11 Formulation Effects on the Lubricity of O/W Emulsions Used as Oil Well Working Fluids

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ABSTRACT

In oil well drilling, completion, and maintenance operations, the rotating pipe
bears against the side of the hole at numerous points, giving rise to two main
friction manifestations known as torque and drag. Torque refers to the pipe
resistance to rotation and drag to hoisting and lowering. Excessive torque and
drag can cause unacceptable loss of power making oil well operations less efficient,
especially in high-angle and extended-reach wells. In these cases, lubricity
becomes one of the main functions of the fluid. In the oil industry, there are oil
well working fluids of different nature, classified according to the external phase
as water-based fluids (WBFs), oil-based fluids, and pneumatic or gas-based fluid
systems. Within WBFs, there are oil-in-water (O/W) emulsions, developed as a
technological solution for oil well operations in low-pressure reservoirs. In this
work, tribological properties of O/W emulsions have been studied as a function
of their physicochemical formulation, especially oil type (nonaromatic mineral
oil [NAM-oil], diesel) and surfactant concentration (1, 2% w/v) along with the
oil/water ratio (70/30, 50/50) as formulation variables. The lubrication
performance was established by measuring the coefficient of friction (CF), and optical
microscopy imaging in conjunction with optical surface profilometry was used
to evaluate antifriction properties. Additionally, contact angle measurements were
performed to correlate the wettability phenomenon with the lubricity of O/W
deposits. Based on the results, it was established that with the surfactants mixture
used in this study, the oil type does not have a significant effect on the CF
of O/W emulsions, due to the similar wettability behavior observed at the
metal surface. However, NAM-oil/W emulsions have better antifriction properties
than the diesel/W emulsions. Also, the lubricity performance and antifriction
properties of O/W emulsions are affected by oil/water ratio and surfactants mixture
concentration, showing a systemic interaction between these two parameters.

11.1 INTRODUCTION

11.1.1 TRIBOLOGICAL PHENOMENA IN WELL CONSTRUCTION

In oil well construction and maintenance processes, particularly during drilling,
al the equipment and fluid systems present different tribological phenomena
and related problems. Table 11.1 summarizes the principal and the particular tribologi­
cal events encountered in the oil well operation system. The dominant wear modes
include impact, abrasion, and slurry erosion [1], and when not controlled or
predicted, they could cause catastrophic failures (Figure 11.1) of the equipment
and the wellbore, with the ultimate loss of the hole.

The main frictional events in oil well operations are torque and drag since they
are caused by the rotation and sliding of pipe inside the well, affecting a large surface
(3 km of pipe in metal-to-metal contact), and can be minimized by lubricity with a
large volume (600 m³) of the circulating working fluid.

Formulation Effects on the Lubricity of O/W Emulsions

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Main Tribologically Related Problems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engines</td>
<td>Adhesion, abrasion, fretting, corrosion</td>
</tr>
<tr>
<td>Shearing, mixing, and product storage facilities</td>
<td>Abrasion (two and three body), erosion (dry and wet), stamping</td>
</tr>
<tr>
<td>Flowlines, stand pipe, valves, and hoses</td>
<td>Erosion (dry and slurry), abrasion, stamping, corrosion</td>
</tr>
<tr>
<td>Mud and centrifugal pumps</td>
<td>Abrasion (two and three body), erosion (slurry), adhesion, fretting, corrosion</td>
</tr>
<tr>
<td>Hoisting systems (derrick, crown block, traveling block, thread ropes, etc.)</td>
<td>Impact, fatigue, abrasion (two and three body)</td>
</tr>
<tr>
<td>Rotary table or top drive</td>
<td>Abrasion (two and three body), fretting, impact, fatigue, stamping</td>
</tr>
<tr>
<td>Pipes and accessories (heavy wates, centralizers, mud motors, directional controls tools, etc.)</td>
<td>Abrasion (two and three body), fatigue, erosion (slurry), impact, corrosion</td>
</tr>
<tr>
<td>Drill bit</td>
<td>Abrasion (two and three body), fatigue, erosion (slurry), impact, torque and drag, corrosion, oxidation</td>
</tr>
<tr>
<td>Blow-out preventer and kill system</td>
<td>Abrasion (two and three body), fatigue, erosion (slurry), impact, corrosion</td>
</tr>
<tr>
<td>Solid control systems (shakers, hydrocyclones, cutting lines, etc.)</td>
<td>Fretting, erosion (slurry), abrasion (two and three body), fatigue, impact</td>
</tr>
</tbody>
</table>

