



Enhancing Oil Based Drilling Fluids Parameters Using Secondary Synthesized Emulsifiers and Nanoparticles

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Abstract

Emulsion stability of oil based drilling fluids is a critical parameter for ultimate fluid performance, this property is controlled using a powerful emulsifiers. Good formulations of drilling fluid properties are required in the drilling operations which can be achieved by selection of adequate additives. The aim of this work is based on two parts; The first part is to enhance emulsion stability of oil based drilling fluids by series of nonionic secondary emulsifiers developed by esterification & amidation (MEAO, DEAO, DETAOA, DETADS, TEAOE and EGOE) reactions from local materials. The chemical structure for the prepared secondary emulsifiers was elucidated using elemental analysis and FTIR. The second part is studying the mud stability by the secondary synthesized emulsifiers in presences of CuO nanoparticles. Besides, the rheological behavior, filtration loss and gel strength were investigated. The results revealed that, the maximum emulsion stability was achieved with the secondary emulsifiers (DEAO and DETAOA), the addition of CuO nanoparticles to the oil base mud pronounced extremely stability integrated with all mud properties as described in the text.

KEYWORDS: Oil based drilling fluids, Non-Ionic Emulsifiers, Emulsion Stability, Breakdown Voltage, Nanoparticles.

1. Introduction

Drilling fluids are mixtures of natural and synthetic chemical compounds; the drilling fluid mud is pumped from the mud tanks down the drill pipe and being out through nozzles in the drill bit. The flowing mud sweeps the crushed rock cuttings from under the bit and carry them back up the annular space between the drill pipe and the borehole or casing to the surface [1-3]. After reaching the surface, the drilling fluid is passed through a series of vibrating screens, settling tanks or pits, hydro cyclones and centrifuges to remove the cuttings brought to the surface [4]. It is then treated as/if required with additives to obtain a set of desired physical and chemical properties meanwhile pumping it back into the well and the cycle repeated [5]. Drilling fluids has many important functions as remove rock bit cuttings from the bottom of the hole and carry them to the surface, overcome the fluid pressure of the formation, avoid damage of the producing formation, cool and lubricate the drill string and the bit, prevent drill pipe corrosion fatigue, allow the acquisition of information about the formation being drilled (e.g., electric logs, cutting analysis), support the borehole wall [6]. Drilling fluids can be

classified as to the nature of the continuous phase: gas, water, oil, or synthetic [7-9]. Within each classification, there are divisions based on composition or chemistry of the fluid or the dispersed phase. Over a long history of on-land and off-shore drilling operations two types of drilling fluids had been used, water-based drilling fluids/Mud (WBM), non-aqueous-based drilling fluids/Mud (NABM) and/or oil-based drilling fluids/Mud (OBM). Oil-based fluids (OBFs) used today are formulated with diesel, mineral oil, or low-toxicity linear olefins and paraffin. The internal water phase added as part of the formulation or incorporated while drilling, is stabilized using emulsifiers [10, 11]. More costly oil-based mud were used as they were usually more stable than the water-based mud (when drilling a deep well at high temperatures) [12]. Oil-based mud was more advantageous to use when drilling into subterranean formations which contain water swell-able clays in as much as being damaged by water contact. Because of their comparatively lower cost and good availability, crude oil petroleum and diesel oil had been used in the formation of oil-based Mud [13]. All such petroleum-based oils used for drilling mud contain relatively large amount of aromatics and at

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least a substantial concentration of n-olefins both of which may be harmful or toxic to animal and plant life. The drilling industry had developed several types of synthetic-based muds (SBMs) that combine the desirable operating qualities of the oil-based mud, lower the toxicity and environmental impact qualities of the water-based mud. It could also, improve the drilling efficiency without polluting the subsurface structures.

OBM formulation contains water as internal phase which is immiscible with oily base fluid, Surfactants are used in oil-based drilling fluids to emulsify water and to ensure that cuttings are wetted by the oil [14]. Surfactants are essentially the same for oil-based and synthetic oil-based fluids [15]. Emulsions are colloidal systems formed when two immiscible fluids are mixed [16], In W/O emulsions (invert emulsion), water droplets form the dispersed phase while the oil becomes the continuous phase. The type and amount of surfactants and surface active solids have proven effective in ensuring the stability of emulsions [17], For oil based drilling fluids where water is the dispersed phase, The smaller and the more monodispersed the water droplets are, the more stable the fluid becomes. The type of emulsifying agent, salt type, salt concentration and the O/W ratio will influence on the stability of the emulsion. The droplet size and specific surface area are affected by emulsifier concentration. Increasing emulsifier concentration leads to a decrease in the average droplet size. The specific surface area of the droplets increases when increasing concentration of emulsifier [18], Dispersion by mechanical grinding is the most common way to prepare drilling fluid emulsions. A stable emulsion is produced by the use of high pressure pumps and turbulent mixing. The process splits the water droplets into smaller units creating a more stable emulsion, Surfactants are the primary wetting components of drilling mud, the surfactants used in oil-based mud tended [19] to alter water-wet siliceous surfaces to intermediately wet or even oil-wet conditions increasing solid tolerance, reduce high temperature-high pressure filtration properties, improve rheological characteristics, and increase the drilling rate as emulsion stability is the key parameter for OBM stabilization and performance improvement and has a direct impact on rest of parameters such as HTHP fluid loss and rheological properties, Based on the structure of emulsion systems, the following classifications can be made: macro-emulsions (0.1–5 μm),

micro-emulsions (5–50 nm) and Nano-emulsions (20–100 nm) [20].

During drilling, Invasion of mud filtrate into the formation occurs as a result of differential pressure between hydrostatic pressure and reservoir pressure, a filter (mud) cake is formed on the formation face due to the build-up of the mud solids, Satisfactory fluid loss value and the deposition of thin, impermeable filter cake can mitigate the problems of excessive formation damage. In addition, the rheology is a key property that needs to be optimized for the development of stable and effective drilling fluid [21-22].

