IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 10, Issue 4 Ver. I (April. 2017), PP 22-25
www.iosrjournals.org

Investigation of Heavy Organics Precipitation from Nigerian Crude Oil Residue Using Single n-Alkane Solvents

Anuchi S.O.[1] and Chukwu U.J.[1]*
Department of Pure and Industrial Chemistry, University of Port Harcourt, Nigeria

Abstract: *This work investigated the effect of some individual n-alkanes (n-hexane, n-octane, n-decane, n-dodecane, n-tetradecane, and n-hexadecane) on the precipitation of heavy organics (asphaltenes) from crude oil. The crude oil residue sample was sourced from the National Petroleum Corporation (NNPC), Research and Development Division, Port Harcourt, Nigeria. The sample was distilled and approximately 1.0 g was used for precipitation of heavy organics with about 20 mL of the respective n-alkane solvents in three replicates. Quantitative results showed that n-hexadecane (C_{16}) recorded the highest percentage yield (15.40±1.18 %) of heavy organic precipitated from the crude oil, while n-decane (C_{10}) recorded the least percentage yield (1.02±0.18 %). Therefore, an estimated value of 0.45 % for n-undecane (C_{11}) was obtained by extrapolation. The study has shown that heavy organics precipitation decreases with increasing carbon number of n-alkane to a minimum value at C_{11} and starts increasing from C_{12} to C_{16}. Thus, C_{12} and C_{14} show the same property as C_{16} in the precipitation of heavy organics from crude oil.*
(Keywords: *Heavy organics, precipitates, crude oil residue, m-alkane solvents.)*

I. Introduction

The oil and gas industry has recently cut down the costs of operation or production, which is majorly due to the recent fall in crude oil price. This has led to reduction of operational cost in the midstream sector, mainly involving the transportation and storage of crude oil and petroleum products (Toews and Naumov 2015). However, survey of oilfield experiences shows that heavy organic deposition problem results to increase cost of production and transportation in oil industry world-wide (Escobedo and Mansoori 1997). This oilfield problem has affected production facilities such as oil wells, storage vessels, and transportation pipelines (Maqbool, 2011).

Heavy organics (HOs) are the known heavy components of crude oil which are specifically known as SARA-fraction. The fractional components include S=saturates, A=aromatics, R=resins, and A=asphaltenes. These components have different polarity and solubility, which are important for their separation from crude oil. Apparently, heavy organic compounds are quite miscible with the light components of crude oil forming distinct compositional phase under reservoir conditions (Mansoori 2007). However, when variations in physical properties such as temperature, pressure or composition set in, corresponding alterations in the single phase observed in the crude oil, result to aggregation, flocculation and precipitation of the heavy organics out of crude oil, which lead to deposition and blockage of oil wells, transfer pipelines, and processing equipment thus, reducing oil productivity (Kawanaka *et al*. 1991; Escobedo and Mansoori 1997). One major effect of such alteration is the precipitation, flocculation and deposition of HOs (asphaltenes, wax, diamondoids, etc.) in oil well (Branco *et al.* 2001; Mousavi-Dehghani *et al.* 2004; Mansoori *et al.* 2007).

Over some decades, several research works have been carried out to study the causes of the deposition, mechanisms, nature, and behavior of HOs under various operating conditions in order to proffer a solution to the problem of HOs deposition. One of such efforts in recent years is the precipitation of HOs in crude oil in the laboratory using single n-alkane solvents, which would give a better understanding of the deposition phenomena, predict correctly the onset of organic deposition and hence help to avoid getting to the region (Mansoori *et al.* 2007). For example, Kokal *et al*. (1992) studied the precipitation of asphaltenes from two Canadian heavy oils by titration with various n-alkanes (n-pentane to n-decane). They observed a decrease in the amount of asphaltenes precipitated at very high dilution ratios, which can be attributed to a partial re-dissolution of asphaltenes in the organic solvent. The precipitations of HOs from two Mexican crude oils by onset titration with n-alkane solvents were carried out by Eduardo *et al*. (2004). While, Chukwu *et al.* (2011) compared the quantity of HOs precipitated from Nigerian Antan crude oil residue by two slightly polar solvents (ethyl acetate and butanone) and non-polar n-alkane solvents. In addition, Udourioh *et al*. (2014) investigated the precipitation of HOs using three single n-alkane solvents, which includes n-pentane, n-hexane, and n-heptane organic solvents. They concluded that the amount of HOs precipitated decreases as the carbon number of the n-alkane increases (C_5 to C_7).

