



AVERAGE MOLECULAR WEIGHT MEASUREMENTS OF SOME NIGER DELTA CRUDE OIL USING VAPOUR PRESSURE OSMOMETRY AND GAS CHROMATOGRAPHY TECHNIQUES

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Abstract

The average molecular weight measurement of some selected crude oil samples around the Niger Delta region using Vapour Pressure Osmometry and Gas Chromatography has been studied. GC fingerprint spectrum for all the samples was equally obtained and revealed that all samples are of different origin. The densities @25°C and API @15°C values for the samples were also determined. The sample OGB-1 gave the highest API value of 53.31o and density of 0.7569 (g/cm³) thus of better quality than the other samples ADN-2, ADN-3, UDL-4, COY-5 with API values 17.79°, 20.27°, 26.84°, 34.56° respectively. The molecular weight value by VPO technique for all the five samples was comparatively higher than the ones given by GC. Comparing the two techniques, gave a very high correlation with the R² value of 0.998. On the premise of density as a function of molecular weight, the two techniques had a measure of congruence. Thus, VPO and GC methods are plausible for molecular weight determination.

Keywords: (Molecular weight, Vapour Pressure Osmometry, Gas Chromatography, Crude oil)

1.0 INTRODUCTION

Crude oil characterization involves the identification of the physical and chemical properties of crude oil. This is important in estimating feedstock properties for refinery units. In addition, to produce the optimal amount of finished products that will meet product quality specifications and provides an economic assessment for the crude oil [1].

Crude grades differ considerably in yield and properties. The value of any particular crude depends upon the specific product slate and refinery configuration [1]. Knowing what your crude is worth begins by having good crude assay data which provides the basis for economic valuation, engineering design and refinery processing [2].

One essential physical property that should be put into consideration before the completion of any crude oil characterization is the relative molecular mass. The average molecular mass of hydrocarbon is very useful when characterizing reservoir fluids and in the simulation of composition [3, 4].

Molecular weight is a fundamental property in the characterisation of oils and its key in forecasting the composition and the worth of the oil [5]. Molecular weight also suggests the magnitude of a molecule and the configuration of a compound [5]. Molecular weight plays numerous and very vital function chiefly in areas of material and energy balance. Also, its expediency is seen in areas such as thermodynamic phase equilibrium, reaction kinetics

and unit operations [6]. The average molecular weight of petroleum fractions is determined generally from any of the following three methods: Chromatographic method, Vapor Pressure Osmometry method and Cryoscopic method.

The vapour pressure osmometry (VPO) technique relies on the measurement of the difference in the vapour pressure of the sample solution and vapour pressure of a pure solvent. Generally, the surface molecules of liquids tend to escape and evaporate even though the liquids are not at the point of boiling. Surface molecules that have higher energy escapes and thus evaporation occur. VPO technique gives a precise assessment compared to what is obtainable using mass spectroscopy (MS) when used for the analysis of weak or non-polar compounds such as crude oils [7].

For petroleum asphaltenes, measuring its average molecular weight has caused quite a lot of controversies. Reasons being that asphaltenes tend to associate, strongly adsorb on surfaces and are also known to be non-volatile [8, 9]. In defence of vapour pressure osmometry for measuring molecular weight, researchers [8, 10] found that the VPO technique gives a measurement of number molecular weight average that is consistent; this trend is not seen with other analytical methods. VPO technique is extensively used for the molecular weight measurement of asphaltenes and bitumen [10] because it is uncomplicated and cost-efficient. Molecular weight determination of compounds has been carried out using gas chromatographic (GC) and vapour pressure osmometry (VPO) techniques. A previous study [11] determined the molecular weights of the Rattawi vacuum residue fractions and compared the mass spectrometric technique with that of vapour phase osmometry. While another study [12] did a comparative study on castor oil molecular weight using both GC and VPO. From their studies, molecular weight determination using GC techniques gave comparatively higher values than the vapour pressure osmometry technique.

