Title: Development of Organoclays from Nigerian Bentonite Deposits and their Evaluation for Application in High Pressure and High Temperature Drilling Fluids

P. SHALLSUKU

Abstract

This paper reports parts of the research and development activities carried out by the oil field chemicals research Group at American University, Yola, Nigeria. Oil exploration of new oil fields in complex subsurface environments under high pressure and high temperature (HP/HT) conditions, requires the development and use of drilling fluids, which maintain their rheological and filtration properties even in such hostile environments.

Though rheology is a key property that needs to be optimized for the development of any stable and effective drilling fluids, fluid loss is also another property that drillers should minimize in order to promote safer and less expensive drilling activities. Invasion of foreign fluids, such as drilling mud filtrate, in to the newly exposed formations, is one of the most common causes of formation damage, leading to costly stimulation treatments and even loss of production. This problem has been known for decades as a major contributor to the abnormal decline in productivity or injectivity in most reservoirs.

Designing stable drilling fluid systems with high thermal conductivity and optimal cooling properties for drilling in deep oil and gas reservoirs under extreme downhole conditions (HP/HT) is a major challenge. Drilling fluids with optimal heat transfer properties are highly desirable as drilling operations cause excessive heat due to friction between drilling bit and the rock surface. Overheating of equipment can lead to severe drilling problems with direct impact on the cost and efficiency of drilling operations. Therefore, it is important to formulate drilling muds with excellent heat transfer capabilities.

Due to their unique physico-chemical properties, modified bentonite are with tailor-made rheological and filtration properties studies in the literature/highlight that the original organoclays with low thermal stability were modified by a cationic exchange reaction between bentonite clay and different quarternary ammonium chloride ions. Owing to their stable nature, imidazoliums have been suggested for preparation of organo clays that can be used in formulation of drilling muds for harsh environment. This work focused on the modification of Nigerian bentomite clay with renewable ester functionalized oleic and stearic acid based imidazolium surfactants. Oleic acid and stearic acid based cationic surfactants containing imidazolium head group and two-ester functional groups are investigated for their self-aggregation properties and clay organic interactions.

Among various clay organic interactions, the phenomenon of intercalation has led to the development of clay products that exhibit novel rheological, surface and structural properties that can find useful applications in oil –based drilling fluids. These acid based surfactants were able to self-aggregate into micelles at lower concentrations compared to conventional surfactants. Organoclays are clays that contain organic molecules intercalated in their structural layers. The clays are more used in the preparation of organoclays are those derived from the smectite group, mainly bentonites, due to reduced crystal dimensions and high capacity of cations exchange, which facilitate the intercalation of the organic compounds.

In this work, physico-chemical and thermal properties of the clay before and after modification were determined and compared using X-ray diffraction (TGA). The chemical composition of bentonite was determined by X-ray fluorescence (XRF) and the cation exchange capacity (CEC) of the clay was determined by methylene blue method. The CEC value is meg/100g of the sample and the XRD analysis is showed the enhancement of basal spacing from 12.63A to 20.88A revealed that desired modification of bentonite has been achieved. The organoclay was used to formulate a drilling mud system.

Rheological properties of samples were determined using both conventional viscometer at elevated temperature and high temperature and high pressure (HTHP) rheometer.

Fluid loss properties of samples were measured with standard API filter press and HTHP filter press. In addition, the filtration properties were also investigated with a dynamic filtration apparatus. Both rheometer and dynamic filtration apparatus were used to customize the properties of the mud system to mimic real borehole conditions.

Rheological and filtration effectiveness of the drilling muds in harsh conditions have been studied experimentally.

The organic clay improved the rheological properties and high temperature stability as well as lowered the filtrate volume of the drilling fluid.

Key words: Organoclay, Bentonite, Drilling fluids, surfactants.

INTRODUCTION

Bentonite is natural clay whose main component is the mineral montmorillonite; bentonites are valuable mineral class for industrial application because of their high cation exchange capacity and surface area.

Smectite is the group name for several hydrated sodium, calcium, magnesium, iron and lithium aluminium silicates. Those bentonite which are used for drilling industry are principally composed of either sodium montmorillonite, calcium montmorillonite (bentonite) or lesser extent, hecctorite (lithium montmorillonite). The most used commercial clay in drilling fluid is sodium montmorillonite.

According to estimate from the Nigerian mining Corporations and the Raw Materials Research Development Council (RMRDC) , deposits of local bentonite clays in Nigeria has been modestly projected to be above 700 million metric tones (Aigbenedion and Iyayi, 2007 a,b;Raw Materials Research and Development Council, 2007, James et al 2008, Omole et al 2013) with the bulk of it lying in Afuze, Edo state, Mid-western Nigeria which holds about 70 – 80 metric tons of bentonite clay (Nweke et al, 2015; Nweke, 2015). In addition, barites deposits in Nigeria have been identified in Taraba and Bauchi, which hold about 7.5 million metric tons. Other regions with appreciable deposit of bentonite clays are the North-east region which comprises of Borno, Adamawa and Gombe states (Folade et al., 2008; James et al., 2008, Ahmed et al., 2012a,b; Obaje, 2013, Inegbenebor et al., 2014).