Over the past decades, Nanoparticles (NPs) among different additives, were investigated to address these challenges. Nanomaterials, and their associated manufacturing and processing technologies, are the key enablers of Nanotechnology industry and encompass a wide range of materials. Nanomaterials typically measure in the range of 1 to 100 Nanometer (nm). This means clusters of atoms or grains less than 100 nm in size, fibers less than 100 nm in diameters and films with thickness less than 100 nm. Nanomaterials exhibits properties such as being lightweight, ultra-high strength, high electrical and heat conductivity and an increased surface area. The superior behavior of Nanomaterials compared to the parent materials originates from Nanoparticles grain boundary, surface area per unit over mass or volume, size, purity and perfection of the particles. Nanotechnology is not new, but its application in the oil and gas industry certainly in its infancy, including drilling applications [23-25].

The first goal of this work is focusing on the preparation of some secondary emulsifiers based on local materials. The second goal is to pronounce some formulations of oil base mud using the prepared secondary emulsifiers. The stability of mud and effect of CuO Nanoparticles on the oil base mud should be investigated. Our attention may be extend to investigate the plastic and dynamic viscosity, yield value, gel strength, and filtration loss properties of the oil based mud.

2. Materials and Methodology

2.1 Materials

The diesel sample (Grade#3). The oleic acid, mono/di ethanol amine, di ethylene tri amine, Tri ethanol amine, Ethylene Glycol and Dodecyl benzene sulphonic acid were supplied from Sigma-Aldrich, Germany. Xylene, n-hexane (purity >99%) were obtained from Fluka, Germany. The CuO was used in the form of Nanoparticles, High Resolution Transmission Electron Microscopy (HR-TEM) as shown in **Figure (1)** in addition to dynamic light scattering (DLS) and the size distribution has been carried out as shown in **Figure (2)** and **Table (1)**.

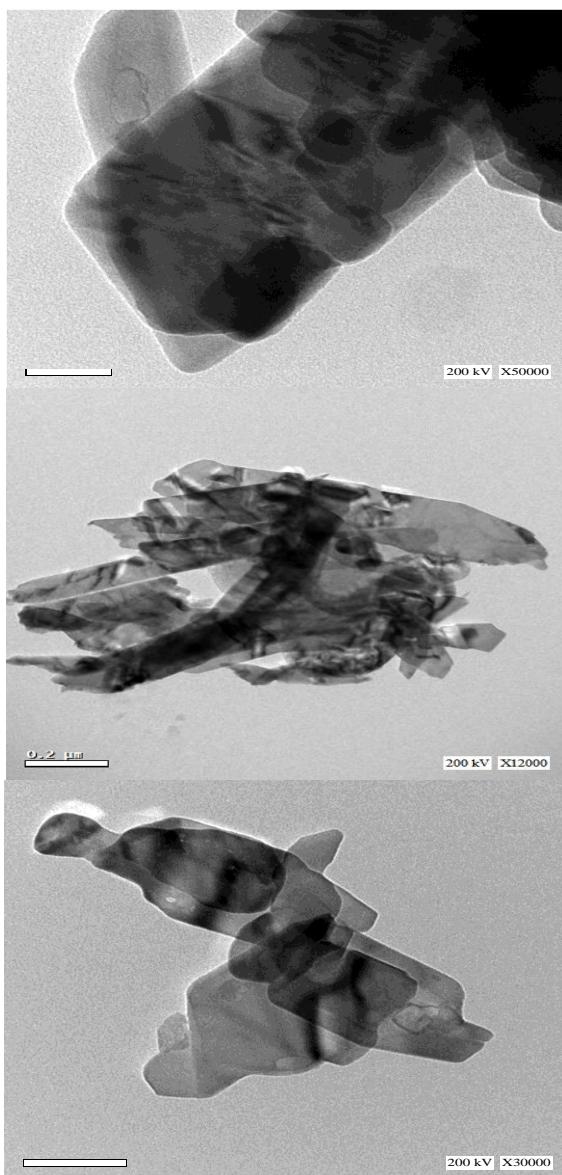


Fig. (1): HR-TEM Image of CuO Nanoparticles with High Resolution Shows Their Grains Morphology and Distribution Different Scales (50nm, 100nm and 0.2mm).

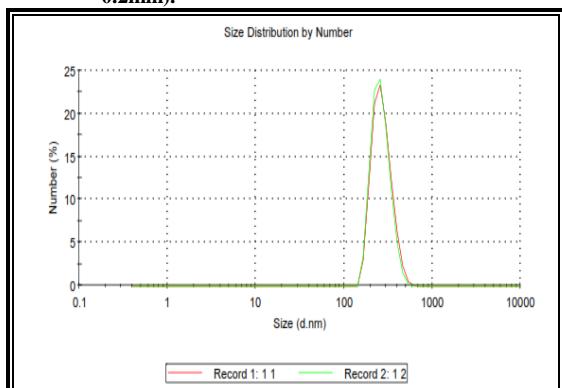


Fig. (2): Size Distribution by Number of CuO Nanoparticles.