In the present study, the average molecular weight of some crude oil samples selected from different

locations within the Niger Delta region of Nigeria will be determined using Gas Chromatography and Vapour Pressure Osmometry techniques.

2.0 MATERIALS AND METHODS

Composite crude oil samples (five) were collected at different locations within the Niger Delta region (onshore and offshore). The samples were properly labelled OGB-1, AND-2, AND-3, UDL-4 and COY-5; and carefully stored for analysis. The sampling locations are as indicated in picture 1 below:

All reagents used were of analytical grade from BDH chemicals.

The density and the API gravity were obtained using the DMA 4500 Density analyser. A Gas chromatograph (Star-lite Air compressor model 1120926 GC) with an FID (flame ionization detector) was the device used for the compositional analysis.

The Knauer Vapour Pressure Osmometer (VPO) instrument model K-1000 was used for Vapour Pressure Osmometry measurements in accordance with Knauer Guide of VPO (2007)[13]. Here, Naphthalene was used as the reference standard, and benzene was the solvent. Different concentrations of Naphthalene in benzene solution and the crude oil samples in benzene were prepared, after which the Osmometry analysis of the solutions was determined according to its standard operating procedure. The measurements were done in triplicates and the average value was taken. Two curves were generated for the reference standard data and crude oil data. The first one is the graph of the osmometer reading on Y-axis which was plotted against the weight % of the standard of the on the X-axis to obtain the reference standard slope. The second is a graph of the osmometer reading on Y-axis plotted against the weight % of the crude oil samples on the X-axis to obtain the crude oil samples slope. The Molecular weight (Mw) was determined by the relationship below:

$$Mw (g/mol) = \frac{\text{Calibration slope} \times Mw \text{ of Naphthalene}(128.1705 g/mol)}{\text{Sample slope}} \dots\dots 1$$



Picture 1: Map of Niger-Delta of Nigeria showing the sampling locations

3.0 RESULTS

The average molecular weights obtained using the two techniques (VPO and GC), their respective API gravities and densities are presented in table 1. A bar chart comparing the average molecular weight obtained by the two methods from the various points of sampling is equally shown in figure 1. On the other hand, figure 2 shows the graphical correlation of average molecular weights by gas chromatography

and vapour pressure osmometry. The plots correlating density and molecular weights by VPO and GC are presented in figures 3 and 4 respectively. Figure 5 presents plots of osmometry reading versus concentration in weight%, while the fingerprints spectrum for GC analysis of the crude oil samples is described in figures 6 - 10.

Table 1: Densities, API gravities and Molecular weights of Crude Oil Samples from OGB-1, ADN-2, ADN-3, UDL-4, and COY-5 Wells

Sample Id	Density@ 25°C (g / cm ³)	API @ 15°C	Mol. Wt. by Gas Chromatography (g / mol)	Mol. Wt. by Vapour Pressure Osmometry (g/mol)
OGB-1	0.7569	53.31	122.065	124.910
ADN-2	0.9405	17.79	214.262	215.230
ADN-3	0.9249	20.27	205.099	210.770
UDL-4	0.8859	26.84	185.660	187.599
COY-5	0.8441	34.56	158.626	162.080

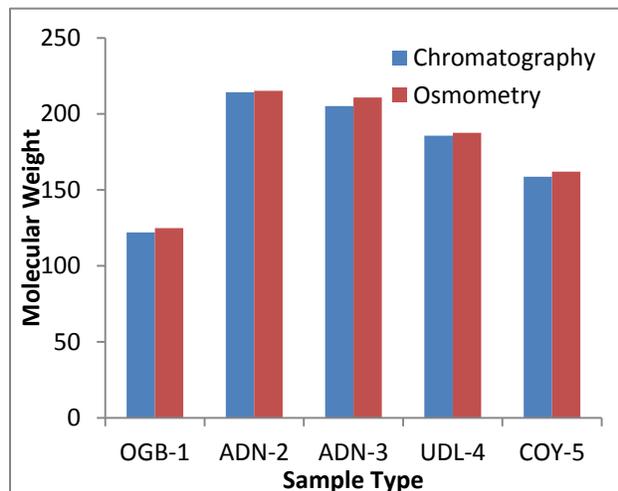


Figure 1.0: Bar Chart showing Molecular weight by Gas Chromatography and Osmometry

