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THE EFFECT OF DIFFERENT SOLVENT POLARITY ON THE PRECIPITATION OF HEAVY ORGANICS FROM A CRUDE OIL DEPOSIT IN THE NIGER DELTA.

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ABSTRACT

The precipitation of heavy organics (Saturates, Aromatics, Resins and Asphaltenes) from the Niger delta (Atan crude oil residue) was studied. Two C_4 *organic polar solvents (ethyl acetate and butanone) were used to investigate the effect of polarity of the precipitating solvents. The heavy organics precipitated from Antan crude residue were 3.34% and 3.76% for ethyl acetate and butanone respectively. Asphaltenes were precipitated from the heavy organic precipitates using n-*C_5 *and n-*C_6 *alkanes. Chromatographic separation and spectroscopic analysis of the deasphalted soluble filtrate were carried out. The results identified the presence of saturates, aromatics and resins in the* C_4 *heavy organic precipitate.*

Key words: Heavy Organics, Precipitates, Saturates, Aromatics, Resins, Asphaltenes

INTRODUCTION

Crude oil is a naturally occurring flammable liquid consisting of a complex mixture of hydrocarbons and heteroatomic organic compounds of various molecular weights. It is found in geologic formations beneath the earth's surface (Hyne, 2001).

For petroleum fluids, composition and properties vary continuously from the simplest structures to macromolecules. The common problem consists then of identification of the discrete components of the crude, the definition of families or fractions of similar components and understanding the nature and role of interactions between various species. The heavy end is assumed to consist of four major fractions of similar species which are: saturates aromatics, resins and asphaltenes (SARA). At the condition of the original oil in the reservoir the light and heavy ends are mutually soluble forming one phase so long as certain conditions are maintained in the reservoir (Mansoori et al., 2006) Variations in temperature, pressure or composition may alter this balance and some of the species may segregate and form another liquid or solid phase. Once separated, the complex species may aggregate due to their large size differences, hydrogen bonding or polar group interactions and form larger particles, named flocs (or supramolecules). Flocs could precipitate out of the mixture as solid deposits which in many cases would plug wells, pipelines and processing equipment (Kawanaka et al., 1991).

In SARA, asphaltenes are removed by precipitation with a paraffinic solvent and deasphalted oil (DAO or maltenes) is separated into saturates, aromatics and resins (SAR) by silica gel chromatography.

Due to the complexity of heavy organics as well as limitations of analytical instruments, the nature of heavy organics (soluble and insoluble) in crude oil, is still not well understood. However, there is some information on the chemical composition of resins and asphaltenes, but little is known about the nature of aggregation process and solvent effects on their solubility, dispersion and their tendency to precipitate from crude oils, which are not well studied and documented. Therefore, butanone and ethyl acetate, two solvents of different polarity were used to investigate the soluble and insoluble heavy organics present in the crude oil. The result of this study would be specifically useful in understanding the behaviour of heavy organics in petroleum fluid.

MATERIALS

Experimental

The atmospheric residue from Atan crude oil used in this study was supplied by the Nigerian National Petroleum Corporation (NNPC), Research and Development Division, Port Harcourt.

METHODOLOGY

Precipitation of Heavy Organics Using C_4 Polar Solvents

Approximately 5g of the residue was added to 100cm^3 of ethyl acetate and butanone respectively. The mixtures were shaken vigorously in a mechanical shaker for 30min and allowed to stand for 48hr before filtration. After filtration, the precipitates contained in the filter paper were oven dried and weighed. The filtrates were concentrated and weighed prior to further precipitation in n-alkanes (n-C_6 and n-C_5).

Dissolution of Precipitates in n-C_6 Alkane

The solid precipitate was added to 15cm^3 of n-C_6 alkane (non-polar solvents). This was followed by vigorous shaking in a mechanical shaker for 30min, and the solution was allowed to stand for 48hr before filtration.

Dissolution of Filtrates in n-C_6 Alkane

The filtrates were evaporated and solid recovered in each case was added to 30cm^3 of n-C_6 alkane (non-polar solvents). The solution was vigorously shaken for 30min and allowed to stand for 48hr before filtration. After filtration, the precipitates contained in the filter papers were oven dried for 30min and weighed. The filtrates obtained (maltenes) were concentrated for SARA (saturates, aromatics, resins and asphaltenes) analysis and identification using chromatographic and spectroscopic techniques.