Table (1): Number of CuO Nanoparticles Distribution

Size (d.nm)	Mean Number	Std. Dev. Number
164.2	3.3	0.3
190.1	12.7	1.0
220.2	22.0	1.1
255.0	23.6	0.5
295.3	18.7	0.3
342.0	11.7	0.8
396.1	5.7	0.9
458.7	1.9	0.6
531.2	0.4	0.2

2.2 Methodology

2.2.1 Preparation of Nonionic Emulsifiers

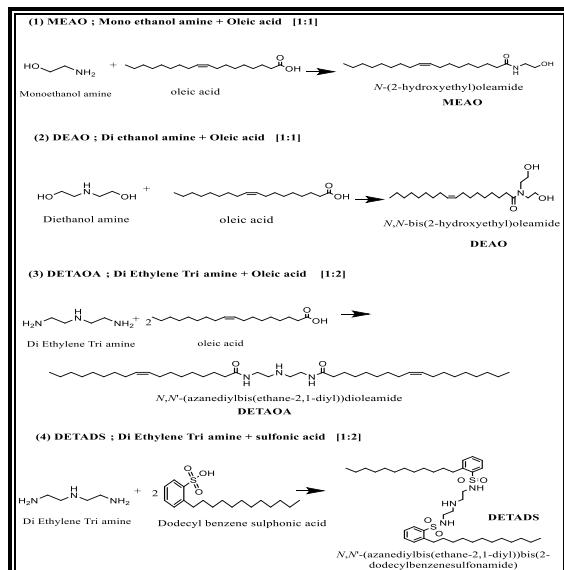
Mono, di ethanol amine, di Ethylene tri amine were amidated individually with oleic acid. Whereas di ethylene tri amine was amidated with the alkyl benzene sulfonic acid, using different molar ratios of the reactant as shown in **Table (2)**, The reaction mixtures were heated to 140 °C (284 °F) in Xylene as solvent using p-toluene sulfonic acid (PTSA) as a catalyst, with continuous stirring until the theoretical amount of water was collected in the Dean–Stark tube. The amide products were purified by washing with sodium chloride supersaturated solution, the organic layer was separated and the solvent was distilled off to obtain the planned amide (MEAO, DEAO, DETAOA, and DETADS). The designation emulsifiers were; TEAOE and EGOE by the same reaction vessel, solvent, catalyst, method and purification the tri ethanol amine with ethylene glycol were esterified with oleic acid in different molar ratios as shown in **Table (2)**, chemical reactions for amidation process is represented in **Scheme (1)** while chemical reactions for esterification process represented in **Scheme (2)**.

The FT-IR spectrometer was utilized to confirm the chemical structure of the prepared emulsifiers.

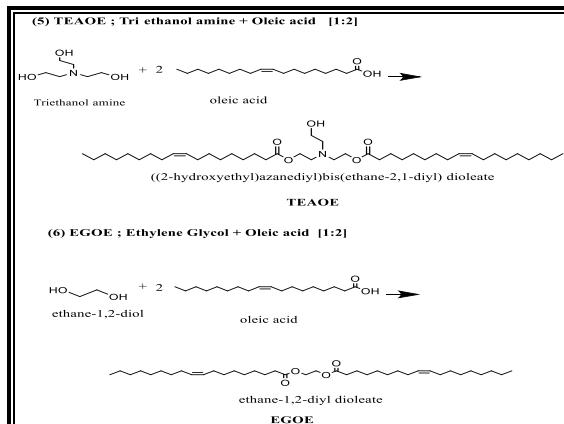
Table (2): Series of Laboratory Synthesized Emulsifiers

No.	Reactants, mole	Product	Description
1	Mono ethanol amine + Oleic acid (1:1)	Mono ethanol amine Oleic acid amide	MEAO
2	Di ethanol amine + Oleic acid (1:1)	Di ethanol amine Oleic acid amide	DEAO
3	Di Ethylene Tri amine + Oleic acid (1:2)	Di Ethylene Tri amine Oleic acid amide	DETAOA

4	Di Ethylene Tri amine + Dodecyl benzene sulphonlic acid (RQSO3H) (1:2)	Di Ethylene Tri amine Dodecyl benzene sulphonlic acid amide	DETADS
5	Tri ethanol amine + Oleic acid (1:2)	Tri ethanol amine Oleic acid ester	TEAOE
6	Ethylene Glycol + Oleic acid (1:2)	Ethylene Glycol Oleic acid ester	EGOE



Scheme (1): Chemical Reactions for Amidation

Scheme (2): Chemical Reactions for Esterification
2.2.2 Preparation of Oil Base Mud Samples (OBM)

Un-weighted oil based mud samples have been prepared throughout pilot test methodology, Pilot test of the drilling fluids is a testing performed on proportionately small scale samples. It is an essential part of drilling fluid preparation, testing and treating .Therefore, it is necessary to know the most suitable formulation to prepare stable drilling fluids with response and adjusting mud properties. The Pilot test design requires calculating amount of

materials to put into the test samples. In the pilot tests, the gram is equivalent to 1b and 350 cm³ is equivalent to one bbl (42-gal) as oilfield barrel (1b/bbl. (42 gal) = 1g/350 cm³).

A control sample using industrial primary and secondary emulsifiers was prepared as following: 266 ml of diesel (0.84 SG) as base fluid for 1 bbl lab work , 1.8 lb/bbl blend of oxidized tall oil Polyaminated fatty acid as primary emulsifier , 4 lb/bbl of Polyaminated fatty acid as a secondary emulsifier , 1.4 lb/bbl liquid based synthetic polymer as a fluid loss reducer , 6 ppb of Ca(OH)₂ as alkaline source followed by 70 ml of CaCl₂ brine solution at 1.18 SG then 6.2 lb/bbl of organophilic clay viscosifier, mixing carried out for several hours to ensure a good emulsion has been pronounced.

Industrial secondary emulsifier has been substituted by synthetized secondary emulsifiers, Oil based mud properties have been evaluated at different concentrations of synthetized emulsifiers and nanoparticles individually and in-conjunctions. All chemical additives were added slowly using stirring and mixed well in the Hamilton Beach mixer. CuO Nanoparticles has been added at different concentrations (0.1, 0.3 and 0.5% by weight) to oil based drilling fluid samples for both control sample and alternative samples prepared using synthetized emulsifiers.

