

Friction mechanisms by carboxylic acids in aqueous lubricants

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Abstract

Carboxylic acids are well known for their friction-reducing abilities driven by the formation of low-shear-strength films on the steel surface. However, understanding of the adsorption mechanisms especially in polar solvents is yet not well explored. In this work Atomic Force Microscopy (AFM) was used to visualise the adsorption behaviour of various carboxylic acids in both polar and less-polar solvents. The work was continued with a tribological study of the lubricants additivated with carboxylic acids in a laboratory scale ball-on-disc tribometer. During this study, the effect of concentration and carboxylic acid chain length was studied in polar media (water-based lubricants) and compared with commonly used synthetic non-polar lubricant (poly- α -olefin, PAO). It was observed that for both polar and less-polar lubricants, surface coverage of carboxylic acids increased with increasing length of hydrocarbon tail. In less-polar lubricants carboxylic acids adsorbed to the surface by spreading on it evenly, whereas in polar lubricants very dense multi-layered formation was promoted. Friction reduction achieved with the use of carboxylic acids in the non-polar lubricant was not as efficient as in the case of the polar lubricant. This was associated with the more pronounced multilayer formation of carboxylic acids in the polar lubricants, facilitating higher friction reduction as compared to the adsorption of carboxylic acids in a dense monolayer form seen in the less-polar lubricant.

Keywords: Aqueous lubrication, PAO, boundary additives, carboxylic acid, polarity

1 Introduction

In tribological systems, a significant amount of energy is lost due to the high frictional forces and the wear of sliding components. It has been estimated that more than 5% of the gross national product losses of industrialized countries can be related to friction and wear [1]. To minimize these costs, mineral or synthetic lubricants are used. However, many concerns have been raised due to their biodegradability, health or other environmental aspects, setting a target to develop new lubricants fulfilling more restrictive environmental criteria. It would seem like substituting classical mineral or synthetic oils with water-based lubricants is environmentally beneficial with a much lower cost. Nevertheless, despite the fact that water is the main lubricating media in human body and in many offshore hydraulic systems, aqueous lubricants have not gained much popularity due to their low viscosity and poor corrosion performance in most engineering systems [2][3]. However, developments of new water-based additives like pour-point depressants, friction modifiers, viscosity improvers, corrosion inhibitors and anti-wear additives have permitted formulation of lubricants for a wide range of applications [4][5][6][7]. Since the frictional characteristics of water-based lubricants are almost entirely attributed to water-soluble additives whose composition is constantly being improved [5][8][9][10][11][2], friction modifiers are the most crucial additives, ultimately affecting the decision of selecting specific lubricants.

On the other hand the increased focus on energy efficiency and environmental safety poses new challenges for lubricant formulators, restricting the use of certain chemistries such as zinc, phosphor, sulphur or chlorinated additives [12]. Therefore, taking into account these restrictions only a few environmentally acceptable additives are available in the market. One of the examples is carboxylic acids, which are well known for reducing friction under boundary conditions. The mechanism of friction reduction lies in its amphiphilic nature. These additives tend to physisorb on metallic surfaces by forming a thin mono or multilayer assembly preventing true contact between the sliding counterfaces of a mechanical moving system [13][14]. When certain conditions are met, such an assembly may generate an easy slip plane thus reducing frictional forces. This phenomenon has been exploited to design various lubricious coatings [15][16], however in the presence of high loads most of the organic coatings tend to fail, therefore a need for developing new environmentally acceptable additives which are more versatile should still be prioritized.

Carboxylic acids as friction modifying additives fulfilling environmental criteria have attracted many interests [17][18][19][20][21][22][23], however due to its importance in industrial applications, a mineral oil has been a typical choice as base lubricant to study their performance. As a general rule, the adsorption of a carboxylic acid to the steel surface is driven by physisorption or chemisorption of the acid group to iron oxides and hydroxides present on the surface. The way carboxylic acids adsorb to the surface is strictly dependent on the activation sites, temperature or lubricating media (base fluid). At room temperature carboxylic acids (R-COOH) tend to physisorb by formation of hydrogen bonds with the surface atoms, whereas when carboxylic acids are deprotonated forming carboxylate anions (R-COO⁻), chemisorption with the formation of iron carboxylates in a monodentate form can be expected [24][25]. Some studies also report that carboxylic acids can bond both oxygens from the carboxyl group with the iron atoms of the surface and thus forming a bidentate configuration [26]. Most of these studies have also shown that the adsorbed amount of carboxylic acid decreases as the number of double bonds (unsaturation) in the hydrocarbon chain increases [27]. This indicates that more efficient surface packing is observed for saturated hydrocarbon chains and therefore better surface protection should be expected for straight molecules.

