Resins In The Heavy Organics Precipitate From Crude Oil With Single N-Alkane And Binary Mixture N-Alkane Solvents

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ABSTRACT: Heavy organics from crude oil was precipitated using single n-alkane and binary mixtures of n-alkane solvent of varying ratios. Precipitation can occur due to changes in composition, temperature or pressure during crude oil production and transportation. The heavy organics Precipitates were studied and fractionated using column chromatography to separate them into different components. The focus of this research is to determine the resin content of the solid precipitate from the various ratios of the different binary mixtures using uv-visible spectroscopy. The results obtained showed increase in the absorbance of the resin content with decreasing carbon numbers for both single nC_5, nC_6, nC_7 and binary mixtures (3:1) of nC_5: nC_6, (3:1) of nC_5:$nC_7$and (3:1) of nC_6: nC_7.

KEYWORDS: Absorbance,Binary mixture,Heavy organics, n-alkane, Resin.

INTRODUCTION

Mechanical and chemical cleaning methods are employed to maintain production, transportation and processing of petroleum at or close to economical level. Due to various factors, precipitation, flocculation and deposition of heavy organicsoccur. The major interest in the oil industry is when and how much heavy organics will precipitate, flocculate and deposit under operating conditions. Laboratory and field data have proven that heavy organic substances in the oil consist of particles with molecular weights from one thousands to several hundred thousand [1],[2]. Crude oil at atmospheric pressure and ambient temperature contains three main fractions mainly oils (saturate and aromatic), resin and asphaltenes [3]. Resins are fractions soluble in light alkanes like pentane and heptane but insoluble in liquid propane [6], [7], [8]. Resins are fraction of deasphalted oil that is strongly adsorbed in surface-active materials such as fuller's earth, alumina or silica and can only be desorbed by a solvent such as pyridine or a mixture of toluene and methanol. They have several functional groups including ketones, acid, ester, hydroxyl, nitrogen and sulfur-oxygen. Resins are a solubility classthat overlap both to the aromatic and asphaltene fraction and little work has been reported on its characteristics compared to aspaltenes. Since asphaltene and resin form the most polar fraction of crude oil, resin have a strong tendency to associate with asphaltene and such association determines to a large extent their solubility in crude oil [2], [9], [10]. They are the very aromatic component and their structure is not well defined. They are polar, polynuclear molecules consisting of condensed aromatic rings, aliphatic side chains and few heteroatoms. Asphaltenes are fractions separated from crude oil or petroleum products upon addition of light hydrocarbon solvent such as n-heptane.

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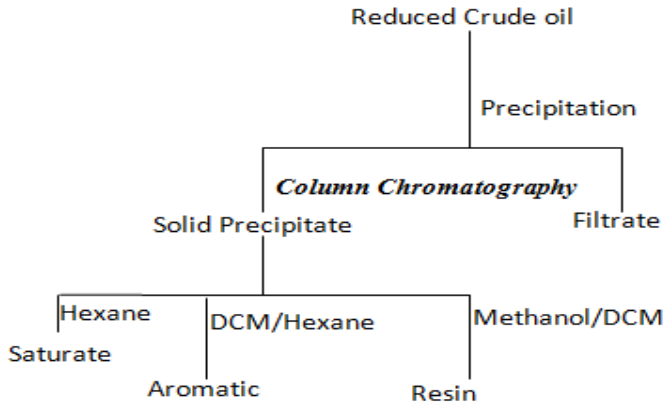
They are solid particles which are suspended colloidally in crude oil and are stabilized by large resin molecules. Asphaltene precipitation is a complex phenomenon that involves asphaltene and resins. [1], [6] .During production of crude, water/ oil emulsions are formed. They are stabilized by asphaltenes and resins which are colloidally dispersed in the crude oil [4]. Resins are one of the crude oil constituents that have impact on petroleum refining operation. Crude oil stability is dependent upon the molecular relationships of asphaltene and resin constituents and the balance with the other constituents of petroleum [5]. Since crude oil is a continuum of several thousands of molecules, it is very difficult todefine a cut off between asphaltene, resin and oils. The variables introduced in each method may generate different fractions of asphaltene with different methods. Like asphaltene, resins are defined according to the solvents used for their separation. In chromatograghic elution, discrepancies in the amount and chemical composition can be found if adsorbents are different or elution time is varied [11]. Direct current (DC) conductivity studies showed that resins are unlikely to coat asphaltene nanoaggreagates in anhydrous organic solvents and Nellensteyan hypothetical model of resin adsorbed on asphaltenes to provide a steric stabilizing layer is not valid [12]. However the roles of resin on asphaltene adsorption at the solvent/ water interface becomes important when in the presence of water or a solvent, thus providing resin and natural surfactants to diffuse first to the interface before being replaced by asphaltene [13]. The amount of adsorbed asphaltene on water equally depends on the resin to asphaltene ratio [3], [14]. The molecular weight distribution of nC_5,nC_7 and nC_9asphaltene fraction was reported with expectation of three different molecular weight distribution of asphaltene. The molecular weight distributions will depend on the level of interactions among asphaltene, resin and co-precipitated high molecular weight paraffin. When n-pentane was used high molecular weight paraffin co-precipitated with the asphaltene and resin. The resin contents of the precipitate for different precipitating solvents increases as the number of carbon atoms in the precipitating solvent decreases [15]. The fact that asphaltenes, resins, diamondoids, waxes or high molecular weight paraffin etc can be precipitated makes it safer to refer to the precipitate simply as heavy organics precipitate.