3. Evaluation of Oil Based Mud by using the Synthetized Surfactant

3.1 Properties and testing procedures

3.1.1 High Pressure- High Temperature (HTHP) Fluid Loss

The HTHP was measured for the oil base drilling fluid. The HTHP fluid loss was measured in volume of fluid that passed through the filter cake at 500 psi differential pressure and 120°C (250°F). The filter cake was built on Fann 2.5" (6.3 cm) Diameter and 2.7 micron filter paper, A filter cake will be formed allowing solids free liquid to easily pass through, No water fraction observed at all HTHP tests indicating a strong well emulsified fluid.

3.1.2 Rheology

Drilling Fluids viscosity was measured using Chandler viscometer 3500 model [26]. Most successful drilling fluids are non-Newtonian. Pseudo plastic is a general type of shear-thinning, non-Newtonian behavior that is desirable for drilling fluids. The Bingham plastic and power-law models [27] describe a pseudo plastic behavior of the drilling fluids.

A- Bingham Plastic Model

$$\eta_{pl} = R_{600} - R_{300}$$

$$\tau_B = R_{300} - PV$$

$$\eta_{app.} = R_{600}/2$$

Where, η_{pl} is the plastic viscosity (cp), R_{600} is the dial reading at 600 r/min, R_{300} is the dial reading at 300 r/min, τ_B is the yield point (lb/100 ft²), $\eta_{app.}$ is the apparent viscosity (cp).

B- Power Law Model

$$\tau = k \gamma^n$$

$$\log \tau = \log k + n \log \gamma$$

Where k , and n are consistency and flow index respectively, τ is the shear stress, and γ is the shear rate.

3.1.3 Determination of Gel Strength

The gel strength of the mud is a measure of the minimum shearing stress necessary to produce slip-wise movement of fluid. Two readings are generally taken, One after 10 s (G10 s) and the second after the mud in the cup has been rested for 10 min (G10 min).

3.1.4 Electrical Stability (ES)

Electrical stability (E.S.) meter measures the fluid stability by increasing the voltage across a probe until the emulsion breaks and a current is established. The electrical stability will vary with the amount of water, the more water generally the lower the stability. Presence of conductive solids such as hematite and insoluble salt will result in low E.S. readings. Falling E.S. readings and the presence of water in the HTHP filtrate indicate weakness of the emulsion. Emulsifiers and lime additions are usually required. The relative stability of a water-in-oil emulsion mud is indicated by the breakdown voltage at which the emulsion becomes conductive, The ES test utilizes a probe with a pair of electrodes which are placed in the oil mud. A voltage is applied until the emulsion breaks and the mud conducts a current. The ES value is indicated by a LED display on the instrument. This test procedure is for the Fann Model 23C. Stability measured at 50 °C (120 °F) the test measures the voltage required to break the emulsion (Break down voltage, BDV) between standard electrode configurations. Samples evaluated have been prepared at moderate oil (80) / water (20) ratio (OWR) ~ 80/20, without presence of conductive solids and insoluble salt to avoid their negative impact on emulsion stability.

All above testing procedures as per API RP 13B-2 procedure for field testing Oil-Based Drilling Fluid [28].

4. Result and Discussion

4.1 Confirmation the Chemical Structure of the Prepared Secondary Emulsifiers

The chemical structure of the prepared compound (MEAO, DETAOA, DETADS and

TEAOE) was confirmed by FTIR as shown in Figure (3) (a, b, c and d). Disappearance band at 1700 cm⁻¹ and appearance of a new band at 1640 cm⁻¹ this confirmed formation of the corresponding amide (a, b and c). For ester compound d-(TEAOE), also disappearance band at 1700 cm⁻¹ and appearance a new characteristic band at 1730 cm⁻¹, This confirm formation the corresponding ester.

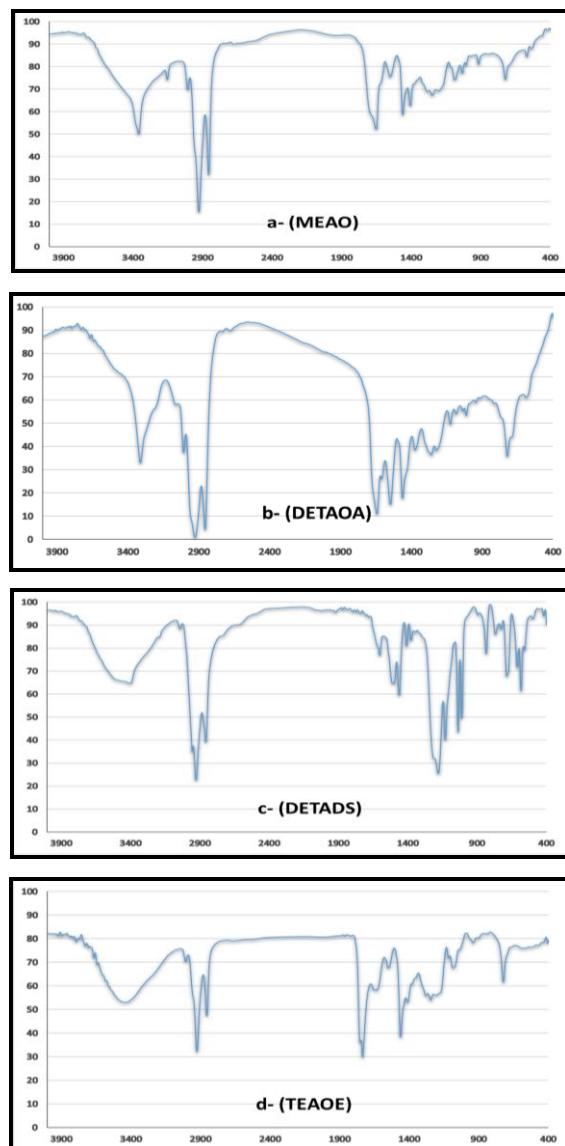


Fig. (3): FT-IR Confirmation the Chemical Structure of the Prepared Secondary Emulsifiers

