

Distribution of Some Diamondoids in Crude Oils from Niger Delta Basin

S. Abrakasa & H.O. Nwankwoala*

Department of Geology, University of Port Harcourt, Port Harcourt, Nigeria

***Corresponding author**

H.O. Nwankwoala, Department of Geology, University of Port Harcourt, Port Harcourt, Nigeria, E-mail: nwankwoala_ho@yahoo.com

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Abstract

Some Niger Delta oils were studied for the presence of diamondoids in the oils. Oils were obtained from a well each from their respective oil fields. The objectives of the study include identification of diamondoids in the oils, use of parametric ratios to delineate biodegradation and maturity of the oils. The m/z 136 show the presence of Adamantane and the m/z 135 showed the presence of 1-Methyladamantane, 2-Methyladamantane, 1-Ethyladamantane and 2-Ethyladamantane in the oils. The nC_{17}/Pr and $nC_{17}+nC_{18}/(Pr+Ph)$ showed good biodegradation trend for the oils. IMA/nC_{11} and $nC_{17}+nC_{18}/(Pr+Ph)$ plot did not show a good biodegradation gradient though of similar trend. IMA/nC_{11} showed a restricted spread. The plot IMA/nC_{11} and $IMA+2MA/A$ showed a better spread for $IMA+2MA/A$. The $IMA/IMA+2MA$ (Methyladamantane index) showed a better maturity gradient and is good for the Nigerian oils but the $1EA/1EA+2EA$ (Ethyladamantane index) showed restricted spread for a good maturity gradient and may be better for higher matured oils than the Niger delta Oils.

Keywords: Diamondoids, crude oil, biodegradation, sediments, Niger Delta

Introduction

Diamondoids are aliphatic hydrocarbon compounds that are cyclic, with the general formula chemical formula $C_{4n}+6H_{4n}+12$. Structurally, they consist of cyclohexane rings in chair configuration, which has an outlook of a 3-dimensional diamond subunit. They were first isolated in crude oils in 1933. The mechanistic pathway to explain the occurrence of diamondoids is the Schleyer's Lewis acid-catalyzed carbocation rearrangement, an example is the rearrangement of Schleyerendotrimethylenenorborane to Adamantane when refluxed overnight with aluminum bromide or aluminum chloride [1]. The diamondoids group is consist of Adamantane (tricyclo[3.3.1.1] decane) ($C_{10}H_{16}$), diamantane ($C_{14}H_{20}$) and Triamantane ($C_{18}H_{24}$) and higher polymantane homologues.

Some of their properties include their natural occurrences which are crude oil, sediments, natural gas and condensates. Their sizes vary between less than 1nm and 2nm, while their solubilities in various solvent varies between 10–11.6% Adamantane in pentane and hexane, 6.3% of diamantane in cyclohexane and 5.0% in tetrachloromethane [1]. They can be obtained by extraction from crude oils and by organic synthesis. Their morphology is that of crystalline structure in normal conditions.

The stability of diamondoids has provided for its uses in maturity evaluations and biodegradation studies [2]. Adamantane and diamantane are the most frequently found in petroleum and natural

gas pipeline deposits, due to their solubility in light hydrocarbons at high pressures and temperatures [3]. When petroleum fluids are produced from the reservoir they are displaced from a higher temperature and pressure regimes to low temperature and pressure environment. The deposition of diamondoids is enhanced basically by phase transitions resulting from changes in temperature and pressure [4].

Diamondoids are present in crude oils and their distribution may be explained by the organic matter that generated various oils that are studied.

The Niger Delta Basin is the most active petroleum basin in Nigeria. The mechanism for deposition of the basin can be explained by the depobelt concept, this concept postulates that the Niger delta basin was deposited in mega sequences, it is based on the conceptual model that rate of deposition is greater than the rate of subsidence, this explains that progradation of the delta in a seaward direction [5]. The lower rate of subsidence results in a reduced rate of sediment compaction, which consequently results in ineffective dewatering of the sediment resulting in overpressure of the basin [6]. The various sequences were formed as a result of the Delta wide sea-level cyclicity of transgressive and regressive sea level changes. The changes were observed to be over intervals of 5Ma, and subsequently resulted in deposition of formations with significant lithological variations, this also brings to bear the fact that the organic matter that could have deposited will have some significant differences hence, may explain differences in compositional variations of diamondoids that may be present in various oils that are analyzed

in this study. The objectives of this study include identifying Adamantane and Methyl analogues in the oils studied, using various ratios to delineate biodegradation and maturity of the oils studied.