Interestingly, the concept of using carboxylic acids as friction modifying additives in polar lubricants has not been well studied. This might be explained by the fact that the solubility of carboxylic acids in polar (i.e. aqueous) media decreases with increasing hydrocarbon chain length. This is not desirable since the tribological performance of a lubricated system with carboxylic acids is improved for longer carboxylic chains. Therefore, this implies the use of carboxylic acids consisting of less than 16 carbon atoms as friction modifiers in polar (aqueous) lubricants. Whereas carboxylic acids consisting of 18 carbon atoms are

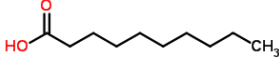
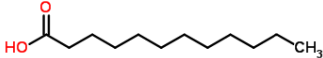
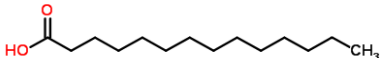
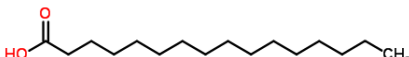
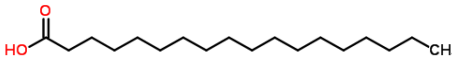
typically chosen in non-polar lubricants. Naturally, a question should be raised if shorter carboxylic acids with a specific concentration could effectively reduce friction in polar (aqueous) media. At the same time, one can expect that the friction reduction related to the adsorption mechanism of carboxylic acid will change due to the high polarity of aqueous solution as compared to the nonpolar solvents (i.e. mineral oils). Therefore, it is the aim of this paper to study the adsorption and the friction reduction mechanisms of carboxylic acids in polar media (i.e. water-based lubricants) and compare it with commonly used synthetic non-polar lubricants (i.e. poly- α -olefin PAO).

2 Experimental procedure

2.1 Materials

Straight-chain (saturated) carboxylic acids with chain length varying from 10 to 18 carbon (C) atoms were used for the tests (Table 1). Capric acid with 10 C atoms (99% purity, molar mass of 172.26 g mol⁻¹ and density of 893 kg/ m³), lauric acid with 12 C atoms ($\geq 99\%$, 200.32 g mol⁻¹, 880 kg/ m³), myristic acid with 14 C atoms ($\geq 99\%$, 228.37 g mol⁻¹, 862 kg/ m³), palmitic acid with 16 C atoms ($\geq 99\%$, 256.42 g mol⁻¹, 853 kg/ m³) and stearic acid with 18 C atoms ($\geq 98.5\%$, 284.48 g mol⁻¹, 941 kg/ m³) were purchased from Sigma Aldrich and used as supplied without further purification.

Table 1 Molecular structure and chemical formula of the carboxylic acids used in this study.

IUPAC name	Other names	Chemical formula	Molecule structure
Capric acid	C10 - Decanoic acid	CH ₃ (CH ₂) ₈ COOH	
Lauric acid	C12 - Dodecanoic acid	CH ₃ (CH ₂) ₁₀ COOH	
Myristic acid	C14 - Tetradecanoic acid	CH ₃ (CH ₂) ₁₂ COOH	
Palmitic acid	C16 - Hexadecanoic acid	CH ₃ (CH ₂) ₁₄ COOH	
Stearic acid	C18 - Octadecanoic acid	CH ₃ (CH ₂) ₁₆ COOH	

Type-C water-based hydraulic fluid (HFC) was formulated by mixing distilled water, glycols, amines and organic thickener in accordance to ISO 12922:2012, to reach the dynamic viscosity of 58 mPa s (500 s⁻¹ shear rate at 40 °C). For the tribological tests, carboxylic acids of various chain lengths were added to the water-glycol fluid at 0.05, 0.1 and 0.5 wt.% concentrations.

The non-polar base oil investigated in this study was poly- α -olefin (PAO, hydrogenated oligomers of 1-decene, purchased from Sigma Aldrich) with a viscosity of 42 mPa s. For the tribological tests, carboxylic acids of various chain lengths were added to the PAO at 0.05, 0.1 and 0.5 wt% concentrations.

The ethanol and acetone of analytical grade used for the adsorption study was acquired from VWR Chemicals and used without further purification. Extremely even and flat (RMS roughness of ca. 0.1 nm) muscovite mica surface (Agar Scientific, Stansted, UK) was used for the spread-coating (adsorption) study. Prior to each experiment a mica surface was freshly cleaved with the use of adhesive tape, and immediately spread coated with the solution of carboxylic acids in ethanol or acetone.

For the tribological testing, substrates made of super duplex stainless steel (SDSS) machined from grade UNS S32750 sheet were used. The plates were ground and polished to obtain a surface finish of R_a=0.03 μ m. Prior to each test, the steel substrate was ultrasonically cleaned in ethanol (analytical reagent

grade acquired from VWR Chemicals) for ten minutes, subsequently rinsed with fresh ethanol and dried with pressurized air.

2.2 Testing and characterization methods

The dynamic viscosity of formulated lubricants was measured with a rheometer (Haake Mars Rotational Rheometer with a CC27 cylinder measuring system, with built-in Peltier element) at 40 °C in humid air. During the test, the shear rate was increased from 0.01 to 500 s⁻¹ and was then held at a constant shear rate of 500 s⁻¹ for 30 seconds. The reported viscosity was measured by calculating the average value of 15 measurements taken after reaching a constant shear rate of 500 s⁻¹. The shear ramp time was set to 180 seconds before and after testing.

