

Effect of Surfactants on the Performance of Water-Based Drilling Fluids



Basim Abu-Jdayil and Mamdouh Ghannam

Abstract In the formulation of drilling fluids, different additives are used to optimize their rheological behavior and control the fluid loss throughout the drilling process. Surfactants, as one of these additives, play a vital role in sealing off the lost circulation zones and in controlling the rheological properties of the dispersions to meet the specification of the desired applications. This chapter is divided into three sections. The first section reviews the definition, functions, and properties of drilling fluids, bentonites and surfactants. The second section provides an overview on the main and recent research on utilization of surfactants in drilling fluid formulations. The last section describes an experimental work on the effect of cationic surfactant CTAB and anionic surfactant SDS on the performance of water based drilling fluid. Adding of CTAB surfactant to water-based drilling fluid reduced significantly its viscosity and shifted its rheological behavior from shear thinning fluid with a yield stress towards Newtonian behavior. On the other hand, the SDS surfactant was effective in modifying the rheological properties of water-based drilling fluid in the concentration range that corresponds to critical micelle concentration (CMC) and critical coagulation concentrations (CCC) of SDS.

Keywords Water-based drilling fluid · Bentonite · Surfactants · CTAB · SDS · Rheology

1 Introduction

Human survival and economic activities all depend on the supply of energy. Nowadays, the worldwide industrial growth led to increase the global demands of energy while the production of conventional crude oil throughout the world has almost reached to its peak. Recent reports claim that there is a decrease in light oil production, while the composition of produced oil is getting heavier [1]. Therefore, the utilization of the unconventional hydrocarbon resources such as heavy oil and tight

B. Abu-Jdayil (✉) · M. Ghannam
Chemical & Petroleum Engineering Department, UAE University, Al Ain, UAE
e-mail: babujdayil@uaeu.ac.ae

reservoirs would play an important role in the future of the ever-growing world's energy consumption [2]. The unconventional hydrocarbons are known as one of the major energy source in the twenty first century [3], where their reserves account for more than 80% of the total quantity of petroleum in the world [4]. It is expected for oil and gas industry to transform exploration development domain from conventional to unconventional hydrocarbon accumulations that are different in types, geological features and genesis [5]. Drilling in unconventional reservoirs can help to meet the world's energy demand. Although the concept of drilling fluids remained the same, their technology became much more complex. Drilling fluids are necessary to drilling success, both maximizing recovery and reducing the time it takes to achieve first oil [6].

1.1 Drilling Fluid

A drilling fluid, also known as drilling mud, is defined as the fluid that is used in a drilling operations, where the fluid is circulated from the surface, down the drill string, through the bit, and pumped back to the surface via the annulus [7]. Drilling fluids are suspensions of clays in liquid phase with chemical additives used to modify their properties. There are many types of drilling fluids including water-based, oil-based, synthetic-based, and air drilling fluids such as mist, foams, and stiff foams [7]. In water-based drilling fluid (WBDF), the carrier fluid is fresh water or brine, while those with oil as a continuous phase are called oil-based fluids. In most drilling processes, water-based fluids are used, owing to the simplicity of their preparation, low cost, environmental friendliness, cutting based removal and fast formation/breaking-down rate [8].

Clay minerals are the basic elements of drilling fluids. Clays provide and maintain a suitable rheological behavior for drilling fluid and control the fluid loss throughout the drilling process. Selecting the type of clay and its quantity are critical factors for successful drilling process [9]. In most of drilling fluids, the used clay is sodium bentonite which is naturally occurring clay mineral contains mainly sodium montmorillonite. In some cases, the palygorskite-sepiolite group clay minerals are used in drilling fluid formulations [8]. Owing to their absorptive properties, sepiolite and palygorskite are used in different applications as carriers, fillers, clarifying agents, and lubricant reclamation.

Additives including electrolytes, polymers, surfactants and nanomaterials were used to optimize the performance of the drilling fluid, most likely to modify its rheological properties [9–12].

Drilling fluid plays an important role in oil and gas exploring process. In addition to carry out effective drilling operations, drilling fluids improve the productivity of wells. The main functions of drilling fluids are to carry the rock cuttings to the surface (needs a minimum yield stress), to maintain a sufficient pressure against the rock formation (needs a viscous fluid), to lubricate and cool the bit (need enough fluidity that comes from the shear thinning behavior) [13].

In addition to the characteristics and chemical composition of the well, the environmental impact should be taken into consideration, when the drilling mud engineer is prescribing the type of drilling fluid necessary in a well. While water-based drilling fluids have generally less impact on the environment during offshore drilling, oil-based drilling fluids may work better with a saltier rock.. Disposal of the used drilling fluids can also be another challenge. Recently, new methods have been established to recycle drilling fluids [14].

The properties of drilling fluids, namely the rheological properties (plastic viscosity, apparent viscosity and yield stress), mud density, fluid loss, pH and gel strength, have been investigated extensively in the literature. Most of the studies, focused on the rheological behavior of drilling fluids, as they are often used in a variety of changing environmental conditions, such as changing pressure and temperature, and inflow through various geometrical shapes of a conduit (e.g. in pipes and strange annuli for oil and gas wells and in rivers and hills) [15].

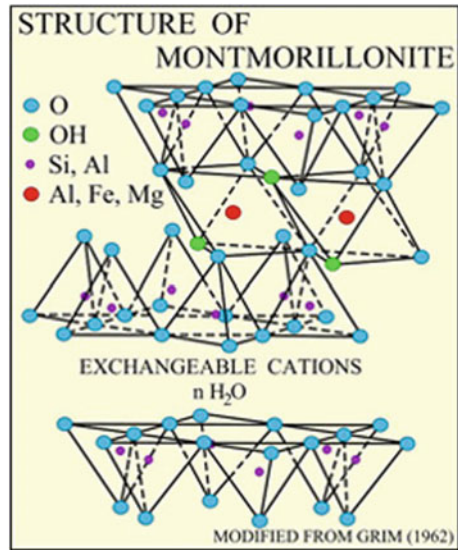
The temperature, type and concentration of clay and additives, and pH are important factors influencing the rheological properties of the drilling fluids.

1.2 Bentonite

Drilling fluids are mainly based on dispersed sodium bentonites. Bentonite is a clay generated often from the alteration of volcanic ash and consisting mainly of montmorillonite that consist of individual crystallites with dimensions are less than 2 μm . Montmorillonite crystallites themselves are three-layer clay minerals: two tetrahedral layers and one octahedral layer. In montmorillonite tetrahedral layers consisting of $[\text{SiO}_4]$ —tetrahedrons enclose the $[\text{M}(\text{O}_5, \text{OH})]$ -octahedron layer, where M is mainly Al, Mg, but Fe is also found, see Fig. 1 [16]. The small negative charge of the silicate layers is usually compensated by exchangeable ions in the intercrystallite region. The charge is so weak that the cations like Ca^{2+} , Mg^{2+} or Na^+ can be adsorbed in this region with their hydrate shell. The intercrystalline swelling results from the extent of hydration [17]. The contact between montmorillonite and water leads to swell montmorillonite particles several times by its original volume. However, the wide range of industrial applications is related to the cation exchange in the interlayer space of montmorillonite with two compositional endmembers (Na-bentonite and Ca-bentonite). While Na-bentonites exhibit great swelling capacity, Ca-bentonites can be considered as non-swelling clays [18]. Moreover, other impurities can be found bentonite such as feldspar, calcite, quartz, cristobalite,, mica, pyrite and ferrous carbonate [19].

With exceptional rheological behavior, bentonites are utilized in different industries including drilling fluids, paper, dyes, pharmaceuticals, cement, composites, and ceramics (e.g. [20–26]). In addition and owing to the fact that bentonite is a porous material with high capability of adsorption, it has an application in environmental engineering as a sorbent for different heavy metals and organic pollutants (e.g. [27–29]).

Fig. 1 Schema of bentonite structure [14]



One of the most important and efficient applications of sodium-bentonite suspensions Fig. 2 is their use as drilling fluid in the oil and gas industry [30–32]. Sodium bentonite’s main feature in drilling comes from its excellent colloidal properties and its unique rheological behaviour, where small solid concentration (2.0–9.0 wt%) in water can form a viscous, shear thinning material with significant yield stress [11], Abdou and El Sayed Ahmed [33, 34]. High viscosity with yield stress behaviour exhibited at low shear rates is representing solids lifting capacity away from the drill bit, and relatively low viscosity at high shear rates (shear thinning behaviour) in the vicinity of the drill bit is necessary to reduce torque requirements. In addition, dispersions of bentonites in water exhibit a thixotropic behaviour, which is often observed at high enough concentrations [11, 35–37].

1.3 Surfactants

On daily basis, surfactants are one of the most chemicals that are consumed in large quantities. Surfactants are substances that create self-assembled molecular clusters called micelles in a water or oil solution and adsorb to the liquid–gas/solid interface. To exhibit these two behaviors, a surfactant molecule should have a chemical structure with two different functional groups that have different chemical affinity. Usually the surfactant molecules have both an alkyl chain with 8–22 carbons, which is called a hydrophobic group (does not show affinity to water). The surfactant molecules also have a functional group, which has affinity to water and it is

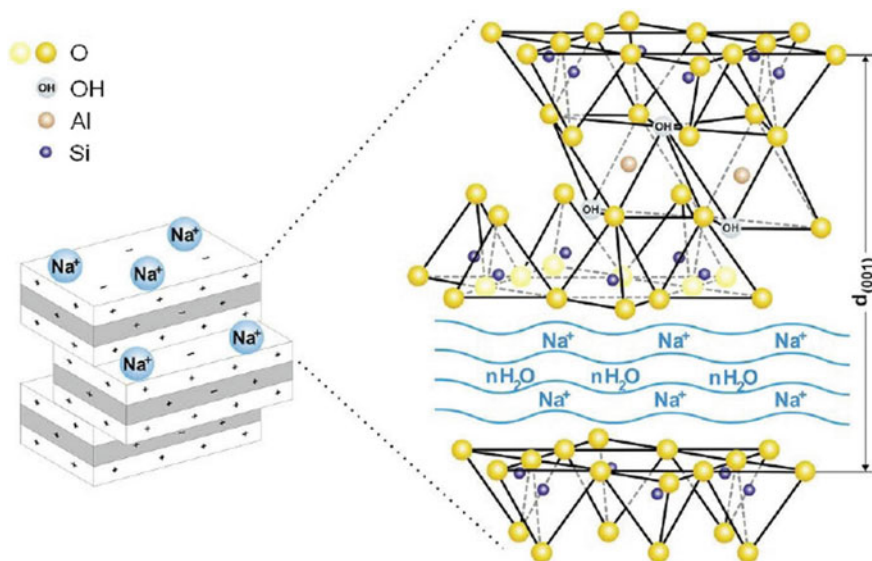


Fig. 2 Schema of sodium montmorillonite structure [38]

called the hydrophilic group [39]. Based on this behavior, surfactants are classified as amphiphilic molecules. As shown in Fig. 3, and due to the different chain lengths in many surfactants, reference is often made to a hydrophilic “head” and a hydrophobic “tail”.