![Examples of catastrophic failures due to tribological problems in oil well construction: (a) erosion failures by drilling fluids, (b) sliding and fretting wear on thrust-bearing racetrack, (c) sliding and fatigue wear on drill pipe by metal-metal contact, (d) impact and sliding wear at PDC bits, (e) two-body abrasion wear at mud pump liners, and (f) fatigue and two-body abrasion on mud pump liners.](See color insert.)
Torque and Drag
Torque and drag are two frictional forces that appear during many oil well operations (drilling, completion, and maintenance), produced by the resistance to rotation (torque) and to raising and lowering (drag), in contact with either the wellbore (metal-to-rock) or the casing (metal-to-metal) [2–4] (Figure 11.2).

Management of torque and drag is a crucial part of well design and well operations, for complex well architectures and extended reach wells (ERWs). For example, rig limits can be compromised by excessive torque surpassing topdrive capacity and excessive drags that can lead to the inability to slide pipe for oriented drilling or failure to land a casing or completion string. Similarly, high overpulls can exceed downhole frictional forces can compromise pipe limits, leading to problems arising from pipe failures (i.e., twistoffs, collapse, buckling, and fracture) or stuck pipe [5].

For this reason, it is important to understand the mechanisms related to torque and drag frictional forces and lubrication by different working fluids, and how these affect the wellbore stability and components in the oil well operational system, in relative rotation or sliding movements.

Lubricity by Oil Well Working Fluids
One of the functions of oil well working fluids is to cool and lubricate the string pipe. Conventionally, the lubricity coefficient is used to quantify the lubricating properties of fluids, and it is measured as the coefficient of friction (CF) of a steel test block pressed against a test rotating ring by a torque arm, to simulate metal-to-metal friction between the pipe and the casing. Lubricity coefficient values are on a scale of 0.01–0.50 and low coefficient denotes good lubricity by a fluid [6].


Formulation Effects on the Lubricity of O/W Emulsions
It is known that the behavior of a lubricant can be classified into three separate regimes depicted in the Stribeck curve as follows: (a) the hydrodynamic regime, suitable at high speeds, in which the surfaces are fully separated and the lubrication is governed by bulk rheological properties of the lubricant; no direct physical contact interaction between surfaces occurs, so wear process cannot take place except surface fatigue wear, cavitation, or fluid erosion. (b) The boundary lubrication regime is present at low sliding speeds and high loads, where friction is determined by both surface–surface asperities interaction and ability of the lubricant to adsorb chemically onto the surface and form an interfacial film. Different sliding wear mechanisms may occur in this regime such as corrosive, fatigue, and adhesive wear depending on the dynamic conditions. Increasing sliding speeds, loads, and operating temperature will establish the extreme pressure (EP) lubrication regime, which is based on the concept of a sacrificial film generated by the reaction between lubricant additives and exposed metal surface, preventing metallic contact and severe wear of the surface. (c) Between these two regimes, a mixed regime can be recognized, where the pressure of the fluid carries only part of the load, while the other part is sustained by the surface asperities [7,8].

The lubricity test simulates load conditions present in oil well operations (pipe weight against casing), corresponding to EP lubrication mechanism [3] and it is currently limited to steel-on-steel testing. It is believed that this is adequate for most lubricant screening purposes, as the cased hole section constitutes 85% of the total hole length [9].

Although oil-based fluids (OBFs) have lower CF values, there are wellbore conditions and environmental requirements that will limit their use. This is the case of oil well operations in low-pressure reservoir that require fluids with density lower than that of oil and adequate rheological properties, especially for critical high-angle and ERWs, where lubricity is also a main design criterion.

