1. DRILLING WASTE PROBLEM

When drilling for oil and gas, more than 75% of the drilled sections contain shales which are the major source of wellbore instability problems\(^1,2\). Borehole instability and related drilling problems while drilling shales is a continuing hurdle in drilling operations. Such problems result in substantial annual expenditure (estimated to cost more than US $ 1.3 billion per year) for the petroleum industry\(^1\). Such technical challenges have led to the requirement of non-aqueous-based drilling fluids (NABDFs). However, the unacceptable environmental impacts of drilling waste (oily drillcuttings and drilling fluid itself) generated from non-aqueous based liquids NABFs (Diesel-based liquids “DBLs” and Synthetic-based liquids “SBLs”) use and discharge were recognized.

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POTENTIAL OF SURFACTANT WASHING TO SOLVE DRILLING WASTE ENVIRONMENTAL PROBLEMS OFFSHORE

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Increasingly, stringent regulations and much legislation have been enforced in response to these environmental concerns and led particularly to continually tightening the discharge limits of allowable oil on cuttings. Regulatory bodies nearly all around Europe specifies that oily cuttings generated offshore have to be cleaned to a limit of 1% residual oil on cuttings (10g oil per Kg dry cuttings) following the pioneering ban imposed offshore North Sea countries by 1997 for DBLs and 2001 for SBLs\(^4\)-\(^7\).

For offshore drilling in the Gulf of Mexico, the EPA’s Effluent Limitation Guidelines (2000) defines the amount of oil in drillcuttings as the Retention on Cuttings (ROC), defined by mass of oil/Mass of cuttings and reported as percentage. For offshore drilling, the ROC of DBFs cuttings is set to 0%. For SBFs the discharge regulations require either containment of contaminated cuttings or drying below 6.9% ROC for base fluids that meet the environmental performance criteria for Internal Olefins 1618, and 9.4% ROC for base fluids that meet the environmental performance criteria of esters. For land-based drilling, the ROC values for DBLs and SBLs are similar\(^8\),\(^9\),\(^10\),\(^11\),\(^13\).

Although, most African, Middle East, and South East Asia petroleum countries do not have such strict regulations\(^5\), it is widely believed that it is only a matter of time until the North Sea and/or Gulf of Mexico regulations be adopted and applied in these countries.

Drilled cuttings from the solids control separation process typically retain (10-25%) oil by weight\(^10\)-\(^12\). Many methods and systems have been developed and millions of dollars have been spent to find the best way to reduce the amount of ROC offshore. Systems involve mechanical separation of oil from cuttings (e.g., drying shakers, drying centrifuges), however, even after treatment, cuttings retain (5-10%) oil by weight\(^9\),\(^11\),\(^13\). Such equipments are extensively used for SBLs drilling operations offshore Gulf of Mexico.

Current waste treatment technology is unable to clean oil out of cuttings to 1% retention, this leads to a discharge prohibition offshore. Contaminated cuttings may therefore, be taken onshore for treatment and disposal. However, bringing this problem ashore is thought to be environmentally and economically imprudent\(^14\). Apart from Cuttings re-injection (CRI), all the treatment methods require land-based waste treatment.

Shipping drilling waste to shore for treatment is a costly and a risky operation. The most important components of onshore disposal are the marine transport and the onshore treatment and/or disposal method selected. It involves a substantial amount of equipment, effort and cost. It also widely depends on the availability of facilities and local regulations. In ultra deepwater drilling operations and heavy sea conditions logistics are difficult, boat trips are long, mud volumes are high, and deck loads are limited\(^8\),\(^9\),\(^10\),\(^16\). Furthermore, given the regional differences in current waste management practices, the cost of complying with local environmental regulations varies widely. Land treatment methods (such as bioremediation, incineration and phytoremediation) which destroy the contaminants are time consuming and not cost effective when handling large volumes of the contaminated materials\(^17\),\(^18\).

Taking into account the scarce or absence of inland treatment facilities and various inland disposal options in vast majority of less developed countries in one hand and the rising cost of handling drilling waste in more developed countries in the other hand, it seems more likely that the industry will face excessive pressure as to implement cost effective and novel technologies and approaches to meet ever tightening regulations. Therefore, for offshore cuttings treatment especially when CRI is not available, there is an urgent need for offshore cuttings treatment.