Surfactants are soluble in both aqueous and organic solvents. The surfactant reduces the surface tension of saqueous solution by adsorbing at the interface of liquid–gas system. By adsorbing at the liquid–liquid interface, surfactant can also reduce the interfacial tension in oil–water system [40]. When there are a sufficient concentration of surfactant in a solution, the surfactant molecules combine together to form certain structures called micelles, see Fig. 4. When the micelle forms, the surfactant heads position themselves so they are exposed to aqueous phase, while the tails are grouped together in the center of the micelle structure far away from the aqueous sphase [41]. Many factors play significant role in the determination of the critical micelle concentration (CMC) where micelle formation becomes significant in liquid phase. The most important factors that are known to have an influence on the CMC in aqueous solution are (i) the chemical structure of the surfactant, (ii) nature of counter ions in the case of ionic surfactants the presence of electrolyte in the solution, especially in the case of ionic surfactants, (iii) the presence of electrolyte in the solution, especially in the case of ionic surfactants, (iv) the presence of different organic compounds in solution, and (v) solution temperature [42]. Moreover, it was found that different types of aggregates can be formed in surfactant solution that depend on the surfactant geometry. Different possible aggregate morphologies in surfactant solutions were identified by Kunitake et al. [43], which are including vesicles, globules, rods, lamellae, tubes, and disks. Varying the length of the tail and/or

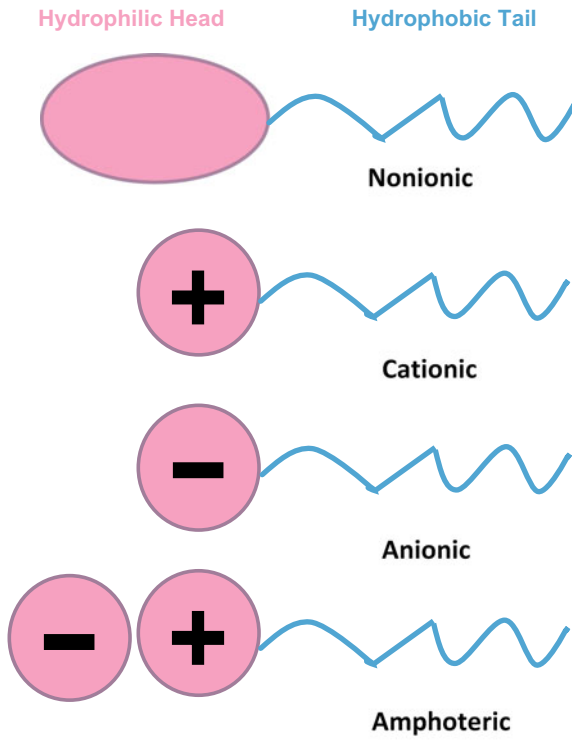


Fig. 3 Types and schematic structure of surfactant

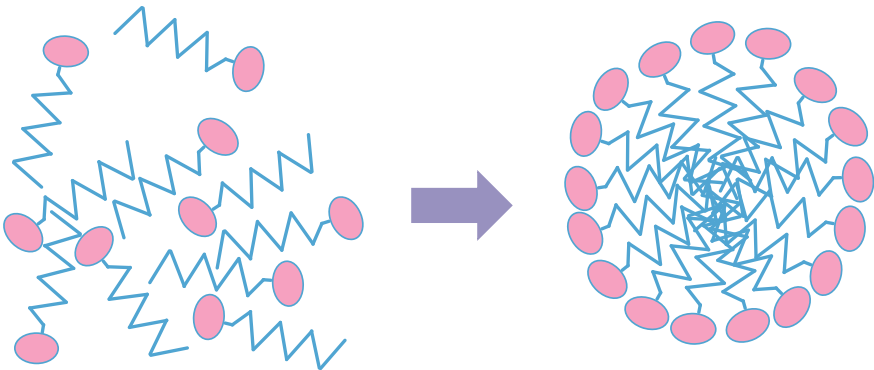


Fig. 4 With high enough concentration, individual molecules of surfactant aggregate to form a micelle (right)

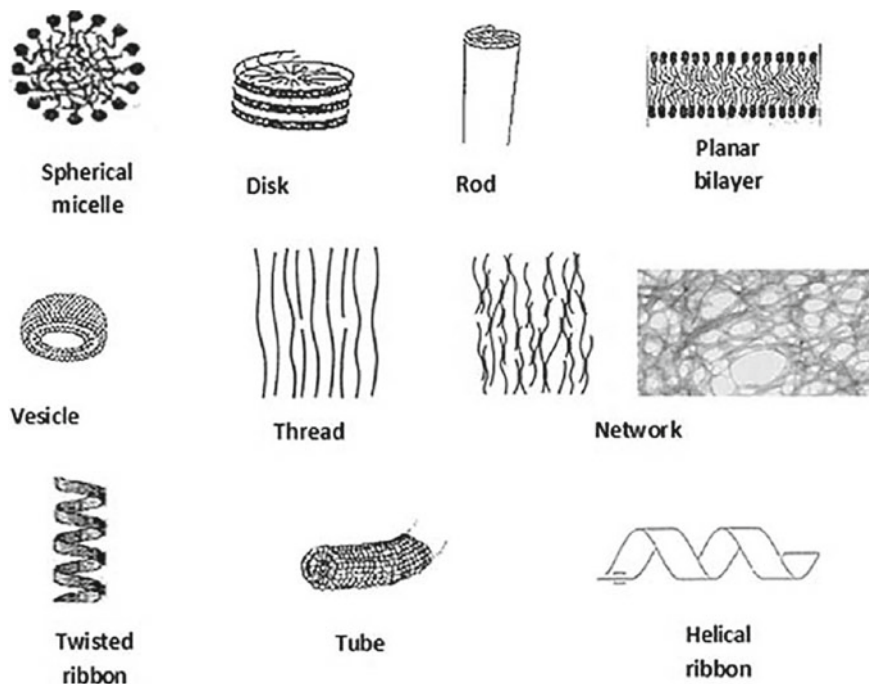


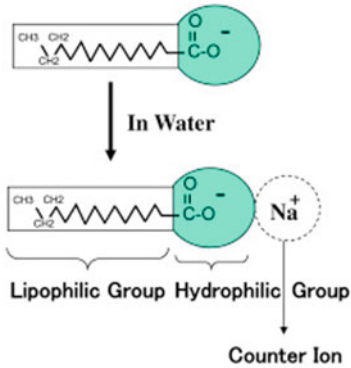
Fig. 5 Shapes of aggregates formed by surfactants in water [42]

the flexible linker can lead to change the structure of the aggregate. Some possible types of aggregates formed in aqueous solutions are shown in Fig. 5.

According to the nature of the hydrophilic group, surfactants are classified into ionic and nonionic surfactants, see Fig. 3. Ionic surfactants are sub-classified into anionic, cationic and amphoteric surfactants. In anionic surfactants, the hydrophilic group dissociates into anions in aqueous solutions (e.g. carboxylates (COO^-) or sulphonates (SO_3^-)), while in cationic surfactants the hydrophilic group dissociates into cations (e.g. quaternary amines ($-\text{R}_4\text{N}^+$)). The hydrophilic group in amphoteric surfactants dissociates into anions and cations often depending on the solution pH (frequently carboxylate and quaternary amine group). On the other hand, nonionic surfactants do not dissociate into ions in aqueous solutions, where they bond with polar, non-ionic groups such as ether, alcohol, or ethoxylate. (see Fig. 6 [39]).

Other types of surfactants called Zwitterionic, double chain, gemini and bolaforms can also be found. The Zwitterionic surfactant molecules contain both anionic and cationic centers at the head group. In double chain surfactants, the polar head is attached with two hydrocarbon chains. On the other hand, “gemini” surfactants contain two hydrophobic and two hydrophilic groups. The gemini surfactants can be thought of “twin” surfactants as being made up of two typical surfactant molecules chemically linked at or near the head group. “Bolaforms” surfactants have two head groups (both cationic, both anionic, or one anionic and the other cationic) joined by

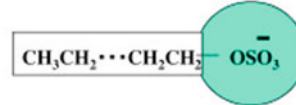
In an amphiphilic structure there are groups with opposite properties, one group that has affinity to water and a group that has affinity to lipids.



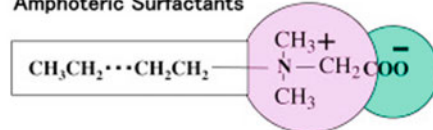
Nonionic Surfactants



Anionic Surfactants



Amphoteric Surfactants



Cationic Surfactants

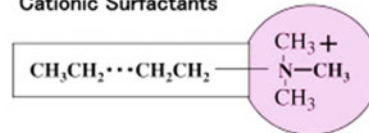


Fig. 6 Classification of surfactants [39]

hydrophobic spacer. The nature of head group(s) and the hydrocarbon chain length control the surface activity of “bolaforms”. Surfactants with longer hydrocarbon chains are found to be more surface-active than those with shorter hydrocarbon tail [42].

Most of the surfactants have similar tails that consist of a hydrocarbon chain, which can be linear, branched or aromatic. For example, Fluoro-surfactants have fluorocarbon chains and Siloxane surfactants have siloxane chains. However, surfactants with mixed chains and complex structures have been recently developed [44]. In Table 1, most famous surfactants with their applications are summarized.

2 Effect of Surfactants on Drilling Fluid Performance

Many difficulties face the drilling fluid engineers such as developing a drilling fluid system that yields acceptable well stability and prevents fluid invasion. One of the main challenges faces the drilling fluid engineers is the loss of drilling fluid, due to the formation openings. The loss of drilling fluid results in loss of hydrostatic pressure at the bottom of the well and allows influx of formation fluids and finally could lead to loss of well control. It is essential that circulation of drilling fluid be regained for drilling process to continue. Formation of filter cake or formation of mud solids layer on the wall of the hole in the formation can cause stuck drill pipe problem, which can occur after drilling has been halted due to a rig breakdown or when conducting other nondrilling operations [7]. Therefore, different additives, mainly polymers and

Table 1 Examples of surfactants [44]

| Surfactant type | Structure/name | Applications |
|--------------------------|---|---|
| Nonionic surfactant | Polyoxyethylene glycol octylphenol ethers: C ₈ H ₁₇ -(C ₆ H ₄)-(O-C ₂ H ₄) ₁₋₂₅ -OH | Wetting agent and coatings |
| | Polyoxyethylene glycol alkylphenol ethers: C ₉ H ₁₉ -(C ₆ H ₄)-(O-C ₂ H ₄) ₁₋₂₅ -OH | Spermicide |
| | Polyoxyethylene glycol sorbitan alkyl esters | Food ingredient |
| | Sorbitan alkyl esters | Polishes, cleaners, and fragrance carriers |
| | Block copolymers of polyethylene glycol and polypropylene glycol | Various |
| Anionic surfactant | Dioctyl sodium sulfosuccinate (DOSS) | Wetting agent, coatings, and toothpaste |
| | Perfluorooctanesulfonate (PFOS) | Scotchguard™, and Skydrol™ |
| | Linear alkylbenzene sulfonates | Laundry detergents, and dishwasher detergents |
| | Sodium lauryl ether sulfate | Shampoos and bath products |
| | Lignosulfonate | Concrete plasticizer, plasterboard, and DMSO |
| | Sodium stearate | Handsoap and HI&I products |
| Cationic surfactant | Quaternary ammonium cations include: Cetyl trimethylammonium bromide (CTAB) Cetyl trimethylammonium chloride (CTAC) | Softeners in textile, and anti-static additives |
| | Benzalkonium chloride (BAC), Cetylpyridinium chloride (CPC), Benzethonium chloride (BZT) | Anti-microbials, and anti-fungals |
| Zwitterionic surfactants | Sultaines; CHAPS (3-[(3-Cholamidopropyl)dimethylammonio]-1-propanesulfonate) | Cosmetics, and in special use |
| | Bataines: cocamidopropyl betaine | |

surfactants, have been used in drilling fluids to seal off the lost circulation zones and to control the rheological behaviour of the suspensions to fit with the specification of the desired applications, such as poly vinyl pyrrolidone [45], poly vinyl alcohol [46, 47], xanthan [48], polyanionic scellulose [49], polyethyleneimine [50], poly (ethylene glycol) [51], polypropylene glycol [52] and carboxymethyl cellulose sodium salt

[12, 53], polyacrylamide [54], polyethyleneimine [55], and sodium dodecyl sulphate (SDS) [56]. In addition, the reduction of bentonite concentration in the mud system is another target of the mud engineers to avoid the undesirable effects of high bentonite concentrations. High solid concentration in drilling fluid leads to a reduction in the drilling rate of a wellbore a given depth. Moreover, the high bentonite concentration in drilling fluids has two other main disadvantages that the high cost of transportation and storage, which can be critical for offshore drilling sites and sites located in distant and hostile environments [57].