Lubricants are often added to the oil well working fluids to reduce friction and minimize torque and drag. They are additives generally available as film-producing liquids or solid beads, powders, or fibers. Liquid additives include glycols, oils, esters, fatty acid esters, surfactants, and polymer-based lubricants and solid additives, such as graphite, calcium carbonate flakes, glass, and plastic beads [5].

Oil-in-Water Emulsions Used as Oil Well Working Fluids
O/W emulsions have been specifically developed to drill, complete, and maintain oil wells in low-pressure or depleted reservoirs [10], where water-based low-density fluids (lower than water's) are required.

O/W emulsions, used as oil well working fluids in low-pressure reservoirs, are designed with a high internal oil phase concentration (HIPC:50%–90%) to both lower the density by substituting water by oil mass, and impart the required rheological properties to the emulsion. The HIPC-O/W emulsion stability and viscosity greatly depend on the type and concentration of the surfactant system used as emulsifier [11,12]. Other additives such as salts potassium chloride (KCl) and pH modifiers (monoethanolamine [MEA]) are incorporated in oil well working emulsions for specific purposes like clay modification.
Most studies published on lubricating behavior of O/W emulsions have been done under metal working, rolling-cooling, drilling, and cutting conditions, where they have been specifically designed as lubricant fluids, with a low emulsified oil concentration (3%–5%). Combination of oil lubricity and the latent heat of water provides the optimum fluid for this application. Mining and petroleum machinery is also lubricated by water-based fluids (WBFs) to minimize the risk of fire from leakage of lubricants [7]. The most severe limitation of these lubricants is the temperature range in which they can be successfully applied [17].

The main objective of this work was to study the influence of oil type, dispersed oil fraction, and surfactant concentration on the tribological behavior of O/W emulsions, designed to drill, complete, and maintain high-angle and extended reach wells, located in low-pressure reservoirs, where high lubricity and low density are primarily design criteria. No additives were added to the O/W emulsion formulations, assuming that the dispersed oil and/or the surfactant will provide the lubricity required, without increasing the cost of the formulation.

11.2 EXPERIMENTAL DETAILS

11.2.1 MATERIALS

11.2.1.1 Surfactants
The emulsifier system was a hydrophilic anionic/nonionic mixture at a specific mass ratio of two commercial surfactants: an alkyl ether sulfate sodium salt and an alkyl ethoxylated alcohol (made by Clariant, Venezuela); and they were used as received. The critical micelle concentration (CMC) of the aqueous surfactant solutions (ASS) and interfacial tension between the base oil and the aqueous surfactant solution were determined for the individual surfactants and the mixture, using a Dataphysics DCAT11 tensiometer, employing the Wilhelmy plate technique (Table 11.2). Deionized water was used for preparing the solutions.

11.2.1.2 Oils and Other Chemical Additives
A nonaromatic mineral oil (NAM-oil) and diesel were used as the dispersed phase in the O/W emulsions. They were used as received. Table 11.3 shows the characteristics of the dispersed phases used. The salt evaluated was KCl (Sigma-Aldrich, 99% purity), and MEA (Sigma-Aldrich, 98% purity) was used to adjust the pH in a range from 8 to 10.

11.2.2 PROCEDURES

11.2.2.1 O/W Emulsion Preparation
The corresponding amount of oil (50% or 70%) was slowly added to the aqueous surfactant solution (1% or 2%), while stirring at 10,000 rpm, room temperature, for 10 min. To characterize the emulsions, average drop diameter ($D_{\text{avg}}$) was determined by laser-scattering technique with a Malvern Mastersizer Hydro 2000G and viscosity by a Physica MCR 301 rheometer, Anton Paar, at 180 s$^{-1}$ and 49°C. Table 11.4 shows the characterization results of the emulsions with surfactant concentration of 1% and 2%.

