Effect of contamination on the frictional and wear ability of carboxylic acids in aqueous lubricants

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Abstract

The friction and wear mechanisms of water-based fluids consisting of various types of carboxylic acids have been systematically investigated using a ball-on-disc tribometer on a super duplex stainless steel under boundary lubricating conditions. Under water-based lubrication a decrease in friction was found for each of the tested carboxylic acids with a hydrocarbon chain longer than 12 carbon atoms. However, wear reduction was only seen for the carboxylic acids with a hydrocarbon chain longer than 16 carbon atoms and when the concentration of the shorter carboxylic acids increased above a critical value. In addition, it was found that when the lubricant is contaminated with bivalent metal ions like Ca²⁺ or Mg²⁺, the frictional performance becomes worse however, wear improved. Indeed, by increasing the concentration of bivalent alkaline metal ions, the adsorption ability of carboxylic acids to the steel surface decreased leading to higher friction and the presence of Na⁺ ions facilitated the wear improvement. This is explained by the formation of polyelectrolyte complexes between the metal ions dissolved in the lubricant and the carboxylic acid molecules. To compensate for the detrimental effects in friction, a chelating strategy has been implemented and explained in detail.

Keywords: Friction, wear, lubrication, chelation, carboxylic acids, seawater
1 Introduction

Due to a growing demand for energy and a depletion of onshore reserves, offshore oil and gas exploration activities are anticipated to retain its momentum in the next years. Unfortunately, many of the machineries operating in the offshore drilling vessels are suffering wear due to the harsh operating conditions making offshore oil extraction economically unprofitable [1]. The lubricity of such systems plays an important role in reducing the losses related to energy or servicing costs. In addition, a well-selected lubricant reduces the maintenance time and increases the overall efficiency of a drilling process.

The continuous pursuit for improving the performance of the lubricated systems operating in offshore conditions together with the increase in environmental restrictions set by the Environmental Protection Agency pushes lubricant formulators to shift to safer water-based or synthetic ester formulations [2][3][4]. The environmentally acceptable lubricants are typically more polar than classical mineral oils or synthetic oils used in machine elements. This directly influences the selection of additives responsible for frictional reduction, corrosion protection, pour point depression or the viscosity of the lubricant. While ester-based oils have been designed to perform in nearly any environment and application, their poor hydrolytic stability does not allow using them in applications where there is a contact with highly aerated seawater environment like offshore vessels [5][6]. For such applications, water-based lubricants should be selected [7][8][9]. Indeed water-based lubricants are not only used in offshore drilling conditions but also in other applications where high ignition risk is at stake. Here, among the most common are metal-working fluids, hot rolling or casting machines, or various types of welding and annealing processes.

Water-based lubricants used in offshore vessels essentially consist of water, glycols, thickeners, corrosion inhibitors and friction modifiers [10]. The main constituent of the lubricant is water, which in normal operating conditions is set to 35-45 wt.% of the whole lubricant composition. Besides the environmental aspects of using water in a lubricant, high water concentration decreases the production costs, allows the lubricant to mix with water without sheen formation and finally increases the flash point of the lubricant. Unfortunately, water has never been considered as a good candidate for tribological contacts due to its poor corrosion and frictional properties. The performance of water-based lubricants must be therefore improved by carefully selecting the additive package to best match the operational conditions. So far, a typical choice for reducing friction and wear in water-based lubricated systems has always been an aliphatic acid with a short alkyl chain not exceeding 18 carbon atoms [7][11]. These carboxylic acid molecules are desirable in the boundary lubricating region due to their ability to adhere to metallic surfaces with their polar carboxyl group, forming a closely packed mono- or multi-layer assembly responsible for friction and wear reduction [12][13]. Unfortunately, the cleanliness of the lubricating system has an effect on the performance of such additives, specially for systems operating offshore. In offshore applications, most of the lubricating systems are constantly exposed to seawater, which contains significant concentrations of ionic salts such as NaCl, MgCl₂, CaCl₂, etc. It is well known that bivalent metal ions such as Ca²⁺, Mn²⁺ or Mg²⁺ can react with carboxylic acids to form polyelectrolyte complexes (i.e. carboxylic salts), deactivating the frictional reducing ability of the carboxylic acids [14]. It is therefore important to control the cleanliness of the system and to know the critical threshold at which friction modifiers (i.e. carboxylic acids) are completely depleted and inactive. Therefore, methods to solving this problem are necessary to increase the lifespan of tribological components used offshore and therefore potentially save costs. One approach to solve the problem of lubricant contamination is the use chelating agents as additives in the lubricant. Chelating agents such as ethylenediaminetetraacetic acid (EDTA) can efficiently catch the bivalent metal cations present in the lubricant and therefore allow surface-active molecules (i.e. carboxylic acids) to freely adhere to the tribological contact area [15].