4.2 Evaluation of the Prepared Non-Ionic Emulsifiers in Oil Based Mud Properties

The key technology of oil-based drilling fluid is the stabilization technology of emulsion. Emulsifier is the main treatment agent in oil-based drilling fluid, so its emulsifying ability and high temperature stability directly affect the performance of drilling fluid [29], The electrical stability (E.S) in the term of break down voltage for oil base mud samples in presence and absence of synthetized

secondary emulsifiers at two concentrations (4 ml and 8 ml) was initially tested as screen test was measured and the obtained data listed in **Table (3)**, The screening test showed that, the stability is ranking as; MEAO, DETAOA > DEAO > 1107 > DETADS (the blank exhibited 1027V). It seems that, the amide (MEAO) pronounced the maximum mud emulsion stability at the two concentrations 4, 8 ml (1135, 1420V) while in the blank sample exhibited 1027 V. The breakdown voltage of the mud emulsion (BDV) referring to the stability of the emulsion in term of the electrical double layer which was formed as the results of the charging materials in the mud formulation. The suitable BDV to pronounce mud stability starts from 1000V, at the same time all mud properties should be appropriate. The (DETADS) decreased the BDV down to 850V.

Table (3): Screening Test of Emulsion Stability

Sample	BDV (ES) 4 ml of SE	Extra screening for Blank-B samples by duplicating SE concentrations	BDV (ES) 8 ml of SE
Blank (Industrial SE)	1027		-
MEAO	1135		1420
DEAO	1116		1315
DETAOA	1123		1310
DETADS	850		560
TEAOE	1007		1202
EGOE	1107		1180

The data shown in **Table (4)**, show the proper concentration effect on the mud emulsion stability in presence of emulsifiers, the first sample which exhibited the best BDV stability (MEAO), the second is intermediate (DETAOA) and the third one which exhibited the lower BDV (DETADS). By analyzing the data, it was found that by increase the secondary emulsifier the BDV increased. But this behavior was seen vice versa with the (DETADS), at which by increasing concentration the stability decreased. This may be due to sulfonic moiety with the aromatic moiety of the benzene ring in the molecules causes dispersion of the negative charge on the molecule. The p_z orbital of benzene ring may cause a synergism with the sulfonic group to support the existing of this negative charge. As the result of the stability of the electrical double bond of the mud emulsion coming by the negative charge of the organophilic clay in the mud formulation, fourth may be the repulsion force exhibited between the electrical double layer and the negative charge of the secondary emulsifiers (DETADS) consequently the stability decreased BDV = 560 at 8ml emulsifier concentration.

It is remarked that, at instance of MEAO and DETAOA, by increase the concentration from 1ml up to 4ml the BDV increased quietly (small amelioration) but when the concentration increased from 4 to 8ml the BDV increased by significant

values. This means that at low concentration, The secondary emulsifier molecules take place their deployment on the electrical double layer to fix it this happened from 1 to 4ml and then the BDV increase significantly because the increase of these molecules on the interface of the electrical double layer supported it to be more stable and this reflected on the BDV values, 1420V and 1315V for the MEAO and DETAOA respectively.

Table (4): Break Down Voltage for the High and Low Stability Oil Base Mud at Different Concentrations of Synthesized Secondary Emulsifiers (SE) Substituting Industrial Emulsifier in Blank Sample

Blank	SE Concentration (ml)	MEAO	DETAOA	DETADS
1027	1	1020	1050	880
1027	2	1030	1060	975
1027	3	1065	1090	940
1027	4	1135	1123	880
1027	5	1200	1140	810
1027	6	1270	1165	765
1027	7	1350	1215	681
1027	8	1420	1315	560

* Blank sample has been prepared at 4 ml concentration of industrial secondary emulsifier.

The action between two secondary emulsifiers was investigated between MEAO with both of DEAO and DETAOA. The data are shown in **Table (5)**. By analysis of these results, it was found that, in the two mixture of secondary emulsifier the increase of BDV Vs increase of concentration was seen as a great significant by comparing with the secondary emulsifier individually. The BDV for (MEAO + DEAO) at (1:1) concentration was 1240V, this results may be pronounced for the individual emulsifier at more than 6ml concentration. This result means that, a great synergism to stabilize the electrical double layer was obtained with mixture of secondary emulsifier to save materials and save cost. This synergism may be due to the monoester of mono ethanolamine and (MEAO) with oleic acid and the Di ester of di ethanol amine make strongly adsorption on the electrical double layer interface causing high values of BDV, consequently stabilizing the mud emulsion. The same behavior was obtained in the mixture of (MEAO + DETAOA). The mixture exhibited BDV at 1ml concentration of mixture (1190V). This value may be exhibited at more than 5ml concentration for the individual emulsifier.

Table (5): Emulsion Stability (BDV) of Mixing Secondary Emulsifiers.