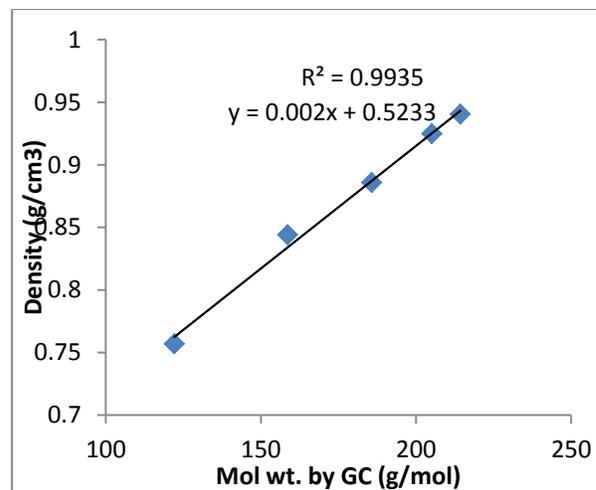


Figure 4: Correlating Density and Molecular weight by GC

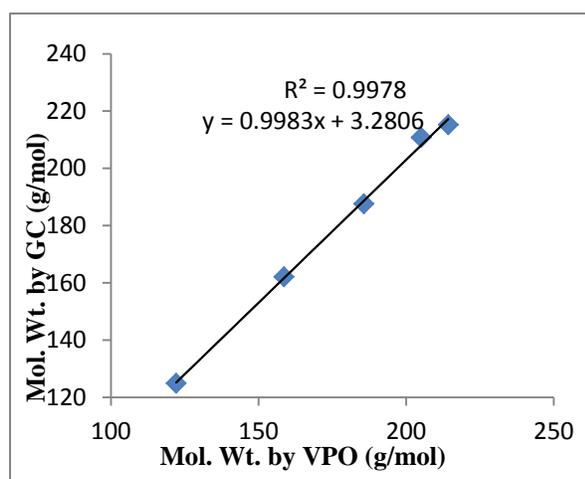


Figure 2.0: Graphical Correlation of Molecular weights by Gas Chromatography and Osmometry