Therefore, this study aims at investigating the role of carboxylic acid chain length on frictional and wear performance of water-based lubricants with and without the presence of bivalent metal cations. In addition, a strategy involving EDTA chelation allowing the capture of the bivalent metal cations will be presented and explained in detail.
2 Experimental procedure

2.1 Materials

Carboxylic acids with hydrocarbon chain length varying from 10 to 18 carbon atoms were used for the tests. Decanoic acid with 10 C atoms (99% purity and a molar mass of 172.26 g mol⁻¹), dodecanoic acid with 12 C atoms (≥99%, 200.32 g mol⁻¹), tetradecanoic acid with 14 C atoms (≥99%, 228.37 g mol⁻¹), hexadecanoic acid with 16 C atoms (≥99%, 256.42 g mol⁻¹) and octadecanoic acid with 18 C atoms (≥98.5%, 284.48 g mol⁻¹) were used as received (Sigma Aldrich) without further purification.

Water-based lubricants were prepared with a mixture of approx. 50 wt.% of distilled water, 40 wt.% of ethylene glycols, amines and a thickener to reach the dynamic viscosity of 60 mPa s at 40 °C. For the tribological tests (friction and wear performance), carboxylic acids of various chain lengths were added to the water-glycol lubricant at 0.05 wt.% and 0.1 wt.%, and in some cases, up to 0.5 wt.%.

As it is seen in the service life of offshore components, the excessive wear of hydraulic cylinders is often initiated through the exposure of hydraulic components to the seawater environment. Therefore, in order to understand the influence of lubricant contamination with seawater, a separate batch of lubricants consisting of approx. 50 wt.% of distilled water, 40 wt.% of ethylene glycols, amines, thickeners and 0.1 wt.% or 0.25 wt.% of C12-dodecanoic acid was prepared. Subsequently, synthetic seawater was added to the fully formulated lubricant and the critical threshold of seawater concentration at which the depletion of carboxylic acid was defined. The synthetic seawater was prepared according to the ASTM D1141-98 (Table 1). In order to avoid the formation of carboxylic acid salts precipitates (i.e. depletion of the friction modifiers), a chelating strategy using ethylenediaminetetraacetic acid (EDTA) was selected to complex the bivalent metal ions present in the lubricant contaminated with seawater. For this 1 wt.% of EDTA (99%, Alfa Aesar) was added to the lubricant containing C12-dodecanoic acid and artificial seawater.

Tribological tests were carried out on substrates made of super duplex stainless steel (SDSS) machined from grade UNS S32750 sheet and subsequently grinded and polished to obtain a surface finish of Rₐ=0.13 μm. Prior to each test, the steel samples were ultrasonically cleaned in ethanol for ten minutes, subsequently rinsed with fresh ethanol and dried with pressurized air.

Table 1 Composition of the synthetic seawater according to ASTM D1141-98.

<table>
<thead>
<tr>
<th>Chemical substance</th>
<th>Chemical formula</th>
<th>Concentration (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Chloride</td>
<td>NaCl</td>
<td>24.53</td>
</tr>
<tr>
<td>Magnesium Chloride</td>
<td>MgCl₂</td>
<td>5.20</td>
</tr>
<tr>
<td>Sodium Sulfate</td>
<td>Na₂SO₄</td>
<td>4.09</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>CaCl₂</td>
<td>1.16</td>
</tr>
<tr>
<td>Potassium Chloride</td>
<td>KCl</td>
<td>0.695</td>
</tr>
<tr>
<td>Sodium Bicarbonate</td>
<td>NaHCO₃</td>
<td>0.201</td>
</tr>
<tr>
<td>Potassium Bromide</td>
<td>KBr</td>
<td>0.101</td>
</tr>
<tr>
<td>Boric Acid</td>
<td>H₃BO₃</td>
<td>0.027</td>
</tr>
<tr>
<td>Strontium Chloride</td>
<td>SrCl₂</td>
<td>0.0025</td>
</tr>
<tr>
<td>Sodium Fluoride</td>
<td>NaF</td>
<td>0.003</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>988.968</td>
</tr>
</tbody>
</table>