Concentration	MEAO	MEAO +DEAO (1:1)	MEAO +DETAOA (1:1)
1	1020	1240	1190
2	1030	1300	1240
3	1065	1380	1345
4	1135	1490	1360
5	1200	1550	1430
6	1270	1610	1585
7	1350	1660	1640
8	1420	1711	1695

The rheological properties (Plastic Viscosity, Yield Point and Gel Strength), HTHP fluid loss and emulsion stability of the prepared oil based mud were measured and listed in **Table (6)**, from this table it can be observed that evaluation of the prepared non-Ionic surfactant at different concentrations (Starting with 1ml up to 6 ml) of DEAO, DETAOA and mixed emulsifiers of both in

OBM key parameters, Effectiveness of chosen synthetized emulsifiers is clearly observed on tighten emulsion and HTHP property as quite reduction observed from 5 to 4.2 ml while using mixed synthetized emulsifiers along with electrical stability increased with addition of synthetized emulsifiers especially mixed emulsifiers (DEAO & DETAOA) this is an indication of how well (or tightly) the water is emulsified in the oil. Higher values indicate a stronger emulsion and more stable fluid, wettability effect of emulsifiers noticed with reduction of plastic viscosity and Gels measurement of the mud meanwhile yield point value remained as was in the blank sample, synthetized emulsifiers are very effective in reducing high temperature-high pressure filtration properties, improve fluids wettability which has direct impact on rheological characteristics and hence increase the drilling rate.

Table (6): Evaluation of Mud Properties using Industrial / Synthetized Secondary Emulsifier

Properties	Blank	DEAO			DETAOA			DEAO + DETAOA		
		1 ml	4 ml	6 ml	1 ml	4 ml	6 ml	(1:1 ml)	(2:2 ml)	(3:3 ml)
Plastic Viscosity, cp	12	12	11	10	12	11	11	12	10	9
Yield Point, 1b/100 ft ²	9	9	9	8	9	9	9	9	8	9
Gels 10 Sec./10 Min ,1b/100 ft ²	8/10	8/9	8/9	7/8	8/9	7/8	7/8	8/10	7/9	6/8
HTHP Fluid Loss, ml/30 min.	5	5	5	4.9	5	4.8	4.8	4.6	4.2	4
Emulsion Stability, volt	1027	1070	1108	1270	1020	1160	1195	1200	1580	1879

4.3 Evaluation of the Prepared Non-Ionic Surfactant in OBM in Presence of Nanoparticle (CuO)

The effect of Nanoparticles on the stability of mud emulsion and other properties is shown in **Table (7)**. The CuO nanoparticles have been tested for their ability to enhance the rheology, gel strength property, filtration loss at high temperature high pressure and breakdown voltage (emulsion stability). The results in **Table (7)** show the impact of CuO in the blank mud sample (Prepared with industrial SE) at different concentrations (0.1, 0.3 and 0.5% by weight). The plastic viscosity decreased from 12 (blank) to 10 at all concentrations. This means that the nanoparticle decrease the value at 0.1% and then being stable at other concentrations (0.3 and 0.5%). The same results were obtained with effect on yield value, it was being stable with different concentration. This behavior may be understanding as the nanoparticles at first addition to the emulsion particles and may cause stability on the electrical double layer, which doesn't effect by the shear and concentration change. The

decrease of gel strength at 10 Sec and 10 min. was seen as the result shown in **Table (7)**, this means that the thickness of the gel formation decrease with nanoparticles increase. This finding is agreeing with the impact of nanoparticles on the plastic viscosity and the yield values. The impact of CuO nanoparticles was tested on the effect of the filtration loss of the drilling mud at high temperature 120° C (250° F) and differential pressure (500 psi). The blank sample recorded fluid loss equal 5ml, but by adding 0.1% CuO nanoparticle. The fluid loss was being 4ml and then decrease ameliorate in the fluid loss was obtained by increase of nanoparticles concentration. At the same time the effect of addition nanoparticles on the emulsion stability was noticed in **Table (7)**. The BDV of the blank mud (1027V), but it increased by increasing of the CuO nanoparticle up to 1350V against 0.5% nanoparticles. This result reflects on the oxide nanoparticles play an important role at the electrical double layer of the formed drilling mud (blank).

Table (7): Mud Properties for the Blank Mud with / without CuO Nanoparticles

Property	Blank	CuO (0.1%)	CuO (0.3%)	CuO (0.5%)
Plastic Viscosity, cp	12	10	10	10
Yield Point, 1b/100 ft ²	9	8	8	8
Gels 10 Sec./10 Min ,1b/100 ft ²	8/10	6/7	5/7	4/6
HTHP Fluid Loss, ml/30 min.	5	4	3.8	3.6
Emulsion Stability, volt	1027	1230	1255	1350

The impact of adding the secondary emulsifier (DEAO) in presence of nanoparticles on OBM key parameters has been illustrated in **Table (8)** as same behavior was remarked in presence of the primary emulsifier as being with the nanoparticles (CuO) only. But the great increase of emulsion stability

(BDV) was obtained. The BDV at 0.1% CuO nanoparticles was 1700V, meanwhile for the blank, was 1027V. At the same time the BDV increased by increase the CuO nanoparticles concentration up to 1910V.

Table (8): Mixing Effect of Secondary Emulsifier (DEAO) on the Blank Mud Sample in Presences of CuO Nanoparticles

Property	Blank	CuO (0.1%)	CuO (0.3%)	CuO (0.5%)
Plastic Viscosity, cp	12	11	11	11
Yield Value, 1b/100 ft ²	9	9	8	8
Gels 10 Sec./10 Min ,1b/100 ft ²	8/10	7/8	6/5	5/5
HTHP Fluid Loss, ml/30 min.	5	4	3	2
Emulsion Stability, volt	1027	1700	1820	1910

Table (9) shows the impact of CuO Nano particles on the drilling mud properties in presence of mixture secondary emulsifier (DEAO + DETAOA). It is seems that, the addition of mixture secondary, emulsifier to the mud containing CuO Nano particles causes a great changes of the mud properties. The concentration of emulsifier at 1ml (total mixture) the increase of CuO concentration led to increase of the plastic viscosity up to 14 cp at 0.5%, and the yield value also increase up to 16 1b/100 ft². The gel strength may be not effected, unless at CuO 0.5%, recorded 10/11 (lb/100ft²). The filtration loss decreased by increase of CuO Nano particles concentration in presence of secondary

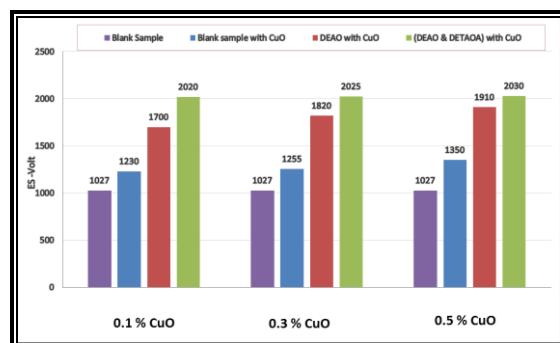
emulsifier mixture, which consider the positive achievement in the mud properties at differential pressure (500 psi) and high temp.120°C (250 °F).