Owing to the fact that bentonites are porous materials with high capabilities for physical and chemical adsorption, they were used extensively as a sorbent for different heavy metals and organic pollutants. However, the efficiency of bentonite as a sorbent was improved by using different kinds of surfactants to switch the surface properties of the bentonite from hydrophilic to hydrophobic [28, 58]. This process allows the pollutants to be adsorbed on the hydrophobic bentonite surface, where the pollutants are captured by hydrophobic interaction between alkyl chains. Many investigators have used the cationic surfactant cetyltrimethyl ammonium bromide (CTAB) and the anionic surfactant sodium dodecyl sulphate (SDS) to modify the surface properties of bentonites and to improve their sorption properties (e.g. [28, 59–61]).

On the other hand, the addition of surfactants to bentonite suspensions can influence their stability. It is expected that the surfactants can induce flocculation of bentonite particles by bridging, charge neutralization, surfactant-particle surface complex formation and depletion flocculation, or by a combination of two or more of these mechanisms.

The first important flocculation mechanism, which is the bridging mechanism needs that the surfactant chains be adsorbed on the bentonite surface with only a few points of attachment, while the bulk of the surfactant chains projecting into the solution for contact and adherence to other bentonite particles. It should be mentioned that the strong adsorption of surfactants on bentonite surface can cause surface saturation, preventing effective bridging and destabilizing bentonite suspension [62]. This means that the strong adsorption of surfactants on bentonite particles does not support the flocculation process. Cationic and anionic surfactants can have clear effect on the flow properties of bentonite suspensions, which is more complex than the surfactant effects on other clays. Vali and Bachmann [63] found that delamination of bentonite produces very thin particles, where the flow behavior of these particles can be changed by modest changes in experimental conditions, such as pretreatment reactions, degree of dispersion, and pH. In the presence of anionic surfactants, it has been proposed that the adsorption of surfactant molecules on the bentonite particles and the subsequent flocculation process occur via hydrogen bonding between the solid surfaces and the hydroxyl groups on the surfactant. While in the case of cationic surfactants, adsorption on negatively charged bentonite particles and consequent flocculation occur by simple electrostatic attraction [64].

Modification of the surface properties of bentonite by adding surfactants permits them to be used as rheological control agents in different engineering applications such as drilling fluid, paints, oils, composites and pharmaceuticals.

2.1 Surfactants in Water-Based Drilling Fluids (WBDF)

2.1.1 Ionic Surfactants

Modification of drilling fluid performance with anionic surfactants received little attention comparing to cationic surfactants. The effect of surfactants on the flow behavior of sodium bentonite dispersions (2 wt%) was studied for a cationic (cetylpyridinium chloride, CPC1) and an anionic surfactant (sodium dodecylsulfate, SDS) by Permien and Lagaly [10]. Cationic and anionic surfactants affected the rheological behavior of sodium bentonite suspensions by several mechanisms. In strongly acidic media, where the $\text{pH} < 4$, the surfactants have clear effect on the stability of the card-house structure. The cationic surfactant promoted disintegration of the card-houses. The same also took place at higher concentrations of the anionic surfactant ($>10^{-3}$ M), whereas lower SDS concentrations stiffened the network. The electroviscous effect was responsible for the reduction in the shear stress and yield point at $\text{pH} > 4$, where the surfactants acted as 1: 1 electrolytes. However, at high surfactant concentrations, the alkyl chains of opposed particles interacted and flocs were formed. Still higher concentrations caused reeptization by recharging the particles.

An early study on the effect of the anionic surfactant (linear alkyl benzene-sulfonate, LABS) and the cationic surfactant (distearyl dimethyl ammonium chloride, DDAC) on the rheological behavior of Na-bentonite was carried out by Gungor [64]. The effect of the surfactants have been tested at different concentrations. At low values of pH ($\text{pH} = 2.4$), it was found that the distearyl dimethyl ammonium positive ion was adsorbed on the negative faces of bentonite leading to decrease the negative charge there. This reduction in bentonite negative charge resulted in lowering the face-edge interactions and so decreasing the yield stress. At high values of pH ($\text{pH} = 9.5$), the flow behavior of bentonite changed with the DDAC concentration, as it was governed by the electroviscous effect. At DDAC concentrations $> 10^{-4}$ M, the exchange of the counter ions on bentonite particles by DDA + cations reduced its hydrophilicity, which cause the particles settling as flocs. On the other hand, LABS anions at low concentration ($< 10^{-5}$ M) and low pH ($= 2.4$) were not adsorbed by the bentonite particles and did not affect the flow properties of the dispersions.). At these conditions, the yield stresses were high due to formation of the card-house structure. At LABS concentrations $> 10^{-3}$ M, the yield stress value decreased because the surfactant anions broke up the edge-face contacts. At high pH ($= 9.5$), the values of yield stress were constant up to about 5×10^{-4} M and then increased.

The flow behavior of Egyptian bentonite dispersions was investigated in the presence of cationic polyethylene imine followed by anionic polyacrylamide at different bentonite concentrations and temperatures (20–80 °C) [65]. All tested samples were aged for 24 h. An inverse relation between temperature and dispersions plastic viscosity was detected. Contrary to that, increasing the temperature led to increase the apparent viscosity, yield point, gel strength, and consistency index of the dispersions.. Moreover, the results showed that there was a strong dependence of the zeta

potential on dispersions temperature. The constructed potential energy profile at different bentonite concentrations gave a high-repulsion potential energy between bentonite surfaces by increasing temperature, which means that the dispersions stability improved.

In the study of Yunita et al. [66], a non-ionic and anionic surfactants were used with the aim to optimize the flow and filtration properties of water-based drilling fluid. Alkyl benzene sulphonate was used as anionic surfactant, while 2-hexadecyloxyethanol was utilized as non-ionic surfactant. The results of this investigation showed that both surfactants can improve the rheological and filtration properties of water-based drilling fluid. The filtration loss was improved by 41.3% in the presence of surfactants. It was expected that the long chain of both surfactants increased the drilling fluid viscosity, which has a positive effect in blocking the pores and forming a tight filter cake. Moreover, the addition of these surfactants to the water-based drilling fluids enhanced their resistance at the higher temperature.

Data presented in the work of Elochukwu et al. [67] focused on the using of Methyl Ester Sulphonate (MES) surfactant and nano-polystyrene in water-based drilling mud. The researchers utilized Bingham and Power law models to study the rheology of the drilling fluid, which showed that its formulation was improved in the presence of MES and nano-polystyrene. Filtration experiments under low pressure low temperature (LPLT) and high pressure high temperature (HPHT) conditions revealed that MES and nano-polystyrene reduced the filtration loss of drilling fluid by 50.7% at LPLT and 61.1% at HPHT conditions.

Two series of cationic Gemini surfactants, alkanediyl- α,ω -bis[N,N-dimethyl alkyl (octyl or dodecyl)ammonium] dibromide (R-s-R; s = 6, 10, 12 and R = 8 and 12) were prepared by Ahmed et al. [68] to be used as additives for water-based drilling muds. FTIR and mass spectroscopy were used to confirm the chemical structures of the prepared surfactants, which demonstrated noteworthy surface activity that was more pronounced with those of longer hydrophobic chain length. Moreover, the effect of the prepared Gemini surfactants on the rheology and fluid loss properties of water-based drilling fluid formulated from local sodium bentonite was tested. The results revealed that the Gemini surfactants have improved the rheological and filtration properties of the sodium bentonite according to API specifications.

Three cationic bolaform surfactants with different spacer lengths were prepared by reaction two moles of triisopropanolamine with one mole of each of the following 1,4-dibromobutane, 1,5-dibromopentane and 1,6-dibromohexane [69]. Then, the effect of the prepared surfactants on the properties of water-based drilling fluids was investigated. Weak surface activity of the prepared cationic surfactants was detected from the surface tension measurements. The prepared water-based drilling fluids with the presence of the cationic bolaform surfactants demonstrated an acceptable yield stress, mud density, swelling ratio, rheological and filtration properties. The prepared cationic surfactants qualified a clay sample to be used as drilling mud as the rheological behavior satisfied the API standard and Oil Company Materials Association (OCMA) specification.

The effects of alkali metal, calcium and lanthanum chlorides, alkali metal sulphates, sodium dodecyl sulphate, cetyltrimethylammonium bromide and pH on

the zeta potential and electrical conductivity of sodium bentonite dispersions were studied by Mészáros et al. [70]. The behavior of the dispersion in an external electric field can be summarized as follows: zeta potential of particles displayed relatively high values both in water and in supporting electrolytes solution (from -35 mV to -52 mV) with low sensitivity to pH, the zeta potential dependencies for RbCl and CsCl concentration were characterized by a constant value at concentration of $10^{-5} - 10^{-3}$ mol/L, and for LiCl, NaCl and KCl by a maximum at concentration of $10^{-3} - 10^{-2}$ mol/L, zeta potential in alkali metal sulphates solutions was measured to be higher compared to that for chlorides at equivalent concentration of salts; addition of electrolytes with bi- and trivalent counter-ions or cationic surfactant caused a clear reduction in zeta potential values and surface charge reversal, respectively; while moving from LiCl to CsCl in the lyotropic series, a regular reduction in the surface conductivity of particles was measured. The researchers explained the observed regularities by accounting for two opposite trends related to the polarization of the electrical double layer (EDL) in the external electric field (increase of zeta potential at low concentration) and the effect of the EDL compression (decrease of zeta potential at high concentration) as well as the increase in filling up the Stern-layer with alkali metal ions as their radius increases. It was linked the bigger zeta potential values for sulphates compared to that for chlorides with dehydration effect of sulphate co-ions which results in the thinning the surface hydrate layer and shift of the shear plane toward the surface. The rheological and other drilling fluid properties were not investigated.

Pickering emulsions showed high potential for different applications in the oil and gas industry, especially those with pH-responsive behavior that allows them to be easily implemented. However, the main concern on the pH-responsive emulsions is the narrow pH window in the stabilization of emulsions, which is not preferred for some complicated reservoir conditions. Liu et al. [71] reported recently a Pickering water-in-oil (W/O) emulsion system with a wide pH window, which can be produced from the interactions between fumed silica nanoparticles (NPs) and amine surfactant. FTIR spectroscopy, turbidity, surface tension and other measurements were used to confirm the pH-dependent interaction between NPs and amine surfactant. Liu et al. [71] found that the stable W/O emulsions generated by this system were formed within the pH window that showed strong flocculation of NPs due to the adsorption of surfactant onto the particle surfaces, which imparts a certain hydrophobicity to the NPs. Outside of this pH range, the similar charge of the surfactant and the nanoparticles generates strong repulsion between them, so the fumed silica NPs cannot be supplied with such hydrophobicity. The pH-responsive Pickering emulsion-based drilling fluid exhibited adjustable rheological behavior and was reversible by a cyclic emulsification-demulsification process. Liu et al. [71] anticipated that this system can be switched “off” in follow up procedures and waste disposal at the surface., while it can be switched “on” over a wide pH range with high stability when running underground.