From all the above studies reported, the choice of organic solvents (e.g., n-alkanes) is an important factor that determines the extent or the amount of precipitation of heavy organics from crude oil. Some of these n-alkane solvents with their molecular formulas include n-pentane (C_5H_{12}), n-hexane (C_6H_{14}), n-heptane (C_7H_{16}), n-octane (C_8H_{18}), n-decane ($C_{10}H_{22}$), n-undecane ($C_{11}H_{24}$), n-dodecane ($C_{12}H_{26}$), n-tetradecane ($C_{14}H_{30}$), n-hexadecane ($C_{16}H_{34}$). In addition, the amount of HOs (e.g., asphaltenes) decreases with increasing carbon number of the n-alkane solvents have been reported by many authors. However, Hotier and Robin (1983) found that the volume of n-alkane at the onset of asphaltene precipitation of a crude oil with increasing carbon number of the n-paraffin reaches a maximum at a carbon number of 7 (n-heptane). Whereas, Wiehe *et al* (2004) arrived at carbon number 10 (n-decane) maximum as presented in Figure 1.

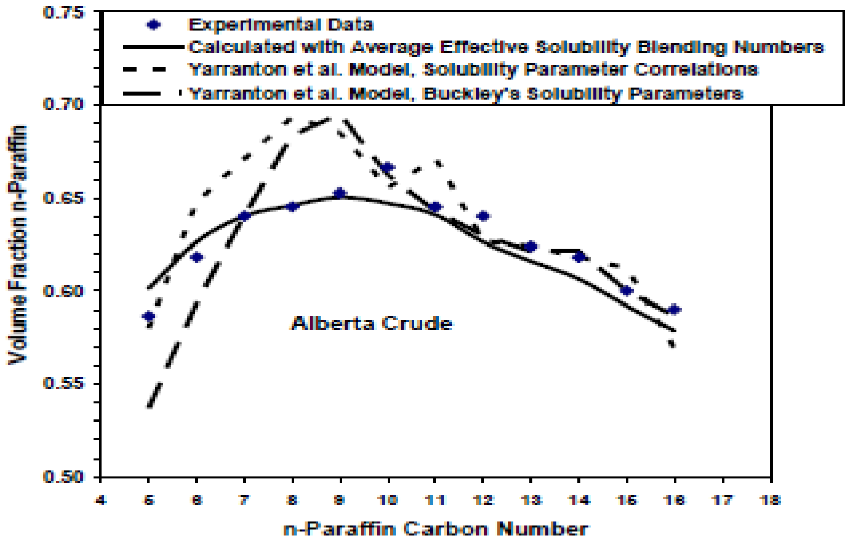

Figure 1: Volume fraction of n-paraffin at the onset of asphaltene precipitation for Alberta Crude (Wiehe *et al.*, 2004).

Figure 1 suggests that n-alkanes with carbon number (> 10) can be poorer solvents for petroleum HOs (asphaltenes) than lower-carbon number n-alkanes, even though the solubility parameters of n-alkanes increase continuously with increasing carbon number (Hansen, 1971). This was observed with C_{16} n-alkane at high n-paraffin/oil volume ratios and was referred to as the paradox of asphaltene precipitation with n-paraffins (Speight, 1999). Tobrise *et al.* (2016) showed that when the number of carbon atoms increase, the percentage weight of the precipitate tends to decrease up to C_{10} indicating increasing solubility, but a sharp increase was obtained with C_{12} to C_{16}. Consequently, crude oils contain n-alkanes C_1 to C_{30} of which C_1 to C_4 are gases at room temperature and atmospheric pressure, C_5 to C_{11} are liquids while others are solids. Under reservoir conditions all these exist in one liquid phase. Hence, n-alkanes C_1 to C_{18} could participate in the precipitation process as precipitants. The aim of this work is to determine the position of n-hexane, n-octane, n-decane, n-dodecane, n-tetradecane, and n-hexadecane in the insolubility (precipitation) curve of heavy organics precipitation from crude oil.

II. Experimental

An atmospheric distilled Nigerian crude oil blend residue was sourced from the National Petroleum Corporation (NNPC), Research and Development Division, Port Harcourt, Rivers. The organic solvents used include analar grade of n-hexane (BDH VWR Analytical, USA), n-octane (Sigma Aldrich, UK), n-decane (Sigma Aldrich, UK), n-dodecane (Alfa Aesar, Germany), n-tetradecane (Sigma Aldrich, UK), and n-hexadecane (Alfa Aesar, German). The single and binary solvent precipitation experiments were each carried out in three replicates according to the method described by Kokal *et al*., (1992) and Eduardo *et al*., (2004) and modified ASTM/IP (American Standard Test Method/Institute of Petroleum) methods. A 20ml of the single n-alkane solvents was added to approximately 1g of oil each in an appropriate flask. The mixtures were agitated for 30mins using mechanical shaker. It was allowed to stand for 48hours. 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 a vacuum oven at 0.1bar (gauge pressure) and 333K over 2hours. It was finally weighed to determine the heavy organic mass precipitate. The weight percent of HOs precipitated from the crude oil sample can be calculated by:

$$\text{Weight } \% = \frac{\text{weight of HO precipitate in mg/L}}{\text{weight of residue in mg/L}} \times \frac{100}{1} \quad [1]$$

III. Results and Discussion

The result of the experiments for single n-alkane (C_6, C_8, C_{10}, C_{12}, C_{14}, C_{16}) precipitation of HOs from about 1.0 g of crude oil residue at room temperature and atmospheric pressure is presented in Figure 2.