2.2 Testing and characterization methods

A unidirectional ball on disc wear test rig (Phoenix tribology) was used to evaluate the boundary lubrication performance of the water-based lubricants. In this configuration, a polished alumina ball with a diameter of 6 mm was pushed against the SDSS plate with a free-weight load. The ball was subjected to a normal load of 30 N corresponding to an effective maximum contact pressure of 2 GPa (Hertz elastic contact equations). To ensure that the boundary lubrication conditions are met, all tests were performed
with a low surface velocity set to 0.26 cm/s. Tribotests performed with the water-based lubricant without carboxylic acids served as a reference. All lubricant formulations were tested at a constant bulk temperature of 25 °C. The duration of the tribological tests was set to 30 min each. Average and standard deviation of data points were calculated and plotted for the last 15 min of the each test. At least three experiments were performed for each condition to verify the repeatability of the tests. The wear volume was quantified with Alicona Infinite Focus optical 3D microscope. Subsequently the specific wear rate was calculated with Archard’s equation:

\[ k = \frac{V}{FS} \]

Where:
- \( k \) – specific wear rate [mm³/Nm]
- \( V \) – volume loss [mm³]
- \( F \) – normal load [N]
- \( S \) – Sliding distance [m]

The investigation of the wear track topography and its cross section was performed with FEI Helios NanoLab DualBeam Scanning Electron Microscope (SEM) and Focused Ion Beam (FIB) respectively. The SEM images were acquired with Everhart–Thornley Detector (ETD) and accelerating voltage of 10 kV. Prior to milling, a protective carbon layer was deposited on the area of 32 × 8 µm² on the surface which is seen as a bright stripe on the top of the FIB images. The deposition of the protective carbon layer, milling and polishing of the wear track was done with the use of gallium liquid metal ion source. More information regarding cross-section preparation can be found elsewhere [16].

Adsorption investigation of carboxylic acids was performed by employing spread-coating technique [17][18][19]. In a previous paper published by the same authors, a thorough adsorption study of all friction modifiers used in this work has been presented [20]. In this work, ethanol with high volatility and polarity was selected to represent water-based lubricant, while dodecanoic acid was selected as a representative friction modifier [20]. During the testing, a droplet of 100 µl of 0.1 wt.% of a C12-dodecanoic acid in ethanol (analytical reagent grade obtained from VWR Chemicals) solution was injected and spread coated on an atomically smooth and freshly cleaved mica surface (Agar Scientific, Stansted, UK). In addition, a separate set of samples was prepared by following the same method to study the influence of seawater contamination on the adsorption mechanisms of carboxylic acids. For this a 0.1 wt.% of C12-dodecanoic acid was mixed with ethanol and synthetic seawater (1 wt.%, 2 wt.% or 4 wt.%). To understand the role of the chelating agent, a 1 wt.% of EDTA was also added to the sample containing 4 wt.% of seawater. After the spread coating technique, the solutions were kept on the mica surface for 120 s and subsequently removed with the use of nitrogen gas and inspected with Atomic Force Microscopy (FLEX AFM, Nanosurf AG). Surface topography images were acquired with tapping mode, using silicon rectangular cantilever with 190 kHz resonance frequency and 58 N/m spring constant. Measurements were repeated several times in order to confirm the repeatability of the experiments.

3 Results

3.1 Effect of carboxylic acid chain length and concentration on friction and wear

The effect of the carboxylic acid hydrocarbon chain length on friction and wear was tested under harsh boundary conditions (i.e. 2 GPa initial contact pressure and 0.26 cm/s sliding speed). Lubricants were formulated by mixing the base fluid (water, ethylene glycol, organic thickener and amines) with 0.05 and 0.1 wt.% of carboxylic acids. The friction and wear results are presented in Figure 1. It can be observed that the base lubricant without any friction modifiers showed the poorest frictional characteristics. For this particular case, the coefficient of friction reached a value of 0.41 while for lubricants additized with
carboxylic acids other than C10-decanoic acid the coefficient of friction was reduced by approximately 70% (i.e. COF of 0.13). As already published and thoroughly explained in a previous work by the same authors, an increase of the hydrocarbon chain length of the carboxylic acids had a great influence on the frictional performance of the fluid [20]. The reason for ineffective lubrication of C10-decanoic acid is the insufficient length of the carboxylic acid molecule with a combination of its low concentration. Very short carboxylic acids with 10 carbon atoms length are not able to promote multilayer formation leading to higher frictional forces due to low surface separation. On the other hand, lengths of C12-dodecanoic acid and above are sufficient enough to activate the friction reduction mechanism (via multilayer or micelle formation) of the carboxylic acid, however the large standard deviation for C12 at 0.05 wt.% indicates that the concentration might be too low for this carboxylic acid. A steady state of friction achieved for lubricants additivated with C14, C16 and C18 indicates the optimal concentrations and operational conditions of the lubricant.