Methods

Samples and Sampling

The samples used for this study were crude oil samples, they are a suite of thirteen (13) oil samples were obtained from thirteen (13) oil fields (figure 1) in the Niger delta basin namely: Nembe Creek, Escravos, Abo, Ahia, Kolo Creek, Usan, Abo, Clough Creek, Tebedaba, Azuzuama, Afremo, Obagi, Rumuekpe, Agbada oil fields. All samples were obtained from wellheads and are representative of the bulk. All samples were stored in glass vials with Teflon cover and preserved in a chest of ice from the field to the laboratory, the samples were further preserved in a refrigerator until samples were retrieved for analysis.

Sample Analysis with GC-MS

Sample analysis was accomplished by whole oil analysis for both aliphatics, aromatics and even the non-hydrocarbon biomarkers since other aspects may be investigated. The sample was diluted in DCM (Dichloromethane) to achieve a concentration of $1\mu\text{g}/\mu\text{L}$, which recommended for GC-MS analysis.

The GC-MS equipment settings

The GC-MS analysis was done using a HP5890 II GC with a split/spiltless injector linked to a HP 5972 MSD (Mass Selective Detector). The GC was temperature programmed for 40°C – 300°C at 4°C per minute and held at final temperature for 20 min. The carrier gas was Helium (flow rate $1\text{ml}/\text{min}$., pressure of 50kPa , slit at $30\text{ml}/\text{min}$).



Figure 1: Map of Southern Nigeria showing the oil fields that were studied

The ionization and identification was carried out in the HP 5972 MSD, which was equipped with electron voltage of 70 eV , filament current of $220\mu\text{A}$, source temperature of 160°C , a multiplier voltage of 1600V and interface temperature of 300°C . The acquisition was monitored by HP Vectra 48 PC chemstation computer in both full scan mode (30ions 0.7 cps 35m dwell). HP is currently known as Agilent, UK. Adamantane and methyl analogues were detected and identified by extracting $m/z=136$ and $m/z=135$ chromatograms respectively and from literature references. Peak integration was done using the RTE integrator [7]. Data was obtained from the percentage report from the Enhanced MSD ChemStation 2011 software by Agilent Technologies.

Result and discussion

Identification of Adamantane and Methyladamantane

Adamantane and Methyladamantanes in Niger Delta oils studied were identified by extraction of their mass chromatogram using m/z 136 and m/z 135 respectively as in figures 2 and 3, their chromatograms were check with their mass spectra from literature [8,9]. Their abundances were extracted from the percent report for each mass chromatogram obtained from the Enhanced MSD Chem Station 2011 software by Agilent Technologies. Figures 4 to 8 show the mass spectra of the various identified peaks in the mass chromatograms in figures 2 and 3. Their fragmentation patterns are consistent with literature [10]. The parametric ratios (as in table 1) were calculated based on the abundances obtained from the percent report using the Enhanced MSD Chem Station 2011 software.

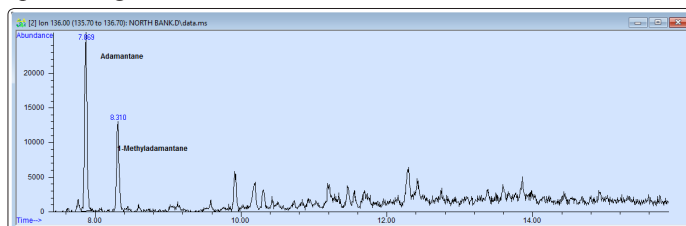


Figure 2: Mass chromatogram for $m/z = 136$. Showing Adamantane and 1-methyladamantane for North Bank oil

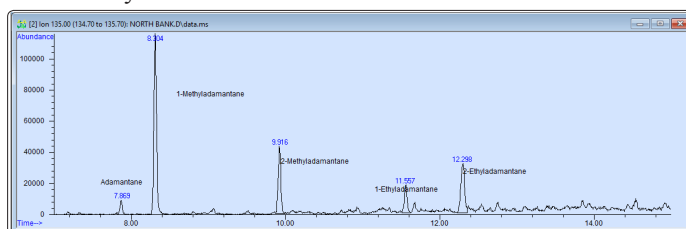


Figure 3: Mass chromatogram for $m/z = 135$, showing the diamondoids as listed in the mass chromatograms for North Bank oil