Cuttings discharge appears to be viable option in many environmental settings and work should focus in developing and implementing new technologies for cuttings treatment to reduce fluid content on cuttings prior to discharge. Several innovative methods are currently under investigation so as to clean oily-cuttings effectively to meet 1% ROC limit. For example use of supercritical carbon dioxide\(^19\),\(^20\),\(^21\) use of Chemical washing including surfactants\(^9\),\(^10\),\(^13\) and thermal desorption by hammer mills\(^22\). However, Supercritical extraction requires expensive high-pressure equipment and is not as familiar a technology as surfactant washing\(^13\). Similarly, thermal desorption does have limitations in terms of health, safety and environment (HSE) issues as well as footprint which make them unsuitable for offshore rigs\(^9\).

2. INTRODUCTION TO SURFACTANTS

Surfactants are amphiphilic molecules having a hydrophilic or water soluble moiety (head group) and a hydrophobic, or water insoluble moiety (tail group). At low concentrations, surfactants exist solely as monomers. The formation of micelles, begins at a specific surfactant concentration termed the critical micelle concentration (CMC), where the physical properties of the solution, such as interfacial tension, electrical conductivity, and light scattering behaviour, often changes abruptly due to the existence of micelles\(^23\).

The CMC concentration corresponds also to the point where the surfactant first shows the lowest surface/interfacial tension\(^23\). Interfacial tension is the tensile force that exists at the interface of two immiscible liquids. This force arises as a result of mutual dislike of molecules, such as oil and water, on two sides of the interface. If the two liquids are fully miscible with each other, there is no interfacial tension between them. The amphiphilic nature of surfactants, which results from their water-like and oil-like components, causes them to accumulate at interfaces and thus reduce the interfacial tension between oil and water.

Beyond the CMC, the aqueous monomer concentration will not increase with any further addition of surfactant since the additional surfactant will form micelles. Spherical micelles orient with
surfactant hydrophobic tails pointed toward the interior and hydrophilic head point outward to the surface of micelles. This creates the hydrophobic interior of the micelle within which hydrophobic organic molecules can partition, thus increasing the aqueous solubility of the none-aqueous liquids (NALs) in the solution. This is referred to as micellar solubilization[22]. Therefore, below the CMC, micelles do not form and the surfactant solution does not enhance the solubilization for NAPL.

Surfactants are classified as ionic and non-ionic with varying chemical structures according to their hydrophilic group. For industrial applications, the ionic surfactants are classified based on the charge they carry when dissociated in water at their neutral pH. These classifications are namely anionic, cationic and zwitterionic or amphoteric[22,23]. Surfactants are also classified according to the balance between the hydrophilic and hydrophobic, or lipophilic, portions of the surfactant molecule. A lipophilic substance is one with a high affinity for fatty or organic solvents and it is essentially a hydrophobic substance[25]. Surfactants with a high hydrophile-lipophile balance (HLB) number are more soluble in water, and a low HLB indicates the surfactant is more soluble in an organic solvent[20].

2.1 Surfactant Enhanced Drillcuttings-Washing

Generally, there is very little research on surfactant-enhanced treatment of oily drillcuttings. Gerard and Antle[9] found out that increasing chemical concentration did not essentially improve reduction of ROC and indeed if too much chemical was added, the ROC increases. This is in contrast with findings of most studies in soil washing as there is always a direct relationship with surfactant concentration[26-40].

Gerard and Antle[9] emphasize that a minimum contact time between the cuttings and the chemical treatment is required to achieve the best reduction in ROC. Further increase in contact time, however, may not decrease the ROC significantly. Similarly, Reddy et al.[13] used aqueous solutions containing a cationic biopolymer in combination with an activator to greatly reduce the oil content of oil-coated drillcuttings. Furthermore, the oil content of the cuttings (ROC) was reduced to 1% or below by the weight of cuttings by using a combination of biopolymer/activator in combination with surfactant mixtures. However, no information was given by both studies about the mechanism of oil removal whether is it rollup or solubilization nor any information was given regarding the type of surfactants and concentrations used. While most studies in soil washing were highlighting subjects such as surfactant sorption to soil, CMCs and interfacial tensions of surfactant with contaminant in absence and presence of soil, the previous studies did not take such subjects into account.