11.2.2.2 Lubricity Test
This device is based on the Amontons friction law [7], where the CF is defined as the ratio of parallel frictional force F and the normal force W applied to the surface.
In order to evaluate the effect of O/W emulsion composition on its lubricating property, the lubricity coefficient was measured as the CF or friction factor, using a block-on-ring tribometer (Fann LUBRICITY TESTER, model 212 E, Figure 11.3). The following recommended procedure was used: apply a constant load (W) of 444.8 N by means of the torque arm, adjust the rotational speed of the ring at 60 ± 10 rpm after 600 s take the ampere reading on the meter, which is converted to the CF. Measurements were performed every 60 s after an equilibration period of 300 s.

The test blocks had 12.2 ± 0.10 mm wide and 19.05 ± 0.41 mm long test surfaces. Each block was supplied with four flat faces and the roughness was between 0.51 and 0.76 μm. The test rotating rings had a width of 13.06 ± 0.05 mm, a perimeter of 154.51 ± 0.23 mm, and a diameter of 49.22 ± 0.125. Both test blocks and rotating rings were made of carburized steel, having a Rockwell hardness C scale number of 58–62 or a Vickers hardness number 653–746 [18,19].

11.2.2.3 Contact Angle Measurements

An optical contact angle device (OCA Dataphysics) was used to evaluate the wetting properties of the oils and ASS on the steel test block surface, at room temperature. The metal surface was immersed in the surfactant solution and then a 2 μL oil droplet was placed on the metal surface with a syringe and allowed to spread until no further change in the contact angle was observed. Images of the solid/liquid/liquid interface were taken. Which represent an entire or part of a scar on the metal surface. Due to the curvature on the metal test block, the edges or part of the pictures may appear blurry; however, this does not have a significant effect on describing qualitatively the wear suffered by the surface.

Additionally, the roughness and texture of the metal test block were analyzed using a Zygo NewView 6000 optical surface profilometer. The studied square area (2.16 x 2.16 mm) in all cases was in the center of the block, assumed as the major friction zone. All metal blocks were cleaned with acetone prior to the profilometry analysis to remove any deposits on the surface. The images were analyzed using the cylindrical filter that allows to flatten the surface.

11.3 RESULTS AND DISCUSSION

O/W emulsions used in oil well operations have been specifically designed for low-pressure or depleted reservoirs, by dispersing a high oil proportion (>50%) to obtain density lower than water, and still being a WBF. These O/W emulsions must be stable under pressure, temperature, shear, and contamination conditions present during operations. To guarantee stability, a high-surfactant concentration is required (>200 CMC). If a low-pressure reservoir is accessed by a high-angle or extended reach well, then lubricity by the O/W emulsions is also a crucial property.

In a previous work [20], hydrophilic surfactants were systematically selected to obtain very stable O/W emulsions. In this study, the effects of oil type, oil/water ratio, and surfactant mixture concentration were evaluated on the tribological properties of the O/W emulsions. The oils and ASS were also evaluated to discriminate the role of each one in the lubricity by the O/W emulsions. Table 11.5 presents the nomenclature of the systems used.

Tribological behavior of the systems was studied by determining the CF and wear of the steel block surface subjected to friction in the lubricity test, following the procedures described in the previous section.

<table>
<thead>
<tr>
<th>TABLE 11.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Systems Nomenclature</td>
</tr>
<tr>
<td>W</td>
</tr>
<tr>
<td>S1</td>
</tr>
<tr>
<td>S2</td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td>V731</td>
</tr>
<tr>
<td>V732</td>
</tr>
<tr>
<td>V551</td>
</tr>
<tr>
<td>V552</td>
</tr>
<tr>
<td>G</td>
</tr>
<tr>
<td>G731</td>
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<tr>
<td>G732</td>
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<tr>
<td>G551</td>
</tr>
<tr>
<td>G552</td>
</tr>
</tbody>
</table>
The mechanisms involved in lubrication using O/W emulsions are far more complex than those involving single-phase hydrocarbon solutions. According to the literature, during O/W emulsions lubrication process, water is partially excluded from the loaded contacts due to an oil pool forming at the interface, and as a result, the performance of an O/W emulsion is close to that of the pure oil at mild operational conditions [7,15,21].

The results presented in this investigation correspond to a boundary and EP lubrication regimes, imposed by the mechanical design, and the medium-to-high pressure operational conditions of the Lubricity Tester, that simulates metal–metal friction between pipes, during oil well operations [6,22,23].