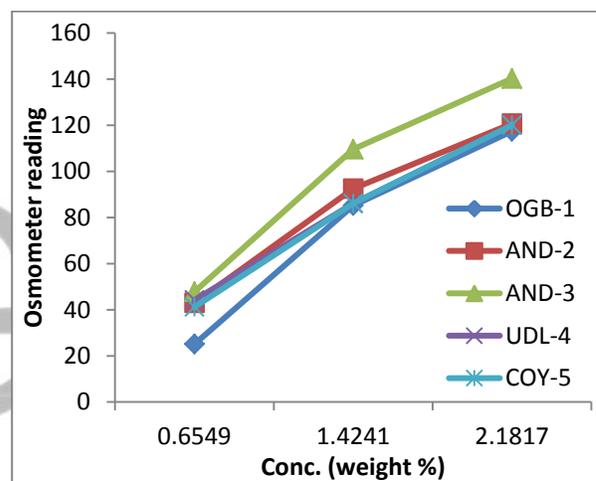


Figure 5: plots of osmometry reading versus concentration in weight%

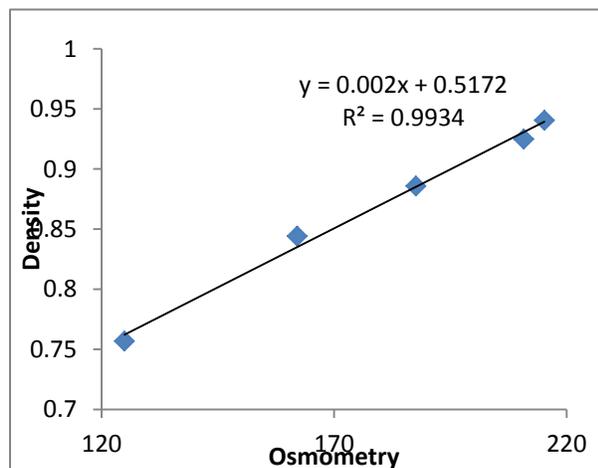


Figure 3.0: Correlating density and molecular weights by VPO

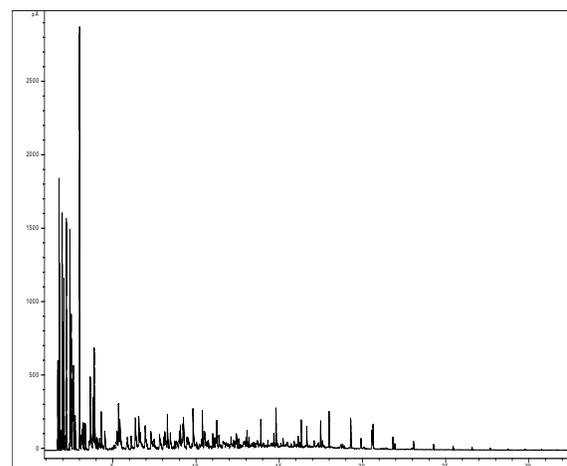


Figure 6: Fingerprint chromatogram for sample OGB-1

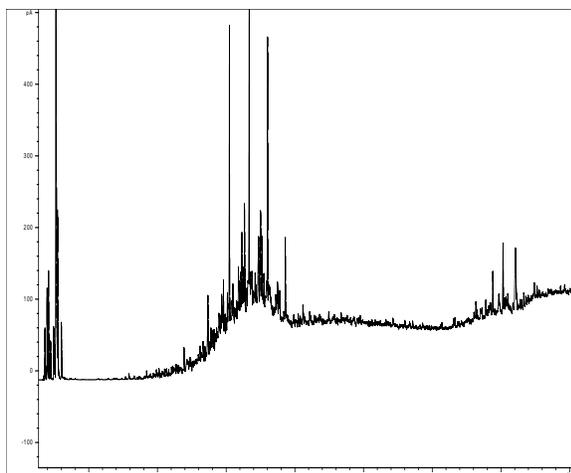


Figure 7: Fingerprint chromatogram for sample ADN-2

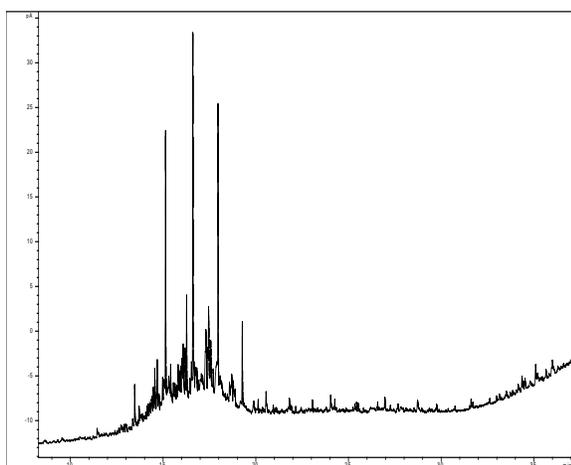


Figure 8: Fingerprint chromatogram for sample ADN-3

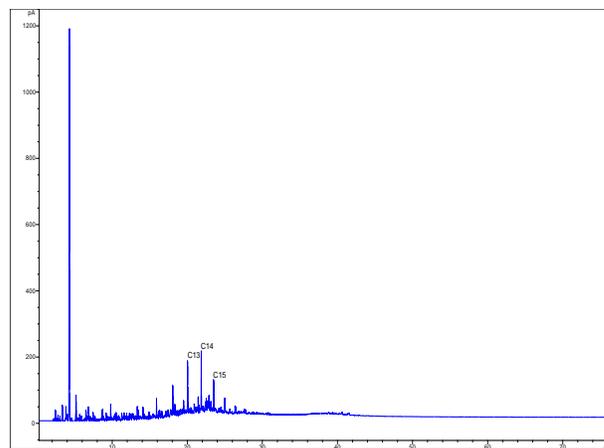


Figure 9: Fingerprint chromatogram for sample UDL-4

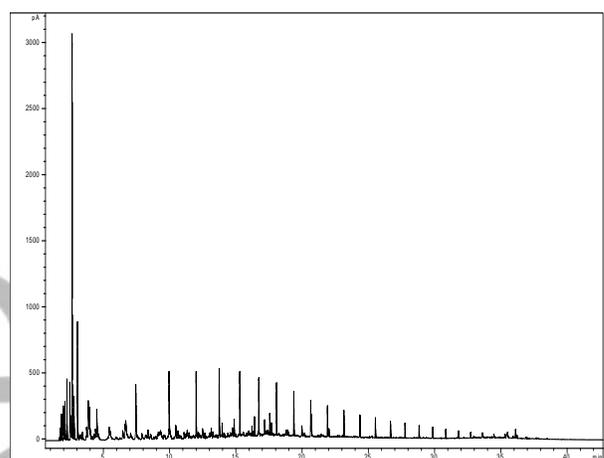


Figure 10: Fingerprint chromatogram for sample COY-5

4.0 DISCUSSION

Results obtained from table 1 shows that the density of the crude oil samples analysed ranged from 0.7569 (g/cm^3) - 0.9405 (g/cm^3), and their API values ranged from 17.79⁰ to 53.31⁰. According to previous authors [3], crude oil can be classified as light, medium or heavy, based on its measured API gravity. Light crude is any crude oil having an API value higher than 31.1⁰API. Medium crude oil is defined as any crude that is having API gravity between 22.3⁰API and 31.1⁰API, while heavy crude oil is defined as one that has API gravity less than 22.3⁰API [6,14]. Similar