On the other hand, wear brings slightly different results than friction and it is investigated for the first time in this work. Wear of the steel plate tested only with the base lubricant showed its poor anti-wear characteristics, reaching a wear rate of approximately $2.57 \times 10^{-4}$ mm$^3$/Nm. Despite the very clear decrease in friction, wear was found to be at the same level as the base lubricant for the shorter carboxylic acids (C10 to C14) at both concentrations. However, a visible decrease in wear rate was found when using carboxylic acids with the longest hydrocarbon tails (C16 and C18). Here for the lower concentration of carboxylic acids (0.05 wt.%) the C18-octadecanoic acid, reduced the specific wear rate by approximately 36% ($1.6 \times 10^{-4}$ mm$^3$/Nm) as compared to the base lubricant, while for the lubricants with higher concentration (0.1 wt.%) of C18-octadecanoic acid, the specific wear rate was reduced by 53%.

![Figure 1](image_url)

**Figure 1** The influence of various carboxylic acids on friction and wear of SDSS. Tests performed under 2 GPa contact pressure, 0.26 cm/s sliding speed, 0.05 and 0.1 wt.% concentration of carboxylic acids and at room temperature.

This concentration dependency of the carboxylic acids (C16 and C18) on the wear rate shows that different mechanisms are playing a role in wear as compared to friction. While friction is mostly driven by the adsorption and hydrocarbon chain length of the carboxylic acids onto the metal surface as already discussed in [20], the anti-wear performance is mostly affected by the concentration and the hydrocarbon chain length of the acids. This latter phenomenon might indicate that the carboxylic acid micelles formation...
might be playing an important role. Micelle formation was already discussed in our previous work focusing mostly on friction performance [20], however the effect was not as clear as it is for wear. Indeed, when carboxylic acids are exposed to polar fluids, specially water, they are prone to the formation of micelles having a dependency with concentration and chemistry (i.e. the presence of metal ions and pH enhances micelle formation) [21][22]. Table 2 shows the critical micelle concentration for each of the tested carboxylic acids and as clearly seen, for shorter carboxylic acids, micelles form only at the highest concentration, whereas for longer carboxylic acids (C16 and C18) lower concentrations are enough. Therefore, to show the effect of micelle formation on wear performance, shorter carboxylic acids like C12-dodecanoic at a concentration exceeding the CMC (i.e. 0.5 wt.% from Table 2) were tested. The results of this test are shown in Figure 2, where it is clearly visible that the highest concentration of C12-dodecanoic acid has an effect on wear performance of the fluid. In this test, by increasing the concentration of the carboxylic acid above the CMC value, a 40% wear reduction was achieved as compared to the base lubricant and was at a similar level as the C16 and C18 carboxylic acids.

Table 2 Critical micelle concentration of carboxylic acids in aqueous solutions. Adapted from [21].

<table>
<thead>
<tr>
<th>Carboxylic acid</th>
<th>Concentration (mM)</th>
<th>CMC (mM)</th>
<th>0.05 wt.%</th>
<th>0.1 wt.%</th>
<th>0.5 wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10 – Decanoic acid</td>
<td></td>
<td>24</td>
<td>2.9</td>
<td>5.8</td>
<td>29.0</td>
</tr>
<tr>
<td>C12 – Dodecanoic acid</td>
<td></td>
<td>12</td>
<td>2.5</td>
<td>5.0</td>
<td>25.0</td>
</tr>
<tr>
<td>C14 – Tetradecanoic acid</td>
<td></td>
<td>13</td>
<td>2.2</td>
<td>4.4</td>
<td>21.9</td>
</tr>
<tr>
<td>C16 – Hexadecanoic acid</td>
<td></td>
<td>2.8</td>
<td>2.0</td>
<td>3.9</td>
<td>19.5</td>
</tr>
<tr>
<td>C18 – Octadecanoic acid</td>
<td></td>
<td>0.45</td>
<td>1.8</td>
<td>3.5</td>
<td>17.6</td>
</tr>
</tbody>
</table>

Figure 2 The influence of carboxylic acid (C12) concentration on wear performance.

Error! Reference source not found. Figure 3 shows SEM images of the worn area on a SDSS tested with unadditivated base lubricant and additivated with 0.05 wt.% and 0.1 wt.% of all carboxylic acids tested in this work. The topography of the wear track produced in the course of a tribological test lubricated with unadditivated fluid, indicates an adhesive wear mechanism. Moreover, traces of abrasive grooves with some delaminated regions can be found. On the other hand, completely different wear mechanism is found for the steel substrate tested in the fluid additivated with carboxylic acids. In this case, a clear smooth and uniform ploughing-like wear marks with signs of plasticity are visible. This indicates a clear effect of the
Carboxylic acid on wear in the boundary regime. Moreover, wear reduction seen as a decrease of the width of the wear track is strongly highlighted for carboxylic acids with longer hydrocarbon chain.
Figure 3 Wear track morphology of SDSS specimens tested with pin-on-disc apparatus with both base lubricant and lubricant additivated with 0.05 wt.% and 0.1 wt.% of various different carboxylic acids. Tests performed under 2 GPa contact pressure, 0.26 cm/s sliding velocity and at room temperature.