11.3.1 COEFFICIENT OF FRICTION STUDIES

11.3.1.1 O/W Emulsions

Figure 11.4 shows the CF values for all studied systems: O/W emulsions, as well as water, ASS and oils, as their main components. The results presented are arithmetic means of CF for the last 5 min of the experiment (total experimental time of 10 min). The error bars shown in Figure 11.4 represent standard deviations of three independent tests. The formulation variables considered were oil type (NAM-oil, diesel) and surfactants mixture concentration (1%, 2% w/v) along with the oil/water ratio (70/30, 50/50).

11.3.1.2 NAM-Oil/W Emulsions

O/W emulsions formulated with NAM-oil have similar or lower CF as that of pure oil (dispersed internal phase), but higher than that of ASS, and show considerable CF reduction, up to three times compared to pure water (Figure 11.4). If it is assumed that water is partially excluded from the metal contact zone [7,21], then surfactant adsorption on the metal surface and its interaction with NAM-oil are responsible almost totally for the lubrication properties of emulsions, as it has been well established in the literature [24–26].

The CF values of the NAM-oil/W emulsion show a small increment when the NAM-oil content is raised from 50% to 70%. Now, the liquid/liquid interfacial area is higher and requires more surfactant to adsorb and stabilize the emulsion suggesting the possibility that less surfactant is available to adsorb and lubricate the metal surface. However, this effect is not so important because the surfactant concentration exceeds 200 times the CMC; hence, there are enough surface aggregates to lubricate the metal surface.

Likewise, increasing surfactant concentration from 1% to 2% does not have a remarkable effect on CF because at 1% the surfactant concentration is already 200 times the CMC, meaning that the interfaces are saturated and the additional surfactant will remain in the bulk.

From these observations, it can be inferred that in NAM-oil/W emulsion, lubricity is provided by interaction between the surfactant aggregates adsorbed at metal surface and the oil molecules present in the system [15,27].

11.3.1.2 Diesel/W Emulsions

Even though diesel has environmental restrictions, there are occasions, like completion and maintenance operations, where diesel/W emulsions can be safely used, because they will be displaced from the well and treated together with the produced oil. In this case, safety and health precautions should be taken to prepare and manage the diesel/W emulsion. For this reason, the tribological properties of the O/W emulsions were also evaluated using diesel as the dispersed phase.

When diesel is added to the ASS, an increase in emulsion CF is observed with respect to both the ASS and pure diesel. The emulsions prepared with 50% of dispersed oil phase show a CF that depends on the surfactant concentration (G51, G52): increasing surfactant concentration from 1% to 2% will render a lower CF. In general, the emulsions prepared with either NAM-oil or diesel show similar CF values (0.14–0.16).

The difference in CF behavior between NAM-oil and diesel, when they are emulsified, could be explained in terms of oil's wettability, i.e., ability of each oil to wet the metal surface.

11.3.2 WETTABILITY STUDIES

Contact angle measurement is a common technique to determine wettability of a solid surface by liquids. Table 11.6 shows the variation of contact angle of NAM-oil and diesel surrounded by water with different surfactant concentrations, measured from inside the oil drop to the oil/water interface. For NAM-oil/ASS, a slight reduction of contact angle was observed, compared with NAM-oil/water system, implying that NAM-oil surface affinity is higher in the presence of the evaluated surfactants. For diesel, an inverse tendency was observed indicating a decrease of diesel wettability on the metal surface with the ASS. Increasing surfactant concentration from 1% to 2% in both systems does not change oil surface wettability.
Two important concepts that need to be considered are oil polarity and orientation and packing of the adsorbed surfactant [11]. Oil polarity will affect oil-surface affinity, as observed in Figure 11.5. The nonpolar NAM-oil, a mixture of saturated hydrocarbon compounds, practically does not wet the metal surface when surrounded by water (Figure 11.5a); but diesel, that contains a high quantity of polar aromatic compounds, shows a high affinity for the metal surface, due to adsorption by polarization of aromatic π electrons [11].

