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Design, Aqueous Properties and Application of Modified Nano-Montmorillonite/Ionic Liquid Nanocomposite Fabricated by Shock Synthesis Using the Leidenfrost Phenomenon.

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ABSTRACT

In the present work we demonstrated for first time for use the Leidenfrost drop as water based green chemical reactor for Design, synthesis, splitting and nanofabrication of Nano-Montmorillonite/Ionic Liquid layers into nanoclay unit (mMMt). The resulting modified mMMt was characterized by various techniques such as infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM), Zeta Size (ZS), and Zeta Potential (ZP) for a better understanding of their chemical and structural properties. Viscosity measurements of the mMMt solution, pH values, antimicrobial effect and mud properties were determined. These prepared new clay nanocomposites possess very interesting physical properties such as good flow which make them suitable for the injection through the gas raw pipeline. The results showed that newly formulated mMMt showed a good ability to act as water soluble types, no-foaming and stable film-persistent corrosion inhibitor for the thermodynamic-hydrodynamic corrosivity predictive models for the assessment of internal corrosion /erosion in the surface production pipelines (flow lines and gathering lines). Furthermore, the newly formulated showed strong antibacterial more than other commercial biocide samples.

Keywords: Nanotechnology, Leidenfrost Phenomenon, Green Chemistry, oil and gas industries, Multifunctional, pH control, Bioresources.

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INTRODUCTION

Nanoparticles are now being used on a large scale, in various industrial applications such as catalysts, electronics, sensors, coatings, petroleum additives, filtration, textiles auxiliaries, cosmetics, medical tools, fuel cells, batteries, oil refinery and solar cells [1-3]. Nanomaterials can be synthesized in several ways[4–7] Nanotechnology includes physical, chemical, and biological techniques for preparing materials within range from 1- 100 nm in diameter nanoparticles [8-10] The physical techniques involved laser ablation,[11] flame pyrolysis,[12] electric discharge,[13] ball milling,[14] ion sputtering [15] and thermal evaporation [16]. These techniques have some drawbacks such as low rate of production, high temperature and pressure requirements which leads to a high energy consumption and ultimately high price for use in bulk production industry.[17,18]. On the other side, there are various chemical methods to synthesize Nanomaterials with desired size, morphology and surface properties by adjusting the solution parameters including temperature, solvents, surfactants, templates and micelles. [19-27] These approaches include sol-gel methods, co-precipitation process, micro-emulsion techniques, hydrothermal and solvothermal methods.[28-31] Chemical methods of Nano-synthesis generally involve wet chemistry, i.e., reducing the metal complexes, thus, forming colloidal dispersions of metal nanoparticles. To prevent coagulation of nanoparticles, a stabilizer or a capping agent is often added. Chemical methods have already proved their unprecedented success in producing novel nanoparticles in an easy and efficient way that it cannot be achieved by other methods of nanosynthesis. But, the problem remains with the inherent use of hazardous chemicals. The use of harmful reducing agents, organic surfactants, solvents and capping agents can easily contaminate the food chain. Another problem is the contamination of nanoparticles themselves by adsorbing toxic byproducts on their surface, thus, negating their biocompatibility. Green chemistry seeks the solutions to these problems through the design and implementation of chemical processes with limited use or generation of substances harmful to the environment.[33-37],The phenomenon of Leidenfrost drops was first reported in the 18th century .When a liquid droplet is deposited onto a hot solid surface the drop may, provided the solid surface is hot enough, levitate on a cushion of its own vapour. This phenomenon known as the Leidenfrost effect. Similarly, the critical substrate temperature above which the ‘film-boiling’ that makes levitation possible is called the Leidenfrost temperature. In everyday life, the Leidenfrost effect is used to test whether a frying pan is hot enough: flicking a drop of water into the pan will lead to the drop skiting about only if the pan is above the Leidenfrost temperature of water (around 200°C). Although classical, this intriguing effect has experienced a renaissance of research effort recently with a number of studies focusing on the origin of the film-boiling regime and its relation to surface properties. Other studies have focused on the possibility of generating motion in this way; it was noted that liquid drops do not touch solid surfaces that are significantly hotter than the liquid’s boiling point. Leidenfrost drops are also seen to last significantly longer than expected, explained by an evaporative flow from the liquid lifting the drop off the plate and creating a gap between the liquid and the solid, filled with vapour. The long lifetime of the liquid drop is due to the layer of gas having lower heat conductivity than the liquid [37-39], so acting as a thermal insulator and protecting the liquid from the hot plate’s effects. Although Leidenfrost drops have been discussed for centuries, many studies have been limited to results using high-speed photography, or applications of the lubrication approximation [40-42]. Meanwhile, recently proposed applications include small-scale pumps using waste heat and since the liquid phase lasts much longer (and is much more mobile) while it floats on a layer of gas a ratchet-like substrate has been used to successfully move drops in desired directions (or even ‘up-hill’) . This recently discovered method of self-propulsion could find extensive applications in micro-fluids, and has attracted significant attention in literature [43-46]. In the last decades extensive research has been devoted to organically modify layered clays as reinforcements for polymers. Their layered morphology, high aspect ratio and the nanoscopic phase distribution lead to improved thermal, mechanical, and gas diffusion barrier properties. One of the most widely used nanofillers is montmorillonite MMt.[46] in nature clay named montmorillonite (MMt) have a porous structure that can accommodate a wide variety of cations, such as Na⁺, K⁺, Ca²⁺, Mg²⁺ and others MMt is a common clay mineral from the smectite family[47]Besides the interlayer cations, the interlayer space contains large amounts of water molecules. To enhance compatibility with organophilic polymers, chemical modification of MMt plays a crucial role in MMt nanocomposites formation. Introducing organic groups on the layered surface increases the interlayer distance, which facilitates the penetration of the polymer chains inside the MMt interlayer spaces. The most commonly used procedure to prepare organophilic MMt and other clay minerals is the cation exchange reaction with a quaternary ammonium salt[48-51] this kind of surface modification does not provide an efficient linkage between the clay mineral and other matrices The grafting/intercalation of the aminosilane inside the Mt interlayer spaces Several organically modified alkoxysilanes have been used to modify layered silicates MMt such as MMt stearylbenzyl dimethyl ammonium chloride and distearyldimethyl