The wear mechanisms were further analysed by cross-section analysis of the wear tracks perpendicular to the sliding direction using FIB (Figure 4). For this, SDSS sample tested in a base lubricant was compared with a sample tested in lubricant additivated with 0.05 wt.% of C18-octadecanoic acid. It can be observed that the combination of the high contact pressures (2 GPa) and shear forces resulted in a subsurface grain recrystallization of the steel substrates for both lubricants. However, as expected, a thicker and finer recrystallized area was found for the test performed with the unadditivated lubricant (base lubricant). For the unadditivated lubricant, the highly refined grain zone has a thickness of approximately 3 µm. It is therefore in agreement with higher shear forces measured during the tests (i.e. higher friction) which resulted in high shear strain accumulation in the subsurface region. At the same time for the tests performed with the additivated lubricant (i.e. 0.05 wt.% C18-carboxylic acid) the thickness of the grain refined zone was 1 µm indicating lower amount of energy supplied to subsurface region (i.e. lower friction and wear measured).

Figure 4 FIB cross section analysis of the wear tracks of SDSS specimens tested with pin-on-disc apparatus with both base lubricant and lubricant additivated with 0.05 wt.% of C18-octadecanoic acid. Tests performed under 2 GPa contact pressure, 0.26 cm/s sliding velocity and at room temperature.

3.2 Adsorption mechanisms of C12-dodecanoic acid in the presence of EDTA and seawater

Many components operating in the splash zone of offshore vessels are constantly exposed to seawater, which might get into the sliding contact and interact with the lubricant. Indeed, it is well known
the very detrimental effect of seawater when in contact with friction modifiers such as carboxylic acids due to the formation of carboxylic salts [23]. The formation of these salts results in a “deactivation” of the friction modifying effect of the carboxylic acids due to a depletion, and therefore a desorption, from the metal surface thus increasing frictional forces [14]. One of the solutions allowing carboxylic acids to operate under seawater offshore conditions is the addition of complexing agents (i.e. chelates), such as ethylenediaminetetraacetic (EDTA). Chelates, and more specifically EDTA, are able to react with bivalent metal ions such as Ca\(^{2+}\), Mg\(^{2+}\) and Mn\(^{2+}\) forming a complex that impedes the reaction of the metal ions with the carboxylic acid.

In order to visualize the chelating performance of the lubricant contaminated with seawater, the spread coating technique and atomic force microscopy were used to investigate the adsorption and desorption mechanisms. In this study, atomic force microscopy (AFM) was used to image the adsorption/desorption behaviour of carboxylic acids (C12-dodecanoic acid) dissolved in ethanol mixed with seawater and EDTA on the mica surface (Figure 5). It can be seen that when only 0.1 wt.% of C12-dodecanoic acid was dissolved in ethanol, carboxylic acids adsorbed to the mica surface in the form of islands. The mechanism of island formation was strongly influenced by the addition of seawater. In this case, adding 1 wt.% of seawater to the solution (Figure 5b), caused precipitation of the salt and its deposition on the mica surface in the form of dendrites. When seawater concentration was slowly increased, adsorbed molecules of carboxylic acids decreased the tendency of island formation (Figure 5c) and finally at the highest concentration of the seawater, the island formation was almost completely suppressed by the crystallization and adsorption of salts on the mica surface (Figure 5d). Interestingly, the process of carboxylic acid island formation was again restored by adding 1 wt.% of EDTA to the solution containing 4 wt.% of seawater (Figure 5e).

**Figure 5** AFM topography images (scan area: 5 µm × 5 µm) showing the effect of artificial seawater addition on the adsorption of 0.1 wt.% of C12-dodecanoic acid in a) ethanol, b) ethanol and 1 wt.% seawater, c) ethanol and 2 wt.% seawater, d) ethanol and 4 wt.% seawater, e) ethanol, 4 wt.% seawater and 1 wt.% of EDTA.
3.3 Effect of seawater, EDTA and carboxylic acid concentration on friction and wear

The AFM study clearly showed the effect of chelants on the adsorption/desorption mechanisms of the carboxylic acids onto the mica surface (Figure 5). This phenomenon should have consequences in the friction and wear ability of the carboxylic acids. In order to study the effect of seawater and chelants on the friction and wear ability of the carboxylic acids in the lubricant, pin on disc tests of the lubricant formulated with different concentrations of C12-dodecanoic acid, with and without the presence of different concentrations of artificial seawater and 1 wt.% EDTA were performed in boundary conditions. The friction and wear results are shown in Figures 6 and 7 respectively.