The spread-coating technique [28][29][30] was employed to study the adsorption characteristics of carboxylic acids. In this study, ethanol with relative polarity (to water) value of 0.654 was selected to represent polar solvents, while acetone with 0.355 relative polarity value was selected to represent less-polar solvents [31]. For this technique, a preheated to 40 °C droplet of 100 µl of 0.1 wt.% of a carboxylic acid solution in ethanol or acetone was poured and spread on a freshly cleaved mica surface. After a specific incubation time the solution was gently removed with the use of nitrogen gas, leaving the adsorbed layer intact. In this work, the incubation time was set to 120 s for ethanol and 10 s for acetone. The incubation time was reduced from 120 s to 10 s in acetone due to the rapid surface coverage seen subsequently on the AFM. A FLEX AFM (Nanosurf AG) was employed to image the surface coverage of the various carboxylic acids on the atomically smooth mica sheets under ambient conditions. All images were recorded in tapping mode, using silicon cantilevers (spring constant of 58 N/m, resonance frequency of 190 kHz) and repeated several times with different samples and tips. Surface coverage and island height were calculated using the average height acquired from histogram of a given image.

For the tribological tests, carboxylic acids with the chain length varying from 10 to 18 carbon atoms were added to HFC type lubricant (water-glycol) or PAO. Prior to each test, the lubricant was preheated to 40 °C to increase the solubility of carboxylic acids. Tribotests with unadditivated lubricant (i.e. no addition of carboxylic acid) served as a reference. A pin-on-disc tribometer (Phoenix tribology) with a ball on disc unidirectional configuration was used, where a polished alumina ball with a radius of 3 mm was pushed against the SDSS plate with a free-weight load. The ball was loaded with a specific weight to achieve 2 GPa maximum initial contact pressure (Hertz elastic contact). In order to study mixed and boundary frictional characteristics of formulated lubricants the sliding velocity was set to 2.6 cm/s at room temperature. The duration of the 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 test. At least three experiments were performed for each condition to verify the repeatability of the tests.

3 Results

3.1 Adsorption study

Originally, polished SDSS surfaces were used for the adsorption study, however due to the high surface roughness exceeding $R_a > 10$ nm (i.e. exceeding the thickness of the single monolayer of a C10-decanoic acid) it was decided to substitute the steel surface with atomically smooth mica surface. This change, allowed to observe the adsorption of short chain carboxylic acids with AFM. Therefore, all of the adsorption experiments presented in this study were performed on mica surfaces. Prior to the adsorption experiments, freshly cleaved mica surface was scanned with the AFM after spread-coating of pure ethanol and acetone to confirm the absence of adsorbed species. Subsequently similar images were recorded for carboxylic acids dissolved in ethanol and acetone solvents, representing the groups of polar and less-polar solvents. The adsorption characteristics of carboxylic acids in polar solvents (0.1 wt.% of a carboxylic acid solution in ethanol) with chain length varying from 10 to 18 carbon atoms, prepared by the spread coating technique is shown in Figure 1. It is clearly visible that all the carboxylic acids have a tendency to adsorb on the mica surface by forming stochastically distributed islands (bright regions) with the height varying

from 1.3 nm (capric acid – C10) to 50 nm (palmitic acid – C16). Due to the thickness of islands formed by the carboxylic acids longer than 10 carbon atoms, it is clear that they adsorb to the surface by forming a very dense multi-layered structure. Since the length of the stretched capric acid (C10) molecule is 1.7 nm (calculated from Van der Waals diameters), it can be concluded that it is adsorbed to the mica surface in a monolayer form with the hydrocarbon chain normal to the surface. Interestingly C12-lauric acid adsorbs to the surface with islands of greater size than any other carboxylic acid. Indeed, by keeping constant the weight concentration of the carboxylic acids the number of adsorbates is influenced. It was therefore, calculated that at 0.1 wt.% concentration, 40% less molecules of stearic acid (C18) as compared to the capric acid (C10) were present in the solution (Table 2). Despite that fact, no significant increase in adsorption rate or surface coverage was observed for the higher number of capric acid molecules.