Re – Precipitation in n-C_5 Alkane

The solid recovered from n-C_6 filtrate was added to 20cm^3 of n-C_5 alkane (non-polar solvent). The solution was shaken vigorously in a mechanical shaker for 30min and allowed to stand for 48hr before filtration. After filtration, the precipitates contained in the filter paper were oven dried for 30min. The filtrates obtained (deasphalted oil fraction) was finally concentrated and weighed prior to SARA analysis and identification using chromatographic and spectroscopic techniques.

RESULTS AND DISCUSSION

Precipitation in C_4 Polar Solvents

The results of the weight and weight percent of heavy organics precipitated by ethyl acetate and butanone are shown in Table 1. The weight percent obtained (Antan crude) ranged between 3.15% to 3.53% (wt/wt), with mean values of 3.34±0.32% for ethyl acetate, while the percentage precipitate by butanone ranged from 3.58 to 3.93% (wt/wt) with a mean value of 3.76±0.30%. The total solid precipitated by these polar solvents are expected to include saturates, aromatics, resins and asphaltenes

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(SARA), in agreement with previous reports (Mansoori, 2007). It is also reported that waxes and heavy aromatics with extensive side chains of n-alkanes are insoluble in polar solvents compared to non-polar n-alkane solvents in which they are soluble (Auflem, 2002).

The difference between the mean values of the heavy organics precipitated by ethyl acetate and that precipitated by butanone is 0.42%, indicating the parity in polarity. Ethyl acetate is slightly less polar than butanone and this difference in polarity is reflected in the comparable total amount of precipitated heavy organics reported in Table 1. As previously stated, waxes and heavy aromatics are known to be sensitive to polarity effect. If this observation was extrapolated to n-alkanes (which are non-polar), the waxes may be soluble even in the lower carbon number n-alkanes. This assertion may therefore imply that the differences in the solubility of heavy organic precipitates in organic solvents of same number of carbon atoms but different functional groups may be as a result of the presence of different groups of compounds in the heavy organic precipitates. (Shehu *et al*., 1991). Mansoori, 2007 showed that the kind and amount of depositions of heavy organics from petroleum fluids vary, depending on the hydrocarbons present in the oil and the relative amounts of each family of heavy organics.

The weight percent of heavy organics (soluble filtrate) in ethyl acetate and butanone solvents are shown in Table 2. The results in Table 2 show that 88.55% and 91.42% (wt/wt) of the Antan crude oil residue were soluble in ethyl acetate and butanone respectively.

Table 1: **Comparison of heavy organics precipitated using ethyl acetate and butanone polar solvents**

Test Crude Oil	**Ethyl acetate**			**Butanone**		
	Wt. of residue (g)	Wt. of HO (g)	Wt. % of HO	Wt. of residue (g)	Wt. of HO (g)	Wt. % of HO
Antan	5.09	0.17	3.34±0.32	5.06	0.19	3.76±0.30

Table 2: Heavy organics soluble in ethyl acetate and butanone polar solvents (Filtrate)

Test Crude Oil	**Ethyl acetate**			**Butanone**		
	Wt. of residue (g)	Wt. of soluble (g)	Wt. % of soluble (g)	Wt. of residue (g)	Wt. of soluble (g)	Wt. % of soluble
Antan	5.09	4.65	91.42±1.56	5.06	4.48	88.55±1.65

Re – Precipitation in n-C_6 Alkane

The results presented in Table 3 show the content of asphaltenes precipitated using n-C_6 alkane. About 37.23% and 21.09% (wt/wt) of asphaltenes were part of ethyl acetate and butanone heavy organic precipitates respectively, and which were insoluble in n-C_6 alkane This indicates that the heavy organics precipitated from crude oil residue (using polar solvents) contained n-C_6 asphaltenes. It was also observed that n-C_6 heavy organics (insoluble) was hard and dark coloured. This n-C_6 precipitates were thought to be principally asphaltenes because waxes, aromatics and resins were soluble in n-C_6 alkane except where co-precipitation occurred (Rossamdana, 1996; Kokal *et al*, 1993).

The amount of n-C_6-asphaltene precipitation from ethylacetate (0.21%) and butanone (0.22%) soluble filtrate are also indicated in Table 3. The results indicated that asphaltene precipitated under this condition are not significant, suggesting that asphaltenes are not soluble in these C_4 organic polar solvents. Previous report by Vazquez and Mansoori (2000) showed that the fraction of heavy organics insoluble in n-pentane is larger than that insoluble in n-heptane and contained wider range of molecules, including the fraction of n-pentane insoluble that was soluble in n-heptane. The n-C_6 soluble filtrates obtained were brown in colour. These soluble filtrates were the maltenes used for uv – spectroscopy and silica gel chromatographic qualitative identification of saturates, aromatics and resins.