The swelling of shale formation when it is exposed to water-based drilling fluids leads to many operational problems. Many common shale inhibitors are used in the industry to overcome this swelling problem, however, they suffer from many

drawbacks, which adversely affect the performance of drilling fluids. The study of Murtaza et al. [72] focused on the development and application of new quaternary ammonium Gemini cationic surfactants as shale swelling inhibitors. The developed cationic Gemini surfactants have similar structure with different spacer lengths. It was found that the new cationic surfactants have the ability to reduce the clay swelling. The increased hydrophobicity of the GS12 surfactant (containing flexible large spacer C12) allowed it to be a beneficial swelling inhibitor as compared to GS8 and GS10 with lower hydrophobicity. In addition, GS12 showed comparable performance with the common shale inhibitor used in the oil industry. SEM images revealed the surfactant-treated clays have fine, dense, and smooth surface. Moreover, it was found that the developed surfactants adsorbed and intercalated between layers of clay through hydrogen bonding and attractive electrostatic forces. Therefore, the orientation of lipophilic tails inhibited the water adsorption in the clay which resulted in decreased clay swelling. It was also reported that the developed cationic surfactants decreased the clay swelling without changing the other drilling fluid properties such as stability, rheology, and filtration properties.

To develop environmentally friendly high performance drilling fluid, effective and green shale hydration inhibitors are needed. For this purpose, Jiang et al. [73] have prepared composites of gelatin and inorganic salt (KCl) or organic salt (2, 3-epoxypropyl-trimethylammonium chloride, EPTAC) as green shale inhibitors. The inhibitive properties of the prepared composites were assessed by comparison with the properties of common inhibitors. Results revealed that when 2.0 wt% gelatin and 1.0 wt% salt were mixed, the composites reduced the swelling height of bentonite to less than 1.70 mm, improved shale recovery to 80% at 150 °C and inhibited 16.0 wt.% bentonite mud-making, suggesting great inhibition performance. Moreover, it was found that the gelatin composite with EPTAC has better synergistic inhibition than that with KCl. The inhibitive mechanisms of prepared composites were also investigated by observing aggregation in the drilling fluid system using electron microscopy, measuring interlayer space through XRD observing hydrophobic modification degree by measuring the water contact angle, and measuring the zeta potential and water activity. Both composites showed lower water activity and effectively prevented water from invading bentonite. In these composites, gelatin mainly adsorbed on the surface of bentonite particles, encapsulated them, and improved their hydrophobic capacity to a certain degree, whereas the salts entered the interlayer, expelled water, and decreased the interlayer space. The main conclusion was that the combinations of gelatin and KCl or EPTAC had significant effect on inhibiting shale hydration.

2.1.2 Nonionic Surfactants

The geological characteristics and the potential formation damage of the Permian formation of the reservoir was investigated by Zhang et al. [74], who identified that the water-blocking due to invasion of drilling or completion fluids is one of the most severe causes of damage to gas well deliverability. Zhang et al. [74] have developed

a low-damage drilling fluid containing efficient water-blocking preventing surfactants, optimized temporary bridging agents (TBAs), and film-forming agents. The development of such drilling fluid was based on the phase trap prevention method, ideal packing theory, and film-forming technology. The results obtained from the evaluation of the new drilling fluid showed that the fluid has acceptable performance in terms of rheological properties, shale-swelling inhibition, temporary plugging effect, ultra-low filtration, and lubricity. Moreover, the developed drilling fluid can efficiently reduce water-blocking. Drilling fluid comprising nonionic surfactants to reduce the interfacial tension between the water-based filtrate and reservoir gas, contributed to mitigation of water-blocking in low-permeability gas reservoirs.

Four vanillin-based nonionic surfactant derivatives were synthesized by Negm et al. [7] to show good surface-active property in solution. These surfactants showed enhancement of the properties of water-based fluid. The results revealed that the performance of water-based drilling fluid formulated with the new prepared surfactants varied within an acceptable range comparable to the performance of field water-based drilling fluid.

In another work, Negm et al. [75] used tannic acid to synthesize a new type of nonionic surfactant. It was found that the ratio of the attached hydrophobic chains controls the surface activity of the produced surfactants. Moreover, the experimental works on the new produced nonionic surfactants proved that those surfactants exhibited good performance when added as viscosifiers to the water-based drilling fluid formulation—Comparing with a reference viscosifier, the rheological and filtration properties of the most synthesized surfactants were very promising.

Using of cost effective and environmentally friendly shale inhibitor in drilling industry steadily increased. Shadizadeh et al. [76] used a newly developed nonionic surfactant (*Zizyphus spina-christi* extract, ZSCE for inhibiting shale hydration. The conductivity technique was used to evaluate the adsorption behavior of ZSCE onto shale cuttings. In addition, different inhibition evaluation methods were used to assess the inhibitive properties of ZSCE. All experimental results showed that ZSCE surfactant can work as a potential shale inhibitor, however, its inhibitive capacity had no clear improvement at concentrations above the CMC. Comparing with polyamine and potassium chloride, ZSCE surfactant showed a better performance. Moreover, it was found that the ZSCE surfactant was compatible with other conventional additives can be found in water-based drilling fluids. The stability of Na-bentonite particles in ZSCE solution was indicated from the SEM micrographs. It was expected that the main inhibition mechanism for ZSCE surfactant is due the hydrogen bonding between oxygen atoms available on silica surface of bentonite and hydrophilic tail of ZSCE molecules, which can produce a hydrophobic shell on the bentonite surface. The results of this investigation opened the door to utilize the plant-based surfactants as shale inhibitors in water-based drilling fluids.

In their recent work, Aggrey et al. [77] reported the utilization of the nonionic surfactant saponins, which was extracted from *Chromolaena odorata* (CO) leaf, as shale hydration inhibitor. The inhibitive performance of the plant-based nonionic surfactant was evaluated through measurements of surface-active, rheological, strength and inhibition properties. It was found that the saponins surfactant has high

compatibility with the water-based drilling fluids and can produce a stable highly effective shale inhibitor. Concentration range of 2.5–3.5 wt% CO could be used as inhibitor component in water-based drilling fluid with a CMC of 3.5 wt% as an optimum concentration to improve the inhibitive properties.

2.1.3 Mixed Surfactants

In the work of González et al. [78], the effects of a surfactant additive (SA) and its dissolution in diesel (SB), on the rheological and tribological properties of WBDFs formulated with hematite and calcium carbonate were investigated. The ionic/anionic mixture (80/20) surfactant was used in this work. The non-ionic surfactant was a lauryl alcohol ethoxilate with an ethoxilation degree of four units, while the anionic surfactant was a Trilaureth-4 Phosphate. SB surfactant was prepared by mixing the surfactant SA with diesel in a ratio of 40:60 (w/v). The tribological properties were determined by measuring the coefficient of friction (CF) in conjunction with optical surface profilometry used to evaluate the wear behavior. In addition, the dispersion stability of solid particles in the aqueous surfactant solutions was identified by light scattering techniques. The findings of this work verified that the used surfactant can reduce significantly the CF, and that SA formulation was much better than SB in CF reduction. Moreover, it was found that the viscosity increases in the polymeric drilling fluids formulated with hematite and SA, reflecting strong interactions in the polymer–surfactant–solid system. However, the kind of these interactions was not discussed. In the case of the drilling fluid containing calcium carbonate the addition of surfactant had no effects on the rheological behavior.

Zhang et al. [79] have mixed the nonionic surfactant Triton X-100 (TX100) with the cationic surfactant hexadecylpyridinium bromide (HDPB) to study their effects on bentonite structure. The findings showed that the surfactant intercalation led to decrease the bentonite specific surface area, pore volume, and surface roughness and irregularities. While the co-adsorption of both surfactants increased the ordering conformation of the adsorbed surfactants on bentonite, it decreased the thermal stability of the clay system. The effect of mixed surfactants on the rheological behavior of bentonite was not one of the objectives of this study.

The effects of anionic sodium tetradecyl sulfonate (NaTDS), cationic tetradecyltrimethylammonium bromide (TDTMABr), and nonionic Brij 30 surfactants on the electro-kinetic and rheological behaviors of sodium bentonite and sepiolite dispersions were studied by Tunc et al. [80]. It has been found that the surface charges of sodium bentonite and sepiolite were negative in water, which converted to positive after the addition of TDTMABr at a certain concentration. As the concentration of NaTDS is increased in the dispersion, the zeta potential value of sepiolite decreased gradually, but that of bentonite did not change significantly. All clay dispersions exhibited Bingham flow behavior in the presence of surfactants. Depending on the surfactant concentration, sepiolite–surfactant suspensions displayed rheopectic or thixotropic behavior, while sodium bentonite–surfactant dispersions showed a thixotropic behavior. On the contrary of sodium bentonite–surfactant system, the

surfactant concentration led to significant changes in the Bingham viscosity of sepiolite dispersions. An evidence about the interactions between clay particles and surfactant molecules had been observed in the FTIR spectra of dispersions. This study concluded that the clay dispersions having the desired rheological properties and zeta potential can be obtained by using different clay–surfactant mixtures.

Colloidal *aphrons* are multi-layered stable bubbles or droplets, surrounded by a thin surfactant film. The ability of two natural surfactants extracted from Henna and *Seidlitzia Rosmarinus* to produce aphronized fluid was investigated by Ahmadi et al. [81]. Both surfactants showed comparable performance in generation Colloidal gas aphron (CGA) fluids with conventional used surfactants in drilling fluids. Increasing surfactant or polymer concentration decreased the average aphron diameters. In addition, more aphron bubbles were generated by increasing the surfactant concentration. On the contrary, increasing the polymer concentration increased the fluid density (less aphron bubbles were generated). While the viscosity of CGA fluid was controlled by the concentration of both surfactant and polymer, the gel strength of CGA fluid depended mainly on the polymer concentration. Comparing to the base fluid, the aphronized fluids generated by both natural surfactants demonstrated their high ability to reduce filtration loss. Stability tests showed that CGA fluid prepared by henna extract has less stability than the fluid prepared by *Seidlitzia Rosmarinus* extract.

The sequential intercalation of three surfactants into calcium bentonite (Ca-Bent) was investigated by Monteiro et al. [82]. These surfactants were the cationic surfactant cetyltrimethylammonium bromide (CTAB), the anionic surfactant sodium dodecyl sulfate (SDS), and the nonionic surfactant lauryl alcohol ethoxylated (ALEO). Three calcium bentonite-surfactant aqueous solutions were prepared: OBent-I with CTAB, OBent-II with CTAB + SDS, and OBent-III with CTAB + SDS + ALEO. The findings of this investigation indicated that OBent-III has the highest values of basal spacing (13 nm), thermal stability (400 °C), superficial lipophilicity index (79.76°) and swelling index in polar or apolar medium (6–10 mL/g).

In a recent study, the effect of temperature (0 to 90 °C) on the drilling fluids phase inversion, and resulting changes in their rheology was investigated [83]. Nonionic (Brij 93: polyoxyethylene (2) oleyl ether, Brij O10: polyoxyethylene (10) oleyl ether, Span 80: sorbitan monooleate) and ionic (SDS and CTAB) surfactants were used to prepare water- (WBM) and oil-based muds (OBM). In addition, the effect of surfactant nature and dispersed phase volume fraction on fluid loss properties was studied. For the range of investigated conditions, phase inversion of WBM samples stabilized by nonionic polyoxyethylene oleyl ether surfactants was noticed. Differences in rheological behavior of the sample, as a result of inversion from one mud type to another, was equally observed. Generally, the findings of this study underlined the importance of evaluating potential application of nonionic surfactants to induce phase inversion in drilling fluids used for offshore operations.

It is expected that the drilling engineers will face more and more and more complex technical challenges with the rapid development of deepwater drilling operations, where hard conditions encountered. One of main challenges is that the drilling fluid used should exhibit the desired rheological properties at low temperatures with high

ability to inhibit hydrate formation. Synthetic biodegradable drilling fluids have been widely used in deepwater drilling operations as they possess acceptable rheological properties, have high penetration rate with good ability to prevent hydrate formation. Calcium phytate and an amide surfactant (CEMU) were used by Hu et al. [84] to prepare a synthetic drilling fluid. It was found that no gas hydrate were formed in the developed synthetic drilling fluid at 20 MPa and 0 °C. In addition, the developed fluid exhibited excellent rheological behavior at low temperatures. The apparent viscosity and the yield stress of the drilling fluid changed significantly with temperature when the content of CEMU was relatively high (~5%). When the CEMU content was 3%, the apparent viscosity and the yield stress of the drilling fluid did not change with temperature. Moreover, the results of this study revealed that increasing the CEMU concentration leads to decrease the average particle size of the dispersed droplets, which can strengthen the interaction between the interfacial area and dispersed droplets and between the dispersed and continuous phases. The authors claimed that this optimized synthetic drilling fluid could be used in deepwater drilling operations.