Laboratory studies by Childs and co-workers[10] showed the branched C14-C15 alcohol propoxylate sulfate (Alfoterra 145-4PO) to be a promising anionic surfactant for liberating oils from drillcuttings. To produce a robust system, calcium sequestrant (Octyl-Sulfobetaine) and a builder (Na2SiO3) was added to the surfactant. Surfactant losses were minimized and oil removal was maximized by using three components.

Childs and co-workers indicated that by washing contaminated cuttings with this three-component formulation, the oil removal was relatively independent of operating conditions such as contact time and agitation energy. This has the added benefit of reducing the fines production during washing operations. Furthermore, oil was liberated from the cuttings as a free phase layer which promotes oil separation and reuse. Oil content of oil-based cuttings was in the range of 2% to 5% (still less than 1% limit). In addition, greater than 85% of the initial surfactant concentration remained in the bath after washing, which minimizes the need for make-up surfactant. Childs and co-workers shed the light on the importance of rollup and snapoff mechanism of oil detachment from cuttings. The rollup and snapoff oil removal mechanisms are desirable because the oil is liberated from the cuttings as a free top layer which can be skimmed from the cleaning tank, hence avoiding the need for surfactant separation from the liberated oil phase. Nevertheless, the authors determined that these mechanisms can be achieved with low surfactant concentrations. Low surfactant concentrations are preferred from the environmental point of view and to ensure the economical viability of the process.

2.2 Surfactant Enhanced Soil Washing

Current interest in surfactants, particularly their application in insitu flushing of contaminated aquifers or ex situ washing of contaminated soils, stems from their ability to reduce interfacial tension between the contaminants and washing system. This facilitates desorption of contaminants or mobilization of trapped ganglia of NALs. Another very important property of surfactants, particularly at higher concentrations many folds their CMC concentration, is their ability to partition NALs into their micellar cores.

Surfactant dosage used in soil cleaning is normally in the range of 0.5-2%. In such cases, surfactant regeneration has to be a part of the process, if costs are to be kept reasonable[23,31]. However, regeneration methods are not efficient enough for practical applications. Another drawback of higher concentration is the formation of stable emulsions of contaminants. Breaking of these emulsions can add significantly to the cost of remediation[10,31].

Implementation of surfactant treatment for soil washing as well as for oilwell drillcuttings decontamination must account for a number of factors, including efficient surfactant recovery and reuse. Other factors that must be considered include the surfactant desorption of contaminant, surfactant-cuttings-water interactions, sorption to cuttings, economic cost, biodegradation, and effects on biota.

Hence, an optimal surfactant would be one that was proven to be effective on contaminant (solubilization and reduction of interfacial tension) yet is fairly non-toxic and will not pose a threat to human health or the environment. Moreover, it is beneficial if the surfactant
is readily available, economically priced and recyclable. Nevertheless, proper surfactant will minimize undesirable surfactants interactions, like sorption to cuttings and interaction with divalent electrolytes and water hardness[32,41].

3. SURFACTANT CLEANING MECHANISMS

When a drop of oil is placed on a solid surface, the oil will either spread across the surface to form a thin, approximately uniform film or it will spread to a limited extent but remain as a discrete drop on the surface. The final condition of the applied oil on the surface is taken as an indication of the wettability of the surface by the oil. The quantitative measure of the wetting process is taken to be the contact angle, θ, which the drop makes with the solid. In the case of a liquid that forms a uniform film (i.e., where θ=0º), the solid is said to be completely wetted by the liquid, or that the liquid wets the solid. Where a nonzero angle is formed, there exists some controversy as to how to describe the system. Some investigators describe the system to be wetting if oil produces a contact angle of 30º or less. While, if θ is between 30º and 89º, the system would be partially wetting, however, if θ is 90º or above, the system is nonwetting. Alternatively, others prefer to describe any system with θ<90º to be partially wetting and only for θ=90º, it would be nonwetting[25].

Several mechanisms have been discussed in the literature in relation to the cleaning of solid surfaces from oily deposits. Depending on the specific system, one or another mechanism can prevail. However, the most popular and well accepted mechanisms are: (1) the rollup mechanism, (2) snapoff or emulsification, and (3) solubilization[10,22,42,43]. Rollup of oil is the primary mechanism, which is facilitated by increase in contact angle exhibited by the oil droplet on the substrate surface in the presence of a wash system. Snapoff is the second accepted mechanism, in which a part of the oil droplet is drawn off into the wash liquor by hydrodynamic forces. The third mechanism is solubilization, in which oil molecules diffuse into the hydrophobic cores of micelles[40].