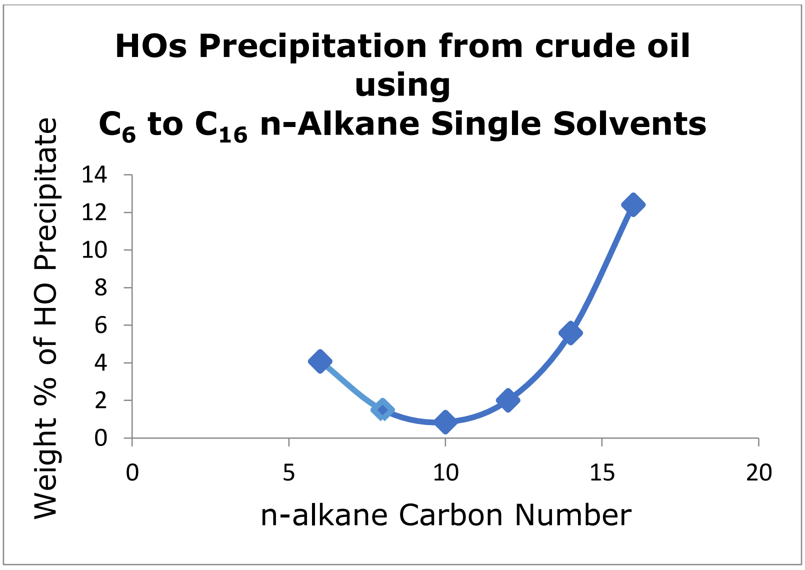

Figure 2: Plot of weight % of HO precipitated against carbon number for single n-alkane precipitants**.**

The HOs precipitation using single n-alkanes (C_6, C_8, C_{10}, C_{12}, C_{14}, C_{16}) for 20mls/g total solvent volume (Figure 2) recorded its highest weight percentage yield of precipitate by C_{16} (n-hexadecane) and least weight percentage precipitate for C_{10} (n-decane). The HOs obtained in this work may be a mixture of co-precipitating species similar to what is obtained in the oilfield.

In comparison to the results found by Wiehe *et al*. (2004), which concluded that the volume of n-alkane at the flocculation point, which is the point of incipient asphaltene precipitation, increases as the n-paraffin carbon number increases, reaching a maximum at a carbon number of 9 or 10, and then decrease (Figure 1). In other words, their conclusion summarizes that with the increase in carbon number of n-paraffin, the asphaltene precipitation of a crude oil reaches a minimum at a carbon number 9 or 10 based on the percentage weight of asphaltene precipitated and then increases.

However, it was observed in this research that the weight percentage yield of HOs decreases from C_6 to C_{11} (estimated value of 0.45%) and then increases beginning at C_{12}. Thus, this work found that with the increase in carbon number of n-alkanes (from C_6 to C_{16}), the HOs precipitation of crude oil reaches a minimum at carbon number 11 with an estimated value of 0.45 weight percent. Then a rise in percentage weight of precipitate is observed from C_{12} and C_{14} to C_{16}, which makes the curve of weight % against n-alkane carbon number a parabola with minima at (0.45) for C_{11} (Figure 2). This curve is similar in shape but inverse of the curve for the volume fraction of n-paraffin at the onset asphaltene precipitation of a crude oil by Wiehe *et al.* (2004) (Figure 1). Consequently, a new concept to divide the range of n-alkane solvents into four major groups of HOs precipitants based on their precipitating power represented as p-factor. The p-factor is defined by the equation:

$$\frac{\text{weight \% of HOs ppt by an n - alkane}}{\text{weight \% of HOs ppt by an n - alkane}} \quad [2]$$

Where C_{11} is assumed to produce the lowest quantity of HOs precipitate.

Assigning C_{11} a p-factor of 1, the values for other n-alkanes used in this work are as follows: $C_6 \geq 10$, $C_8 \geq 3$, $C_{10} \geq 2$, $C_{12} \geq 4$, $C_{14} \geq 16$ and $C_{16} \geq 34$. This result leads to classification of n-alkane precipitants according to their precipitating ability/reverse of solubility properties. This classification is presented in Table 2.