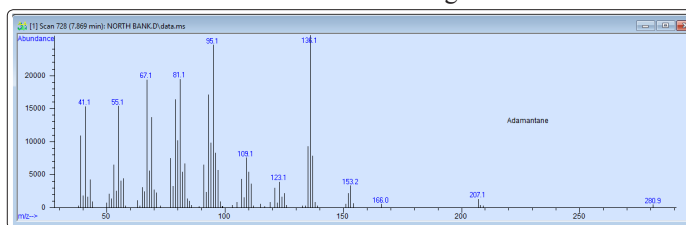


Figure 4: Mass Spectra for Adamantane from North bank oil

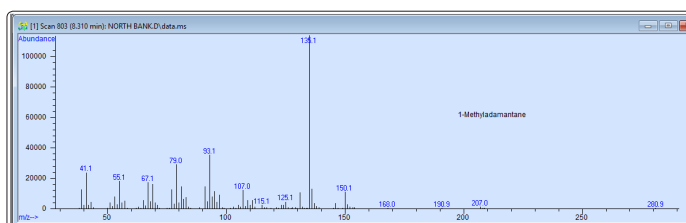


Figure 5: Mass Spectra for 1-Methyladamantane from North bank oil

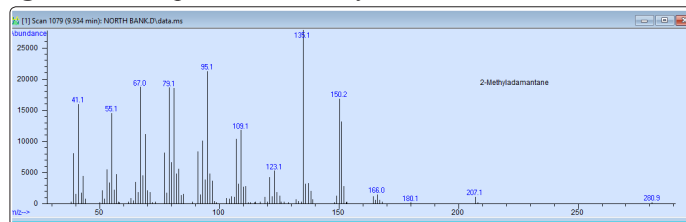


Figure 6: Mass Spectra for 2-Methyladamantane from North bank oil

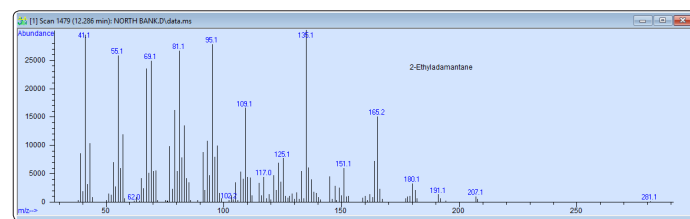
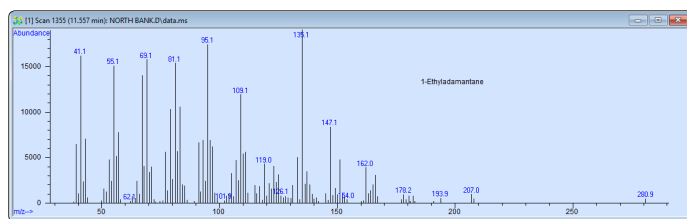


Figure 7: Mass Spectra for 1-Ethyladamantane from North bank oil

Figure 8: Mass Spectra for 2-Ethyladamantane from North bank oil

Table 1: Parametric ratios derived from the percent report obtained. Pr=Pristane, Ph=Phytane, A= Adamantane, 1MA= 1-Methyladamantane, 2MA= 2-Methyladamantane, 1EA=1-Ethyladamantane, 2EA= 2-Ethyladamantane

Wells/Oilfields	nC17/Pr	(nC17+nC18)/(Pr+Ph)	1MA/nC11	2MA/nC11	(1MA+2MA)/A	1MA/(1MA+2MA)	1EA/(1EA+2EA)
Aferemo	0.70	0.75	0.11	0.04	5.82	0.71	0.29
Agbada	0.28	0.36	1.04	0.48	6.95	0.68	0.27
Escravos	1.57	2.16	0.01	0.00	0.35	0.68	0.49
Kolo Creek	0.80	1.41	0.04	0.01	6.37	0.72	0.28
Abo	1.40	1.88	0.03	0.01	5.88	0.67	0.27
Ahia	0.99	1.44	0.06	0.03	6.14	0.68	0.30
Obagi	0.37	0.58	0.09	0.05	7.08	0.63	0.24
Clough Creek	0.92	1.24	0.49	0.18	6.47	0.73	0.25
Azuzuama	0.66	0.87	0.25	0.10	7.13	0.73	0.33
Nembe Creek	1.92	2.29	0.09	0.04	6.42	0.69	0.32
Rumuekpe	0.29	0.38	0.08	0.03	6.76	0.74	0.21
Tebedaba	0.96	0.97	6.32	2.18	6.00	0.74	0.28
Usan	0.59	0.64	0.06	0.03	7.38	0.71	0.17
Adebawa	na	na	na	Na	6.95	0.70	0.21
Beneside	na	na	na	Na	7.26	0.70	0.24
Etelebou	na	na	na	Na	6.65	0.72	0.25
North Bank	na	na	na	Na	6.30	0.73	0.29
Obigbo	na	na	na	Na	7.14	0.69	0.24
Otumara	na	na	na	Na	8.18	0.67	0.24
River Nun	na	na	na	Na	7.03	0.67	0.24
Yokiri	na	na	na	Na	6.65	0.72	0.30
Oloma	na	na	na	Na	7.86	0.63	0.26
Soku	na	na	na	Na	7.90	0.65	0.26
Utorugu	na	na	na	Na	6.29	0.68	0.29