ammonium chloride, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane [52-53] The quaternary adsorption reaction, between the silane coupling agents and reactive silanol groups, located at the broken edges of the clay mineral layers, at the structural defects of the interlayer and external surfaces, has attracted great interest. The condensation between the interlayer surface silanol groups in clay layers and the aminosilanemolecules occurred as schematically shown in **Sch. 1**. [9] However, this kind of surface modification does not provide an efficient linkage between the clay mineral and polymer-matrices. Moreover, most of aminosilanemolecules surfactants are not stable at temperature at which the plastics are commonly processed. In addition to aminosilane surfactant have very complex process for its synthesis. For these reasons, the ionic liquid reaction, between the halogen coupling agents and reactive silanol groups or cation at clay surface, located at the broken edges of the clay mineral layers, at the structural defects of the interlayer and external surfaces, has attracted great interest. Several organically modified quaternary ammonium salt or ionic liquid has been used to modify layered clays such as MMT. quaternary ammonium salt can be represented. Recently, the sustainable technologies became the first priority in all chemicals industry [54]. Ionic liquids (IL) attracted great attentions as sustainable materials alternative for many quaternary compound due to their low volatility (low vapor pressure), thermal stability, low toxicity, high surface activity due to the presence of cations and anions species in the same molecules, and high performance as catalysts, and desulfurization solvents in the petroleum fields [55-59]. ILs are ionic molecules that contain both organic cations and inorganic or organic anions. The difference between inorganic salts and ionic liquids is based on the size of cations and anions when compared with sodium or halides. Commonly, the derivatives organic cations were imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium and sulfonium. The organic anions were alkylsulfate, alkylsulfonate, p-toluenesulfonate (tosylate) and trifluoroacetate. The inorganic anions were halides, tetrachloroaluminate, hexafluorophosphate, tetrafluoroborate and bis (trifluoromethylsulfonyl) imide as examples. The properties of ILs depend on choosing the correct cations and anion for a specific synthesis. There are several petroleum processes used different oil-field chemicals such as emulsifiers, demulsifiers, inhibitors, dispersants and scavengers to modify the crude oils and their products specifications [60-64]. These chemicals are based on amphiphiles or polymeric surfactants mixtures having different hydrophile lipophile balances [65]. They have several advantages over organic surfactants used in petroleum oilfield chemicals due to their excellent rheology, better solubility in oils and solvents, anticorrosion and recyclability [66-68]. Ionic liquids such as melted salts with melting points at or below ambient room temperature are composed of organic cations and various anions. In the chemical structure of common ionic liquids, an organic cation (i.e., imidazolium) is linked with an anion such as bromide, chloride, cyanide. ILs are one of the aims of green chemistry because of their special properties such as high thermal stability, high ionic conductivity. [69] Long chain substituted imidazolines and their quaternized products are of great importance because of their numerous and varied industrial applications. Fatty imidazolines and quaternized imidazolium salts are frequently used as fabric softeners [70], dispersants [71], anti-static agents [72], bleach activators [73], emulsifiers [74,75] and biocide [76] not only because of their good performance but also for their mildness to eyes, skin and clothes [77] and their biodegradability [78]. In addition, imidazolines compounds are gaining importance in the paint and lubricant industries because of their corrosion inhibition properties [79]. The 2-substituted imidazolines and their derivatives exhibit a wide variety of biological activities including anti-percholesterolemic, anti-inflammatory, anti-diabetic and anti-hypertensive properties [80]. Imidazolines are also used as insecticidal agents and disinfectants [81] in agricultural sprays. These compounds are also used as intermediates and catalysts [82] in synthetic chemistry. Several methods for the synthesis of 2-imidazolines from fatty acids, esters, nitriles, or thioesters, hydroxymoyl chlorides, hydroxyl amides and mono- or disubstituted choroidi- cyano vinyl benzene have been reported previously. General methods of preparation of imidazolines involve dehydration between fatty acids and polyamines under vacuum (Scheme 1). The fatty acids generally used are stearic acid, palmitic acid, lauric acid, oleic acid and some oils such as corn oil and rice bran oil. Polyamines used are ethylenediamine (EDA), Diethylenetriamine (DETA), ethylene triamine tetra acetic acid (EDTA), aminoethyl ethanolamine. This conventional thermal method suffers from disadvantages such as long times, low yield of the products and tedious work up [83, 84]. Nowadays, use of microwave irradiation in organic synthesis is gaining special attention due to the generally low reaction time, better yield and high purity of products [85]. In the present work we demonstrated for first time for use the Leidenfrost drop as water based green chemical reactor for Design, synthesis, splitting and nanofabrication of clay MMT layers into nanoclay. In addition to, the evaluation of the prepared modified fatty clay nanocomposites in different petroleum industrial application such as Corrosion inhibitors, Rheology modifier, pH control, Drilling mud Emulsifiers and Biocide. The advantages of petroleum additives based on these simple, green, renewable sources have very low or almost negligible aquatic toxicity and are, in most cases, readily biodegradable. Industrial application in large scale production for some produced materials.

METHODS AND TECHNIQUES

Preparation of Ionic Liquid 1-(2-Aminoethyl)-2-octadecyl-imidazoline

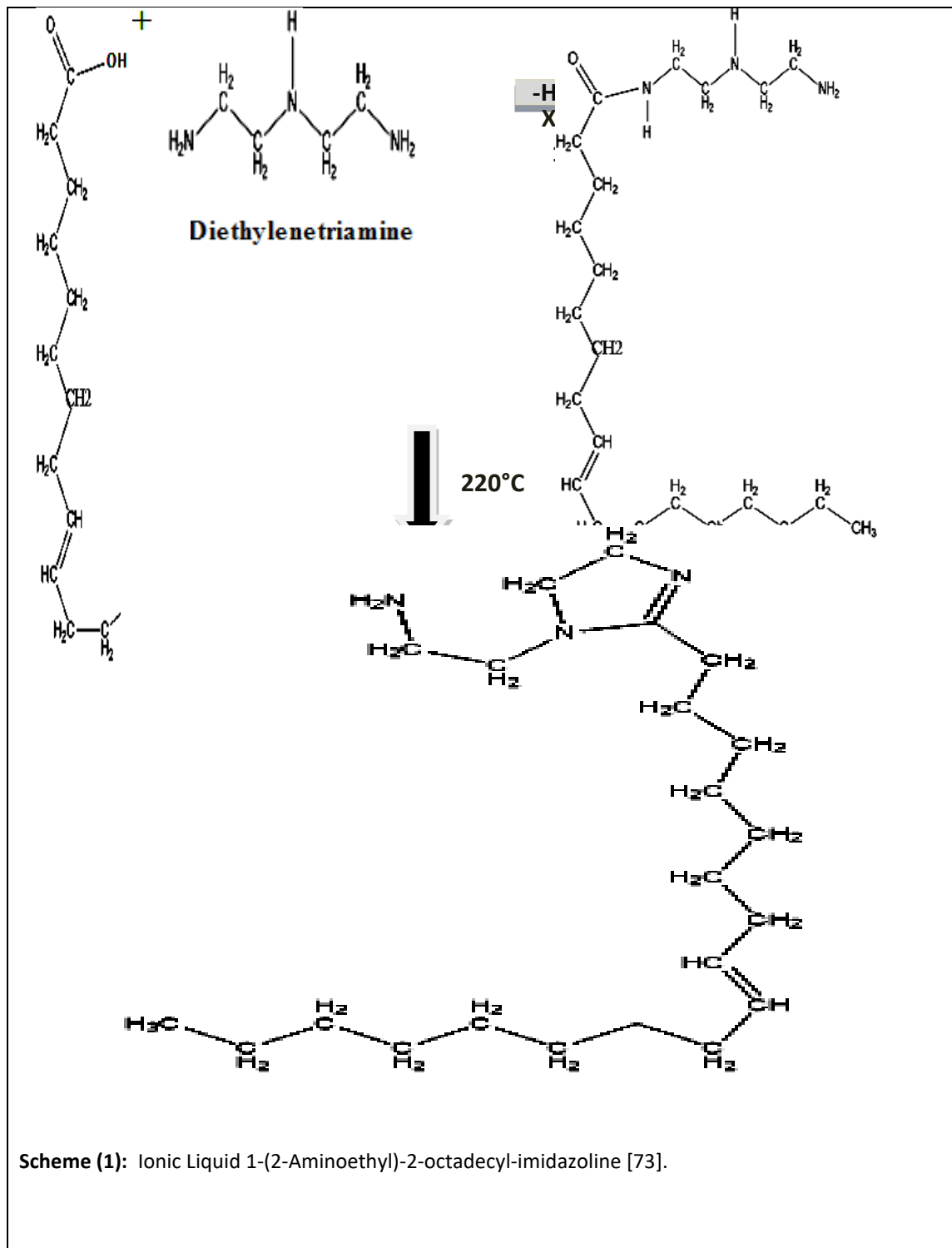
For preparation of Ionic Liquid 1-(2-Aminoethyl)-2-octadecyl-imidazoline (cationic surfactant). Place Into 4-neck round bottomed flask equipped with an overhead stirrer, thermometer, addition funnel and a Dean-Stark trap (water splitter),dropping funnel,73.33 g (0.26 malls) of oleic acid (OA) was added then heated to 60° C in the presence xylene (50 ml) as isotropic solvent and then 26.67 g (0.25 malls) of Diethylenetriamine was added drop wise drop by drop to monocarboxylic fatty acids oleic acid . At the first step, the resulting mixture turned from light yellow to dark red with remarkable increase in viscosity and exothermed to 100°C to form ammonium salt neutralization. The mixture was then heated to 130°-140°C. for 3.5 h. till the calculated amount of water was close to be obtained (1.8 ml) to oleoamide formation process. At the second step, the solvent xylene collected in the trap was returned to the flask. The mixture was thereafter heated to 160° C. for 1 hour while allowing water to collect in the Dean-Stark trap to completely of amid step. The resulting mixture was then heated at 165° C. for 2 hours and then at 240°C for 6 h. till the other calculated amount of water was close to be obtained (1.8 ml)to allow to imidazoline ring formation process for an additional hour during which time any further evolved water was collected. A nitrogen sweep was applied and the speed of the overhead stirrer was increased to facilitate removal of water finally the reaction mixture was cooled down to 70 °C. At third step, the products neutralize by acetic acid which added dropwise into the reaction flask [73].