3.1 Rollup/Snapoff Mechanisms

Rollup may be simply defined as the detachment of an oil droplet from a substrate due to the increase in contact angle between the oil droplet and the substrate. The contact angle (θ) is related to various interfacial tensions by Young’s equation:

\[ \cos \theta = \frac{\gamma_{w/s} - \gamma_{o/s}}{\gamma_{o/w}} \]  

Figure 1 shows the contact angle at the water (w)-oil (o)-substrate (s) junction, measured in the oil phase. The driving force causing the oil to separate from the substrate surface and rollup results from tension at the interfaces between oil, water, and the substrate. In an ideal case, the apparent contact angle of the oil on substrate increases from 0 to 90 and 180º, and the oil rolls up when the resultant force “f” of interfacial tensions is positive (Figure 2):

\[ f = \gamma_{o/w} - \gamma_{w/s} + \gamma_{o/w} \cos \theta \]  

If the resultant “f” become zero before the contact angle θ has increased to 180º, the rollup of oil stops and an external force must be applied to complete the removal of soil.

Equation (2) suggests that the conditions for oil removal by roll-up mechanism are favourable when the interfacial tension between substrate and water is small, the oil/substrate interfacial tension is large, and the interfacial tension between oil and water is small. However, a positive resultant of interfacial tensions is not a sufficient condition for the separation of oil from the substrate surface. The rollup of oil is opposed by the viscosity of oil, which depends on the cohesive energy of oil and the shape of its molecules. If the viscosity is high, the interfacial forces may not be sufficient for rolling up the oil and an external force may be needed to dislodge the oil.

Rollup mechanism is also related to the work of adhesion of the oil and the surface \( W_{w/o} = \gamma_{o/w} (\cos (\theta)+1) \). Non-wetting oil droplets (θ~180º, cos (θ) ~ -1) and/or formulation with low interfacial tension (\( \gamma_{o/w} \sim 0 \)) yields systems with negligible work of adhesion where the oil can be removed from the surface with minimal mechanical agitation (energy). In other words, if the work of adhesion of the droplet to the surface is zero or negative, it becomes easier for the mechanical forces to completely detach the oil droplet from the solid surface[10,22,24,42].

The surfactant helps a hydrocarbon oil to roll up by lowering the water/substrate and water/oil interfacial tensions. In this mechanism the adsorption of surfactant at the oil-water interface increases the contact angle (θ) between the oil and the solid surface and decreases the interfacial tension between oil and water (\( \gamma_{o/w} \)). The repulsion between the monomer head group and the solid surface promotes separation of the oil from the surface[27]. Convective currents created by
agitation and abrasion provide the energy necessary to create additional surface area of the oil phase and thus displace the oil from the solid surface as a free phase layer of oil.

Snapoff or emulsification mechanism occurs when the contact angle is not high enough for the entire droplet to detach from the substrate, but a portion breaks off the oil film that is deposited on the surface as shown in Figure 3. This mechanism is obtained when the mechanical agitation is stronger than the work of cohesion ($W_c=2\gamma_{OW}$) of the droplet, which lead to a break up of the droplet, leaving behind some oil residue[10].

3.2 Solubilization Mechanism

The solubilization mechanism for oil removal is based on the partition of the oil molecules inside the hydrophobic core of surfactant micelles. This mechanism is only relevant at high surfactant concentrations when a large number of micelles are present[10].

The solubilization mechanism is quite effective in removing the oil but it also requires high concentrations of surfactant in the washing solution, and additional separation of the oil dissolved from the surfactant solution. The other two mechanisms rely on the decrease of the work of either adhesion or cohesion, which are in both cases, proportional to the interfacial tension between the oil and water. Surfactant concentrations below CMC were found capable to initiate rollup and/or snapoff mechanisms, however, high surfactant concentration far above CMCs were found necessary to initiate solubilization mechanism[10,23,27,32,36].