The results plotted in Figure 6 show that the addition of 1 wt.% EDTA efficiently suppresses the reaction of the carboxylic acid with the bivalent metals up to a 10 wt.% of seawater. For the two lubricant formulations (0.1 and 0.25 wt.% wt. of C12-dodecanoic acid) contaminated with seawater, the results showed a rise in friction when increasing seawater concentration. At the same time, it was observed that the onset of frictional increase can be postponed by increasing the concentration of carboxylic acid (0.25 wt.%). However, regardless of this improvement, their performance will decrease with time in industrial applications where seawater is involved, since the long operation time of the tribological systems will imply more seawater intake. As consequence, an increase in the concentration of bivalent metal cations in the lubricant implies a desorption of the carboxylic acid molecules from the metal surface eventually increasing friction and therefore leading to power losses of the system.

Surprisingly, when adding seawater to the system the wear results indicate that the lubricant possesses better anti-wear ability than the fully formulated lubricant both with and without 1 wt.% of EDTA (Figure 7).

![Graph showing the effect of seawater and EDTA on friction and wear](image)

**Figure 6** The effect of lubricant contamination with artificial seawater on the friction performance of the lubricants additivated with 0.1 and 0.25 wt.% C12-dodecanoic acid. Tests performed under 2 GPa contact pressure, 0.26 cm/s sliding velocity and at room temperature.
Figure 7 The effect of base lubricant (BL) contamination with 10 wt.% of artificial seawater on the wear performance of the lubricants additivated with 0.1 wt.% of C12-dodecanoic acid (C12) and 1 wt.% of EDTA. Tests performed under 2 GPa contact pressure, 0.26 cm/s sliding velocity and at room temperature.

4 Discussion

4.1 Effect of sweater contamination on friction

Tribological tests performed in this study have shown the importance of the carboxylic acid chain length on the frictional and wear performance on the SDSS in the aqueous media. This observation is possible due to the polar extremity of the carboxylic acid molecule, which allows the carboxylic acid to adsorb onto the metallic surface by forming self-assembled mono- or multilayers or even micelles [24][25]. Indeed, when the shortest carboxylic acids (C10-decanoic acid) were used, the frictional improvement was almost negligible as compared to the base fluid. This result can be explained by the very low surface coverage of C10-decanoic acid [20]. At the same time using carboxylic acids with the hydrocarbon chain length longer than 10 carbon atoms allowed to successfully reduce friction of water-based lubricant to the value of 0.14. Similar results were obtained by Jahanmir [26][27] who also reported a better frictional performance of longer carboxylic acids.

When a lubricant is additivated with carboxylic acids, the driving force for frictional reduction lies on the ability of the carboxylic acids to adsorb onto the surface of mating components. As long as the concentration of carboxylic acid is higher than the concentration of metal cation dissolved in the lubricant, a positive effect on friction can be seen (Figure 6). At the same time, by increasing the concentration of bivalent metal ions like Ca$^{2+}$, Mg$^{2+}$ or Mn$^{2+}$ (seawater), the adsorption ability of carboxylic acids to the steel surface decreases. This behaviour is explained by the formation of polyelectrolyte complexes between metal ions dissolved in the lubricant and the carboxylic acid molecules (Figure 8). The formation of such complexes hinders the ability of the acid to adsorb onto the surface. Even though it was found that some metallic salts tend to reduce the coefficient of friction [28], under the studied conditions such a frictional reduction was not achieved.
In order to mitigate the influence of seawater on the frictional performance of the fluid, a chelating strategy using EDTA was performed. As seen in Figure 6, EDTA has efficiently improved the frictional performance of the fluid containing seawater by suppressing the depletion onset of the carboxylic acid from the metal surface. EDTA can form four or six bonds with metal ions. The number of bonds that EDTA can share with metal ions is mostly attributed to the pH of the solution. In this study due to the high concentration of amines in the lubricant solution, the pH of formulated fluids was in the range of 9.5±0.5. Under these alkaline conditions, the deprotonation of the four carboxylic acid groups of the EDTA molecule occurs, thus causing the EDTA to have four extra unpaired electrons. As shown in Figure 9, EDTA exhibits multiple coordination groups, and therefore can form 1:1 metal-chelator complexes [29].