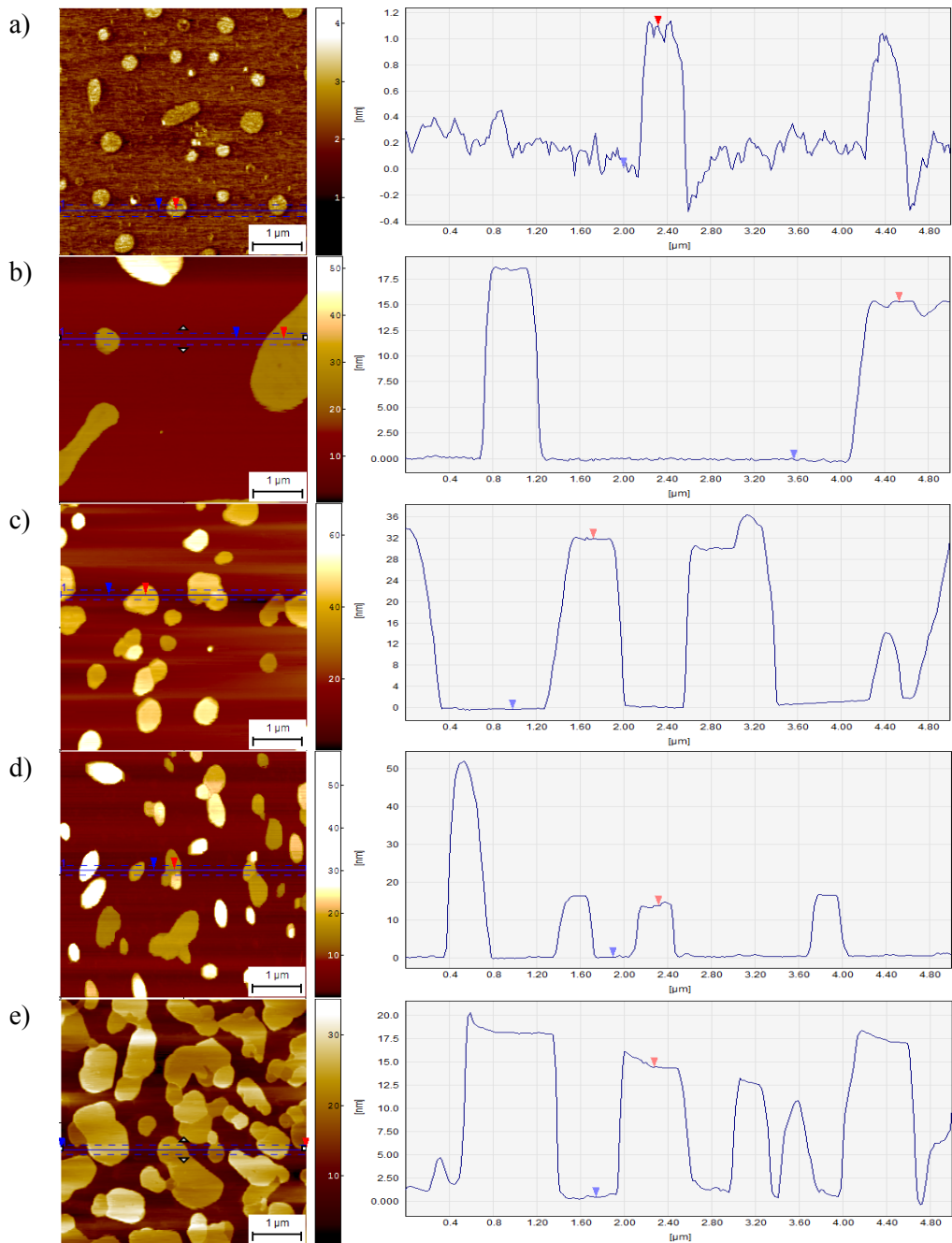
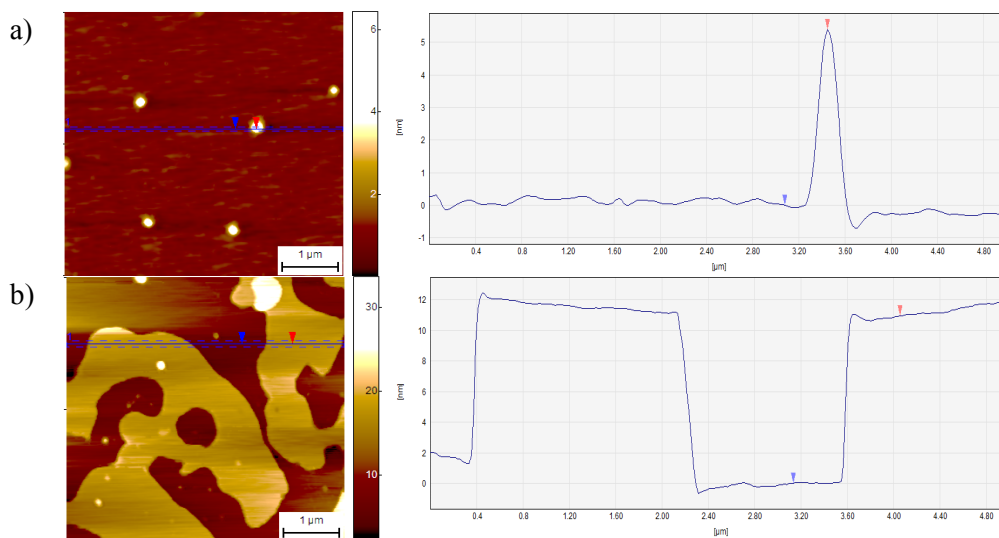


Figure 1 AFM topography images (scan area: 5 $\mu\text{m} \times 5 \mu\text{m}$) of adsorbed carboxylic acids prepared by spread coating technique in ethanol with an incubation time of 120 s using 0.1 wt.% (a) C10-capric acid, (b) C12-lauric acid, (c) C14-myristic acid, (d) C16-palmitic acid and (e) C18-stearic acid-ethanol solutions, and corresponding section analysis. In order to enhance the differences between different carboxylic acids, the scale of each graph has been adjusted to its maximum height.