Rollup is probably the most important mechanism on polar substrates, emulsification and solubilization govern the results on non-polar materials. Rollup is relatively simple to achieve, however, emulsification and in particular solubilization, need fine tuning of the surfactant composition. Effective solubilization is only obtained with surfactants that bring the interfacial tension of oil and water down to ultra-low values. Ultra-low interfacial tensions are possible when microemulsions are formed.

4. HYDROPHILE LIPOPHILE BALANCE AND MICROEMULSIONS

Microemulsions are thermodynamically stable emulsions that contain water and oil domains separated by surfactant films[22]. Forming a middle phase microemulsion requires matching the hydrophile-lipophile balance (HLB) of the surfactant system with that of the oil. The HLB number is an indication of the relative strength of the hydrophilic and hydrophobic portions of the molecule and can be used to characterize the relative affinity of surfactants for aqueous and organic phases. A high HLB number generally indicates good surfactant solubility in water, while a low HLB number indicates a lower aqueous solubility and higher relative affinity for the organic phase.

There are three types of microemulsions: (1) Winsor Type I is an oil-in-water microemulsion in equilibrium with excess oil, (2) Winsor Type III is a middle phase microemulsion in equilibrium with excess oil and water, and (3) Winsor Type II is a water-in-oil microemulsion in equilibrium with excess water[22].

It has been found that the oil-water interfacial tension has a deep minimum in the three-phase region, i.e. $\gamma_{OW}$ decreases as a system goes from Winsor I to Winsor III, has a minimum in the middle of the Winsor III region and increases as it moves on into the Winsor II regime. The Winsor I-III-II transition can be achieved by raising the temperature for a system based on a nonionic surfactant and by increasing the salinity of a system based on an ionic surfactant (Figure 4).

5. SORPTION TO SOIL AND OTHER INTERACTIONS

Three types of interactions are involved in the adsorption of a surfactant at solid/liquid interface: the attractive or repulsive interaction between the hydrophilic group and the surface, the attractive interaction between the hydrophobic group and the surface and the lateral interactions which occur between adsorbed surfactants. For surfactants, the most important interactions between the hydrophilic group and the surface are the electrostatic and hydrogen bonding[45-48].

Electrostatic interactions are most important for ionic surfactants. Most natural surfaces are negatively
charged under naturally occurring conditions. As a result, anionic surfactant will experience a repulsive electrostatic interaction with most natural surface; this serves to make them adsorb to a lesser extent than cationic or nonionic surfactants for most applications. In contrast, cationic surfactants experience an attractive electrostatic interaction and show high levels of adsorption when compared to anionic or nonionic surfactants of the same size hydrophobic moiety. This generalization correctly predicts the relative adsorption of anionics and cationics on SiO₂ surfaces such as are found in sandstone. On dolomite or calcite, however, at low to neutral pH values the solid/liquid interface is positively charged, and anionics will be higher adsorbing than similar cationics[45].

Hydrogen bonding is weaker than electrostatic interactions. Hydrogen bonding between surfactant species and the solid surface species could occur in systems containing hydroxyl, phenolic, carboxylic and amine groups on the surfactant. For instance, adsorption of a nonionic surfactant such as ethoxylate alcohol (e.g., Triton X-100) has proposed to involve hydrogen bonding. It should be noted that for adsorption due to hydrogen bonding to take place, the bond formed between the surfactant functional groups and mineral surfaces should be stronger than that formed between the mineral and interfacial water molecules[48]. Most nonionic surfactants contain polar groups that form hydrogen bonds with the hydroxyl groups on the solid surface. Sorption of nonionic surfactants to soils/sediments is limited by their critical micelle concentrations and reaches a plateau at their equilibrium concentrations about 1.5 CMCs[49].

Hydrophobic bonding can be important for adsorption on solids that possess a fully or partially hydrophobic surface. In this case, surfactant molecules can adsorb flat on the hydrophobic sites on the solid. Such adsorption can also take place on other types of solids that are originally hydrophilic, but that have acquired some hydrophobicity owing to reaction with organic species in solutions[46].

Due to negatively charged surface of most minerals, anionic surfactants and nonionic surfactants can be expected to be sorbed less than cationic surfactants, and have usually been chosen in surfactant enhanced aquifer remediation (SEAR) technology. The amount of a single anionic surfactant or a single nonionic surfactant sorbed to soils/sediments, however, is still significant.