The mineral characterization of bentonite clay deposits in Nigeria in its raw form has indicated that the clays are mainly calcium based montmorillonite and this differs significantly from the industry standard which is a sodium based montmorillonite clay. Beneficiation or activation of these clays with a sodium salt has been largely used by researchers in converting the calcium based montmorillonite clays into sodium based montmorillonite with comparable rheological properties with the API standard Wyoming bentonite clays (Onize 2003., Falode et al 2008., James et al., 2008, Salam et al., 2010; Dewu et al., 2011a,b; Udoh and Okon, 2012). The mechanism through which this occurs is via an ion exchange route that involves the substitution of the calcium ions for the sodium ions. The properties of locally formulated drilling mud that have been researched into include plastic viscocity (PV), Apparent viscocity (AV) Yield Point (YP), Mud density (MD), Fluid Loss (FL), ph and gel strength (GS). A summary of the works done on the rheology of locally formulated drilling are found in the review article of Richard O. Afolabi et al., 2017, evaluated locally bentonite clays obtained from the Pindiga formation in North –east Nigeria for rheological and filtration performance using a Rheometer and an API filter press. The authors considered the rheological properties, free swell volume, gel strength and filtration properties. It was observed that the clays concentration has a direct effect on these properties with noticeable improvement in all of them.

Not much is known about the viscoelastic behavior of the locally formulated drilling mud under challenging downhole environment such as high temperature high pressure (HTHP), deep offshore etc. In addition, the thermal stability of these beneficiated clays has not been well researched into and as a result is still an area of major concern. Furthermore, the beneficiated local clays have most often been used primarily for teaching purpose in institutions of higher learning due to the cost implications of importing foreign grade bentonite. Looking beyond the technique of beneficiation, acid activation and calcination of local bentonite clays have been reported (Ahmed et al., 2012a,b).

The significance of bentonite have increased due to its ability to form organically modified clay or nanoclays, which are gaining a large market place in the field of polymer mono-composites, paints, greases, inks, cosmetics and drilling mud.

Organoclay suspension are commonly used as oil-based drilling fluids due to their capacity to form gels and their suitable viscous properties. These fluids are submitted to high pressure and temperature in the well during drilling operations. The successful completion of an oil well and its cost depend, on a considerable extend, on the properties of these fluids hence, the main objective of this study is to develop a drilling fluid formulation with enhanced thermal and rheological properties, using organoclays prepared with a new generation of renewable surfactants. The functionalization of bentonite by intercalation of these surfactants is described. It has been long known that organoclays can be used to thicken organic compositions and particularly drilling fluids. See J.W Jordan, "Proceedings of the 10th National Conference on Clays and Clay Minerals" (1963) which discusses a wide range of applications of organoclays from high polarity liquids to low polarity liquids.

The central focus of this project is the development of an organophilic clay additive for oil based drilling fluids providing such fluids with improved temperature, stable rheological properties.

More recently, organophilic clay gellants have been developed which are the reaction products of smectite-type clays having a cation exchange capacity with certain organic cations or organic cations and organic cations combination. These gellants have the advantage of being effectively dispersible in particular organic compositions without the need for a dispersion aid under normal shear conditions.

In Nigeria, oil exploration is carried out in hostile environment where oil based drilling fluids are used. The success of drilling operations, and its cost, fundamentally more practical and efficient. Thus, improved rheological properties offer greater efficiency in the activities performed during the drilling process.

The Nigerian Local Content Development Act was signed into law in 2010 with the singular purpose of encouraging the use of Nigerian local resources and content in providing benefits and solutions to the problems confronting the Nigerian Oil and Gas Industry (Ayonmike and Okeke, 2015). The local content act provides a platform not just for Nigerian entrepreneurs in the petroleum industry but also researchers who seek to explore the applicability of the rich and abundant resources of the Nigerian State in Solving problems arising in the oil and gas industry (Richard Afolabi et al., 2017).

Furthermore, as the search for oil and gas reserves shift from the offshore regions, likewise is the associated cost of the overall drilling operation. The cost of drilling operation is also influenced by the performance of the drilling fluid. This in turn makes the design, formulation and maintenance of the drilling fluids important.

Nigeria as a nation is blessed with abundant bentonite resources which if well harnessed will reduce the importation of drilling fluid ingredients and specialized drilling fluids (Richard Afolabi et al., 2017).

Research objectives and aim

This research has the objectives to test and investigate the rheological and filtration properties of oil based drilling fluid formulated from Nigerian bentonite organoclay modified with fatty acid based imidazolium surfactants in HPHT conditions. This paper studies certain effects of the inherent high pressure and temperature present in deep well on the drilling fluid. The parameters that are gauged are viscosity, yield point and gel strength of the drilling fluid when subjected to these conditions. Despite considerable experimental studies over the years, there is relatively little systematic understanding of how the flow behavior changes with downhole conditions. The rheology of the fluid is influenced by many factors including temperature and pressure and salinity.

The aim of this study is to use organoclay of Nigerian bentonite as a main component in drilling fluid system to develop a suitable mud system for high temperature and high pressure environment.

EXPIREMENTAL

Materials and Methods

The Nigerian clay used in this work was obtained from the North eastern part of the country. Its cation exchange capacity (CEC) is 93meq/100g, obtained by methylene blue method. More information about the clay can be found in (James O.O et al., 2008). It is a calcium bentonite.

Oleic acid and stearic acid were obtained from Nigerian cotton seed oil.

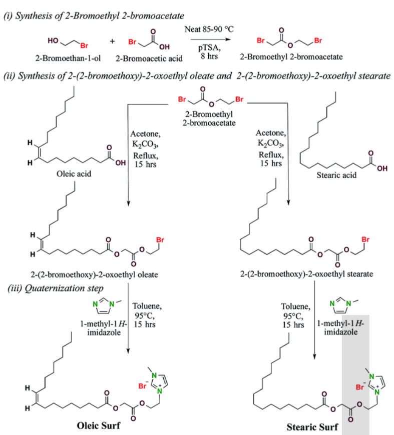
2-bromoethan-1-ol, 2-bromoacetic acid, *p*-toluenesulfanic acid monohydrate, 1-methyl-1*H*-imidazole and potassium carbonate were purchased from Sigma-Aldrich.