Table 2 Weight concentration to mmol/l conversion.

Carboxylic acid	Concentration					
	wt. %	mmol/l	wt. %	mmol/l	wt. %	mmol/l
C10 – Capric acid	0.05	2.9	0.1	5.8	0.5	29.0
C12 – Lauric acid	0.05	2.5	0.1	5.0	0.5	25.0
C14 – Myristic acid	0.05	2.2	0.1	4.4	0.5	21.9
C16 – Palmitic acid	0.05	2.0	0.1	3.9	0.5	19.5
C18 – Stearic acid	0.05	1.8	0.1	3.5	0.5	17.6

The AFM images of adsorbed carboxylic acids from less-polar solvent (acetone) are presented in Figure 2. It is clear that both polar and less-polar solvents are promoting adsorption of carboxylic acids in the form of islands, however the adsorption is faster in the case of less-polar solvents. For this particular reason, the incubation time of carboxylic acids in acetone was reduced from 120 s to 10 s. Despite this, the surface coverage of carboxylic acids in acetone surpassed the one in ethanol (Figure 2 and 4 (b)). Interestingly in the case of less-polar solvents the islands are spreading without a significant increase in height. The overall height of the islands is similar for all of the carboxylic acids (12 nm) apart from capric acid (C10) that is 5 nm. Since the height of the islands is higher than the length of carboxylic acid molecules it can be assumed that multilayer formation takes place in the less-polar solvent for all carboxylic acids tested. In addition, a similar trend as in the case of polar solvent, was seen for the C12-lauric acid which has also adsorbed to the surface in the shape of islands that merged together to form large clusters.



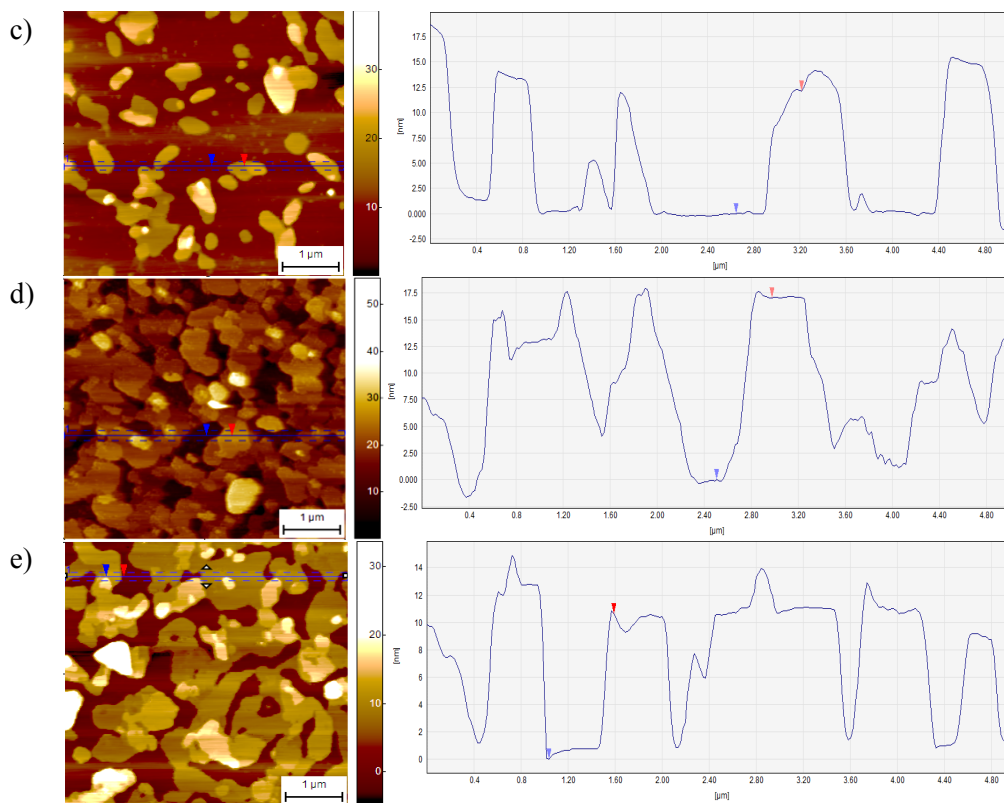


Figure 2 AFM topography images (scan area: $5\ \mu\text{m} \times 5\ \mu\text{m}$) of adsorbed carboxylic acids prepared by spread coating technique in acetone with an incubation time of 10 s using 0.1 wt.% (a) C10-capric acid, (b) C12-lauric acid, (c) C14-myristic acid, (d) C16-palmitic acid and (e) C18-stearic acid-acetone solutions, and corresponding section analysis. In order to enhance the differences between different carboxylic acids, the scale of each graph has been adjusted to its maximum height.