For example, Deshpande et al. [27] observed that increasing the surfactant concentration 25 times above the surfactant CMC increased the efficiency of petroleum contaminants extraction using selected anionic surfactants but had no apparent improvement on the extraction efficiency of selected non-ionic surfactants. They reported that concentrations of nonionic surfactants in the final solution were found to be below their CMC’s and hypothesized that this was due to the sorption of a significant amount of the added surfactant.

Similarly, Zheng and Obbard[50] found the maximum values of sorption for three anionic surfactants (Brij 35, Triton X-100 and Tween 80) on a soil consists mostly of ash to be 2.73, 5 and 7.23 mMol/Kg (3.3, 3.1 and 9.5 g/Kg) respectively. Chu and Chan[34] estimated that nearly 84% (0.839 mol/L) of nonionic surfactant input (Brij 35) was adsorbed or lost to the soil. Childs et al.[50] found that the abstraction losses of an anionic surfactant (Alfoterra 145-4PO) in presence of drillcuttings rich in divalent cations were 20 g/Kg. Zhou and Zhu[51,52] found the maximum sorption amounts of Triton X-100 onto different Soils ranged 5.6 and 14.3 mMol/kg (3.5-8.9 g/Kg).

Furthermore, researchers found that the sorbed nonionic surfactants was more effective as a sorbent for HOCs than was humic matter and enhanced HOC sorption relative to the untreated soils[53-56].

Although anionic surfactants can be expected to sorb less than non-ionic surfactants to most mineral surfaces, they are subject to losses by precipitation[57].

Water/drilling-fluid/rock hardness may be detrimental to the effectiveness of anionic surfactant because anionic surfactant may precipitate. Mineral species, especially multivalent cations (Ca⁺, Mg⁺), can interact with surfactant species and result in precipitation of the surfactants[10,45,57,58]. This is likely to occur below CMC. Above the CMC the cations may associate with the micelles of the surfactant to such extent that the activity of the cations is reduced to the point that precipitation is no longer form[45].

Precipitation of the surfactant in the presence of dissolved mineral species is also considered to contribute to the maximum often observed on the surfactant adsorption isotherms. In most cases adsorption is calculated from the difference between initial and final surfactant concentrations. Since any precipitation in the system can contribute to the observed difference in concentrations, the term “abstraction” is used instead of “adsorption” for systems that have precipitation phenomena.

Furthermore, anionic surfactants possess high CMCs than nonionic surfactants and their solubilization power is significantly less than with nonionic surfactants[59,60]. For nonionic surfactants, aggregation is mainly due to hydrophobic interaction among hydrocarbon chains. These hydrophobic groups are easily separated from the aqueous environment, whereas for ionic surfactants, high concentrations are necessary to overcome the electrostatic repulsion between ionic head groups during aggregation[60].

However, nonionic surfactants are more likely to adsorb onto clay minerals and/or organic matter than anionic surfactants[49,62,68]. Whereas some authors have reported the existence of a positive relationship between adsorption and the organic matter (OM) content of soils[49,64,65], others have found a
relationship between adsorption and the clay content. Cano and Dorn[62], Brownawell et al.[63], Salloum[64], Lee et al.[65], Zhu et al.[49] and Rodriguez-Cruz et al. (2005) showed data that reveal that it is the content of expanding clays (montmorillonite), rather than total clay content that is related to surfactant sorption. Similarly, Zhu et al.[49] and Rodriguez-Cruz et al.[66] concluded that illite also has a strong affinity to nonionic surfactants (Triton X-100). These results imply that the sorption of nonionic surfactants on soils/sediments may be a combination of organic matters fraction and clay minerals fraction.

According to the above literature review, it has been suggested that the sorption of nonionic surfactants by soil surfaces such as clay minerals and/or organic matter content and abstraction of anionic surfactant by multivalent cations may negate their contaminant extraction efficiency.

6. SYNERGISM OF SURFACTANT MIXTURES

When different types of surfactants are purposely mixed, what is sought is synergism, i.e., the condition when the properties of the mixture are better than those attainable with the individual components by themselves[68]. For example synergism in the monolayer formation in aqueous systems containing two surfactants exists when a given surface tension can be attained at a total mixed surfactant concentration lower than that required for either surfactant by itself[68].