The emulsion stability in the term of BDV exhibited a great increase by increase of the CuO nano particles in presence of mixture secondary emulsifiers as shown in **Table (9)**. The BDV increased from 1027V at zero CuO concentration up to 2030V against 0.5% CuO nanoparticles. This results means that the mixture of emulsifiers help to transfer the nanoparticles from the bulk of emulsion to the particles interface to support and enhance to electrical double layers, consequently the stability increased in the term of break down voltage (BDV).

Table (9): Effect of Secondary Emulsifier (Mixture of DETAOA and DEAO) on the Blank Mud Sample in Presences of CuO Nanoparticles

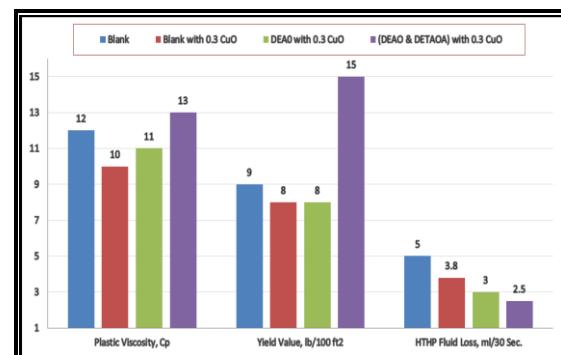
Property	Blank	CuO (0.1%)	CuO (0.3%)	CuO (0.5%)
Plastic Viscosity, cp	12	12	13	14
Yield Value, lb/100 ft ²	9	13	15	16
Gels 10 Sec./10 Min ,1b/100 ft ²	8/10	8/9	8/10	10/11
HTHP Fluid Loss, ml/30 min.	5	3.8	2.5	2.4
Emulsion Stability, volt	1027	2020	2025	2030

In **Figure (4)** it was found that due to positive synergism between the synthesized secondary emulsifiers and CuO nanoparticles, it's clear that as concentration of CuO increases from 0.1 to 0.3 to 0.5% a significant increase in the emulsion stability was observed. The maximum ES was exhibited with 0.5% CuO (2030V.) meanwhile the commercial secondary emulsifier in the blank showed a little increase in the emulsion stability against 0.1, 0.3 and 0.5% of CuO (1230, 1255 and 1350V Respectively). By formulating the drilling fluid using one synthesized secondary emulsifier (DEAO), a unique enhancement in emulsion properties exhibited with different concentrations of CuO (0.1,0.3 and 0.5%), the emulsion stability was 1700,1820 and 1910V respectively but by formulating the drilling fluid using mixed secondary emulsifiers (DEAO & DETAOA), a remarkable enhancement in the emulsion stability exhibited with the minimum concentration of CuO (1%) and the emulsion stability was (2020V), But the maximum enhancement in the ES was pronounced also against 0.5% CuO nanoparticles as 2030 V, By analyzing the effect of nanoparticles (CuO) on the oil base mud emulsion stability point of view, It was found that, The nanoparticles have a great effect and enhancement the emulsion stability of the oil base mud by the synthesized secondary emulsifiers rather than the commercial.

**Fig. (4): Evaluating Emulsion Stability OBM sets**

The evaluation of the rheological properties and high pressure high temperature fluid loss for the oil base mud in presence of 0.3% CuO nanoparticles is

shown in **Figure (5)**. It is clear from regarding to the plastic viscosity that, the secondary emulsifies mixture exhibited the maximum value (13cp) meanwhile the blank sample with commercial secondary emulsifier and without CuO nanoparticles gave PV equal to 12 cp. The blank mud formulation with CuO only and without emulsifier pronounced PV at 10 cp and with individual secondary emulsifier (DEAO) exhibited 11 cp. On the other hand regarding to the yield value, the mixture emulsifier was in the former situation among the other formulation (15 lb/100ft²). From **Figure (5)** also, it was found that, the minimum HTHP fluid loss 2.5 ml was obtained with the 0.3% CuO nanoparticles and mixed emulsifier system (DEAO & DETAOA). This observation proves that, the positive synergism between the two emulsifiers with the 0.3% CuO nanoparticles exhibited the integration properties of the oil base mud. It can be concluded that the mixed secondary emulsifiers with the nanoparticles may be is the best way in the OBM formulations in the next generation of these mud emulsions.

**Fig. (5): OBM Rheology and Fluid Loss Evaluation**

5. Conclusion

The conclusion of this work can be drawn as following points:

1. Six oil soluble emulsifiers based on fatty acid esters and amides were prepared and their chemical structures were confirmed.