Correlation Studies Biodegradation

The peculiar structure of diamondoids provides for their thermal stability due to their recalcitrant nature to biodegradation. Hence diamondoids have been suggested to serve as a good reference compound in the study of biodegradation. In a study, ratios such as the relative abundance of diamondoids to n-alkane have been used to express the degree of biodegradation of Australian oils [8]. In another study, the using of diamondoids in the delineation of biodegradation has been emphasized including maturity, oil-cracking, oil mixing, oil biodegradation, organic facies, TSR (thermo chemical sulphate reduction), gas washing, migration, and oil spill identification

[11-13]. Niger delta oils are prone to biodegradation because of the potential influx of water into the reservoir which provides nutrients to the microorganism will be utilized for the hydrocarbon for generation of energy. The nC₁₇/Pr and (nC₁₇+nC₁₈)/(Pr+Ph) parametric ratios has been used to express biodegradation. The plot of nC₁₇/Pr and (nC₁₇+nC₁₈)/(Pr+Ph) has been used for delineating biodegradation especially in oil spill related studies, In this study, the plot of nC₁₇/Pr and (nC₁₇+nC₁₈)/(Pr+Ph) (figure 9) showed gradual but significant differences in degree of biodegradation of the oils [3]. The suite of oils used for the biodegradation study, the Nembe oil is least degraded while the Agbada and Rumuekpe oils are the most degraded.

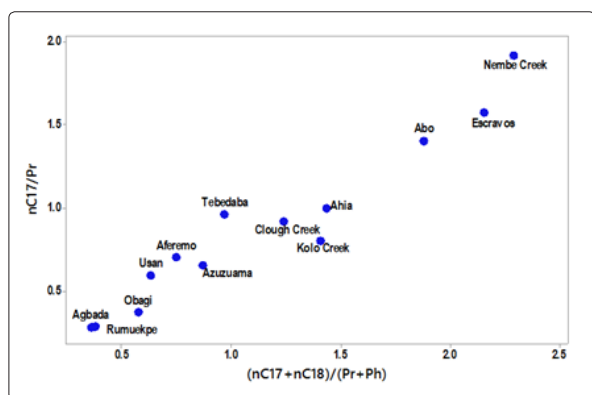


Figure 9: Plot of nC_{17}/Pr and $(nC_{17}+nC_{18})/(Pr+Ph)$

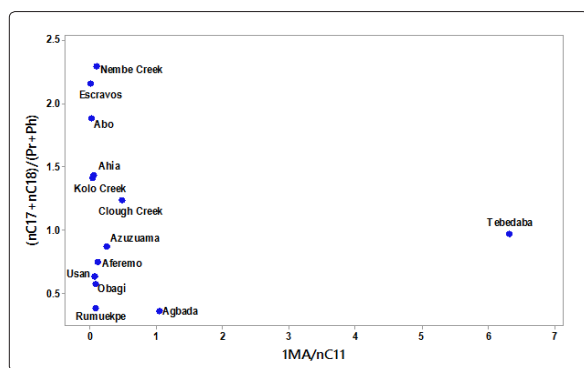


Figure 10: Plot of $1-MA/nC_{11}$ and $(nC_{17}+nC_{18})/(Pr+Ph)$

The use of diamondoid/n-alkane ratio was also tested for the Niger delta basin oils, $1MA/nC_{11}$ ratio was used. Figure 10, which is the plot of $1-MA/nC_{11}$ and $(nC_{17}+nC_{18})/(Pr+Ph)$ show the same trend in terms differences regarding degree of biodegradation. This buttress the fact that $1-MA/nC_{11}$ can be used to evaluate biodegradation for Niger Delta Oils. The plot of $2-MA/nC_{11}$ and $(nC_{17}+nC_{18})/(Pr+Ph)$ also gave the same trend of differences for accessing biodegradation across the suite of oils used for the biodegradation aspect of the study. Another biodegradation parameter which is the $(1MA+2MA)/A$ was also tested, the $(1MA+2MA)/A$ was plotted against $1MA/nC_{11}$ in figure 11 [8]. $1MA/nC_{11}$ showed a restricted spread of data while $1MA+2MA/A$ showed a significant spread of data, inferring subtle changes in biodegradation degree of the oils. This represents the difference in rate of depletion of n-alkanes relative to diamondoid compounds in the oils.