Table 1: Reactant ratios, product name and H₂O off collected during the preparation of fatty imidazoline compounds

Ratio	Reactant		Products	H ₂ O off
	Oliec acid	DET		
Mol	1mol	1 mol	Oleoimidazoline	2 mol
M.Wt. Gram	282 g	103 g	353 g	32g

Table 2: Analytical properties of cationic imidazoline

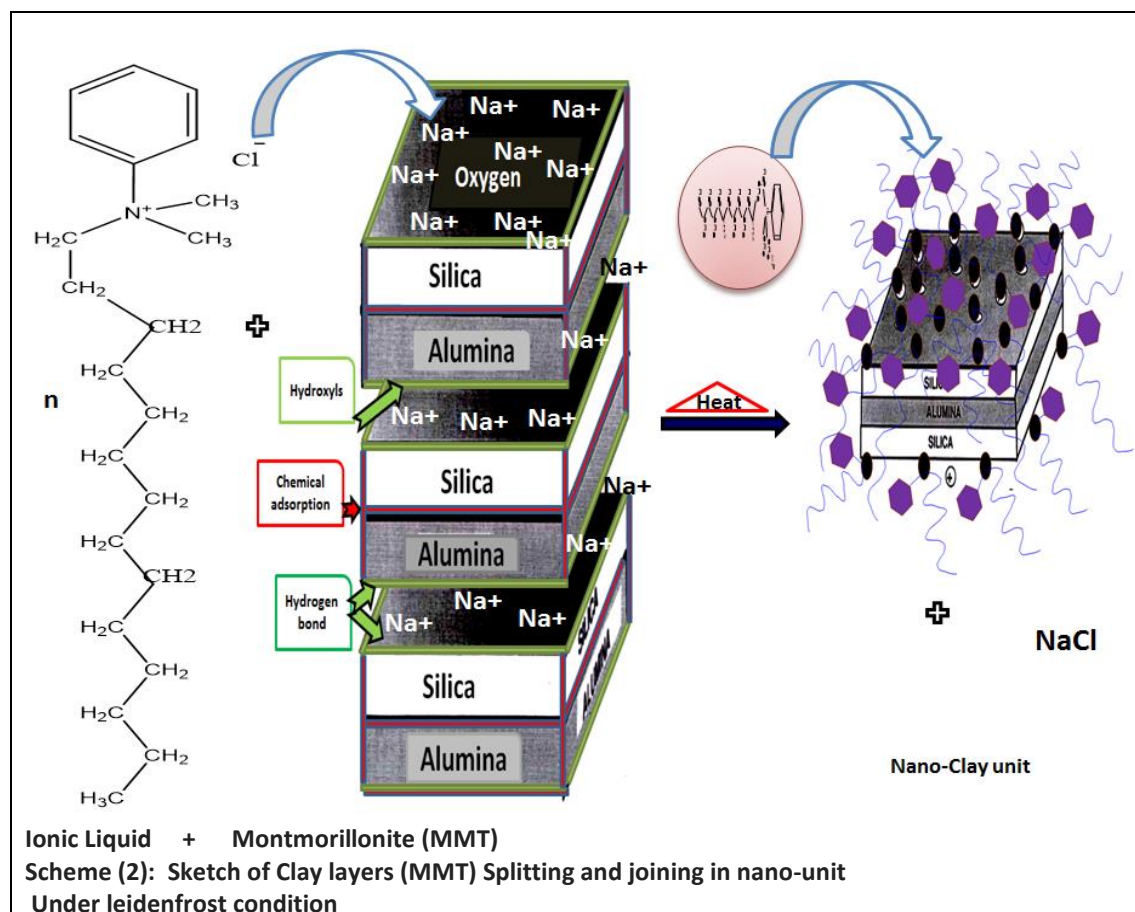
Items	Index
Amine salt %	1.0
PH(1% water solution)	7.0
Density	0.97(±0.01) g/mL



Nanosynthesis of Cationic Surface Montmorillonite/Ionic Liquid Nanocomposite in a Leidenfrost reactor

Rapid splitting of clay layers take place on one step within only 30s, The levitated chemical reactor suggested here can be used to Create of Cationic Surface Modified clay nanocomposites. Clay sample were fabricated into nanoclay unit modified with ionic liquid. a water droplet was loaded with a dispersed clay (10 mg of clay in 100 ml solution of Ionic Liquid N-Benzyl-N,N-dimethylaurayl -1-aminiium chloride aqueous solution in a glass burette placed above a preheated aluminum plate (300 °C). By adjusting the feed rate to be 1 mL per 30 s, the solution forms a Leidenfrost puddle which levitates on its own vapor film. The cold salt solution in contact with the hot surface undergoes a fast evaporation and formation of overheated zone at the base of the

Leidenfrost puddle. Moreover, it experiences a charge separation and self-ionization to produce clay ions (M^+) and anionic ionic liquid ions (Cl^-) lead to splitting and separation of clay into individual unit clay part, this ideal basic Leidenfrost conditions nanoparticles fabrication inside the puddle is created [86-88]. The color of the puddle changes from colorless to be milky as shown in Schem 2. After complete transformation of the precursor to the nano form, the modified nano-clay coagulates and thus precipitates at the bottom of the Leidenfrost reactor. The colloidal modified mMMt can be easily collected in glass tubes, In addition, the mMMt may be extracted by evaporation of the suspension for further investigations and applications. The modified nanoclay MMT then ready to use in multifunctional hydrocarbon drilling industry. The surfactant adsorb at the interface between clay surfaces and prevent the platelets from linking by eliminating electrochemical attractive forces between clay particles, suggest mechanism was reviewed in Schem 2[73].