2.2 *Surfactants in Organic-Based Drilling Fluids*

Different types of surfactants were also utilized extensively in modifications of organic-based drilling fluids. A cationic surfactant was synthesized by alkylation of coal tar phenol with tetradecyl alcohol to be used as an additive for drilling fluids [85]. The produced alkyl phenol was then reacted with formaldehyde and amine to produce the Mannich base product, which was further reacted sodium chloroacetate to produce a cationic surfactant. The prepared surfactant, which was characterized by FTIR analysis, surface tension, emulsification power, and wetting power, displayed promising results when utilized as the primary emulsifier in the formulation of both oil-based drilling fluid and synthetic-based drilling fluid.

The purpose of the study of [86] was to modify a procedure for clay dispersing in the organic phase of a vegetable-oil-based drilling fluid. The drilling fluid formulation consists of bentonite (modified by cationic surfactant CTABr), barite, soybean oil, lauryl alcohol triethoxylate and brine. The bentonite was modified by three different concentrations of CTABr. The measurements of surface tension measurements and contact angles on soybean oil were used to evaluate the surface modification of the bentonite. Increasing amounts of CTABr cations were adsorbed on bentonite surface, led to decrease of the contact angle, suggesting an increasing affinity for soybean oil. The results of the study revealed that temperature is the most controlling factor in the rheological behavior of the developed drilling fluid. Moreover, the results showed that CTABr surfactant modifications enhance the interaction between bentonite and the organic phase of the fluid, which has increased the ability of the drilling fluid to maintain cuttings in suspension, therefore favoring separation.

Zhuang et al. [87] aimed in their work to select appropriate organo-montmorillonites (OMt) for the formulation of oil-based drilling fluids. They studied

also the effects of surfactants' nature on the structure and rheological behavior of oil-based drilling fluids prepared with OMT. The following cationic surfactants were used to modify the surface of OMT: lauryl trimethyl ammonium chloride (C12), octadecyl trimethyl ammonium chloride (C18-A), Benzenemethanaminium, N,N-dimethyl-Noctadecyl chloride (C18-B) and Dimethyl dioctadecyl ammonium chloride (DC18). From the XRD analysis, it was concluded that bigger surfactants produced higher basal spacing and more ordered internal arrangement. On the other hand, the SEM images indicated a trend that surfactants with bigger size and low Hydrophile-Lipophile Balance (HLB) value resulted in more OMT lamellae (thickness of ca. 50 nm) scattered. XRD analysis of OMT in oil-based drilling fluids testified a tendency that modifiers with bigger size and low HLB values led to easier exfoliation in oil. OMT modified with surfactants of small size and high HLB values obviously shrank while OMT modified with surfactants of bigger size and low HLB values kept exfoliation above 180 °C. The surfactants' size and polarity have clear effect on the rheological behavior of oil-based drilling fluids prepared with the modified OMT. Exfoliation of OMT in oil improved the viscosity and thixotropy of oil-based drilling fluids.

Recently, more attention was paid to the utilization of organo-palygorskite (OPal) in oil-based drilling fluids that is derived from palygorskite (Pal), which is a hydrated magnesium aluminum silicate clay mineral. It is expected that the high thermal stability and salt resistance of Pal may make OPal be suitable for offshore and deep drilling operations. The work of Zhuang et al. [88] aimed to reveal the effects of surfactants on the properties of oil-based drilling fluids containing OPal. Three quaternary ammonium salts surfactants with different lipophilicity were used to modify the surface of palygorskite. The same cationic surfactants were used in a previous study [87]. The disparity of OPal in oil increased with increasing the lipophilicity of surfactants. However, high disparity can't provide oil-based drilling fluid with high viscosity and gel strength. In addition, a little polarity can improve the rheological behavior of drilling fluids. Although high temperature facilitates the disaggregation of OPal in oil, it may result in thermal decomposition of surfactants on the surface of palygorskite.

Weng et al. [89] have prepared a group of cationic-anionic organo-sepiolite (CA-OSEP) to be used in oil-based drilling fluids. The following surfactants were used in this investigation: dodecyltrimethylammonium bromide (DTAB), n-octyltrimethylammonium bromide (OTAB), cetyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB), octadecyltrimethylammonium bromide (STAB), and sodium dodecyl sulfate (SDS). The effect of surfactant chain length, concentration of surfactants, and the ratio of cationic to anionic surfactants on OSEP were investigated. Cationic surfactant with long chains showed better adhesion to the sepiolite surface than those with short chains. Moreover, CA-OSEP showed higher thermal stability comparing with cationic organosepiolite (C-OSEP). The effects of OSEP addition on the rheological properties of oil-based drilling fluids were investigated at different temperatures. Results of this work revealed that organic surfactants had been adsorbed on the surface of sepiolite, and the CA-OSEP showed higher surface polarity and thermal stability in diesel oil than C-OSEP. This work

concluded that CA-Osep can be used as rheological control additive for oil-based drilling fluids with very promising thermal stability.

Bentonites modified with nonionic surfactants Ultramine 20 (TA20) and Ultramine 50 (TA50) were used to prepare organic-based drilling fluids [90]. An effective intercalation of the nonionic surfactants in organoclays was observed, and the content of incorporated surfactants was also quantified. Chemical compatibility between diesel and kerosene organic media and the organoclays produced was indicated from the swelling measurements. In terms of rheological properties, some of the tested organophilic clay samples showed a potential for use as additives in organic-based drilling fluids. The investigators claimed that the nonionic surfactants have advantages over ionic surfactants as they have higher ability in improving the thermal and chemical properties of organoclays.

To optimize the new wells performance, the drilling engineers need to choose between drilling with water-based drilling fluid and risk possible drilling instability or drill with oil-based drilling fluid to achieve stability in difficult trajectories and risk permeability impairment. To overcome this problem, reversible emulsion based drilling fluids were suggested in recent studies. By using acid–base chemical switch, reversible emulsion can be converted from water-in-oil (W/O) to oil-in-water (O/W) emulsion.. The reaction this acid–base chemical switch with drilling system was studied by Okoro et al. [91]. Silicon Ethoxide was used in this study as a reversible surfactant to formulate a reversible drilling fluid that will not react with the formation nor the drilling equipment. Different volumes of Silicon Ethoxide ranging from 5 to 45 ml were investigated, where the reversibility was achieved from 30 ml. Three different base oils, namely,EDC-99, Palm Kernel Oil and Polytriethanolamine were also investigated. With the reversed emulsion drilling fluid, reduction in permeability within the range of 16–19 mD was achieved, which facilitates its using close to the reservoir during drilling operation without facing significant permeability impairment.

The work of [92] investigated the effects of carboxymethyl cellulose and tragacanth gum on the filtration, rheological, and interfacial properties of oil-in-water emulsion-based drilling fluids. Tragacanth gum was used as a surfactant in the emulsification process of the drilling fluid. The rheological properties and filtrate loss characteristics of the emulsion based drilling fluid were controlled by adding carboxymethyl cellulose and tragacanth gum. Moreover, the presence and concentration of these polymers affected clearly the stability of emulsion systems. The drilling fluids exhibited a shear thinning behavior in the presence of oil and additives. In addition to its role as an emulsifier for the emulsion-based drilling fluids containing diesel oil, tragacanth gum acted as a perfect viscosifier and filtrate loss control agent. The study concluded that optimizing the concentrations of carboxymethyl cellulose and tragacanth gum in the emulsion system, main properties such as fluid rheology, filtrate loss, and pH can be improved.

Shettigar et al. [93] studied the impact of cationic surfactant cetyltrimethylammoniumbromide (CTMAB) on rheological, filtrate loss and biocide properties of a polymer-based drilling fluid. Inhibitive polymer drilling fluid was prepared using shale inhibitors (KCl, K_2SO_4 and $CaCO_3$) and XC polymer. Addition of CTMAB

enhanced fluid retention capacity of the drilling fluid even at very low concentration 0.1% (w/v) without altering the other properties. In addition, the cationic surfactant showed good compatibility with conventional fluid loss preventers such as pre-gelatinized starch when used in combination. The dissolved oxygen test results revealed that no need for any other biocide to prevent degradation of bio-polymer-based drilling fluid. Moreover, the thermal stability studies showed that the CTMAB is for applications in high salinity conditions and at high temperatures up to 120 °C without effecting the rheology behavior of the fluid.

In another utilization of CTAB, [94] formulated a reversible emulsion system induced by bentonite and the cationic CTAB. In this work, the contact angle and zeta potential measurements were used to evaluate surface wettability of bentonite particles in the process of phase transmission behavior, which was characterized by the electrical conductivity and microscopic analysis. The adsorption behavior and adsorption layer structure of CTAB at bentonite particles were studied at different surfactant concentrations. The results showed that changing the cationic surfactant concentration can reverse the wettability of bentonite particles, and then the two phase transition behavior of bentonite based emulsion can be induced. Additionally, the reversible emulsion oil-based drilling fluid system demonstrated good thermal stability and a small amount of fluid loss, and it reduced successfully the damage produced from the traditional oil-based drilling fluids on oil well completion.

Using of oil-based drilling fluid forms a thin layer of solids adsorbed on the well surface, called filter cake. To obtain acceptable well cementation this filter cake should be removed. Recently, microemulsion systems containing SDS, kerosene as oil phase, n-butanol as co-surfactant and distilled water were developed by da Silva et al. [95] to remove the filter cake from the well surface. The results revealed that the developed microemulsion systems composed of inverse and bicontinuous micelles removed 100% of the filter cake regardless of the content of the constituents in the formulation. It was also found that the co-surfactant/surfactant ratio is a controlling parameter for direct micelles to remove all of the of the filter cake. The compatibility of the developed reversible emulsion with cement, providing desirable thermal stability and enhancing the wettability of the rock in water.

2.3 General Remarks

From the overview presented in the previous section on the main and recent works in the modifications of the WBDF performance by different types of surfactants, we can draw the following remarks:

1. The above studies show that the drilling fluids having the desired rheological properties and stability that satisfies the API standard and OCMA specification can be achieved using different surfactant-clay systems.
2. The using of cationic surfactants in drilling fluid formulations is dominant over other surfactant types.

3. Mixtures of non-ionic and anionic surfactants can be presented as a new kind of potential rheological behavior control additive for drilling fluids, with very promising thermal stability.
4. Environmentally friendly surfactants with additive compatibility, ease of handling and cost for effective placement in water-based drilling fluids are in high demand. Most surfactants currently utilized in drilling systems are inorganic based and very few studies on the bio-based materials were carried out.
5. Surfactants can be also used in drilling fluid formulations to minimize water-blocking problems and to prevent hydrate formation in the deepwater drilling operation, where the temperature is low.
6. The chemical structures of the surfactants used in drilling fluid modifications are confirmed using FTIR and mass spectroscopy. The evaluation of these surfactants includes studying the surface activity of these compounds and their surface properties including surface tension, critical micelle concentration, emulsification power, effectiveness, minimum surface area and maximum surface excess.
7. The modified drilling fluids are evaluated by: XRD analysis to determine the interactions between the surfactants and the inter layers of the clay structure. Rheological properties, thixotropy, gel strength, filtration loss properties and temperature effect on rheological properties (apparent viscosity, plastic viscosity, yield stress, thixotropy and gel strength) of the water-based fluid are usually studied. Zeta-potential measurements are used to evaluate the stability of the drilling fluids in presence of the surfactants. In some cases, contact angle tests are used to characterize surface wettability of clay solid particles. Thermogravimetric Analysis (TGA) can also be used to evaluate the thermal stability of the developed mud.
8. Most of the studies focus on measuring the local rheological properties of drilling fluid like the single point apparent viscosity, plastic viscosity and yield stress. Little number of studies provide full rheological characterization of the drilling fluid, which gives better chance for understanding the fluid behavior and subsequent developments.
9. It is noted the absence of viscoelastic properties of the developed drilling fluid from the investigations, although these properties are very important in drilling fluids used in deepwater operations experience large variations in temperature and pressure.