Additionally, the multilayer binding mechanism of carboxylic acid was significantly reduced by the less-polar solvent demonstrating that the polarity of the lubricant plays an important role in the multilayer build-up and eventually in the frictional reduction. Indeed, the AFM adsorption study for the less-polar solvent was reduced from 120 s to 10 s (Figure 4) and one might expect that in the long term the multilayer formation will be facilitated. However, additional set of experiments performed with longer incubation time confirmed that the carboxylic acids in the less-polar media had a higher tendency to spread on the mica surface than to form multilayers (Figure 3) confirming that the higher solubility of the acids in the PAO promotes surface coverage rather than multilayer formation.

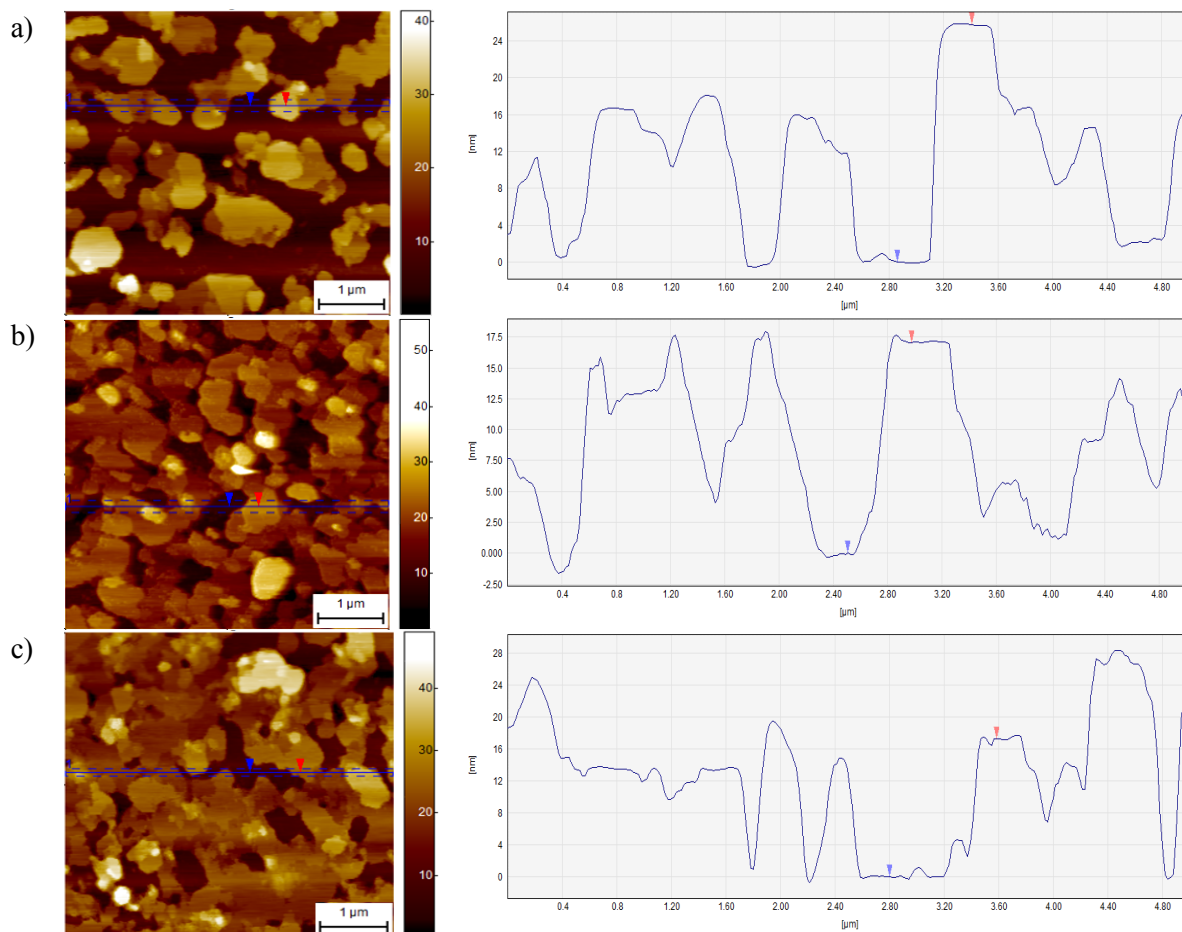


Figure 3 AFM topography images (scan area: $5 \mu\text{m} \times 5 \mu\text{m}$) of adsorbed carboxylic acids prepared by spread coating technique in acetone with an incubation time of a) 5 s b) 10 s and c) 20 s using 0.1 wt.% C16-palmitic acid, and corresponding section analysis.