Synthesis of oleic acid and stearic acid based cations surfactants.

ISSN 2229-5518

The synthesis of oleic acid based imidazolium surfactant 1-methyl-3-(2-(2-(oleoyloxy acetoxy) ethyl)-1*H*-imidazol-3-ium bromide (Oleic surf) and stearic acid based imidazolium surfactants – 1 – methyl-3-(2-(2-(stearoyloxy)acetoxy) ethyl)-1*H*-imidazol-3-ium bromide (Stearic stuff) was carried out according to the method developed by Avinash Bhadani et al., (2017) which is depicted in the scheme shown below.

Experimental details of the procedure of synthesis can be found in the cited reference (Avinash Bhadani et al., 2017).



Scheme 1 Synthesis of oleic and stearic acid based cationic surfactants.

Table 1: Chemical Composition of Nigerian clay bentonite analyzed by XRF

Element oxides	Wt. %
SiO_2	57.32
Al_2O_3	24.87
Fe_2O_3	3.90
MnO	0.00
MgO	2.42
CaO	1.98
N_a2O	1.11
K_2O	0.65
TiO_2	0.27
P_2O_5	0.04
SO_3	0.12
SrO	0.02
LOI	11.36
(%)	103.95

Organoclay preparation.

The smectite clay is polycationic, hence the metallic ions occupying the inter layer space (predominantly Ca^{2+}) had to be changed by sodium ions (Na^{+}): for that the clay is dispersed in deionized water (4wt. % of clay) and Na_2Co_3) at a concentration of 100 meq/ 100g of clay, was slowly added to the suspension. The suspension was stirred for about 30 min at 97^{0}C. Then an aqueous solution of Oleic acid based imidazolium surfactant: 1-methyl-3-(2-(2-(oleoyloxy)acetoxy)-1H-imidazol-3-ium bromide (oleic surf) and stearic acid based imidazolium surfactants: 1-methyl-3-(2-(2-(stearoyloxy)acetoxy)ethyl)-1*H* imidazole-3-ium bromide(stearic surf) was added to the suspension containing sodium smectite clay, at a concentration equivalent to 1.1 CEC of the sodium clay. After stirring for 30 min at a room temperature, the suspension was filtered and washed with deionized water. The organophilic clays were then dried at 60^{0}C for 48h, ground and stored at room temperature.

Characterization by instrumental techniques.

Characterizations: The FTIR spectrum was recorded on Perkin Elmer FTIR 1650 spectrometer at ambient temperature using KBr disk method. The disc containing 0.0010g of the sample and 0.3000g of fine grade KBr was scanned at 16 scans at wave number range of 400-4000cm^{-1}. CHNS analyser (LECO CHNS-932) was used for quantitative analysis of amount of intercalation present in the organoclay. A sample of approximately 2mg of organoclay burned at 1000^{0}c under oxygen gaseous flow was used for this test. The sulfamethazine was used as standard.

X ray diffraction (XRD)

The clays (Sodium and Organo) were analyzed by X-ray diffraction using a Philips X'Pert-MPD diffractometer. XRD Patterns were recorded using Cu k*ol* (π=1.54056 A^O) and scanning rate of 1^o (20)/min. The basal spacing ($d_{(001)}$) of clays was calculated using Braggs law.

Thermogravimetry

Thermogravimetric analysis (TG) and Differential Thermal Analysis (DTA) of the clay before and after modification were obtained in simultaneous TG-DTA. The weight loss arising from the degradation was studied by TGA (Perkin Elmer Diamond TG/DTA instrument). Samples of 5 – 7 mg were heated from 50ºC to 650ºC at a rate of 10ºC/min. The TGA traced was used to determine the % weight loss at 650ºC which is sufficient temperature to degrade the organic content present in modified MMT Clay.

Scanning Electron Microscopy

The morphology of the products was analyzed by Scanning Electron Microscopy (SEM) (Philips XL-30 and Hitachi S400 with EDS system).

Choice of Organic cations

In aqueous solutions, surfactants molecules start to aggregate and form micelle in concentration called Critical Micelle Concentration, and it is one of the most important physical parameters of surfactants. The physical properties of surfactant like viscosity vary markedly when it concentration is higher or lower than its CMC, and the studies and industrial applications of a surfactants are always based on the value of its CMC. Also Micelle formation enables emulsification, solubilisation and dispersion.

The CMC values of these new renewable ester based imidazolium surfactants are lower compared to other types of non-functionalized imidazolium surfactants (i.e 1-alkyl-3-methyl-imidazolium chloride 1-alkyl-3-methyl-imidazolium bromides and functionalized imidazolium surfactants, ester based imidazolium surfactants, aryl group containing imidazolium surfactants etc.) (Avinash Bhadani et al., 2017).

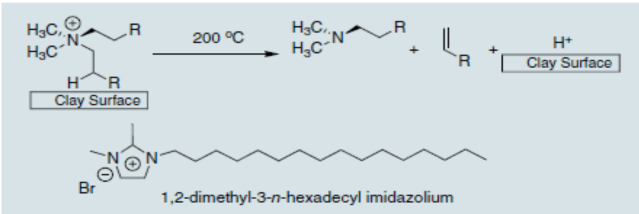
Also, recent studies have established ester based imidazolium surfactants to be bio-degradable. (Avinash Bhadani et al., 2017).