Instruments used in analysis and measurements

The structures of the synthesized materials were confirmed via instrumental analysis as follow:

Weight loss measuring

The carbon steel sheets of 7 cm 9.3 cm 0.5 cm were sequentially abraded with different emery papers cleaned successively with distilled water, ethanol and acetone and finally dried in dry air at room temperature 25. After accurately weighing, the steel specimens were immersed in the CO₂-saturated corrosion 28 solution in 1000 mL PE bottles. The specimens were completely immersed for 12-120 h, with the addition of different concentrations of the synthesized cationic surfactant formula at 50 C°. The experiments were carried out in triplicate to get good reproducibility. The weight loss then was determined and the corrosion rate was expressed and the average value of the weight loss is reported. The specimens were sequentially abraded with different emery papers, degreased with acetone, washed with distilled water and dried. Corrosion parameters such as corrosion rate (CR) and inhibitor efficiency were calculated in the absence and presence of OQI the cationic surfactant corrosion inhibitors at concentrations ranging from 50 to 200 ppm.

Elemental analysis of carbon steel

The chemical composition of carbon steel was the following 0.16 C, 0.26 Si, 1.30 Mn, 0.010 S, 0.009 P, 0.05 Nb , 0.026 Al, 0.007 Co, 0.013 Cu, 0.014 Cr and the remainder iron determined by an ARL™ 4460 Optical Emission Spectrometer(USA).The structures of the synthesized materials were confirmed via instrumental analysis as follow:

Infrared spectra (IR)

Infrared spectra (IR) were performed on a Mattson 5000-FTSFTIR spectrometer. All samples were prepared by mixing FTIR-grade KBr (Aldrich Chemicals) with 1.0 wt. % of the polymer and grinding to a fine powder. Spectra were recorded at 4 cm⁻¹ (128 scans) over the 400 – 4000 cm⁻¹ range without baseline corrections. Bands are given in cm⁻¹.

Zeta size and zeta potential

The particle size of prepared sample was measured by the malvern instrument in the polymer laboratory of the National Institute of Measurement and Calibration, Egypt.

Morphology study

The morphology of prepared sample was investigated by HRTEM (JEOL - JEM- 2100) attached to a CCD camera at an accelerating voltage of 200 kV.

X-ray diffraction analysis

X-ray diffraction analysis was performed at room temperature for the modified sample on a Bruker D8 Avance using CuK α as the target with secondary monochomator to operate at 40 kV and 40 mA.

Determination Total Amine Value

The sample, if it is not already liquid, was melted in awater bath, mixed thoroughly, and accurately 1-4g weighed into a 250-mL flask. Fifty millilitres of alcoholwas added and boiled for 1 min to drive off any free ammonia that may have been present. This was then cooledto room temperature. Five drops of bromophenolblueindicator were added and it was then titrated, whileswirling, with 0.2 N HCl to the yellow end point.

Shear stress

An applied force (F), acting over an area (A), causes the layers to slide past one another. However, there is a resistance, or frictional drag, force that opposes the movement of these plates. This resistance or drag force is called shear stress (τ), in equation form.

$$\tau = F/A$$

With shear stress having typical units of lb_f/100 ft².

Shear Rate

The difference in the velocities between two layers of fluid divided by the distance between the two layers is called the shear rate (γ). In equation form,

$$\gamma = \text{Velocity difference} / \text{distance}$$

With typical units of or, reciprocal seconds. ft. Sec.⁻¹/ ft = Sec.⁻¹

Plastic viscosity

It is an important mud property that gives a measure of the internal resistance to flow due to amount, type and size of solids in the mud. Due to the collision of solids with one another and with the liquid phase of the mud, mechanical friction is produced deterring movement. The plastic viscosity is essentially a function of the viscosity of the liquid phase and the volume of solids contained in a mud. It describes the expected behavior of mud at the bit. In order to minimize high shear rate viscosity, the plastic viscosity has to be minimized. By decreasing the plastic viscosity, a driller correspondingly reduces the viscosity at the bit giving rise to higher ROP.

Rheological properties

Viscosity is defined as the internal resistance to the fluid flow; it is very important property of the mud because it affects the efficiency of the lifting capacity. The most practical instrument for determination of the rheological properties of the mud is the V-G meter, which has been used in this work. In the six-speed DV-III + CP Programmerable Rheometer Brookfield illustrated in **Fig. (7)** are available via synchronous motor driving through precision gearing. The Rheological study were carried out on a DV-III + CP Programmerable Rheometer Brookfield Model LVDV-III + Cp R p 66336 LVD V-3Cp115 Brookfield viscometer with spindle 52 at controlled temperature 25.0 +/- 0.1 °C. The polymer sample was rested for 24 h before measuring by the Rheometer to guarantee no were present in polymer solution. Before the measurement, all the polymer samples were rested for 20 min after the cylinder reached the measuring position to eliminate the shear influences.

Effect of the temperature on the rheological properties

Procedure

- 1- The mud sample was stirred for 15 minutes, before the rheological properties were measured.
- 2- Put the mud in cup heater and gradually raise the temperature from 75 °F to 200 °F

The rheological properties were measured at different temperatures and the results were compared with the reference mud sample (ER)

pH measurements

Drilling fluid and prepared sample pH measurements and pH adjustments are fundamental to drilling fluid control because clay interactions, solubility of additives, and contaminant removal are all pH-dependent. The recommended method for pH measurement is with a pH meter. A portable pH meter consists of a pH probe and an electronic voltage meter. to measure pH of samples after dilution of modified clay 7 % deionized water, with periodic calibration with known accurate standards Using diluted buffers pH 4.01 and pH7.00 to calibrate is recommended for best results there would be three time points .

Testing for oil-based

Crude oil

An asphaltic crude oil was obtained from Gulf of Suez Petroleum Company (GUPCO, Gulf Suez, Egypt). The physicochemical properties of this crude oil and their specifications are shown in **Table (3)**.

Specification	Stander Test Methods	Result
Specific gravity, at 60°F	ASTM D 1298	0.874
API gravity at 60 °F	ASTM D 1298	35.29
Kinematic viscosity, cSt, at 40 °C	ASTM D-445	14.97
Asphaltene content (wt.%)	IP 143/57	7.18
Pour point °C	ASTM D 97	118

Sea water

The average composition of seawater is shown in Table (1). Sea water from Elsewhere Gulf was used to prepare synthetic crude oil emulsions. Its salinity, current resistivity and conductivity are 39.99 g/L, 0.019 Ohm and 2.2 mS/M, respectively.