The surface coverage and island height of adsorbed carboxylic acids from polar and less-polar solvents measured as a function of the carbon chain length is shown in Figure 4. The AFM data in the polar solvent (ethanol) (Figure 4 (a)) indicates that the surface coverage is the lowest for C10-capric acid (7.5%) and increases linearly with the hydrocarbon tail length, reaching maximum of 48.5% for C18-stearic acid. Interestingly an opposite trend is seen for the island height where the height of the island tends to decrease for carboxylic acids longer than 12 carbon atoms. On the other hand, for the less-polar solvent (acetone) (Figure 4 (b)), the surface coverage increases faster than in the case of the polar solvent (ethanol) reaching maximum coverage of 75% for the longest stearic acid (C18). In the case of the island height a constant height of ca. 12 nm is achieved for carboxylic acids with more than 12 carbon atoms and 5 nm is achieved for the shortest carboxylic acid (capric-C10). In all cases this can be accounted as multilayer arrangement, but with less number of molecules in the stacks than in the case of the polar solvent.

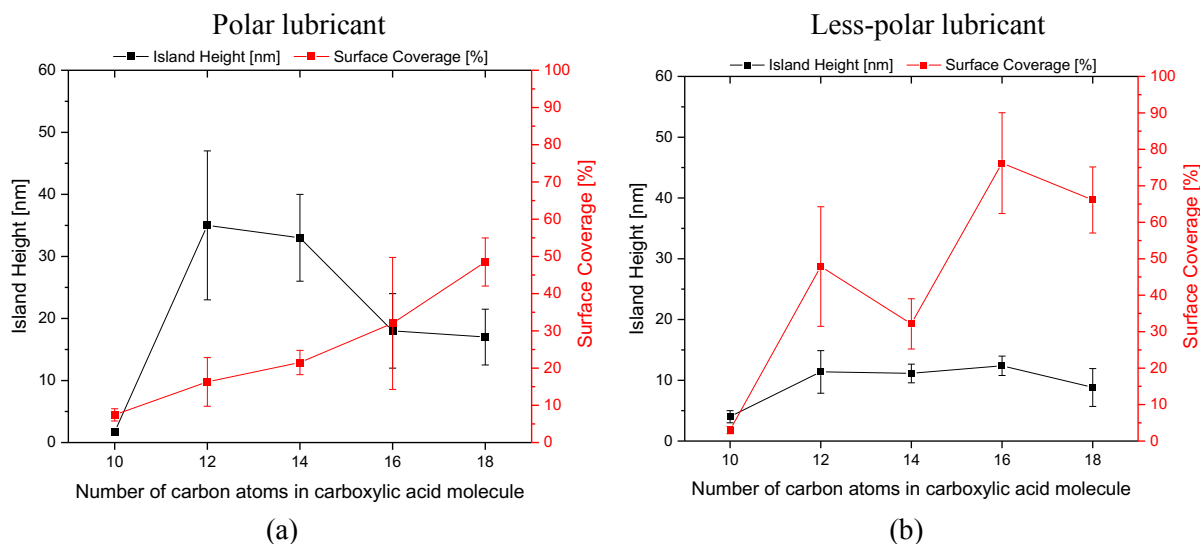


Figure 4 Surface coverage and island height versus carboxylic acid chain length. Carboxylic acids prepared by spread coating technique using 0.1 wt.% of carboxylic acid in ethanol (polar) with an incubation time of 120 s (a) and in acetone (less-polar) with an incubation time of 10 s (b).

It would be reasonable to state that the frictional behaviour of the carboxylic acid is not simply explained by the polarity of the base lubricant or the surface coverage of the reactive species, but rather by the number of adsorbed molecules onto the surface. Therefore, a calculation of number of molecules that adsorbed onto $1 \mu\text{m}^2$ during the incubation time of 120 s for the polar solvent and 10 s for the less-polar solvent has been performed (Figure 5). The calculations were done by analysing the volume of occupied space in a $25 \mu\text{m}^2$ area and the volumetric density of the carboxylic acids. In addition, the number of monolayers were analysed by dividing the island height by the actual length of the fully stretched carboxylic acid molecule, assuming that acids are arranged with their long-axis perpendicular to the surface and are not tilted. The following lengths were used for the calculations: 1.57 nm for C10-capric acid, 1.85 nm for C12-lauric acid, 2.05 nm for C14-myristic acid, 2.3 nm for C16-palmitic acid and 2.56 nm for C18-stearic acid. The length of the carboxylic acid molecules was calculated using the MarvinSketch software from Van der Waals diameters.