Both the Oleic surf and stearic surf containing ester functionality have been found to be readily biodegradable under the experimental condition (Avinash Bhadani et al, 2017).

Furthermore, due to the variety of structures of organic cations available bentonite modification, it is best to refer to literature search for a guide in selecting Organic cations. One other important factor to be considered is thermal stability. For example, Alkyl ammonium's which are widely used for clay modification are thermally unstable above 200ºC undergoing a Hoffman degradation and this temperature (Scheme 2) (Xie, W. et al., 2001).

For higher temperature end use applications, Imidazoliums (Scheme 2) appear to have great promise, capable of handling temperatures; 300ºC or above and available in a variety of structures that can be tailored to high temperature application.

(Gilman J.W et al., 2002, 2003).



Scheme 2. Hofmann Degradation of alkyl ammonium on clay surface and thermally stable imidazolium cation treatment.

Preparation of Drilling Mud

Oil based mud formulation intended for use under high temperature (up to about 500ºF) and high pressure (up to about 25,000 psi) conditions may contain a petroleum oil, a weighting agent, an emulsifier, a gelling or thixotropic agent, salt and fluid loss control agent as the ingredients if desired.

In the formulation of drilling mud, several approaches were investigated in this work. The oil based drilling was formulated according to the latest test methods described in API RP 13B-2: Recommended Practice for Field Testing Oi-based Drilling Fluids (5th Edition). The oil based drilling fluids were then aged for 16h before performance test. The performance measurement was conducted at 50ºC according to API RP 13B-2 (API Institute, 2014). However, for the result reported in this paper, the following approach was used:-

For the preparation of the drilling fluids, 3 wt% organoclay was mixed with the base oil, using a high shear mixer, (Ultraturrax, Ika, Germany), at 9,000rpm, for 5 min and room temperature, before mixing, both organoclays were wetted with oil, for an hour, to guarantee good organoclay dispersion into the oil base. When the dispersion process was finished, the resulting suspensions became viscous and stable. the drilling fluids formulated were stored at a room temperature.

The mud system was formulated without a wetting agent and fluid loss additive; this reduces cost of formulation as shown in the Table 3 below.

Table 3: Composition of Test Fluid

Component	Percent (%)
N – Paraffin (Oil phase)	65
RNX – 40 (emulsifier)	25
Saline solution – 35000ppm NaCl	7
Organoclay, 1 & 2	3

Organocaly 1 - Oleic surf

Organoclay 2 - Stearic surf

The base oil used was crude oil (paraffinic) generally, in practice.

The oil (continuous phase) used is a petroleum oil, diesel oil or mineral seal oil, although lighter oil such as kerosene or heavier oils such as fuel, white oil, crude oil, and the like may also be used.

Determination of Rheological and Filtration properties of formulated drilling fluid.

The rheological and filtration properties of the drilling fluids were determined using traditional procedures and state-of-art equipment for the purpose of comparison.

The Filtration property was checked using the high temperature high pressure (HTHP) filter press shown in Fig. 2 at 120^{o}C and 500psi.

Figure1. High temperature High pressure (HTHP) Filter Press.

Also FANN Model 90, a dynamic radial filtration apparatus, evaluates the filtration properties of a circulation fluid through a ceramic core. It can also be used in the industry for conducting filter cake formation and permeability analysis when drilling fluid optimization through shale sections. Dynamic filtration simulates the effect of fluid movement (shear rate) on the filtration rate and filter cake deposition in an actual well. In addition, the Model 90 can be heated and pressurized to provide the closest possible simulation of downhole conditions. The filter medium is a thick cylinder with rock like characteristics to simulate the formation. The filter medium is available in varying porosities and permeability's (Gursat Altun et al., 2015).

A high pressure high temperature (HPHT) viscometer (Candler Viscometer 7600) is used for the rheological analysis. The viscometer is designed for rheological studies of drilling fluids while subjected to varying drilling well conditions in accordance with ISO 10414-1, 10414-2, and API 13 recommended practices. As the variation of the pressure and temperature would influence the measured viscosity values of the suspension, two independent experimental schedules are performed. Automated measurements were recorded once the pressure and temperature values of the sample have reach the test values. Viscosity values are measured at a maximum pressure of 170MPa with temperature ranging from ambient to 180^{o}C.

This viscometer was capable of measuring the rheological properties of drilling fluids under high temperatures up to 600^{o}F and high pressure up to 40,000 psi (Amani and Al-jubouri, 2012).

ISSN 2229-5518

the rheological property (plastic viscosity, Yield point and apparent Viscosities) of the formulated mud sample was also examined after aging for 16 hours. The 8-speed viscometer was used for the measurement at the following dial settings 600, 300, 200, 60, 30, 6, and 3 in rotation per minute (RPM). The mud was allowed to gel for 10 seconds and 10 minutes respectively. The plastic viscosity and yield point were evaluated using the following relationships:

Plastic viscosity (PV) = dial reading for 600rpm – dial reading for 300rpm (1)

Yield point (YP) = dial reading for 300rpm – PV (2)

Apparent viscosity (AV) = 600rpm/2 (3)

The PV and AV were measured in centipoise (cP) while the yield point was measured in (Ib/100 ft^2). The work was completed with the help of using Fan 35A and M50 viscometer, which measures the rheological properties of the drilling fluid up to (200^{o}C) and (500psi). Understanding the Influence of this two factors is crucial for the purpose of designing acceptable drilling fluids that can function properly in such environment. This system uses a rotor and bob geometry for rheology parameters measurement and applicability approved for applications in Petroleum industry.