Gas production characteristics

Characteristics, Experimental conditions for corrosion measurements and Analytical data of the Assessment of internal corrosion in the surface production pipelines of the gas well indicate that the thermodynamic corrosivity predictive model has found that, under the thermodynamic operating conditions in the full length of the pipeline, the corrosivity of the flowing fluid due to carbon dioxide (0.4-0.5mole% , 3.42-5.64 psi partial pressure) is rated as slightly corrosive with a possibility to cause general pitting to the carbon steel of the pipeline .the thermodynamic- Hydrodynamic prediction model established based on multiphase flow for the pipelines found that, for the whole length of the pipeline, the multiphase mixture flow velocity is always above both of the API-14E critical velocity and the service velocity limit for sand erosion, and therefore neither flow induced corrosion (erosion corrosion by liquid droplets impingement)nor sand erosion is predicted to occur.

Mud formulation

Each batch of base mud used in each experiment was prepared by adding 80 g bentonite together with 4 g of sodium carbonate into 1000 mL water before aging it for more than 24 hours. Evaluate the thinning performance at room temperature and at different aging temperature for 30 minutes. This experiment was designed to observe the influence of temperature towards the performance of each thinner, when 0.3% thickener was added to the mud [90-91].

Testing for water-based mud

Work for water base mud was performed by using the new prepared fatty additives with different ratio as multifunctional compared to the commercial sample. The formulation of oil base water base mud is tabulated in **Table (4)**.

Table (4): Mud formulation

Formulation	Amount
sodium montmorillonite	80g
Tap water	1000 ml
Viscosifiers	0.3 %
Sodium carbonate	4 g.

RESULTS AND DISCUSSION

Infrared spectroscopy of Ionic Liquid

The structure of the prepared Ionic Liquid compound was verified using (FTIR) spectrum as shown in Fig.(1) Absorption bands for Ionic Liquid compound C–H, CH₃ at 2847, 2919 cm⁻¹, (CH₂)_n skeletal 722 cm⁻¹, the IR band at 1744 cm⁻¹ for ester disappears, and the IR band for primary amine materializes at 3293 cm⁻¹, the strong IR band at 1642 cm⁻¹ for C=N. There relatively weak IR band at 1604 cm⁻¹ for imidazoline ring.

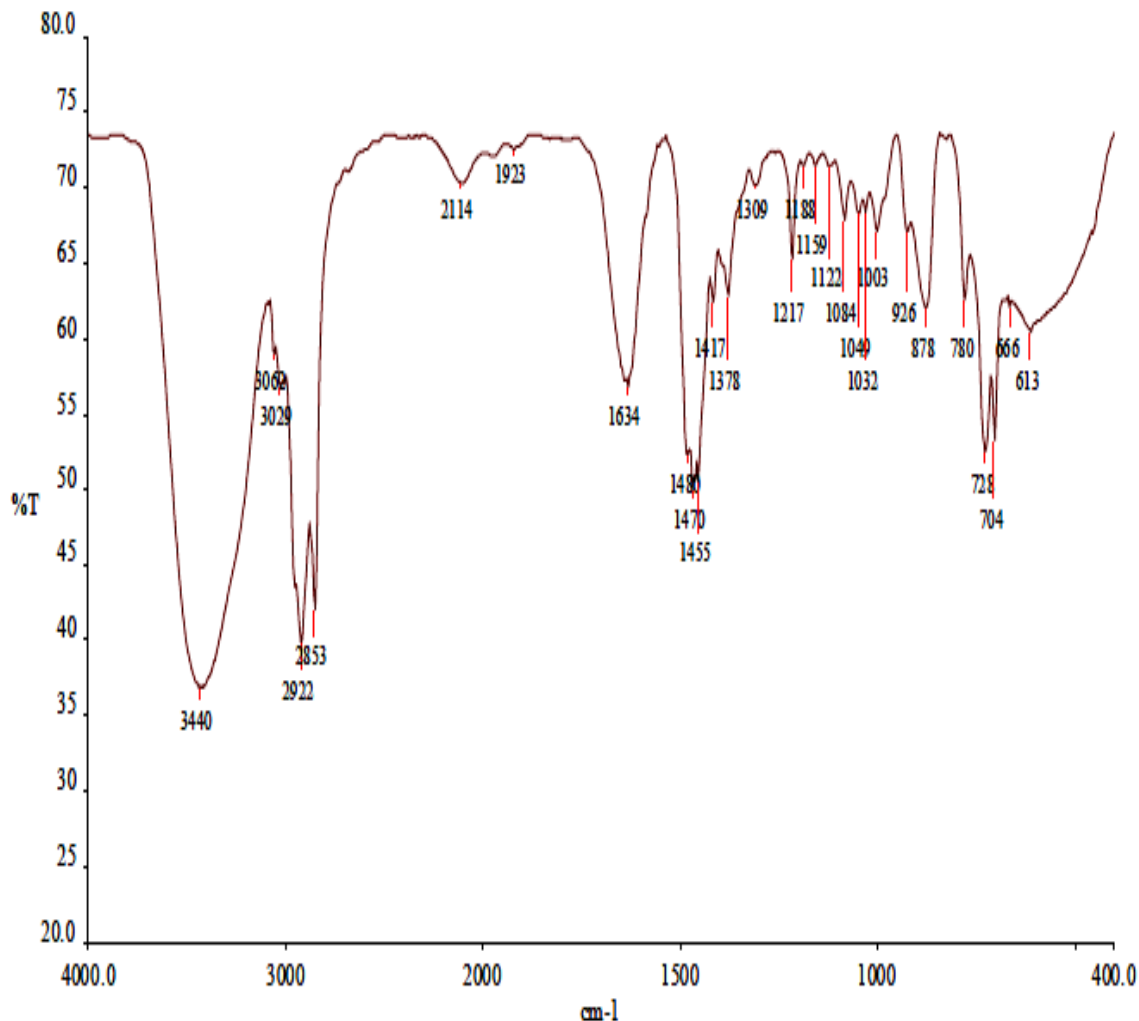


Figure 1. FTIR spectra of Ionic Liquid

Zeta Size and zeta potential for prepared modified surfactant nanoclay mMMt

The behavior of the colloid the particle size of the modified nanoclay mMMt was measured by the malvern instrument. The zeta potential is a key indicator of the stability of dispersions the magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent Zeta potential [mV] Stability relationship and particle size can be showed in Fig.2 and Fig.3 the results of the modified nanoclay MMt which show that the modified clay in nano particle sizes (30-100 nm) modified with high emulsion stability. The magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent Zeta potential [mV] Stability relationship can be shown as the following behavior of the clay modified dispersion

From 0 to ± 5 ,	Rapid coagulation or flocculation
From ± 10 to ± 30	incipient instability
From ± 30 to ± 40	Moderate stability
From ± 40 to ± 60	Good stability
more than ± 61	Excellent stability