3 Cationic Surfactant CTAB and Anionic Surfactant SDS in Water-Based Drilling Fluid

Although the effects of CTAB and SDS surfactants on the rheological and physical properties of clay dispersions were presented in many reports in the literature [56, 82, 83, 86, 89, 94, 96, 97], low solid concentrations were used in these investigations. Moreover, most of the conducted rheological studies did not include the

time-dependent behavior of clay suspensions, which is an a main property for many industrial applications including the drilling fluids. Therefore, this work aims at investigating the impacts of the anionic surfactant SDS and the cationic surfactant CTAB as additives on the rheological behavior including thixotropy of water-based drilling fluids.

3.1 Experimental

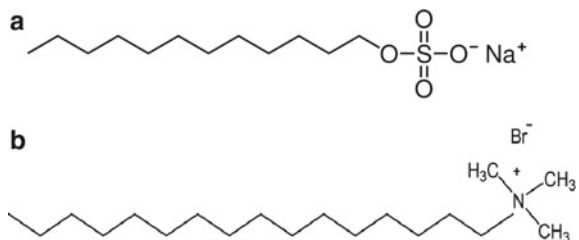
3.1.1 Materials

Sodium-bentonite used in this investigation was a laboratory grade clay, which was supplied by Sigma-Aldrich CHEMIE GmbH (Germany). The bentonite sample has the following chemical composition (wt.%): SiO₂ 63.020; Al₂O₃ 21.080; H₂O 5.64; Fe₂O₃ 3.250; MgO 2.670; Na₂O 2.425; CaO 0.650; FeO 0.350; and K₂O 0.245. The average particle size of bentonite was 5.34 μm, where all particles were less than 74 μm. Cetyltrimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) surfactants were supplied by Sigma-Aldrich CHEMIE GmbH (Germany). The chemical structure of SDS and CTAB are shown in Fig. 7.

3.1.2 Drilling Fluid Preparation

Two water-based drilling fluids with bentonite concentration of 4.0 and 8.0 wt% were prepared in this work. To avoid the formation of aggregates and ensure homogeneous suspension, surfactant free drilling fluids were prepared by adding bentonite particles gradually to deionized water under continuous mixing conditions. For drilling fluid-surfactant suspensions, the following surfactant solutions were prepared in advanced: 1.0×10^{-3} , 2.0×10^{-3} , 5.0×10^{-3} , 1.0×10^{-2} , 2.0×10^{-2} , 5.0×10^{-2} and 1.0×10^{-1} M. Then, the clay particles were added gradually to the surfactant solution under mild continuous mixing conditions. After receiving a homogenous suspension, the sample was kept in a closed container for 24 h at room temperature before conducting the rheological tests. Before start recording the rheological properties, the sample was stirred in the rheometer at shear rate of 5 s^{-1} for 1 min, followed by a rest time for two minutes to remove the stress history from the sample.

Fig. 7 Chemical structure of **a** SDS, **b** CTAB



3.1.3 Measurements of Rheological Properties

Rheolab QC viscometer (Anton Paar, Germany) equipped with coaxial cylinder measuring system was used to measure the rheological properties of the prepared drilling fluids. The Coaxial cylinder measuring system has the follow dimensions: the radius of the measuring cup = 14.460 mm; and the radius of the measuring bob = , 13.329 mm. The gab width available with this geometry a was 1.132 mm. The flow curves (shear stress (τ) versus shear rate ($\dot{\gamma}$)) of drilling fluid samples were measured at a constant temperature of 25 °C \pm 0.1 in the shear rate range of 500–1500 s⁻¹. Many industrial applications are covered in the tested shear rate range. Among of these applications is the drilling fluid which is usually tested at shear rate of 511 and 1022 s⁻¹ [98]. All flow curves were measured by increasing (forward measurements) and decreasing (backward measurements) shear rates. The hysteresis area formed between the forward and backward flow curves was determined as a measure of thixotropy using data analysis option of RHEOPLUS/32 V3.31 software. All flow curves measurements were performed in duplicate and the average values were reported. The measured shear stresses exhibited less than 3% difference. Eliminating of slip conditions in the used concentric cylinder measuring system was conducted by following the prehearing approach prior to measurements and using of coated measuring system. However, the absence of slip conditions from the used system was further confirmed from comparative measurements on the same suspension using different measuring system, which showed no significant difference between the reported stresses.

3.1.4 Measurement of Zeta Potential

Zeta/nano particle analyzer (NanoPlus, Otsuka Electronics CO LTD, Japan) was used to measure the zeta potential values of the prepared drilling fluids. The zeta potential values were used to evaluate the effect of surfactant type and concentration on the stability of the drilling fluid. In these measurements, the bentonite concentration was kept at 4.0 wt%. The zeta potential of fluid samples was measured at 24 h after preparation.

3.2 Investigation of Surfactant-WBDF Properties

3.2.1 Rheology of Surfactant Free Drilling Fluids

The rheological properties of surfactant free drilling fluid (SFDF) were discussed in details for bentonite concentration of 0.5–10.0 wt% in former studies [10, 11]. Figure 8a shows the flow curves of the SFDF with 4.0 and 8.0 wt% bentonite concentration. SFDFs tested in this work exhibited non-Newtonian rheological behavior at both concentrations. The flow curves of the prepared SFDFs were fitted well with

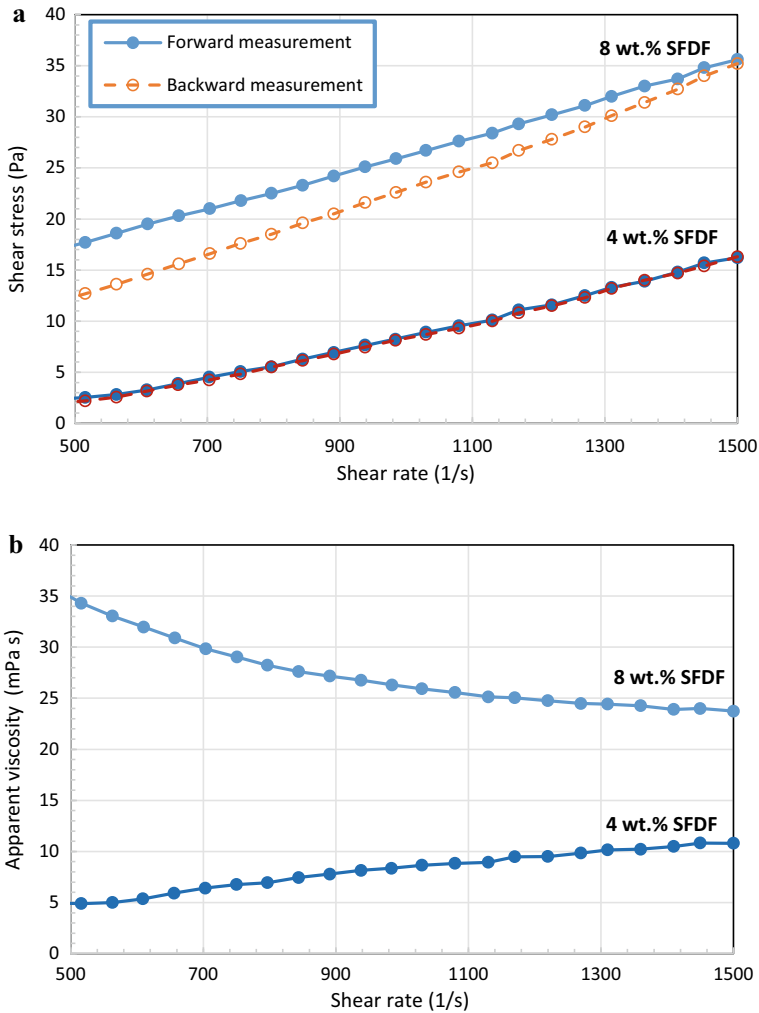


Fig. 8 a Flow curves of SsFDF at different solid concentration, **b** Apparent viscosity of SFDF

the Herschel-Bulkley model:

$$\tau = \tau_0 + m\dot{\gamma}^n \tag{1}$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate, τ_0 is the yield stress, m is the consistency coefficient and n is the flow behavior index. As can be seen in Table 2, where the regressed parameters of Herschel-Bulkley model are reported, that the 8 wt% SFDF demonstrated pseudo-plastic behavior (shear thinning) with a noticeable yield stress. On the other side, the 4 wt% drilling fluid behaved like a shear thickening material

Table 2 Herschel-Bulkley parameters of WBDF for different surfactant concentration

| Bentonite Conc. (wt%) | Surfactant Conc (wt%) | SDS | | | CTAB | | |
|-----------------------|-----------------------|---------------|--|------|---------------|--|------|
| | | τ_0 (Pa) | $m \times 10^5$ (Pa · s ⁿ) | n | τ_0 (Pa) | $m \times 10^5$ (Pa · s ⁿ) | n |
| 4.0 | 0.0 | 0.0 | 10.0 | 1.65 | 0.0 | 10.0 | 1.65 |
| | 1.0×10^{-3} | 0.0 | 12.5 | 1.60 | 0.0 | 5.7 | 1.71 |
| | 2.0×10^{-3} | 0.0 | 13.1 | 1.58 | 0.0 | 2.3 | 1.82 |
| | 5.0×10^{-3} | 0.0 | 6.6 | 1.66 | 0.0 | 1.6 | 1.85 |
| | 1.0×10^{-2} | 0.0 | 9.0 | 1.63 | 0.0 | 1.9 | 1.84 |
| | 2.0×10^{-2} | 0.0 | 8.3 | 1.64 | 0.0 | 2.1 | 1.78 |
| | 5.0×10^{-2} | 0.0 | 7.7 | 1.65 | 0.0 | 1.3 | 1.85 |
| | 1.0×10^{-1} | 0.0 | 6.3 | 1.67 | 0.0 | 1.2 | 1.84 |
| 8.0 | 0.0 | 8.65 | 2618.9 | 0.95 | 8.65 | 2618.9 | 0.95 |
| | 1.0×10^{-3} | 6.90 | 2333.6 | 0.98 | 0.91 | 1508.0 | 1.0 |
| | 2.0×10^{-3} | 6.40 | 1875.0 | 1.0 | 0.0 | 1400.0 | 1.0 |
| | 5.0×10^{-3} | 2.74 | 1690.3 | 1.0 | 0.0 | 1380.0 | 1.0 |
| | 1.0×10^{-2} | 4.37 | 2070.0 | 1.0 | 0.0 | 1220.0 | 1.0 |
| | 2.0×10^{-2} | 11.5 | 2149.0 | 1.0 | 0.0 | 1190.0 | 1.0 |
| | 5.0×10^{-2} | 7.31 | 1994.0 | 1.0 | 0.0 | 1010.0 | 1.0 |
| | 1.0×10^{-1} | 6.67 | 1660.0 | 1.0 | 0.0 | 975.3 | 1.0 |

in the tested shear rate range without remarkable yield stress. These behaviors can also be seen in Fig. 8b, where the apparent viscosity of 8 wt% SFDF decreased with shear rate (shear thinning behavior), while the apparent viscosity of 4 wt% SFDF increased slightly with shear rate presenting a shear thickening behavior.