It becomes expedient to show if this heavy organic precipitate which consist of mainly asphaltenes also contains some percentage of resin using single n-alkane and binary n-alkane mixtures. The contributions by the different compound types to this variation had never been studied. The aim of this research therefore is to determine the resin content of the precipitate obtained from both single n-alkane and binary mixtures of n-alkanes solvents at various ratios.

METHODOLOGY

Crude oil used for this research was obtained from NNPC research and development laboratory, Port Harcourt, Rivers State, Nigeria. The reduced crude oil was obtained by removing the distillate at 260^{0}C using atmospheric distillation. Precipitation of heavy organics was carried out using both the single n-alkane and binary n-alkane mixtures of different ratios. 30mlof each of the single solvents (pentane, hexane and heptane) and 30ml of each of the binary mixtures (C_5:C_6, C_5:C_7 and C_6:C_7) of varying ratios were added to 1g of the oil in the appropriate flasks. The mixtures were mechanically shaken for 30minutes and kept for 48hrs before filtration. Each of the solutions obtained after precipitation was filtered using vacuum filtration system with 0.45nm membrane filter to separate the solid precipitate from the filtrate. The solid precipitate was dried in an oven, weighed and kept in a dessicator for further analysis. Solid precipitates obtained from the precipitation process using single n-alkane and binary n-alkane mixtures of were removed from the membrane filter using tetrachloroethylene and kept in their appropriate flask. 0.5g of the precipitate was dissolved in tetrachloroethylene and introduced into a column packed with silica gel with a syringe, for saturate, aromatic, resin and asphaltene (SARA) analysis, affording different fractions from the column. The saturate (aliphatic) fraction was eluted with 50ml hexane, while 70ml of 1:1 dichloromethane/ hexane was used for the elution of the aromatic fraction. A mixture of (1:2, 60ml) of methanol/dichromethane was used to elute the resin. Elution of the different fractions was monitored using a uv-visible spectroscope. The resin fraction was scanned at several wave lengths using uv-visible spectroscope and absorption at 450nm was selected. Each of the fractions of resin obtained from the SARA analysis was measured. The scheme below summaries the methods adopted for this work.



Scheme 1: *Chromatographic separation of n-alkane Precipitate from Crude Oil.*

RESULT AND DISCUSSION

The results obtained are shown in table 1 and the figures below

TABLE 1: *Absorbance of Resin from Heavy Organics Precipitation using different mixtures of n-alkanes Solvent*

	PRECIPITANTS		
Vol.Ratio	C_5&C_6	C_5&C_7	C_6&C_7
0:1	1.567	0.324	0.324
1:0	2.17	2.17	1.567
1:1	2.041	1.796	1.008
1:2	2.041	0.644	0.35
2:1	2.116	0.825	0.551
1:3	2.089	0.711	0.373
3:1	2.117	2.082	1.42