Figure 2: Zeta size of the modified nanoclay mMMt

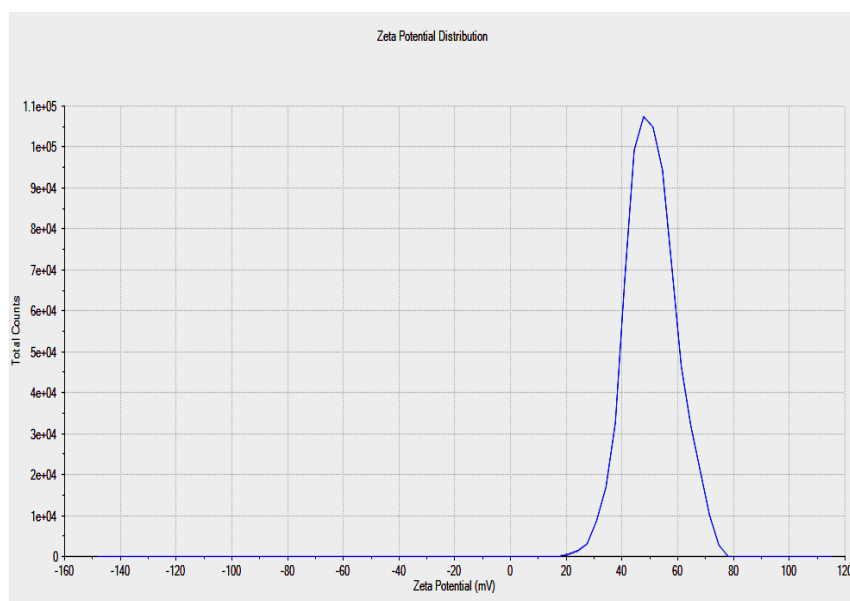
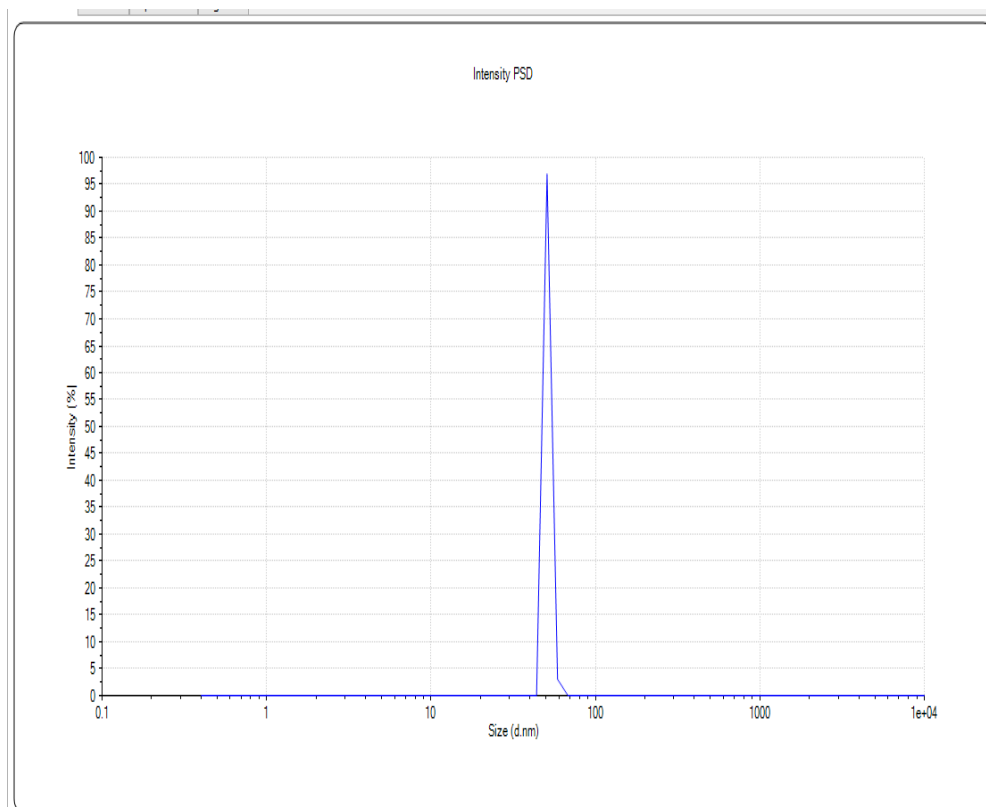


Figure 3: Zeta potential of cationic Ionic Liquid sample

Thermogravimetric analysis (TGA)

The effect of cationic modifications on the thermal behavior of clay nanocomposites was analyzed by thermo-gravimetric analysis TGA. The TGA are shown in **Fig. (4)**. considering thermal stability of the modified imidazolines the mass loss decomposition started almost; such behavior is typical for a barrier effect due to the remaining silicate layers, acting as diffusion barriers for the oxygen. The maximum degradation temperature also showed an improvement from (Fatty clay-modified). This is attributed to the effective exfoliation into the fatty matrix during the melt.

Without any notable decomposition. These results and interpretations are in good correspondence with the results found for the thermal and thermal oxidative decomposition of fatty nanocomposites. the initiation and maximum temperatures are shifted towards higher temperature; the polymer permeability to both oxygen and the volatile decomposition products. The small volatiles which were raised during the thermal decomposition process and hence enhances the thermal stability of the nanocomposites.

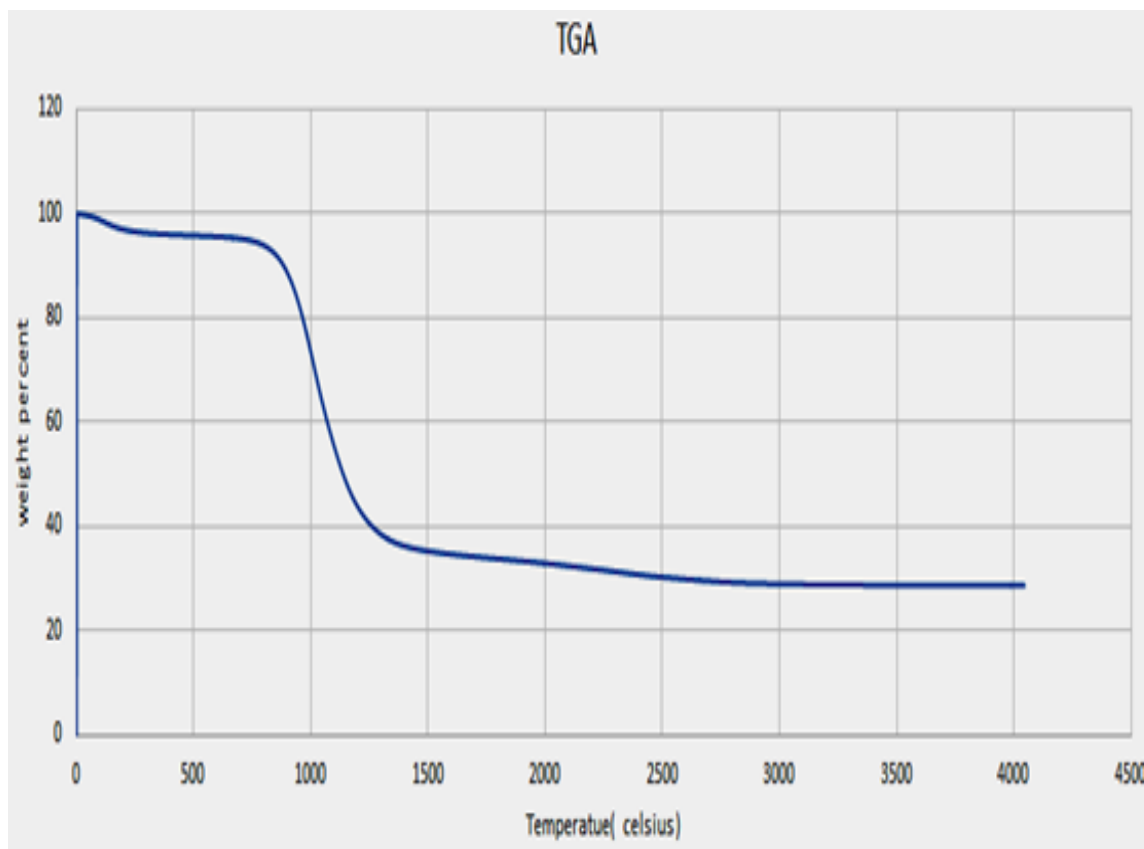


Figure 4: Thermo gravimetric Analysis (TGA) of modified mMMt. clay nanocomposites.