2. A sets of oil based mud were formulated using these esters and amides as secondary emulsifiers, The ES, HTHP filtrate and rheological properties were evaluated.
3. DEAO and DETAOA showed the optimum parameters for oil based mud (E.S~1879 volt & PV~9 cp , YP~9 lb/100 ft²& HTHP~4 ml/30 min. and Gels~6/8 lb/100 ft²)
4. The effect of adding CuO nanoparticles for some selected OBM formulations exhibited promising enhancement results, The maximum integrated results for OBM properties were obtained with 0.1& 0.3 & 0.5% by weight of CuO in the OBM formulation which made by mixture of (DEAO & DETAOA)
5. Nanoparticles at different concentrations (0.1, 0.3 and 0.5% by weight of CuO) exhibited a unique enhancement on emulsion stability for oil based mud formulated using prepared synthetized secondary emulsifiers rather than commercial emulsifiers.

6. Conflict of Interest

There is no conflict of interest.

7. References

- [1] Darley H. C. and Gray, G. R., Composition and properties of drilling and completion fluids. Gulf Professional Publishing, (1988).
- [2] Fink J, Oil field chemicals. Elsevier, (2003).
- [3] Adams N. and Charrier T., Drilling engineering: a complete well planning approach. Pennwell Corp, (1985).
- [4] Moore P. L., Drilling practices manual, (1986).
- [5] Bourgoyn A. T., Millheim K. K., Chenevert M. E., and Young F. S., Applied drilling engineering (Vol. 2, pp. 137-144). Richardson, TX: Society of Petroleum Engineers (1991).
- [6] Horton D. P., Drilling fluids, drilling fluids additives and methods useful for limiting tar sands accretion on metal surfaces, U.S. Patent No. 7081438. , Washington, DC: U.S. Patent and Trademark Office, (2006).
- [7] Clark R. K., Scheuerman R. F., Rath H., and Van Laar H. G., Polyacrylamide/potassium-chloride mud for drilling water-sensitive shales. Journal of Petroleum technology, 28(06), 719-727(1976).
- [8] Steiger R. P., Fundamentals and use of potassium/polymer drilling fluids to minimize drilling and completion problems associated with hydratable clays, Journal of Petroleum Technology, 34(08), 1-661(1982).
- [9] Bennett R. B., New drilling fluid technology mineral oil mud, Journal of petroleum technology, 36(06), 975-981 (1984).
- [10] Hughes T. L., Jones T. G. J., and Geehan T., The chemical logging of drilling fluids. SPE Drilling & Completion, 10(04), 255-264 (1995).
- [11] Kang K. S., Pettitt D. J., Whistler R. L., and BeMiller J. N. Polysaccharides and their derivatives. Industrial Gums. Academic Press, Inc.: San Diego, CA, 341-397 (1993).
- [12] Hall J., Ester-based drilling fluids-still the best environmental option, Canadian technical report of fisheries and aquatic sciences, 21-21(2000).
- [13] Tapavicza S., and Hall J., Development of environmentally safe drilling fluids based on esters. Presentation at the OFiC, 7-10 (2002).
- [14] Dardir M. M., Preparation of some new emulsifying agents for oil-well drilling fluids (Doctoral dissertation, Ph. D. thesis, Ain Shams University, Faculty of Sciences), (2001).
- [15] Dardir M. M., Synthesis and Evaluation of Some Local Surfactants and Additives for Oil-Well Drilling Fluids, Ain Shams University (Doctoral dissertation, Ph. D. Thesis) (2005).
- [16] Jha P. K., Mahto V., and Saxena V. K., Emulsion based drilling fluids: an overview. International Journal of ChemTech Research, 6(4), 2306-2315 (2014).
- [17] Smith H. V., and Kenneth E. A., Crude oil emulsions (1987 PEH chapter 19)." Petroleum Engineering Handbook (1987).
- [18] Al-Mutairi S. H., Nasr-El-Din H. A., Hill A. D., and Al-Aamri A., Effect of droplet size on the reaction kinetics of emulsified acid with calcite. Spe Journal, 14(04), 606-616 (2009).
- [19] Skalli L., Buckley J. S., Zhang Y., and Morrow N. R., Surface and core wetting effects of surfactants in oil-based drilling fluids. Journal of Petroleum Science and Engineering, 52(1-4), 253-260(2006).
- [20] Tadros T. F., Emulsion formation, stability, and rheology. Emulsion formation and stability, 1, 1-75 (2013).
- [21] Hoberock L. L., and Bratcher G. J., Dynamic Differential Pressure Effects on Drilling of Permeable Formations , 118-123 (1998).
- [22] Civan F., A multi-purpose formation damage model. In SPE Formation Damage Control Symposium. Society of Petroleum Engineers, SPE-31101, (1996).
- [23] Mokhatab S., Fresky M. A., and Islam M. R., Applications of nanotechnology in oil and gas E&P. Journal of petroleum technology, 58(04), 48-51 (2006).
- [24] Nabhani. N., Emami M., and Moghadam A. T., Application of nanotechnology and nanomaterials in oil and gas industry. In AIP Conference Proceedings, 1415(1), 128-131 (2011).
- [25] Amanullah M. and Al-Tahini, A. M., Nanotechnology-its significance in smart fluid development for oil and gas field application. In SPE Saudi Arabia Section Technical Symposium. Society of Petroleum Engineers, SPE 1261102, (2009).
- [26] Cooper D. G., Zajic J. E., Cannel E. J., and Wood J. W., The relevance of "HLB" to de - emulsification of a mixture of heavy oil, water and clay. The Canadian Journal of Chemical Engineering, 58(5), 576-579 (1980).

- [27] Jayakumar R., Balaji R., and Nanjundan S., Studies on copolymers of 2-(N-phthalimido) ethyl methacrylate with methyl methacrylate. European Polymer Journal, 36, 1659-1666 (2000).
- [28] API R., 13B-2: Recommended Practice for Field Testing Oil-Based Drilling Fluids. API, Washington DC, (2005).
- [29] Evans N., Langlois B., Audibert-Hayet A., Dalmazzone C. and Deballé E. , High performance emulsifiers for synthetic based muds. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers, SPE 63101, (2000).