Table 3: n-C_6 Asphaltenes content of heavy organics (HO) precipitates and soluble filtrates obtained in C_4 polar solvents (ethyl acetate and butanone)

	Precipitate (via Ethyl acetate)	**Precipitate (via Butanone)**	**Filtrate (via Ethyl acetate)**	**Filtrate (via Butanone)**
Total Heavy organics (SARA/g)	0.17	0.19	4.65	4.48
n-C_6 Asphaltene(g)	0.06	0.04	0.01	0.01
n-C_6 Asphaltene %)	35.29±3.06	21.05±1.87	0.21±0.01	0.22±0.01
A/SAR (asphaltene/saturates, aromatics and resins)	0.353	0.211	0.0022	0.0022

Table 4: n-C_5 Asphaltene precipitated from Antan Crude by n-C_5 via n-C_6 filtrate

	Ethyl acetate			**Butanone**		
Test	Wt. of filtrate solid (g)	Wt. of asphaltene (g)	Wt. % of asphaltene	Wt. of filtrate solid (g)	Wt. of asphaltene (g)	Wt. % of asphaltenes
1	0.09	0.03	33.33	0.13	0.04	30.77
2	0.09	0.03	33.33	0.14	0.05	35.71
3	0.09	0.03	33.33	0.15	0.05	33.33
Mean	0.09	0.03	33.33±0.00	0.14	0.05	33.27.07±4.17

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Re – Precipitation in n-C_5 Alkane

The results of weight percent of n-C_5 asphaltenes precipitated from n-C_6 filtrates are presented in Table 4. It was observed that 33.27 to 33.33% (wt/wt) of the solid recovered from n-C_6 soluble filtrates containing C_4 heavy organic precipitates were insoluble in n-C_5 solvent. Thus, n-C_6 soluble filtrates contained n-C_5 insoluble asphaltenes. It also showed that both ethyl acetate and butanone precipitates include n-C_5 insoluble precipitates (or n-C_5 asphaltenes). In essence, the dissolution and re-precipitation using n-C_5 alkane is to investigate the effectiveness of n-C_6 alkane as a heavy organic precipitant. Asphaltenes were part of the hydrocarbon types as defined by SARA responsible for the differences in the quantity of heavy organics precipitated by organic solvents of different carbon chain lengths and polarity. It was also observed that the n-C_5 insoluble precipitates obtained were hard and dark in colour and the precipitates were n-C_5 asphaltenes in accordance with similar report by Vazquez and Mansoori, 2000. The mean values of n-C_6 and n-C_5 asphaltenes is 37.23±3.06% (for ethyl acetate); 21.09±1.87% (for butanone) and 33.33±0.00% (for ethyl acetate); 33.27±4.17% (for butanone). The total n-C_6 and n-C_5 asphaltenes obtained from ethyl acetate heavy organic precipitate is 1.93 while 1.78 was obtained from butanone heavy organic precipitate (Table 5). The differences between the total asphaltenes is negligible (0.15) compared to 0.42 in the total heavy organics precipitated by C_4 solvents. This suggests that the other compound types – saturates, resins and aromatics were a large part of the precipitates by C_4 solvents. The absorbances (340 – 550nm) of the maltenes and deasphalted oil, after fractionation showed the presence of saturates, aromatics and resins.

Table 5: Comparism of SARA content in C_4 HO precipitates

C_4 HO PPT (%)		**n-C_6 PPT From C_4 HO (%)**		**n-C_6 Asphaltene From C_4 HO (%)**		**n-C_5 PPT From C_4 HO (%)**		**n-C_5 Asphaltene From C_4 HO (%)**	
Ethyl acetate	Butanone	Ethyl acetate	Butanone	Ethyl acetate	Butanone	Ethyl acetate	Butanone	Ethyl acetate	Butanone
3.34	3.76	37.23	21.09	1.24	0.79	33.33	33.27	0.69	0.99

CONCLUSION

This investigation showed that butanone being more polar, produced greater quantity of heavy organic precipitates than ethyl acetate because waxes and heavy aromatics with extensive side chains were insoluble in polar solvents. It is noted that n-C_6 alkane failed to precipitate all nC_5-asphaltenes. Since asphaltenes were defined as the component of crude oil which are insoluble in n-pentane, the n-C_5 filtrates were regarded as the deasphalted oil because the asphaltenes have been removed. It contains the remaining three fractions; saturates aromatics and resins, which were separated and identified using silica-gel chromatographic and spectroscopic techniques. Quantitative analysis of the saturates, aromatics, resins and asphaltenes (SARA) can be carried out using high performance liquid chromatography (hplc) and/or gel permeation chromatography (gpc).

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