Scanning electron microscopy (SEM) modified clay nanocomposites

The Scanning Electron Microscopic technique was used to explore the surface morphologies of the prepared nanoclay Imidazoline sample. The surface morphologies of nano Imidazoline obtained approximately the same surface morphologies seen with the exception of more aggregates in Fig. 19 The structure of the nanoclay modified by ionic liquid shows a massive thin layered structure and some interlayer spaces; this may be attributed to the chemical modification by large alkyl moieties in the imidazolie galleries. All the samples show angular particles and aggregates with particle sizes around 100 Nanometer.

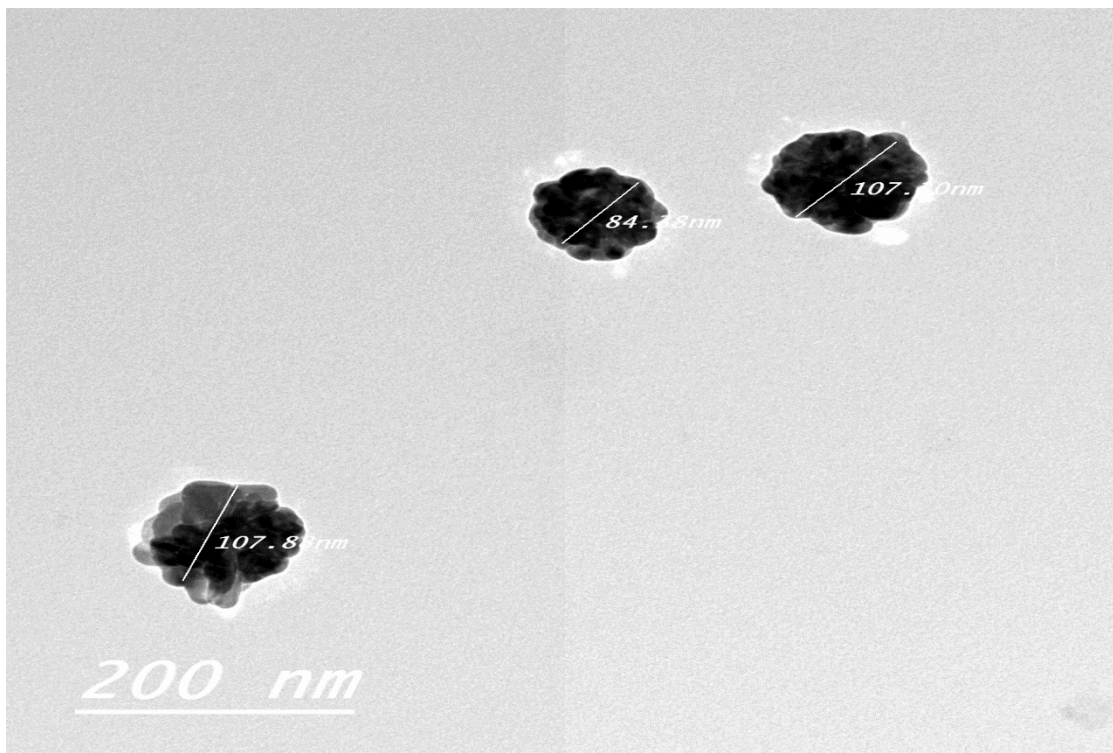


Figure 5: Scanning Electron Microscopy (SEM) of modified clay nanocomposites mMMt.

Evaluation of new prepared modified mMMt. clay nanocomposites as multifunctional for hydrocarbon fluid

The new prepared ionic liquid and clay were mixed together with certain proportion in one formula under leidenfrost temperature for only 30 sec. to convert into modified mMMt clay nanocomposites that suitable for multifunctional applications in hydrocarbon industry, which evaluated as new formula with multifunctional properties. The new prepared formula incorporated into mud formulations and oil and gas production pipelines compared with the commercial sample. The efficiency of the prepared formula in comparison with commercial sample was investigated by studying the following properties:

- 1- Corrosion inhibitor
- 2- Antimicrobial
- 3- Ph Control
- 4- Rheology modifier

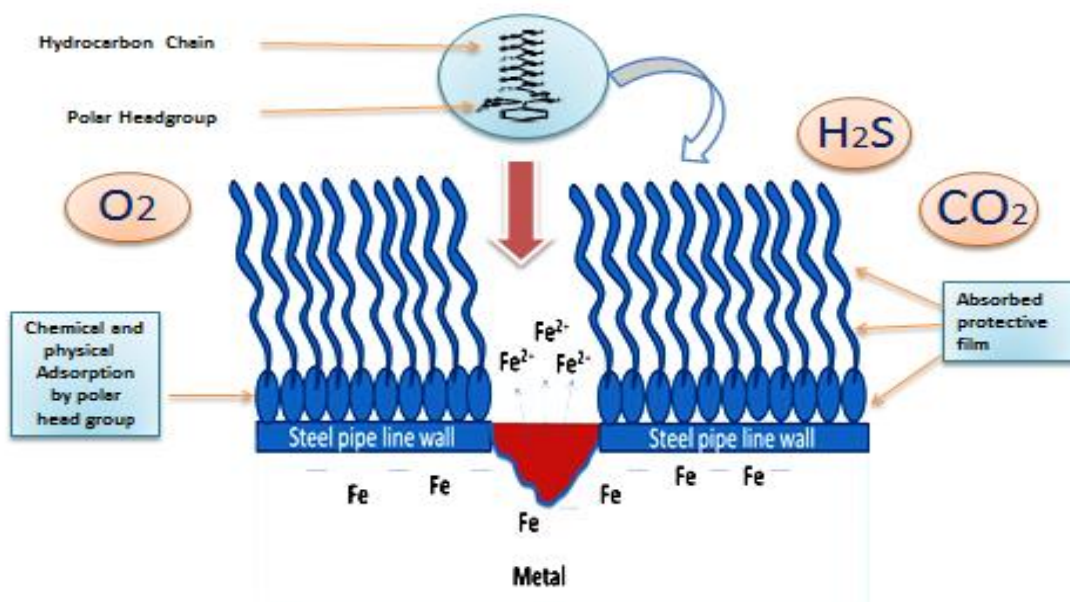
Evaluation of corrosion inhibitor property

Imidazoline derivatives, a kind of environmental-friendly corrosion inhibitors, can effectively inhibit metals corrosion in CO₂ environment. Corrosion test have been carried out in formation water at 50 C° is shown in Table 5. In the absence and presence of inhibitor using static and linear polarization (L.P) methods. Table (5). clearly shows that the inhibition efficiencies increased with the increasing concentration at 50°C. The increasing number of molecules of inhibitor covering the surface area of metal with the increase of its concentration resulted in a decrease of the corrosion rate and increase of inhibition efficiency. The newly formula represent an environmental alternative and effective for the protection of metallic surfaces against corrosion.