Table 2: precipitating properties versus solubility properties

Group	precipitating properties/ solubility properties for HOs	Factors
C_1 to C_4	Gases at room temperature and pressure.	Not determined
C_5 to C_8	moderate precipitate/ moderate solubility	$\geq 3 \leq 10$
C_9 to C_{11}	Low precipitate/ high solubility	$\geq 1 \leq 2$
C_{12} to C_{16}	High precipitate/ low solubility	$\geq 4 \leq 34$

IV. Conclusion

The trend of precipitation by single n-alkane solvent which shows corresponding decrease in the quantity of precipitate is extended to a minimum at carbon number 11 (C_{11}) in this work. The heavier molecular weight n-alkanes: C_{12}, C_{14} and C_{16} follow a trend of increasing heavy organic precipitation from crude oils. Hence, the assignment of precipitating factors to n-alkane precipitants as defined therein.

Referencies

[1]. Branco, V.A.M., Mansoori, G.A., De Almeida, XavierL.C., Park, S.J., Manafi, H. (2001). Asphaltene flocculation and collapse from petroleum fluids, *J. Petrol. Sci. & Eng.*, Vol. 32, pp.217–230.

[2]. Chukwu, O. C., Ofodile, S.E., Okoye, I.P. (2011). The Effect of Different Solvent Polarity on the Precipitation of Heavy Organics from a crude oil deposit in the Niger Delta. *Scientia Africana,* vol. 10 (No.2) pp9-15. P.

[3]. Eduardo, B.G., Carlos, L.G., Alejandro, G.V., Jianzhong, Wu (2004). Asphaltene Precipitation in Crude Oils: Theory and Experiments. *Journal of AIChE,* Vol. 50, No. 10 pp 2552-2570.

[4]. Escobedo, J., Mansoori, G.A. (1997). Viscometric principles of onsets of colloidalasphaltene flocculation in paraffinic oils and asphaltene micellization in aromatics, *SPE Prod. Facil.*, May, pp.116–122.

[5]. Hotier, G. and Robin, M. (1983): *Rev. Inst. Fr. Pet,* pp 38, 101-110.

[6]. Kawanaka, S., Park, S.J., Mansoori, G.A., 1991. Organic deposition from reservoir fluids. SPE Reservoir Eng., 185–192, May.

[7]. Kokal, S.C., Nayman, J., Sayeh, S.G. and George, A.E., 1992. Measurement and Correlation of Ashphaltene Precipitation from Heavy Oils by Gas Injection. Journal of Canadian Petroleum Technology, 31, 24. http://dx.doi.org/10.2118/92-04-01

[8]. Maqbool, T. (2011). Understanding the kinetics of asphaltene precipitation from crude oils. ProQuest Dissertations and Theses.

[9]. Mansoori, G.A. (2007) "Diamondoid Molecules", *in Advances in Chemical Physics,* Vol.136, pp 207-258.

[10]. Mansoori, G.A., George,T.F., Zhang, G., Assoufid, L. (2007a). *Molecular Building Blocks for Nanotechnology: From Diamondoids to Nanoscale Materials and Applications*, Topics in Applied Physics109, Springer, New York.

[11]. Mansoori, G.A., Vazquez, D., Shariaty-Niassar, M. (2007b). Polydispersity of heavy organics in crude oils and their role in oil well fouling, *J.Petrol. Sci. and Eng'g*, September, Vol. 58, Nos. 3–4, pp.375–390.

[12]. Mousavi-Dehghani, S.A., Riazi, M.R., Vafaie-Sefti, M. and Mansoori, G.A. An analysis of methods for determination of onsets of asphaltene phase separations, J. Petrol. Sci. & Eng., 42 (2-4): 145-156, 2004.

[13]. Mullins OC, Sheu EY, Hammami A, Marshall AG (2006). *Asphaltenes, Heavy Oils, and Petroleomics*, Springer

[14]. Tobrise, O.O ;Ofodile, S.E ;Osu, C. and Achugasim, O. 2016. Comparative Evaluation of Asphaltene Precipitation from Nigerian Crude Oil Residue Using Intermediate and Long Chain Single and Binary N-Alkane Solvent Mixtures. IOSR Journal of Applied Chemistry (IOSR-JAC) Volume 9, Issue 5 Ver. I, PP 82-86

[15]. Toews G. and Naumov. A., 2015. The Relationship Between Oil Price and Costs in the Oil and Gas Industry. *OxCarre Research*. 152, 1-23.

[16]. Udourioh, G., Ibezim-Ezeani, M. I. and Ofodile, S.E. (2014). Comparative Investigation of Heavy Organics Precipitation from Crude Oil Using Binary Mixtures and Single n-Alkane Organic Solvents. *Journal of Petroleum and Gas Exploration Research.*Vol. 4(4) pp. 53-59.

[17]. Wiehe, I. A., Yarranton, H. W., Akbarzadeh, K., Rahimi, P. M. and Teclemariam, A. (2004) "The Paradox of Asphaltene Precipitation with Normal Paraffins". *Energy & Fuels*, 19, pp. 1261-1267.