It is obvious that increasing the bentonite solid concentration will lead to increase all rheological parameters like the yield stress τ_0 , the apparent viscosity and the consistency coefficient (m). It is expected that in dispersions with high solid concentration (like 8.0 wt% SFDF), a continuous networked structure will be formed as a result of solid particles flocculation instead of individual flocs that usually observed in dispersions with lower solid concentrations. In dispersions with high solid concentration, the particles orient themselves towards positions of minimum free energy under the effect of Brownian motion to build up slowly the network structure [31].

To test the thixotropic behavior of the SFDF, the flow curves were measured by increasing shear rate values in the forward measurement followed by decreasing the shear rate values in the backward measurement), see Fig. 8a. The form of hysteresis loops between the flow curves of the forward and backward measurements, indicates that the SFDF exhibited a thixotropic behavior. It should be recalled that if the apparent viscosity of a material decreases and immediately recovers after shearing, the material has a shear thinning not a thixotropic behavior. As can be seen in Fig. 8a, the thixotropic behavior of the 8.0 wt% SFDF is very clear, while that for 4.0 wt% SFDF is not detectable. In addition, the calculated area of hysteresis loops for both

fluids shows that the extent of thixotropy of 8.0 wt% sample (3189 Pa/s) is orders of magnitude higher than that of 4.0 wt% sample (577 Pa/s). The thixotropic behavior has been reported for many clay dispersions [99], Besq et al. [51, 100, 101], which was solid concentration dependent. Dispersions with higher solid concentration showed pronounced thixotropic behavior [11]. This behavior can be attributed to the fact that the pieces of the network structure which are broken under shearing effect, need time to be rebuilt again the network structure [31]. The thixotropic behavior of a material means that the rate of bonds breakdown in the network structure of this material is higher than the rate of restructuring process.

3.2.2 Rheology of Surfactant-WBDF

The effect of different SDS concentrations on the flow curves of WBDF is shown in Fig. 9. Addition of SDS surfactant to 4.0 wt% bentonite dispersion led initially to decrease the viscosity/shear stress values to reach a minimum at 0.005 M of SDS, then these values moved up to show a maximum at 0.01 M SDS concentration and decreased again at higher SDS concentration, see Fig. 9a. The same trend was detected in 8.0 wt% bentonite dispersion with one difference that the maximum shear stress, which was higher than the pure bentonite shear stress, shifted to 0.02 M SDS concentration, see Fig. 9b. The effects of SDS concentration on the apparent viscosity of WBDF at shear rates of 511 s^{-1} are shown in Fig. 10. This value of shear rate is usually used to evaluate the apparent viscosity of water-based drilling fluids [98]. The apparent viscosity of drilling fluid showed a minimum at 0.005 M SDS concentration and a maximum at 0.01 and 0.02 for 4.0 wt% and 8.0 wt% bentonite concentration, respectively. The apparent viscosity of 8.0 wt% WBDF in the presence of 0.02 M SDS is 43 mPa s, which is greater than that of SFDF (35.8 mPa s).

It was reported in the literature that the surfactant concentration has pronounced effect on the behavior surfactant based formulations [102]. As the concentration of a surfactant in aqueous phase increased, the individual surfactant molecules began to aggregate, with their hydrophilic heads being housed by the aqueous phase and their hydrophobic tails extending out of the aqueous phase to minimize the system free energy. These aggregates are called micelles and occur at the critical micelle concentration (CMC). Micelles have, in general, spherical shape with a diameter about 4–10 nm [103]. These micelles can act as barrier between bentonite-bentonite solid particles and can also reduce the bridging mechanism between the surfactant and bentonite. Increasing the surfactant concentration above the CMC, other strong and elastic micelle forms (cylindrical, hexagonal-packed, and lamellar structures) may produce, which would improve the bridging mechanism between the solid particles and the surfactant leading to increase the system viscosity.

It can be seen that the SDS concentration range tested here 0.001–0.1 M covers both the CMC of SDS in water which is around 0.0095 M according to [104], and the critical coagulation concentration of SDS, CCC, which is the minimum surfactant concentration needed to origin coagulation of a colloidal dispersion like bentonite dispersion [97]. Three kinds of interactions between anionic surfactant SDS and

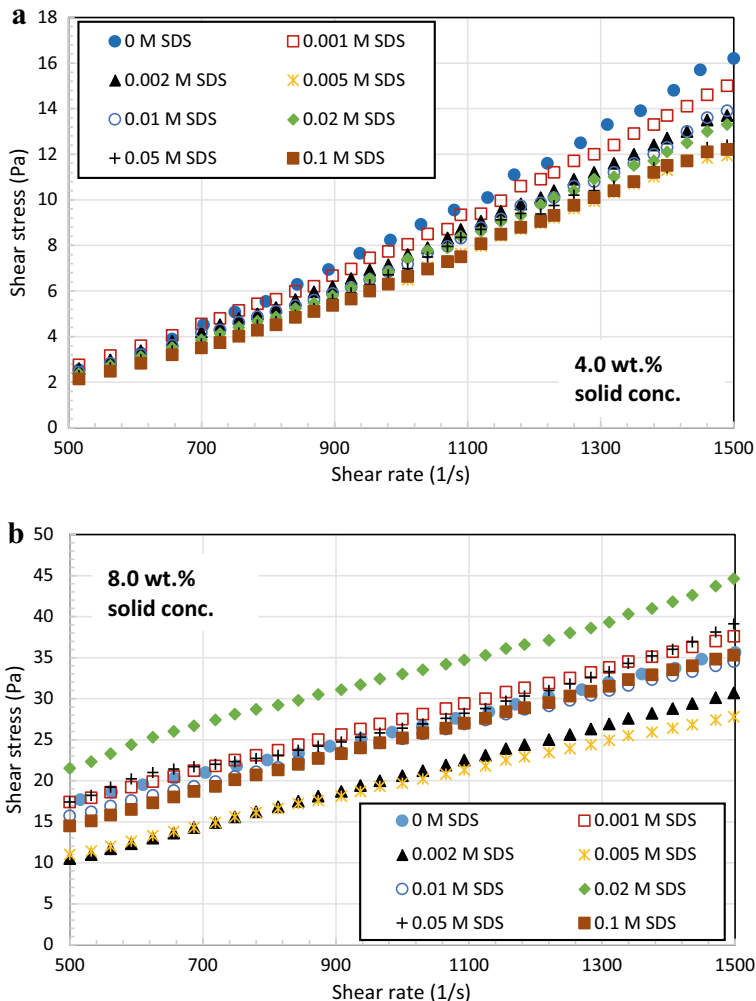


Fig. 9 Flow curves of SDS-drilling fluid for **a** 4.0 wt% bentonite concentration, **b** 8.0 wt% bentonite concentration

negative charged bentonite particles can take place [97]. The first kind is that ion exchange can take place between the anionic part of surfactant $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-$ and the OH^- ions on the surface of bentonite particles. The second type of interactions is the formation of hydrogen bonding between bentonite particles and SDS molecules. In addition, it is possible that Na^+ cation on the bentonite surface can establish electrostatic bridges between the surface of bentonite and the anionic part of SDS. All these three kinds for the interactions between the surfactant SDS and bentonite particles can occur in the current system. It is clear from the rheological

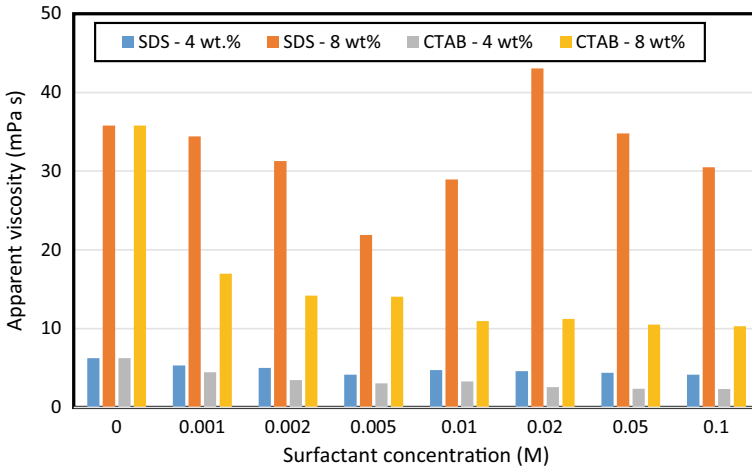


Fig. 10 Apparent viscosity of SDS-drilling fluids at 511 s^{-1}

results that the SDS surfactant is adsorbed by bentonite particles in the concentration range of 0.01 and 0.02 M producing aggregates as a result of the interactions between the hydrophobic tails of the anionic surfactant and the positive edge of the bentonite particles, which resulted in the formation of a structure with higher resistance against shearing process. Increasing the SDS concentration from 0.05 M to 0.1 M, decreased the drilling fluid viscosity. The adsorption of SDS surfactant on the bentonite surface will be increased by increasing the surfactant concentration. However, this strong adsorption can cause surface saturation, preventing later the effective bridging between the bentonite particles and causing reduction in the dispersion viscosity. Tunc et al. [80] have observed similar behavior.

Adding the cationic surfactant CTAB to the bentonite dispersions resulted in a clear decrease in the shear stress values of the WBDF, see Fig. 11. The effect of CTAB concentration on the apparent viscosity of WBDF at 511 s^{-1} is presented in Fig. 10. The apparent viscosity of CTAB-drilling fluid system decreased clearly with surfactant concentration until the addition of 0.02 M of CTAB. Beyond this concentration, the effect of cationic surfactant CTAB on the apparent viscosity of bentonite dispersions was insignificant. Adding of surfactant CTAB reduced the degree of flocculation in the bentonite dispersion which was resulted in viscosity decrease.

It has been shown that the replacing of exchange ions on the surface of clay by a cationic surfactant will change the clay surface properties from hydrophilic to hydrophobic [28]. This should result in an increase in the viscosity of clay dispersion due mainly to the electrostatic interactions that will produce from binding of positively charged surfactant molecules onto the negatively charged clay particles. In addition, the hydrophobic tails of CTAB molecules adsorbed onto the clay particles surface interact with each other by hydrophobic interaction mechanism to produce large flocs [58, 80]. In the current study, it is expected that the previous discussed

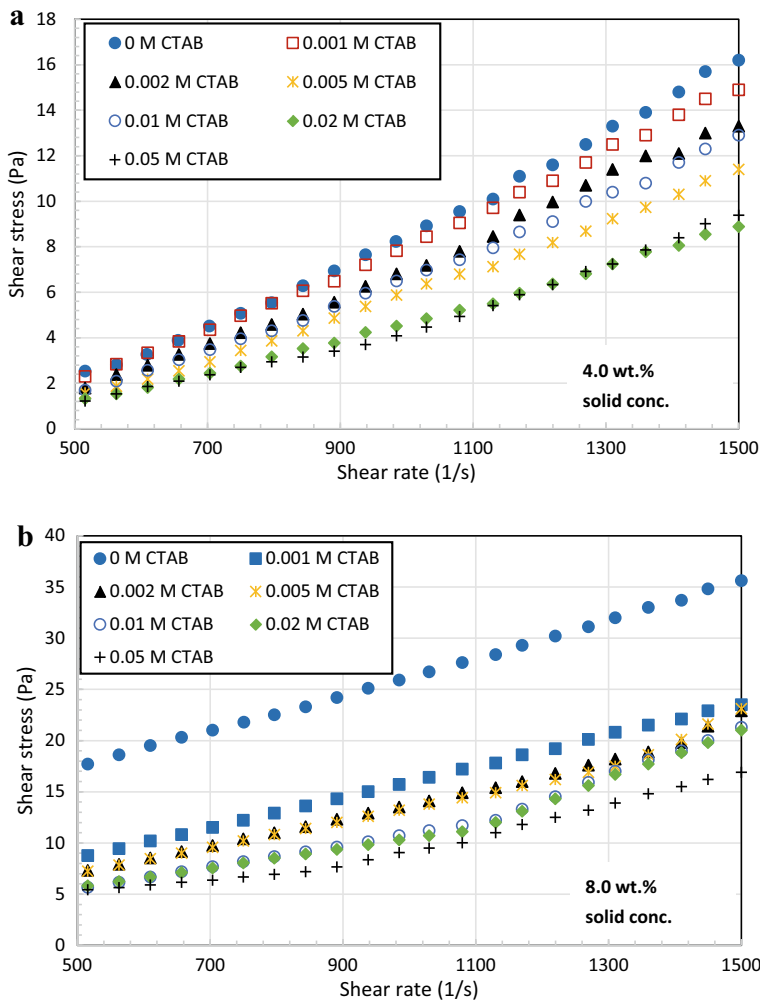


Fig. 11 Flow curves of CTAB-drilling fluid for **a** 4.0 wt% bentonite concentration, **b** 8.0 wt% bentonite concentration

mechanisms were not dominant in the tested CTAB concentration (0.001 – 0.10 M). The same tend of viscosity reduction upon addition of cationic surfactant to clay dispersion was also observed by Isci et al. [58] when they tested the effect dodecyltrimethylammonium bromide (DTABr) on the rheological behavior of sodium bentonite. This decrease in viscosity was attributed to the formations of second layers onto the bentonite particles with positive excess charges that produced dense aggregates and settled to sediment. In our study, the initial increase in the viscosity of bentonite-CTAB system was not detected as it occurs usually at very low surfactant concentration, which was out of the concentration range investigated here.