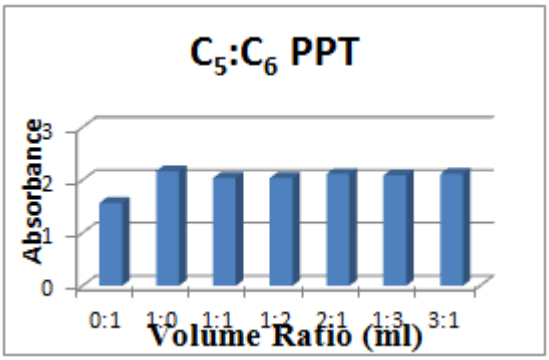


FIGURE 1: *Absorbances of Resin in Solid Precipitate from different Ratios of (C5:C6) Binary Mixtures of n-Alkane*

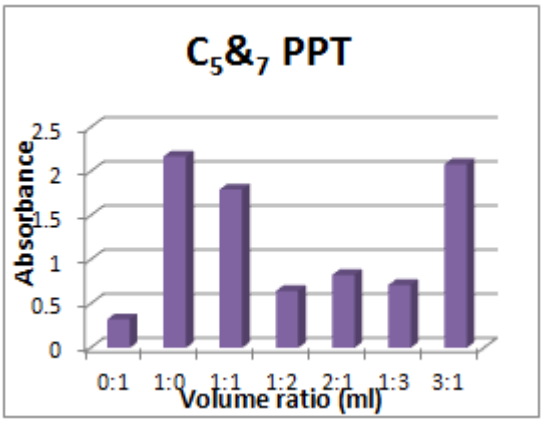


FIGURE 2: *Absorbance of Resin in Solid Precipitate from Varying Ratios of (C5:C7) Binary Mixtures of n-Alkane*

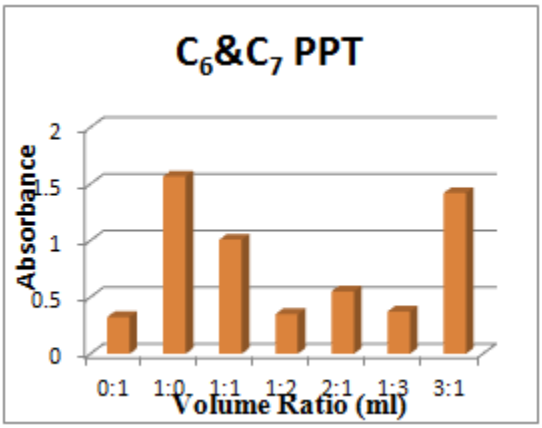


FIGURE 3: *Absorbance of Resin in Solid Precipitate from Varying Ratios of (C6:C7) Binary Mixtures of n-Alkane*

The results of the resin content of precipitates obtained with single n-alkane and binary n-alkane mixtures of various ratios are shown in figure 1, 2, 3 and table 1.The result shows that the highest absorbance (highest quantity) was recorded in single pentane (nC_5) solvent precipitate in figure1 followed by nC_6 in figure 3 while the least amount was observed in single n- heptane (nC_7) infigure 3. In figure 1, the result for the binary mixture (C_5:C_6) shows that the ratio with the higher volume of the lower carbon number recorded the highest amount of resin in the precipitates compared to lower volume of a higher carbon number. For the binary mixture of nC_5:nC_7 in figure 2 and that of nC_6:nC_7 in figure 3, the same trend of the result observed. From the above results, it was observed that the C_5:C_6 binary mixture recorded the highest absorbance (highest resin content) and the least absorbance was shown in C_6:C_7. The results for the resins in single solvent precipitates in figure 1, 2, 3 and table 1 equally follows the same trend observed with the single solvent precipitates in heavy organics. The result of this work supports a previous report that resin content in precipitates increases as the number of carbon in the precipitating solvent decreases [15]. It was equally observed that the precipitates obtained from heavy organic precipitation from crude oil using both single n-alkane and binary n-alkane mixture of various ratio showed increase in the precipitate with decreasing carbon numbers (16,17). It has been reported that the phase envelope of heavy organics precipitate with binary mixture with more of the lower carbon number recorded a larger envelopes compared to phase envelopes with higher carbon number and equally concluded that the phase envelope gives a qualitative evidence of the asphaltene and resin content of crude oil precipitates [18].