Concerning orientation and packing of the absorbed surfactant, it is known that above the CMC surfactants will aggregate in different geometrical forms (spherical, cylindrical and others) called micelles, and when adsorbed at a metal surface these have been designated as surface aggregates to distinguish them from micelles in solution [11].

Since the highest surfactant proportion is anionic, the surface aggregates will have a negative charge, which will be imparted to the metal surface. If the metal surface is now negatively charged, diesel will have less metal surface affinity (Figure 11.5d and f) due to repulsion between aromatic π electrons and the negative charge of surface aggregates. In the case of NAM-oil, which contains a high percent of saturated organic compounds, the addition of surfactant slightly increases the oil surface affinity (Figure 11.5b and c). It is believed that this occurs due to the possible interaction between oil molecules and the hydrophobic groups of the surface aggregates adsorbed on the metal surface.

According to the literature, the wettability phenomenon is related to the tribological properties of O/W emulsions [28]. In this study, both oils achieve similar metal surface wettability (151.1°–156.9°), when surfactants mixture is present in the oil–water–metal system. This wettability behavior is in correspondence with the similarity of CF values obtained for O/W emulsions (Table 11.6 and Figure 11.4).

Improving oil wettability will decrease the CF of emulsions. Compared with pure oils as lubricants, similar to lower CF values would be obtained for NAM-oil/W emulsions as NAM-oil wettability slightly increases (Figure 11.5). Likewise, oil wettability decreases in the diesel–metal–ASS system, then similar to higher diesel/W emulsions CF values would be obtained (Figures 11.4 and 11.5).

### WEAR EVALUATION

Wear was qualitatively evaluated by analyzing and comparing several consecutive pictures of the metal block surface wear scar, taken with an optical microscope, after completing the lubricity test. Additionally, the roughness and texture of the metal test block were analyzed using an optical surface profilometer.

Optical profilometry test includes a roughness index (Ra), which is an arithmetic mean roughness. In this study, roughness index was not considered as a parameter because steel blocks had a rough surface in the original state (before lubricity test) (Figure 11.6) and comparison could be misleading or ambiguous. After the test, what is relevant is the scar or wear pattern characteristics, i.e., whether it is homogeneous, symmetrical, flat, or with crest and valleys.

Figure 11.6 is the optical microscope image of the center of an unused metal test block, which is presented as a reference pattern of the metal surface. The surface profilometry images are also shown (Figure 11.7).

#### NAM-OIL/W EMULSIONS

Figures 11.8 through 11.11 are the optical microscope pictures of the different steel test blocks after performing the lubricity test, where 50/50 and 70/30 NAM-oil/W emulsions stabilized with 1% and 2% surfactant concentrations were used as lubricants. Pictures with less amount of dispersed NAM-oil (50/50) show that...
FIGURE 11.7 (See color insert.) Optical surface profilometry images of an unused metal test block: (a) areal view and (b) profile.

FIGURE 11.8 (See color insert.) Metal surface after the lubricity test for lubricant V731.

FIGURE 11.9 (See color insert.) Metal surface after the lubricity test for lubricant V732.

FIGURE 11.10 (See color insert.) Metal surface after the lubricity test for lubricant V551.

FIGURE 11.11 (See color insert.) Metal surface after the lubricity test for lubricant V732.

an oxidation process occurred with deposition of debris on the steel test block surface, possibly due to metal asperities contacts; in these emulsions, increasing surfactant concentration from 1% to 2% reduces surface's oxidation (Figures 11.10 and 11.11). For emulsion V731 (more oil, less surfactant) lower oxidation and no debris are observed, but when raising surfactant concentration from 1% to 2% (V732), the oxidation product is higher and homogeneously distributed along the surface (Figure 11.9).

Figures 11.12 through 11.15 are the optical surface profilometry images of the steel test block surface used with the NAM-oil/W emulsions. In general, low wear is observed in these pictures, the most damaged surface being the one that uses emulsions with less oil and less surfactant (V551) and more oil and more surfactant (V732). This analysis is in agreement with the optical microscopy results previously discussed. No metal mass transfer is noted with NAM-oil/W emulsions.