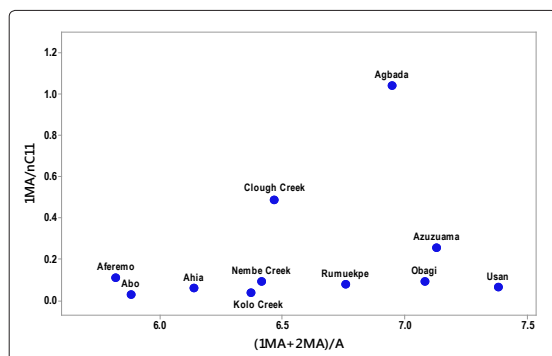


Figure 11: $1MA/nC_{11}$ and $(1MA+2MA)/A$

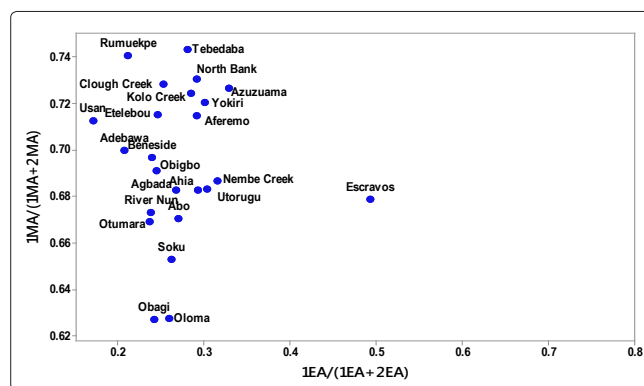


Figure 12: $1MA/1MA+2MA$ and $1EA/1EA+2EA$

Maturity of the Oils

The MA index (methyladamantane index) which is expressed as $1-MA/(1-MA + 2-MA)$ was used to access the maturity of the oils [8,9]. Though the 1-Methyladamantane is more stable relative to 2-Methyladamantane, the relative abundance of 1-Methyladamantane increases with maturity. The EA index (Ethyladamantane index) was also calculated for the oils. The two parameters were plotted against each other in figure 12. The $1MA/1MA+2MA$ (Methyladamantane index) showed significant spread of data points, portraying subtle maturity differences implying maturity gradient for the oils, this could be used to expressed maturity of the Niger Delta oils, by this Tebedaba and Rumuekpe oils are the most mature, while Oloma and Obagi oils are the least mature. The $1EA/1EA+2EA$ (Ethyladamantane index) had a limited spread of data points, inferring that the index did not vary much with the level of maturity of the Niger delta oils, and it would be better used for higher matured oils than the Niger delta oils [2,4].

Conclusion

The GC-MS analysis provided for identification of Adamantane and 1-Methyladamantane, 2-Methyladamantane, 1-Ethyladamantane and 2-Ethyladamantane by obtaining the EIC (extractible ion chromatogram) for $m/z=136$ and $m/z=135$ respectively. The mass spectra were also obtained from mass chromatograms for Adamantane and 1-Methyladamantane, 2-Methyladamantane, 1-Ethyladamantane and 2-Ethyladamantane. The oils were also evaluated for biodegradation. The ratios nC_{17}/Pr and $(nC_{17}+nC_{18})/(Pr+Ph)$ gave a plot that showed gradual biodegradation of the oils. The plot of $1-MA/nC_{11}$ and $(nC_{17}+nC_{18})/(Pr+Ph)$ also showed similar trend. However, the maturity parameters ($1MA/1MA+2MA$ and $1EA/1EA+2EA$) showed a trend from their plot for which $1MA/1MA+2MA$ (Methyladamantane index) had wider spread of data points, this could be used to expressed maturity of the Niger Delta oils, by this Tebedaba and Rumuekpe oils are the most mature, while Oloma and Obagi oils are the least mature. The $1EA/1EA+2EA$ (Ethyladamantane index) had a limited spread data points, preferably should be used for higher matured oils than the Niger delta oils.

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