CONCLUSION

Total heavy organics precipitates consist of different compound type saturate, aromatic resin and asphaltene. Quantity of total heavy organics precipitate varies with the number of carbon atoms in the precipitating n-alkane solvent. Asphaltene content follow the same trend as the total heavy organic. From this research it has been proven that the resins in total heavy organics obtained from both single and binary mixture n-alkanes solvent of various ratios follows the same trend of increase in carbon number of solvent resulting in the decrease. in the amount of resin /asphaltene precipitated..

REFERENCES

[1] Ashoori S. Mechanisms of Asphaltene Deposition in Porous Media, A Thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, School of Engineering, University of Survey, (2005).

[2] Asok K. Tharanivasan Aspahaltene Precipitation from Crude Oil Blends, Conventional Oils and Oils with Emulisified Water, A Thesis submitted to the faculty of Graduate studies in partial fulfilment of the requirements for the degree of Doctor of Philosophy, Department of Chemical and Petroleum Engineering, Calgary, Alberta, (2012).

[3] Lamia Goual. Petroleum Asphaltene. University of Wyoming USA (www.intechnopen.com),(2012).

[4] P. C Schorling, D. G kessel and I Rahimian, Influence of the Crude Oil resin/ asphaltene ratio on the Stability of oil/ Water Emulsions,(1999).

[5] D. Mason Part 10: Resins and Polymers in Crude Oil Refining, (2016).

[6] J.G Speight, The Chemistry & Technology of Petroleum, Marcel Dekker, New York,(1999).

[7] E.Y. Sheuand O.C. Mullins, ''Asphaltenes: Fundamentals and Applications'', New York, Plenum Press,(1995).

[8] S.I Andersen and J.G Speight, Petroleum Resin: Separation, character and Role in Petroleum, Petroleum Science and Technology,19(1&2) pp 1-34, (2001).

[9] J.A Koots and J.G Speight, Relation of Petroleum Resins to Asphaltenes, Fuel. 54, 179, (1975).

[10] EduardoB.Gonzalez,CalosL.Galeana, Alejandro G. Villegas andJianzhong Wu, Asphaltene precipitate in crude oils. Theory and experiments. Al CHE journal, (2004).

[11] L. GoualandA. Firoozabadi, Asphaltenes and Resins Separated from Crude oils,(2002).

[12] F.J. Nellensteyn, The colloidal structure of Bitumen, in The Science of Petroleum, Vol. 4, 2760, Oxford University Press, London, UK,(1938).

[13] A. Mangual, G. Horvath- Szabo, J.H Masliyah, Acoustic and Electroacoustic Spectroscopy of Water –in-Diluted- Bitumen Emulsions. Langmuir, Vol. 21, No. 19, pp. 8649-8657, (2005).

[14] L. Goual, G.Horvath- Szabo, J.H MasliyahandZ. Xu, Adsorption of Bituminous Components at Oil – Water Interfaces Investigated by Quartz Crystal

Microbalance: Implications to the Stability of Water-in –Oil Emulsions. Langmuir, Vol. 21, No. 18, pp. 8278-8289, (2006).

[15] D. Vazquez and G.A Mansoori (2000). Identification and Measurement of Petroleum Precipitates. Journal of Petroleum Science and Engineering. **26**, 49-55, (2000).

[16] G. Udourioh; M. Ibezim-Ezeani; and S. Ofodile, 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 **4**(4) 53-59,(2014).

[17] G. Udourioh; M. Ibezim-Ezeani ; U. Millicent and S. Ofodile, The Effect of Compositional Changes of Binary Mixtures of n-alkane Solvents on the Precipitation of Heavy Organics from a Solution of Crude Oil Residue, (2015).

[18] M.C. Utin, S.E Ofodile, L.C. Osuji, G.I. Ndukwe and V.J. Aimikhe, Comparison of the Phase Changes of Binary Mixtures n-alkanes of Lower Carbon Numbers, Journal of Applied Chemistry (IOSR-JAC) Vol.9, Issue 9, pp132-137, (2016).