It was reported by Tunc et al. [80] that the rheological properties of bentonite dispersions have not been affected by the addition of cationic surfactant tetradecyltrimethylammonium bromide. However, adding low concentration of the same surfactant (0.0001 M) to sepiolite increased slightly the dispersion viscosity. Further addition of surfactant led to pronounced reduction in sepiolite viscosity. On the other hand, [89] found that the addition of CTAB to sepiolite had no effect on clay structure. When the concentration of CTAB reached to 20 wt% of sepiolite, the CTAB-Sepiolite system had the biggest surface contact angle, lowest surface energy and highest decomposition temperature. In addition, the 20 wt% CTAB-Sepiolite-diesel oil system exhibited optimum rheological properties, with an apparent viscosity of 50 mPa s, a plastic viscosity of 45 mPa s, and a yield stress of 5 Pa.

The flow curves of CTAB- and SDS-WBDF dispersions were fitted well with Herschel-Bulkley model (Eq. 1), and the regressed parameters are reported in Table 2. For 4.0 wt% bentonite, the shear thickening behavior is still dominated in the presence of both surfactants. While the addition of SDS did not change significantly the flow behavior index, n . On the other hand, the CTAB surfactant has increased the n values, which means that the addition of CTAB to the bentonite suspension has improved the shear thickening properties.

More pronounced effect of surfactants was observed with the 8.0 wt% bentonite suspension. Initial addition of SDS surfactant led to diminish the yield stress of 8.0 wt% bentonite dispersion, which then increased suddenly at SDS concentration of 0.02 M demonstrating a maximum value of 11.5 Pa. This behavior goes along with the trend of the apparent viscosity. Moreover, the rheological of 8.0 wt% bentonite dispersion changed gradually from shear thinning behavior ($n < 1$) with a yield stress to Bingham behavior ($n = 1$) upon the addition of SDS surfactant. On the other hand, the addition of CTAB surfactant to 8.0 wt% bentonite suspensions resulted in removing completely the yield point and changing the rheological behavior from shear thinning to Newtonian ($n = 1$). This behavior along with the apparent viscosity results suggested that the interactions between the bentonite particles in the presence of CTAB surfactant were reduced to the minimum.

The evaluation and analysis of the time-dependent rheological behavior of surfactant-WBDF is another aspect of interest in this discussion. The thixotropic behavior, which is defined as an increase in the system viscosity with time of shearing at constant shear rate, was more noticeable in SDS-WBDF than that in CTAB-WBDF, as most of the CTAB-WBDF samples showed Newtonian behavior. The areas of hysteresis loops presented in Fig. 12 for both bentonite samples are in accord with the trend of the steady rheological properties (apparent viscosity vs. shear rate). In general, the thixotropic behavior of 4.0 wt% surfactant-WBDF was unnoticeable and the addition of either anionic or cationic surfactant did not affect the time-dependent behavior of bentonite dispersions.

On the other hand, the 8.0 wt% drilling fluid demonstrated clear thixotropic behavior in the presence of the SDS surfactant. The formation presence of flow curves hysteresis loops is an indication of the effects of shearing process on the surfactant-bentonite molecular structure. This means that the rate of structure damaging due to the shearing process is greater than the rate of rebuilding. Figure 12 shows that the

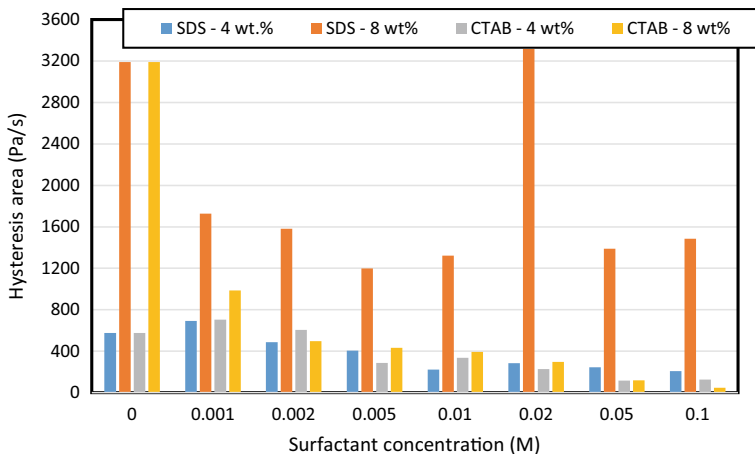


Fig. 12 Hysteresis Area of surfactant-drilling fluids

maximum degree of thixotropy occurred at 0.02 M SDS concentration, which is very close to the thixotropy extent of SFDF, see Fig. 13. The area of hysteresis loops For 8.0 wt% CTAB-bentonite dispersions decreased gradually with CTAB concentration to reach negligible value at high surfactant concentration. It should be mentioned that most of the calculated area of hysteresis loops for CTAB-bentonite dispersions are within the error range of the experimental results and can be neglected.

It is clear from the above results that using SDS surfactant will be very useful in WBDF where it needs to increase the yield stress of the drilling fluid and keep

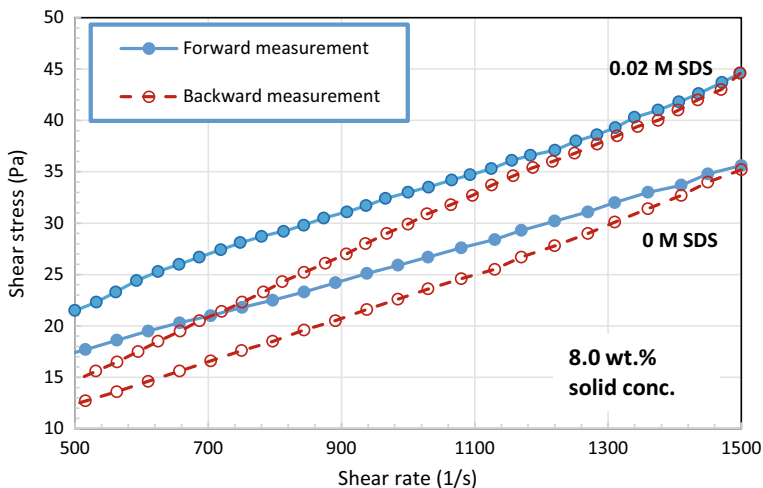


Fig. 13 Hysteresis loops of SFDF and drilling fluid containing 0.02 M SDS

good thixotropic behavior. On the other hand, adding cationic surfactant like CTAB into bentonite-based dispersion will be advantageous in other applications such as in slurry transportation, where minimum resistance to flow is required to facilitate the mixing and filtering processes.

3.2.3 Zeta Potential

The zeta potential is used as an indicator of the stability of clay suspensions system. The zeta potential value reflects the degree of electrostatic repulsion between similarly charged, adjacent particles in suspension. Figure 14 shows the measured zeta potential of surfactant-drilling fluid dispersions as a function of surfactant concentration. Increasing the SDS concentration led to increase the absolute value of zeta potential. The WBDF becomes more stable by adding 0.02 M of SDS surfactant as the zeta potential values increased from -7.4 to -36.4 mV. This increase in zeta potential value was accompanied with general decrease in the bentonite dispersion viscosity. Moreover, switching of the rheological behavior of drilling fluid from shear thinning with a yield stress to Bingham behavior upon the addition of SDS surfactants indicates that the dispersion system became less flocculated.

On the other hand, the zeta potential values of CTAB-bentonite dispersion decreased with CTAB concentration, indicating that the system became less stable and more flocculated. Formation of flocculated particles led to increase the sedimentation of solid particles, which can explain the observed rheological behavior of bentonite dispersions in the presence of CTAB surfactant, as it changed from non-Newtonian to Newtonian. CTAB surfactant forms second layers onto the bentonite particles with positive excess charges that lead to decrease the dispersion viscosity [58].

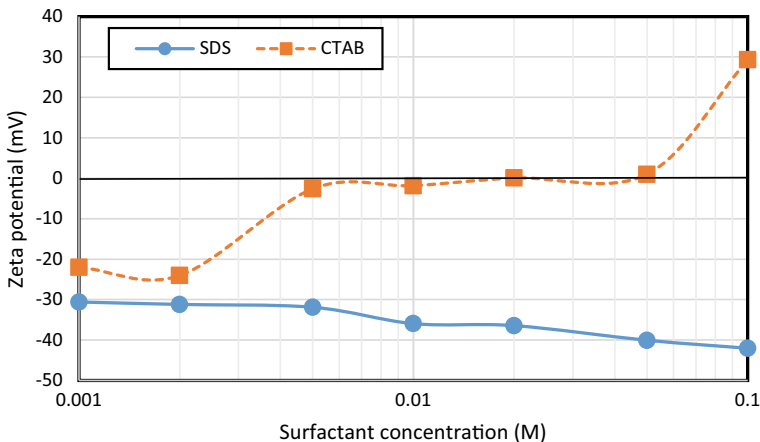


Fig. 14 Hysteresis loops of SFDF and drilling fluid containing 0.02 M SDS

It is well known that if a dispersion has a large positive or negative zeta potential, the particles within it tend to successfully repel each other and there will be no tendency for the particles to come together. On the other hand, smaller negative or positive zeta potential values increase the likelihood of flocculation. The dividing line between stable and unstable suspensions is generally taken as ± 30 mV. In the current study, the zeta potential of SDS-bentonite system was in the range of -30 to -42 mV providing stable dispersions. In the case of CTAB, the zeta potential was very close to zero for most of surfactant concentrations indication aggregates formation in the dispersion.

3.3 Conclusions

Addition of the anionic SDS surfactant in the concentration range of 0.01–0.02 M to the water-based drilling fluid which contains sodium bentonite particles led to increase the dispersion viscosity and improve its degree of thixotropy. This range of surfactant concentration corresponds to the CMC and CCC values of SDS surfactant, respectively. Moreover, the presence of SDS surfactant in WBDF system switched its modified the rheological behavior from shear thinning to Bingham plastic. The zeta potential measurements indicated that SDS-drilling fluid is stable in the SDS concentration range of 0.01 – 0.10 M. On the other hand, adding the cationic surfactant CTAB with concentration range of 0.001 – 0.1 M to the WBDF decreased its viscosity and diminished its yield stress and thixotropic behavior. The CTAB-WBDF dispersions demonstrated a Newtonian rheological behavior in the most of the tested surfactant concentration. The addition of cationic surfactant CTAB to the bentonite particles formed dense aggregates in the dispersion with higher tendency for sedimentation, which led to reduce the dispersion viscosity and reflected on the low value of zeta potential.

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