Figure 2: Fann 35A and M50 Viscometer

The Fann 35A viscometer was used for measurement of rheological and thixotropic parameters. Samples were prepared in Hamilton Beach Stirrer Model 936 with 13000 rpm for 5 minutes.

Equipment for evaluating drilling fluid at HPHT conditions

The main equipment for this experiment is CHANDLER Model 7600 High Pressure High Temperature Viscometer.

New testing equipment and new laboratory techniques that can measure the rheological properties of drilling fluids at conditions up to 600 F and 40,000 psi have recently become commercially available (Lee and Shadravan, 2012).

Figure 3: Chandler 7600, Extreme HPHT Viscometer

Figure 4. Chandler 7600 HPHT Viscometer

Figure 5. HPHT Filter Press

Results and discussion

Intercalation of oil surf and stearic surf into bentonite clay (Montmorillonite)

The reaction of intercalation of the two surfactants was studied at concentration ranging from 0mg/l to 10000mg/l.

Measurement for basal spacing's (*d* spacing) of the clays were performed by X-ray powder diffraction (XRD). The *d* spacing was calculated according to the Bragg's equation ($n\lambda = 2d\theta$), where the value for $n = 1$ was assigned by calculating the observed peak pattern for fitting $n = 2, 3$, or 4.

Enlargement of clay linter layer spacing correspondent well with incorporation of the amount of surfactant into the clay layer, as displayed in table 4.

Table 4: Intercalation of Stearic surf.

Concentration of stearic surf	d_{001} (Å)
0mg/L	12.63
50mg/L	14.68
100mg/L	14.82
500mg/L	14.92
2000mg/L	17.58
5000mg/L	20.86
10000mg/L	20.88

Table 5: X-ray analysis of Na^+ - MMT intercalated by Oleic surf

Concentration of Oleic surf	D spacing (Å)
0mg/L	12
50mg/L	28
100mg/L	28
500mg/L	30
2000mg/L	34
5000mg/L	34
10000mg/L	34

As can be seen in both tables 4 and 5, the *d* spacing of the clay changed accordingly, expanding in organoclays after intercalation and then further to a higher interlayer spacing after absorbing the surfactant in the clay galleries.

Overall result for both Oleic surf and Stearic surf confirmed that the process of intercalation was successful.

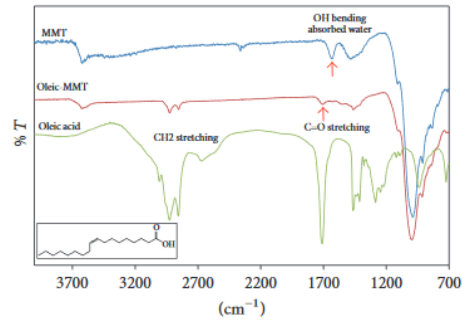


Figure 6: FTIR Spectra of oleic acid, MMT and modified clay.

FTIR spectra of oleic acid, MMT and MMT Modified with oleic acid base surfactants are shown in figure 1. In the spectrum of MMT, the peak at 3619 cm^{-1} is related to O-H stretching. The Si-O out-of-plane and in plane stretching bonds are observed at 1110cm^{-1} and 996cm^{-1} , respectively. The Al-O and Mg-O stretching bonds are assigned to the peaks between 836 and 910cm^{-1} . The strong peak at 1630cm^{-1} is assigned to the bending mode of absorbed water (Zhu J. et al., 2003, 2001).

The spectrum of oleic acid shows a peak at 1710cm^{-1} which is related to the vibrations of C=O groups. Two peaks at 2932 cm^{-1} and 2856 cm^{-1} are related to the symmetric and asymmetric vibrations of methylene ($-CH_2$) present in the fatty acid (Amanullah M., 2005).

Characteristic peaks of the oleic acid are included in the spectra of the modified clay, indicating the presence of oleic acid in the gallery spacing of the organoclays. These peaks are indicative of surfactants (oleic surf) associated with the clay surface.

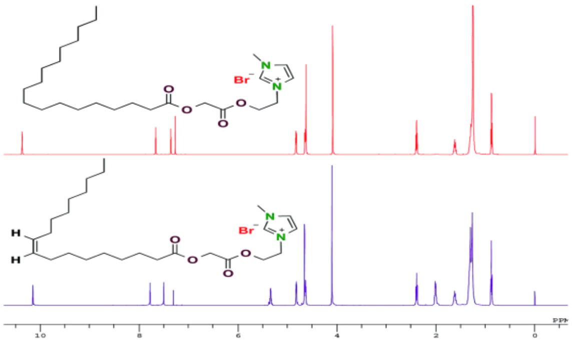


Figure 8: ^{1}H NMR spectra of oleic acid and stearic acid based surfactants.

(Taken from Avinash Bhadani, et al., 2017).

Evaluation of rheological and filtration properties of formulated drilling fluid.

For the purpose of accuracy, both traditional procedures and state-of-the-art equipment were used. The dial readings of the various samples were taken by the use of the Fann Viscometer Model 3500 at readings 600,300,200,100,60,30 and 3 rpm as indicated by API to measure the rheological properties of mud samples. Overall, to ensure the accuracy of the experimental result, API standard procedures for preparing mud and determining the mud properties were followed throughout the experimental work. The plastic viscosity, apparent viscosity and yield point values were calculated using equation 1, 2 and 3 respectively as shown above.

Table 6. Rheological behavior at different viscometer readings for stearic surf and Oleic surf.