Table 5: Laboratory evaluation of corrosion inhibitor property

Method	Blank Corr. Rate, mpy	% Inhibition, at:		
		50	100	200 ppm
Static	2.3	29	37	26
L.P	49	17	16	10

The Conclusion of corrosion inhibitor according to Concerning start up Quaternary amine-cationic imidazoline Corrosion Inhibitor the chemical injection with the chemical injection rate optimized based on continues treatment injection and the coupons had been installed for at injection The carbon steel coupons are weighted and installed for the trilled wells at the end of each trial by our lab staff. (Multiphase flow) operation conditions in these pipes. the imidazoline ring adsorb on metal Fe surface by donating electrons to metal atoms and accepting electrons from 3dorbital of Fe atoms Some researchers believe they block the active sites and generate a barrier to reduce the transport of corrosive species to the metal surface, the mechanism of corrosion and adsorption of imidazoline on the surface of mild steel as showed in **scheme 3**.



Scheme 3: Adsorption mechanism of the on the carbon steel surface

Evaluation of Antimicrobial Property

This series is involved in the comparative study between prepared quaternized inhibitor formula quaternized ammonium salt and some other commercial Biocide samples such as BAG80 .the results showed in Table 6.indicate that prepared new modified nano-formula showed strong antibacterial more than other commercial biocide samples BAG-80 the prepared cationic imidazoline surfactant ammonium chloride have very effect on microorganisms (Escherichia coli ATCC13706, Pseudomonas aeruginosa ATCC15442, Listeriamono- cytogenes ATCC25152 Staphylo-coccus aureus ATCC6538), Thus can be used as antimicrobial in the newly corrosion inhibitors formulation.in addition to their compatible with nonionic, ampholytic and cationic surface active agents . It is can be used in many oilfield formulations such as hydrocarbon drilling fluid additives and refinery industry. The antimicrobial formulation has an important role in formulation of long term corrosion Inhibitor exposure increase amines and their derivatives molecules in formulation lead to the increase antimicrobial activity and long term storage [90].

Table 6: Antibacterial analysis

Samples	Tested bacterial strains			
	E.Coli ATCC13706	Pseudomonas aeruginosa ATCC15442	Listeria monocytogenes ATCC25152	Staphylococcus aureus ATCC6538
BAG-80	++	+++	++	++
QIF	+++	+++	++	++

Where (+) =
 *(++) Moderate effect on microorganisms
 *(+++) High effect on microorganisms
 *(++++) Extreme effect on microorganisms

Determination of hydrogen ion concentration

The degree of acidity or alkalinity of drilling mud or hydrogen ion concentration (pH) was measured by the electrometric method using a glass electrode instrument. Drilling fluid pH measurements and pH adjustments are fundamental to drilling fluid control because clay interactions, solubility of additives, and contaminant removal are all pH-dependent. The addition of different dosage of nano modified nanocomposites to mud formulation, under the aging process at different temperatures from (30 to 90 °C) was studied, the results showed that the newly formulated has multifunctional properties, it may be employed as pH controlling in addition to their application as viscosity modifier for water base drilling mud at low and high-temperature degree without further additives which added to control pH of the water base drilling mud. The data listed in a table.13. Shows the new formulated maintained the pH of the drilling mud within the desired drilling pH range and showed that, the pH value was slightly deviated after the aging at high temperature. This also reveals the thermal stability of the polymers. The thermal stability may describe to unique chemical structure of new formulated inhibitor which comprised different functional groups such as imidazoline, ester and ethoxylated groups

Table 7: Hydrogen ion concentration

Mud formulation	T(°C)	pH
Base mud + 0.1% (QIF)	50	12.37
Base mud + 0.5%	50	11.97
Base mud + 0.7%	50	11.77
Base mud + 0.1%	70	12.24
Base mud + 0.5%	70	11.78
Base mud + 0.7%	70	11.67
Base mud + 0.1%	90	12.15
Base mud + 0.5%	90	11.99
Base mud + 0.7%	90	10.89

Relation between shear stress and shear rate

The Aqueous properties and Rheology performance and physical Properties of the new prepared green multifunctional formula based on clay-sliver nanocomposites as water soluble type, no-foaming, demulsifying agent for corrosion inhibitor formula for treating crude oil emulsion with associated water, salinity and clay deposit shown previous in Table .15.,and its properties at the solution/air interface were investigated by measuring dynamic viscosity (Cp) at low and pediment temperatures, Pour point(°C), density at 40°C, Refractive index at 20°C and pH using standard test methods are shown in Table .15. Which indicate that demulsifier have optimum properties for the filling in the chemical skid during field trials demulsifier long term exposure. The evaluate fluid properties have an important role in the recommended dosage for each well field trial conditions to customize a corrosion-treatment program specific to The chemical injection rate optimized

needs. The effect of share rate on viscosity of the selected mMMt demulsifier sample was studied at 1-60 rpm using spindle 52 at 25 oC, decrease viscosity values with increase share rate that is mean share thinning or in other words Pseudo-plastic behavior, this drop in viscosity may be due to destroying the networks formed by the association between the hydrophobic chains presented in thickener molecules leading to drop in viscosity.

Table 8: Effect of share rate

Speed (Rpm)	Viscosity (cp)	Share stress (1/sec)	Share rate (D/Cm3)	Torque (%)
1	7987	190.0	2	85.0
2	5678	178.3	4	79.2
5	3650	150	10	73.1
10	1987	137.6	20	79.7
20	784	135	40	81.2
30	345	121.3	60	83.1
40	276	143.1	80	78.3
50	219	160.2	100	88.2
60	110	190.1	120	96.1

CONCLUSION

The main goal of this study is to prepare a new Green Modified nanoclay composite mMMt multifunctional property to replace the existed commercial formulation for gas and oil-field industries. Toward this goal, two different specialty chemicals in this formulation were synthesized using a novel, simple, economic, eco-friendly and green chemical method was applied for synthesis, design and fabrication of new modified clay nanocomposites mMMt with a controlled size under leidenfrost drop temperature. The first ingredient is Ionic liquid with corrosion inhibition property and antimicrobial properties, which synthesized from renewable sources. The other ingredient is clay layers, which act as stabilizer, rheology modifier and pH control. Then, in the next section the obtained products using leidenfrost drop rector were characterized and evaluated in formulation as multifunctional formulation for oil and gas industries.

From the data of the evaluation of the new synthesized surfactant utilized as multifunctional in oil and gas industries we can conclude the following:

- The prepared that newly formulated possess very interesting physical properties such as good flow which make them suitable for the injection through the oil and gas raw pipeline.
- The results showed that newly formulated CORRICHEM compound showed good corrosion inhibitors with chemical injection rate optimized showed that the inhibition efficiencies increased with the increasing concentration at 50°C.
- The results showed that new formula have better rheology property as compared with commercial samples and hence can be used as nano modified thickener. Furthermore, the newly formulated possess very interesting rheological and remarkable ph controlling properties at both room and high aging temperature which make it suitable for the injection through the oil and gas production pipelines.

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