classifications have also been documented by the Louisiana Department of Natural resources [15]. Thus from our study, OGB-1 and COY-5 samples with densities of 0.7569 (g/cm^3) and 0.8441 (g/cm^3), and API values of 53.31⁰ and 34.56⁰ respectively, indicates that the crude oil samples can be classified

to be light. UDL-4 sample with a density of 0.8859 g/cm^3 and API of 26.84⁰ falls in the medium crude category while the ADN-2 and ADN-3 crude samples having densities of 0.9405 (g/cm^3) and 0.9249 (g/cm^3), and API gravities of 17.79⁰ and 20.27⁰ respectively suggests they are heavy crude. Thus we have two light crudes (OGB-1 and COY-5), one medium (UDL-4) and 2 heavy crudes (ADN-2 and ADN-3).

The specific gravity of crude oil gives a rough measure of the quantity of lighter hydrocarbons present [2]. The lower the value of the specific gravity (which is a function of density) and higher the API gravity, the higher is the yield of light fractions by distillation [5, 16]. According to other authors [2], any crude oil with higher API gravity tends to have a higher price and is of good quality. This implies that crude oil sample collected from OGB-1 is of better

quality and invariably of higher market price than the crude oil samples obtained from ADN-2, ADN-3, UDL-4, COY-5.