Dial setting (RPM)	Mud type	
	Stearic surf	Oleic surf
600	89	79
300	53	48
200	38	40
100	23	26
60	15	16
30	9	11
6	3	9
3	2	6
Gel Strength, 10 seconds ($Ib/100ft^2$)	10.5	6
Gel Strength 10 minutes ($Ib/100ft^2$)	23	7
Apparent Viscosity (cP)	44.5	39.5
Plastic viscosity (cP)	36	31
Yield point ($Ib/100ft^2$)	17	17

The plastic viscosity, yield point and gel strength were determined with a Fann viscometer. The yield point is reported in terms of pounds per 100 square feet, the plastic viscosity in centipoises (cps), and gel strength as pounds per 100 square feet.

Many drilling fluids are thixotropic; the ability of drilling fluids to form a gelled structure over time when not subject to shearing and then to liquefy when agitated. This gelling behavior aids the suspension of cuttings while fluid motion is stopped. A drilling fluid must be able to transport the cuttings under dynamic conditions and suspend them under static conditions. Gel strength is one of the important drilling fluid properties because it reveals the ability of the drilling mud to suspend drilling cuttings and weighing materials when circulation is ceased and is measured with a viscometer after varying lengths of static conditions (generally at 10s and 10min) (Lee J. et al, 2012).

Although gel strength is a crucial property for optimal drilling operations, it is ultimately a compromise; it should be carefully monitored (Rossi et al., 1999, Ronald P. et al., 1981).

Excessive gel strength can lead to retention at the surface, which in turn can cause severe drilling problems such as ineffective solids control, fracturing of the formation, and fluid loss. Low gel strength values indicates that the fluid will not efficiently suspend the cuttings leading to the build-up of the cuttings bed within the bore path resulting in an increased possibility for stuck drill pipe.

Filtration and filter cake

There are many definitions of filtration both in the chemical engineering and petroleum engineering industries. Filtration or fluid loss is a relative measure of the fluid that could invade a permeable formation through deposit and mud solids. Fluid loss is the measurement of filtrate passing from the drilling fluid into a porous permeable formation. Low fluid loss is characteristic of good drilling fluids and the key to borehole integrity. The goal of good drilling fluids is to create a thin filter cake on the side of the borehole. This prevents the excessive loss fluids into the formation". A desirable filter cake is achieved by minimizing the drill solids content of the drilling fluid and maintain the proper concentration of filtration control additives (Moussa, M.M, 1985).

Filtration experiments were carried out at HTHP conditions (300psi differential and 250°F) both at static and dynamic conditions.

Based on drilling fluids reference manual, two types of filtration are considered: Static and dynamic. Static filtration occurs when the fluid is not in motion in the hole (Moussa M.M, 1985).

Table 7. Filtration characteristics of the test drilling fluids at 300psi differential pressure and 250 temperatures.

Stearic surf					
Concentration (wt%)	Mode	Filter Cake Thickness (in.)	Percentage change in Thickness (%)	Cumulative Filtrate Volume (cm^3)	Percentage Change in Filtrate Volume (%)
0.0	Static	0.3084	-	12.0	-
0.03	Static	0.3123	1.25	10.0	-16.67
0.5	Static	0.3618	17.32	6.9	-42.50
1.5	Static	0.4330	40.40	9.0	-25.00
2.5	Static	0.4760	54.35	11.9	-0.83
0.5	Dynamic	0.2958	-18.24	12.4	79.71
Oleic Surf					
0.5	Static	0.3462	12.26	13.6	13.33
1.5	Static	0.4280	38.78	18.9	57.50

Table 8. Filtration properties of optimum concentrations

Organoclay	Concentrations in drilling fluid	Filtration volume (ml)
Stearic surf	3%	4.0
Oleic surf	5%	5.6

The result in table 8 above shows that drilling fluids formulated with oleic surf and stearic acid have excellent filtration property as its filtrates volume is (150°C) and high pressure (3.5MPa). The high –temperature and high Pressure condition are usually encountered when drilling when drilling deep formation.

A comparative study was undertaken for a conventional drilling fluid containing organic lignite and the test fluids of this work. The results are shown in Table 9 below.

Table 9. Comparison of Performance of different filtrate reducers for drilling fluid.

Type of filtrate reducers	API filter loss-mL	High temperature High pressure filter Loss/mL
3% organic lignite	6.4	40.8
3% Oleic surf	6.7	7.1
3% Stearic surf	3.4	4.4

API filter loss (FL_{API}) and high temperature high pressure (HTHP) filter loss (FL_{HTHP}) of the drilling fluid after aging at the high temperature of 220°C for 16h are shown in Table 9. The HTHP filter loss was measured at 180°C and 3.5 MPa.

The stearic surf fluid loss reducer has a very good filtration reduction performance.

Table 10: Comparison of organoclay based test drilling fluid oil –based drilling fluid properties.

Type	Condition	Apparent Viscosity/ (mPa·s	Plastic viscosity (PV)/(mPa·s)	Yield Point (YP)/Pa (mPa·s)	YP/PV/ (Pa(mPa.s)$^{-1}$)	Gel Strength /Pa	High Temp/ High pressure Fluid loss/mL
Traditional drilling	Before aging	78.5	72	6.64	0.092	2.0/3.5	-
	After aging	91.0	85	6.13	0.072	2.5/3.5	8.6
Organo clay Stearic surf	Before aging	62.0	50	12.26	0.245	5.5/7.0	-
	After aging	55.0	45	10.22	0.227	5.0/6.5	4.2

Compared with the traditional drilling fluid, the organo (stearic surf) drilling fluid has the following advantages:

Has lower viscosity, which is good for increasing the rate of penetration. The traditional drilling fluid has high viscosity before and after aging, which has negative effect on increasing rate of penetration. Besides, the organoclay test drilling fluid has higher yield point, gel strength and higher ratio of yield point to plastic viscosity before and after aging than traditional drilling fluid which is conducive for cutting-carrying.