As mentioned above, in the lubricating condition where seawater is added to the lubricant containing carboxylic acids, the most probable reactions are between carboxylic acids and Mg$^{2+}$ or Ca$^{2+}$ bivalent ions. The addition of EDTA to a lubricant containing seawater and carboxylic acids will cause it to react with bivalent ions present in the solution avoiding the neutralization of the negative charge of the carboxylate ion. Under such conditions, EDTA acts as an effective chelator for the bivalent ions and can be used safely [30][31]. A schematic illustration of the adsorption of carboxylic acids in the presence of metal ions and EDTA is presented in Figure 10.

![Chemical structure of metallic salts (magnesium, calcium, manganese) of carboxylic acids.](image)

**Figure 8** Chemical structure of metallic salts (magnesium, calcium, manganese) of carboxylic acids.

![Chemical structure of deprotonated EDTA molecule at pH of 9.5 and its complexation with metal ion M in 1:1 stoichiometry.](image)

**Figure 9** Chemical structure of deprotonated EDTA molecule at pH of 9.5 and its complexation with metal ion M in 1:1 stoichiometry.
In order to estimate the critical threshold of seawater concentration at which a frictional increase is likely to happen, a calculation was made for different cases and it is presented in Figure 11. In this calculation, an assumption determining that each of the bivalent ions in the solution react with two carboxylic acid molecules was made. In addition, in order to calculate the critical seawater concentration for which 1 wt.% of EDTA is not sufficient to compensate the cationic charge of the bivalent ions, the reaction ratio between bivalent metal and chelator was set to 1:1. For the calculations of the number of bivalent cations present in the seawater, a concentration specified in ASTM D1141-98 standard were used. As seen in Figure 11, the threshold for depletion of all carboxylic acids present in a lubricant consisting of only 0.1 wt.% of C12-dodecanoic acids is approximately 3 wt.% of seawater. The results fall in agreement with the experimental data shown in Figure 6. Exact reproducibility of results was also reported for higher concentration (0.25 wt.%) of C12-dodecanoic acid. The calculation also indicates that the addition of the EDTA to the lubricant allowed it to operate under 30 wt. % and 36 wt.% of seawater for 0.1 wt. % of C12 and 0.25 wt. % C12 respectively. Unfortunately, the chelating performance of EDTA cannot be maintained for higher concentrations of bivalent metal ions. In this case, the concentration of EDTA should be increased or additional system for filtration of the seawater should be considered.
0.10 wt.% C12
0.25 wt.% C12
0.10 wt.% C12 + 1 wt.% EDTA
0.25 wt.% C12 + 1 wt.% EDTA

Figure 11 Seawater threshold for the deactivation of carboxylic acids in various lubricants.

4.2 Effect of carboxylic acid length, concentration and seawater contamination on wear

Interestingly, the very similar frictional performance of lubricants additivated with C12, C14, C16 and C18 was not accompanied by similar wear loss, showing reduced wear only for the longest carboxylic acids and a higher concentration of C12 (Figures 1 and 2). There are two possible explanations for these phenomena: (1) attributed to the formation of carboxylic acid multi-layer assembly and (2) carboxyl micelle formation in the presence of water and alkali media.

For the first hypothesis, a multilayer assembly might be strongly attached to the metal surface and weakly physically adsorbed to the next carboxylic acid monolayer [20]. Such a multilayer should provide with a reduction in friction due to low shear forces between multilayers and with sufficient surface separation to keep wear at a lower level than in a monolayer assembly. In addition, it has been shown that longer carboxylic acids might appear in the solution in the form of dimers, held together by the hydrogen bonds, thus providing higher separation of the mating components [32] [33] [34]. Such a thick multilayer assembly might generate enough surface separation to limit the asperities of the counter surfaces. Whereas the reason for the ineffective wear reduction of the shorter carboxylic acids at lower concentrations might lie in the insufficient surface coverage combined with the formation of monolayer assemblies [20]. However, when the concentration of the shorter carboxylic acids was significantly increased (0.5 wt.%), wear reached similar values as found for the longer carboxylic acids (Figure 2). This can be attributed to the multilayer formation as concentration increases however, the second hypothesis (micelle formation) becomes more plausible since the wear rate improved at same levels as friction only when the concentration of carboxylic acids exceeded the critical micelle concentration (CMC) (Table 2 and Figure 2). Indeed, in a previous paper by the same authors [20], the concentration and length of carboxylic acids and the amount of micelles formed in aqueous lubricant were closely related. This phenomenon might be the main reason for the lower wear rate since micelles are expected to be strong agglomerates of carboxylic molecules (specially in alkali media) and therefore can keep the separation of surfaces for much longer time than a multilayer of carboxylic acids, which is mostly an easy-shear assembly assisting low friction.