Based on the experimental objective of determining the average molecular weight of crude hydrocarbon oil samples, figure 1 clearly reveals that GC and VPO techniques are plausible for determining molecular weights. Sample ADN-2 with a molecular weight of 214.262 g/mol by GC and 215.230 g/mol by VPO gave the leading value. This was followed by sample ADN-3 and UDL-4 with molecular weight of 205.099 g/mol by GC; 210.770 g/mol by VPO and 185.660 g/mol by GC; 187.599 g/mol by VPO respectively while sample COY-5 with molecular weight of 158.626 g/mol by GC and 162.080 g/mol by VPO was next. Sample OGB-1 with 122.065 g/mol by GC and 124.910 g/mol by VPO had the smallest value. From the results so far, sample ADN-2 tends to be the heaviest while the sample OGB-1 is the lightest. However, VPO technique gave relatively higher values for average molecular weight determination than results obtained with GC technique. This corresponds to a previous report [12] on castor oil molecular weight by VPO and GC which gave values of 928.88g/mol and 928.30g/mol respectively. Furthermore, graphical correlation of molecular weights by gas chromatography and vapour pressure osmometry indicates an R^2 value of 0.993 (close to 1) for both VPO and GC with a constant correction factor of 3.280 as presented in figure 3 and 4.

Additionally, figures 3 and 4 which describes the plots that correlate the molecular weights by the two techniques (VPO and GC) and their densities reveals that the data can be modelled by a straight line fit. From the plots, we observed that density increased with an increased molecular weight, which shows that density is directly related to molecular weight [5].

Also, it further corroborates with the equation of state in which:

$$PV = nRT \dots \dots \dots 2$$

Where n = number of moles and can be expressed as mass/molar mass.

$$\text{Then, density} = \text{mass}/\text{volume} \dots \dots \dots 3$$

From equation (3),

$$\text{mass}(m) = \text{density} (\rho) \times \text{volume} (V) \dots \dots \dots 4$$

$$\begin{aligned} &\text{Number of moles } (n) \\ &= \frac{\text{mass} (m)}{\text{Molar mass } (MM)} \dots \dots \dots 5 \end{aligned}$$

Substituting (5) in (2) we have,

$$Pv = \frac{mRT}{M.M} \dots \dots \dots 6$$

$$\text{Thus, } M.M Pv = mRT$$

$$\text{Putting (4) in (6) we get; } M.M Pv = \rho VRT$$

$$M.M P = \rho RT \dots \dots \dots 7$$

From equation (7) we see the directly proportional relationship between M.M (Molecular mass or weight) and the density (ρ)

Also, carefully looking at the graphical representation of all the five samples analysed for VPO in figures 5 revealed that the osmometer reading increases with an increase in solution concentration in weight %. The straight line shows proportionality between the measured value and the concentration [12]. This corroborates the theoretical assertion which states that vapour pressure is a colligative property and its lowering is a function of the number of solute particles per the number of solvent molecules in solution [17].

Finally, figures 6 to 10 presents the fingerprint gas chromatogram for the five samples (OGB-1, ADN-2, ADN-3, UDL-4, COY-5) respectively. The fingerprints of all the samples are distinctly different from one another an indication that all five crude oil samples originate from different sources and thus unique.

5.0 CONCLUSION

From the study, results obtained show that the densities and the API gravities of the crude oil samples indicate two of the crude oil samples OGB-1 and COY-5 as light crude oil, UDL-4 as medium crude oil, while samples ADN-2 and ADN-3 as heavy crude oil. The sample OGB-1 gave the highest API value of 53.31° and thus of better quality than the other samples ADN-2, ADN-3, UDL-4, COY-5 with API values 17.79°, 20.27°, 26.84°, 34.56° respectively and invariably of a higher market price.

The molecular weight value by VPO technique for all the five samples was comparatively higher than the ones given by GC. Since previous research [12] showed that VPO presents a more accurate result for molecular measurement, it can, therefore, be said that molecular weight obtained by VPO could be more reliable than the ones obtained by GC. The weights were estimated within the limits of experimental errors. Comparing the two techniques, there is a correlation between them. On the premise of density as a function of molecular weight, the two techniques had a measure of congruence.

The VPO plots for the analysed samples show that the osmometer reading increases as the solution concentration also increases. The vapour pressure of a solution reduces as the number of solute particles increases [5].

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

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