A very interesting observation is that, even though there is low plastic deformation in all the samples, surfaces that were lubricated with V731 and V552 present a symmetrical wear pattern, with crest and valleys, even more homogeneous than the reference pattern (Figures 11.6 and 11.7). It seems that the V731 and V552 lubricant emulsions uniformly distribute the load applied.

FIGURE 11.12 (See color insert.) Optical surface profilometry images of the metal block after the lubricity test for lubricant V731: (a) areal view and (b) profile.
Formulation Effects on the Lubricity of O/W Emulsions

To explain the difference in wear behavior as a function of emulsion formulation, the individual performance of all the systems was studied: water (Figures 11.16 and 11.17), the ASS (Figures 11.18 through 11.21), and pure NAM-oil (Figures 11.22 and 11.23).

The ASS with 1% surfactant concentration has the best performance of all evaluated systems (Figures 11.18 and 11.19). A higher surfactant concentration has a detrimental effect on antiwear properties (Figures 11.19 and 11.20).
Surfactants in Tribology

**FIGURE 11.20** (See color insert.) Optical surface profilometry images of the metal block after the lubricity test for lubricant S1: (a) areal view and (b) profile.

**FIGURE 11.21** (See color insert.) Optical surface profilometry images of the metal block after the lubricity test for lubricant S2: (a) areal view and (b) profile.

**FIGURE 11.22** (See color insert.) Metal surface after the lubricity test for lubricant V.

Figure 11.16 shows the optical microscope picture taken of the steel test block using water (W) as the lubricant. In the middle of the picture, part of the scar can be seen caused by possible metal–metal contact, and between the block and the ring the metal looks polished. In the outer area of the scar, the metal suffers an oxidation process with deposition of fine wear debris on the surface.

The profilometry shows severe wear on the center of the metal block evidencing metal–metal asperities contact (Figure 11.17); such pattern could be generated by the existence of adhesive wear mechanism initiated by lubricant film failure due to the poor load-carrying properties of pure water [7].

The optical microscope picture of the steel test block surface after using 1% ASS (S1) as the lubricant (Figure 11.18) shows debris and fine oxide particles dispersed over the surface. Also, a colored film (light blue with patterns on light yellow and red) can be seen in the friction zone. This colored film could be a result of a possible chemical degradation of the sulfate group of surfactant molecules adsorbed onto the metal surface [8, 26, 29]. This chemical reaction may allow the formation of a sacrificial film on the surface. It is known that additives with sulfur, chlorine, or phosphorus and others may react with exposed metallic surfaces creating protective, low shear strength surface films, which reduce friction and wear; these additives are termed as EP additives [7, 30]. If this presumption is true, the surfactant evaluated acts like a boundary and EP additive in water, under the experimental conditions evaluated [7].

Figure 11.20 shows surface plastic deformation in an even more homogeneous and very symmetrical wear pattern, than the one produced with V731 and V552 NAM-oil emulsions (Figures 11.12 and 11.15). It is known that surfactants may adsorb onto the surface, depending on the surface affinity, whereas the monomers and micelles will fill up microasperities generating a film. This film strongly bonded with the surface may enlarge the real area of contact distributing the load and thus, improving the load-carrying capacity of the system [7, 24].

When the surfactant concentration was increased in the aqueous solution (Figure 11.19), the colored film was still present, but in this case, a significant area of wear was noted. Increasing surfactant concentration (Figures 11.19 and 11.21) has a detrimental effect on the wear reduction properties of the ASS, probably due to a change in the aggregation size and geometry of the adsorbed surface aggregates, producing a weaker unstable film, with a loss in load-carrying properties allowing contact between the sliding surfaces [7, 24, 25].

Likewise, metal surface tested with pure NAM-oil (Figures 11.22 and 11.23) shows no debris, low-to-moderate wear, and no colored film. This last observation is in correspondence with the absence of S-, Cl-, and P-compounds in the NAM-oil.
which would react with the metal surface [8]. Profilometry analysis (Figure 11.23) presents a symmetrical and homogeneous wear pattern, similar to S1, implying that NAM-oil also possesses good load-carrying capacity under the experimental conditions evaluated.