The rheological properties of the drilling fluid will remain stable during drilling operations even if it is contaminated by NacL or drilling cuttings.

CONCLUSION

The ease of synthesis combined with optimum surface properties and biodegradability establish these new renewable fatty acid based surfactants to be good alternative to conventional petrochemical based surfactant.

The bentonite (montmorillonite) has been successfully modified using these organic cationic surfactants. The XRD results show intercalation of the organic cations between the clay mineral layers, hence basal spacing increased. The organoclays prepared in this study can be used for the formulation of HPHT drilling fluids.

A major constituent of oil based drilling muds is colloidal or gelling agents, normally organophilic clays. Large amount of the clays are often required to obtain the desired thixotropic properties in the mud formulation.

The aim of this work is to provide improved formulations using less of the clays without loss of the required thixotropic and thermal properties of the oil-mud formulations. A typical oil mud formulation was prepared and evaluated for applications in HPHT oil & gas wells. High Pressure and Temperature (HPHT) wells have bottom hole temperatures of 300°F (150°C) and bottom hole pressures 10,000psi (MPa) or higher.

Drilling into reservoirs with elevated pressures and temperatures requires a fluid with stable rheological properties. This study shows that the oil-based mud is tolerant to high temperature/high pressure conditions, because the experiment was designed to mimic real conditions. The drilling fluid formulated herein showed good rheological and filtration properties as well as strong anti-aging properties and anti-pollution ability under high pressure and high temperature conditions.

Filtration properties of the drilling fluid used at high temperature and high pressure conditions (above 300°F) and especially with high salinity conditions are reported in this work.

Investigation on HTHP rheological properties of the drilling mud indicates more realistic results compared to traditional method. Despite the large work done in the area of improving the rheological properties of the locally sourced Nigerian bentonite clays, little attention has been given to studying the characteristics of drilling mud prepared from Nigerian bentonite clays and evaluating rheological properties of the drilling fluid when exposed to high pressure high temperature (HPHT) conditions and/or contaminated with salts as it comes in contact with deep formations.

Acknowledgment

The properties of the formulated drilling fluid under high pressure high temperature conditions were studied using state-of-the- art equipment - Chandler 7600 HPHT Viscometer. This was facilitated by the Petroleum Engineering Department, Texas, A&M University of Qatar, Qatar. The Author is grateful.

The author is also thankful to Dr. Zhenghe Xu, Department of Chemicals and Materials Engineering, University of Alberta, Edmonton, Canada for his valuable advice.

REFERENCES

1. A.P Institute, API recommended practices 13B-2 Recommended Practice for Field Testing Oil-Based Drilling Fluids, API (2014) Washington D.C, USA. 2014, pp. 141
2. Aghamelu, O. P, and Okogbue, C.O. "Characterization of some clays from Nigeria for their use in drilling mud.". *Journal of Applied Clay Science.* doi:10.1016/jclay.2015.08.025, 2015.
3. Ahmed A.S, Salahudeen , N. Ajinonomoh C.S Hamza., H. Okihere., A. 2012a. Studies on the mineral and chemical characteristics of Pindiga bentonitic clay. Petrol Technol. Dev. J. 1. 1 – 8.
4. Aigbedion I., Iyayi S.E., 2007a. Formation evaluation of Oshioka field using geophysical well logs. Middle – East J. Sci. Res. 2. 107.
5. Aigbedion I., Iyayi S.E., 2007b. Formation evaluation of Oshioka field using geophysical well logs. Middle – East J. Sci. Res. 2. 107.
6. Alexander B. Morgan, Material Matters. Volume 2 Issue 1.
7. Amani M, (2012) Rheological Properties of Oil-Based mud under High Pressure and High Temperature conditions. *Advances in Petroleum Exploration and Development, 3(2), 21 – 30.*
8. Amani M, Al-Jubouri M, Shadravan A. Comparative study of using oil-based mud versus water-based mud in HPHT fields. *Adv Pet Explor De.* 2012;4(2)18 – 27.
9. Amani M, and Hassiba, K.J. 2012. Salinity Effect on the Rheological Properties of Water-based Mud under High Pressure and High Temperature of Deep Wells. Presented at the SPE Kuwait international Petroleum.
10. Amani M., Al-Jubouri, M. Shadravan, A. (2012). Comparative study of using Oil-based Mud versus Water-Based mud in HPHT Fields. Advances in Petroleum Exploration and Development 4(2): http://dx.doi.org/1-.3968/j.aped.1925543820120402.987
11. Amanullah MD, (2005) Physio-chemical characterization of vegetable oils and preliminary test result of vegetable oil based muds. SPE/IADC (97008) paper presented at the SPE/IADC Middle East Drilling Technology Conference and Exhibition in Dubai. U.A.E September 12th – 14th.
12. American Petroleum Institute (2014). Recommended Practice for Field Testing Oil-based Drilling Fluids, API recommended Practice 13B-2. Fifth Edition.
13. Avinash Bhadani, Kazuki Iwabata, Kenechi Sakai, Setsuko Koura, Hideki Sakai and Masahiko Abe. The Royal Society of Chemistry, 2019.
14. Dewu, B.B, Arabi, S.A Oladipo, M.O., Funtua, I.I., Mohammed Dabo, I.A., Muhammad A.M., 2011a, improvement of rheological properties of bentonitic clays using sodium carbonate and synthetic viscosifier. Int. Arc. Appl. Sci. Tech. 2 (2) 43 – 52.

