Athabasca Bitumen and Maya Crude oil. *Energy Fuels*, 21(5), 2795-2804.

Nalwaya V., Tangtayakom V., Piumsomboon P., Fogler S. (1999): Studies of Asphaltenes through Analysis of Polar Fraction. *Ind. Eng. Chem. Res.* 38(3), 964-972.

Shkalikov, N.V., Ganeeva, Y.M., Yusupova, T.N. and Skirda, V.O.(2008): Magnetic Resonance in Solids. *Electronic Journal*, Vol.10,No.1, pp. 11-19.

Asok Kumar Tharanivagan (2012): Asphaltene Precipitation from crude oil blend, Conventional oils and oils with Emulsified water .Phd Thesis in department of Chemical and Petroleum Engineering University of Calgary, Alberta.

Ayers G.W and Krewer W.A, (1959): A method of preparing natural oils. US Patent 2,878,181.

Bristow D. J., Achia, Lawrence J.E, Bright G. (1986): Process for increasing bright stock raffinate oil production. US Patent 4,592, 832.

Gonzalez E. B. Galeana C. L. Villegas A. G. and Wu. J. (2004) Asphaltene Precipitation in Crude Oil: Theory and Experiments. *Alche J.* 50: (10) 2552-2570.

Kokal, S. L., A1-Ghamdi, A., Krinis D, and Saudi Aramco Source,(2008): Asphaltene Precipitation in High Gas-Oil Ratio Wells, Middle East Oil show 9-12 June 2008, Bahrain.

Mansoori G. A. (1996) Asphaltene, Resin and Wax Deposition from Petroleum Fluids, the *Arabian Journal for Science and Engineering* 21, no. 48, 707.

Rassamandana, H., and Sahimi m., (1996). Asphaltene Flocculation and Deposition: Onset of Precipitation, *Alche, J.* 42, 3318.

Speight J. G. (2004). Petroleum Asphaltenes part 1, Asphaltenes, Resins and the Structure of Petroleum, Oil & Gas Sc. and Tech. 59 (5), 467-477, USA.

Standard Test Method for Determination of Asphaltene in Crude Petroleum and Petroleum Products. D6560, (2000), ASTM, International, West Cônshohocken, United States.

SPE (2010): Asphaltene studies on-shape Abu Dhabi oil field, Part II: Investigation and Mitigation of Asphaltene Deposition- A case study, SPE conference paper.