These results allow to propose that the film with the best performance is an ordered structure formed by the adsorbed surface aggregates and oil molecules, which is determined by oil and surfactant concentrations [11,27,28].

11.3.3.2 Diesel/W Emulsions

Figures 11.24 through 11.27 are the optical microscope pictures of the different metal blocks, where diesel/W emulsions stabilized with 1% and 2% surfactant concentrations used as lubricants. In all pictures, fine oxidation particles are observed distributed along the surface. Except for system G731, a colored film (light blue with patterns on light yellow and red) is formed, similar to the ASS systems (Figures 11.18 and 11.19).

Formulation G731 permits generation of a lubricant film strongly bonded to the surface, which distributes more effectively the load applied than the other diesel/W formulations, avoiding metal–metal contacts and hence the formation of sacrificial film is obviated.

Figures 11.28 through 11.31 are the optical surface profilometry images of the metal blocks after the test where diesel/W emulsions were used as lubricants. High to severe wear process was observed in these pictures. Adhesive wear with metal mass loss was present with system G551 as lubricant (Figure 11.30), like what was observed when water was used as lubricant (Figure 11.17), which is an evidence of lubricant film failure [7].

Similarly to NAM-oil/W emulsions, the surface deformation depends on the evaluated formulation: low plastic deformation was observed with higher diesel/W ratio (G731) and lower surfactant concentration (Figure 11.28), while high to severe plastic deformation was observed in other formulations (G732, G551, and G552) (Figures 11.29 through 11.31).

Pure diesel was also evaluated and the optical microscope image (Figure 11.32) shows the oxidation process suffered by the metal surface after using diesel (O) as lubricant, producing a large quantity of fine oxide particles deposited on the metal surface. Although, diesel has traces of sulfur compounds and other impurities, the
FIGURE 11.29 (See color insert.) Optical surface profilometry images of the metal block after the lubricity test for lubricant G732: (a) areal view and (b) profile.

FIGURE 11.30 (See color insert.) Optical surface profilometry images of the metal block after the lubricity test for lubricant G551: (a) areal view and (b) profile.

FIGURE 11.31 (See color insert.) Optical surface profilometry images of the metal block after the lubricity test for lubricant G552: (a) areal view and (b) profile.

FIGURE 11.32 (See color insert.) Metal surface after the lubricity test for lubricant G.

FIGURE 11.33 (See color insert.) Optical surface profilometry images of the metal block after the lubricity test for lubricant G: (a) areal view and (b) profile.

colored film was not observed, meaning that the colored (sacrificial) film is produced by the possible reaction of the adsorbed surfactant molecules with surface metal atoms, producing colored metallic sulfur salts [7,8,29].

Optical surface profilometry image (Figure 11.33) of the metal block tested with diesel (G) presents high wear accompanied by high plastic deformation bordering the friction zone.

11.4 CONCLUSIONS

With the surfactants mixture used in this study, the oil type does not have a significant effect on the CF of O/W emulsions due to the similar wettability behavior observed at the metal surface. However, NAM-oil/W emulsions have better antiwear properties than the diesel/W emulsions. This implies that conventional CF measurements are not enough to evaluate lubricating properties of oil well working fluids. Surface analysis must be done to compare antiwear performance.

Under the evaluated test conditions and with the specified surfactants mixture, the lubricity performance and antiwear properties of O/W emulsions are affected by oil/water ratio and surfactants mixture concentration, showing a systemic interaction between these two parameters. Being under a boundary and EP lubrication...
regimes, emulsion viscosity and droplet size do not have any effect on the lubricating properties. The film formed at metal surface with all NAM-oil/W emulsions and diesel (70)/W(30) emulsion with 1% surfactant concentration can withstand loads higher than 488 N before entering in the EP lubrication regime. All other evaluated systems fail in the EP lubrication regime at lower loads and where they will form a sacrificial film if surfactant is present. The 1% surfactant mixture studied could be used as a lubricant additive for pure water-based oil well working fluids.

REFERENCES


Formulation Effects on the Lubricity of O/W Emulsions