Generally, anionic and nonionic surfactant solutions usually form mixed-micelle aggregates that frequently exhibit properties remarkably different from those of the individual components. The attractive interaction between the components of mixed surfactants results in the changes of structure and properties of mixed micelle. Upon mixing several properties were observed to change, of which the negative deviation of the CMCs from ideal mixtures, increasing or decreasing contaminant solubility, reducing precipitation of anionic surfactants and sorption of nonionic surfactants to soil[22,68-73]. Anionic-nonionic surfactant mixtures are also found to exhibit cloud points higher than those of the single nonionic surfactant, along with Krafft points lower than those of the single anionic surfactant[69].

Zhao and co-workers[70,73] studied the mixed surfactant systems of an anionic surfactant, Sodium Dodecyl Benzene Sulfate (SDBS), and a nonionic surfactant, Triton X-100 (TX100). The mixed TX100-SDBS was found superior to the relevant single ones mainly due to the reduction in nonionic surfactant partition and/or sorption to soil as well as the high solubilization capacity of the mixture. It is shown that the amounts of both TX100 and SDBS sorbed to Ca-montmorillonite are significant. However, the amount of either TX100 or SDBS sorbed can be decreased and minimized when they are mixed with each other[70]. Furthermore, the extent of TX100 partition into the organic matter was found to decrease if the amount of SDBS increased[73,74]. Decreasing loss of surfactant due to partition and/or sorption and the greater apparent solubilization of the mixture will reduce surfactants volumes needed and thus the capital expenditure and operation cost[72].

Surfactant mixtures of Triton X-100 and Sodium Dodecyl Sulfate (SDS) have also been studied. Synergism was found as the critical micelle concentrations (CMCs) of mixed surfactants were sharply lower than that of sole SDS. With the increase in mole fraction of TX100, the CMCs decrease continuously from the CMC of pure SDS down to the CMC of pure TX100. Furthermore, the experimental CMCs are lower than the ideal CMCs[51,67,68,89,71,75-79]. The experimental results showed that the presence of SDS not only reduced the sorption of TX100 onto the natural soil, but also enhanced the solubilization of TX100 for phenanthrene, both of which resulted in the distribution of phenanthrene in soil-water systems decreasing with increasing mole fraction of SDS in surfactant solutions[51,79]. Furthermore, the mixed surfactants exhibited no inhibitory effect on biodegradation by phenanthrene-degrading microorganisms with 96 hours. The results suggested that anionic-nonionic surfactants would improve the performance of remediation of PAH-contaminated soils[79].

7. SUMMARY

This review presented offshore oily drilling waste problem, surfactant-enhanced washing of drillcuttings, surfactant-enhanced soil washing, surfactant loss due to sorption and precipitation and synergism of surfactant mixture. Special emphasis has been put on proper selection of surfactants and factors that must be considered for an optimal surfactant washing process. It has been shown that a successful surfactant washing is affected by many factors. A full understanding of all the complex interactions of surfactant-soil/drillcuttings-water/drillingfluid could lead to new approaches and insights that are needed to optimized the washing process. The following could be concluded from the previous review:

- While offshore direct discharge of oily drilling waste is deemed as the least expensive disposal option, current waste treatment technology is unable to clean oil out of cuttings to 1% ROC limit.
- Shipping the contaminated-cuttings to shore for treatment and disposal are expensive, operationally difficult, and depend on availability of treatment and disposal equipment and locations available onshore.
- Surfactant-enhanced washing for remediation of oily drillcuttings offshore were seen to be
promising. The rollup and snapoff oil removal mechanisms are desirable because the oil is liberated from the cuttings as a free phase top layer which can be skimmed from the cleaning tank, circumventing the need for surfactant separation. Also these mechanisms are preferred because they can be achieved at low surfactant concentrations. The economics are then improved.

- Estimation of amount of surfactant adsorbed to specific drillcuttings is necessary for the success of the process. It is believed the sorption and abstraction of surfactants has a strong effect on the efficiency of surfactant in drillcuttings remediation. Adsorption of surfactant is due to clay minerals (particularly montmorillonite and illite) as well as organic matter content. While abstraction is mainly due to hardness (divalent cations).

- Mixing anionic and nonionic surfactant can greatly improve their washing properties over individual surfactants. The CMCs, adsorption and precipitation tendencies of individual surfactants are reduced through mixing. Similarly, solubilization power of mixtures was found to be greater than individual ones.

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