15. Dewu, B.B., Funtua , I.I., Oladipo, M.O., Arabi, S.A., Mohammed-Dabo, I.A.,, Muhammad, A.M., Hamidu, 1., 2011b. Evaluation and beneficiation of bentonic clays from Pindiga formation in Benue trough. Am. J. Eng. Appl. Sci.4 (4), 497 – 503.
16. Dewu, B.B., Funtua , I.I., Oladipo, M.O., Arabi, S.A., Mohammed-Dabo, I.A.,, Muhammad, A.A., 2012. Evaluation of rheological and other physical properties of bentonic clays from Fika formation in parts of North-eastern Nigeria. Pet. Tech. Dev. 1.1
17. Falode, A.O., Ehinola, O.A., Nebeife, P.C., 2008. Evaluation of local bentonitic clay as oil well drilling fluids in Nigeria. Appl. Clay Sci. 39:19-27. http://dx.doi.org/10.1016/j.clay.2007.04.011.
18. Hughes B. Drilling Fluids Reference Manual. Houston, Texas; 2006.
19. Jahan S.A, Parveen S., Ahmed S, Kabir H, (2012). Development and characterization of organophilic clay from bentonite. Mater Sci 8:67-72.
20. James, O.O., M. Adediran Mesubi, F.A Adekola, and Odebunmi, J.I.D. Adekeye. Beneficiation and Characterization of a bentonite from North-eastern Nigeria. Journal of the North Carolina Academy of Science. 124 (4). 2008, pp. 154 – 158.
21. L.B. de Paiva, A.R Morales, F.R.V Diaz, Organoclays: properties, preparation and applications, Appl. Clay Sci. 42 (2008), 8 – 24.
22. Lee J, Shadravan A, and Young S. 2012. Rheological Properties of Invert Emulsion Drilling Fluids under Extreme HPHT conditions. Presented at the IADC/SPE Drilling Conference and Exhibition, San-diego, California, U.S.A., 6 – 8 March. SPE-151413-MS.
23. Lee J., Shadravan A., and Young S., (2012). Rheological properties of invert Emulsion Drilling Fluid Under HPHT Conditions. *Society if Petroleum Engineers*. DOI:10.2118/151413-MS
24. Moussa M.M.: Dynamic Measurement of Drilling Fluid Rheology at Elevated Temperature and Pressure. Proceedings Mid East Oil Technical Conference and Exhibition, Bahrain, (1985).
25. Nweke., O.M, Igwe E.O., Nnabo, P.N., 2015. Comparison evaluation of clays from Abakili formation which with commercial bentonite for use as drilling mud. Afr. J. Environ. Sci. Technol. 9 (6) :508-518.
26. Obaje, S.O., 2013. suitability of Borno bentonite as drilling mud. Int. J. Sci. Technol. 3(2), 151 – 152.
27. Okorie, O., 2009. Modification of Drilling Fluid pH with local Nigerian Additives. Pet. Technol. Dev. J. 1, 1- 16.
28. Omole, O., Adeleye, J.O., Falode, O., Malomo, S., Oyedeji, O.A., 2013. investigation into the rheological and filtration properties of drilling mud formulated with clays form Northern Nigeria. J. Petrol. Gas Eng. 4 (1), 1 – 13.
29. Omole., O. Molomo, S., Akande, S., 1989. The Suitability of Nigerian black soil clays as drilling mud clays. Nature and technical properties. Appl. Clay Sci. 4, 357 – 372.
30. Onize D.E., 2003. Production of Drilling mud from local clays. B. Engg. Thesis Federal University of Technology, Minna, Niger State. Department of Chemical Engineering (unpublished).
31. Ouellet – Plamondon, C.M., Stasiak, J.; Al- Tabbaa, A. The effect of cationic, non-ionic and amphiphilic surfactants on the intercalation of bentonite. Colloids and surfaces. A: Physicochem. Eng. Aspects, v.444. p. 330 – 337, 2014.
32. Raw Materials Research and Development Council. *Technical brief on mineral raw materials in Nigeria*. Abuja: RMRDC, 2011.
33. Ronald P., Bernard., BS (1981). Rheological properties of high-temperature drilling fluids, pages 11 – 12.
34. Rossi S., Luckman, P.F., Zhu, S. et al. 1999. High Pressure High Temperature rheology of Na Montmorillonite Clay Suspensions. Presented at the SPE International Symposium on Oil Field Chemistry, Houston, Texas 16 – 19 February. SPE-50725.
35. Terry Hemphi, Prediction of Rheological Behavior of Ester-Based Drilling fluids Under downhole conditions. SPE 35330. Paper presented at .s1 Ihe 1996SPE International Petroleum Conference and

Exhibition of Mexico held in Villerhamosa, Tabasco 5-7 March, 1996.

36. Udoh, F.D Okon., A.N., 2012. Formulation of Ware based drilling fluid using local materials. Asian J. Microbiol. Biotechnol. environ. Sci. 14 (2) . 167 – 174.

37. Xie W, Gao Z, Pan W-P, Doug H, Vaia R (2001). Thermal Degradation Chemistry of alkyl quaternary ammonium montmorillonite. Chem matter 13:2979-2990.

40.244.

38. Zhu J, He X, Guo J, Yang G, Xie D (2003) Arrangement Models for alkylammonium cations in the interlayer of HDTMA + pillared montmorillonite. Chin Sci Bull 48:368-372.

39. Zhu J, He X, Zhu L, Wen X, Deng F (2005) Characterization of Organic phase in the interlayer of montmorillonite using FTIR and CNMR. J Colloid interface Sci. 286:239-