Interestingly, wear was highly reduced when the base lubricant consisting of 0.1 wt.% of C12-dodecanoic acid was contaminated with 10 wt. % of seawater as compared to the base lubricant consisting of only C12-dodecanoic acid (Figure 7). Seawater, containing a high concentration of Na ions, promotes the micellar aggregation by forming sodium dodecanoate. Micelles formed in the presence of Na ions are
more stable than the ones formed only in water and this is reflected in the lowest wear rate measured when seawater was added to the lubricant (Figures 2 and 7). Interestingly, Steigman et al. [22] showed that the critical micelle concentration of both cationic and anionic surfactants in water can be lowered by the addition of salts like NaCl, eventually leading to higher number of available micelles in lubricating systems. Therefore, the presence of micelles in the lubricant should not be neglected as the main factor to reduce wear since their bigger size will have a clear effect on the surface separation in the tribological contact. The effect of micelle formation on surface separation and thus wear rates are schematically presented in the illustration shown in Figure 12.

Figure 12 Schematic illustration of the wear mechanism of SDSS in aqueous solution a) unadditivated with C12-dodecanoic acid and b) additivated with C12-dodecanoic acid below CMC concentration and c) additivated with C12-dodecanoic acid above CMC concentration in water-based fluid.

SEM observations of the wear tracks from tests performed with unadditivated lubricant (Figure 3) show clearly an adhesive wear mechanism. Presumably due to the high shear forces, a rubbing-induced material transfer to the alumina counterpart appeared, thus causing localized adhesive bridges which further increased the resistance of the material to slide. In addition, a visible irregular surface indicates smearing-like action and formation of folds and cracks that promote detachment of the material. Under the same sliding conditions a different wear mechanism was seen for the stainless steel lubricated with C18-octadecanoic acid. In this case a predominant ploughing-like wear mechanism in combination with low frictional forces suggest either a thick multilayer assembly of carboxylic acids which only allow the asperities to get in contact in small areas or micelle formation which also promotes lower frictional forces. The FIB results (Figure 4) also confirmed the beneficial low-shear-strength of the carboxylic acid adsorbates either in the form of multilayer or multilayer assisted with micelles. The low-shear-strength of the carboxylic acid depressed the shear stresses which in consequence reduced the grain refinement in the subsurface of the steel counterpart. Similar behaviour was observed by Zavieh and Espallargas [9] who reported lower degree of recrystallization of the steel surface for lubricant additivated with hexadecanoic acid.

5 Conclusions

Saturated carboxylic acids with various hydrocarbon chain lengths were dissolved in a water-based lubricant. Their frictional and wear performance was studied under boundary lubricating conditions against SDSS on a pin-on-disc tribometer. The following conclusions can be drawn from this work:

1. Under boundary lubricating conditions an effective frictional reduction is achieved for carboxylic acids with a chain length longer than 12 carbon atoms.
2. The concentration of the shorter carboxylic acids in water-based systems plays a major role in reducing wear of the sliding components. While frictional reduction for the lubricants was already seen for the lowest tested concentrations (0.05 wt.%), the anti-wear performance was only seen
when the concentration of carboxylic acids exceeded critical micelle concentration. This confirms, that micelles play important role in separating counter surfaces.

3. In the case of the longer carboxylic acids (C16 and C18), the wear reduction was seen at both low and high concentration, which it is attributed mainly to the multilayer formation and partly to the micelle formation.

4. Lubricants additivated with carboxylic acids are susceptible to harmful effects of seawater contamination (i.e. the presence of bivalent metal ions), which can deactivate its friction-reduction ability. As long as the concentration of carboxylic acid is higher than the concentration of metal ions dissolved in the lubricant, a positive effect on friction can be seen.

5. Chelating agents, such as EDTA, are successful in preventing the harmful effects of seawater contamination in the frictional performance of carboxylic acids. AFM technique showed that the adsorption of carboxylic acids decreases with increasing concentration of seawater and can be reversed by the addition of EDTA. EDTA combines with metal cations through its two amine groups and four carboxylate groups. The salt-immune behavior of lubricants modified with EDTA can be a potential solution for minimizing negative effects of the seawater.

6 Acknowledgments

This research was sponsored by the Norwegian Research Council (NFR NANO2021). The Research Council of Norway is also acknowledged for the support to the Norwegian Micro- and Nano-Fabrication Facility, NorFab.

7 References