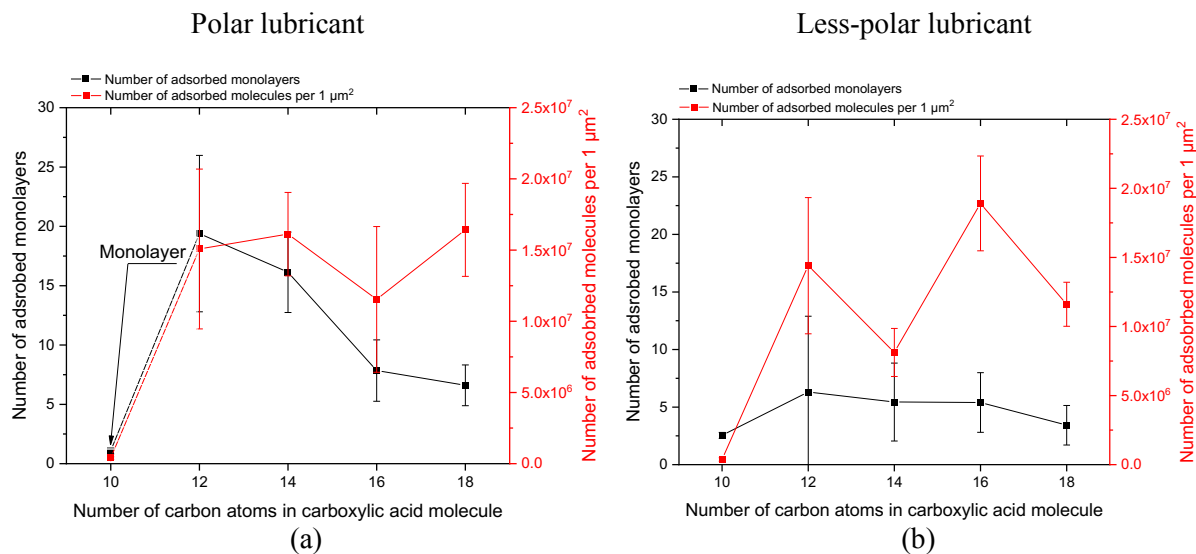


Figure 5 Number of adsorbed molecules and corresponding adsorbed monolayers for the different carboxylic acids for the polar solvent (a) and less-polar solvent (b).

As seen in Figure 5 (a) a multilayer formation for carboxylic acids with more than 10 carbon atoms for the polar solvent is found at the carboxylic acids concentration used in this adsorption study. However, the number of adsorbed monolayers decreases with increasing the number of carbon atoms, whereas the surface coverage increased (Figure 4 (a)). Therefore, it can be assumed that for longer carboxylic acids, a faster transportation of the carboxylic acid molecules to the surface-active sites occurs, but less molecules are attracted to the previously formed carboxylic acid monolayer. One might thus assume that as soon as the metal surface is covered with the first layer of the carboxylic acid, the process of adsorption becomes slower for longer carboxylic acids because of their lower solubility in the polar solvent. Figure 5 (a) also shows that for carboxylic acids other than C10-capric acid almost a similar number of molecules is involved in the adsorption even though the surface coverage is increasing.

The adsorption of carboxylic acids in less-polar solvent seems to be more effective in densely covering the surface within a shorter time (Figure 4 (b)), but the number of adsorbed molecules in the same area is similar to what was observed for the polar solvent (Figure 4 (b)). However, worth noticing is the different incubation times, i.e. for 10 s in acetone the same number of molecules adsorb on the surface as for 120 s in ethanol. As seen in figure 3, as incubation time increases the thickness of adsorbed layers does not increase. The islands are spreading but without increasing thickness. Therefore, in the non-polar lubricant it should be expected more molecules as time increases but without a thick multilayer formation. This might be a drawback since it seems from the frictional results (Figure 6) that both high surface coverage and thick multilayer aggregation must be met in lubricants modified with carboxylic acids in order to facilitate lower friction.

3.2 Tribological testing

The effect of carboxylic acid on the frictional reduction of the sliding pair was tested under harsh boundary conditions (i.e. 2 GPa initial contact pressure and 2.62 cm/s sliding speed). Lubricants were formulated at different carboxylic acid concentrations (0.05, 0.1 and 0.5 wt.%) in both polar (water-based) and non-polar (PAO) lubricants. During the formulation in the water-based lubricant, it was observed that as the chain length increased cloudy lubricants were obtained when using the highest concentrations. This indicates that the solubility of the carboxylic acids in water decreases with the carboxylic chain length as described in [32]. Also important to take into account is the critical micelle concentration (CMC) for the

carboxylic acids in the aqueous media [32]. According to literature [33], for the concentration of 0.5 wt.% the CMC is reached for all of the used carboxylic acids and therefore the micelles formation is expected (Table 3). Under the boundary lubrication, micelle generation might also have a detrimental effect on the frictional performance of the system. As shown by the Gilad et. al [34] surfactants can enormously reduce friction when dissolved in aqueous lubricants by forming micelles or bilayers maintaining high integrity even at high pressures.

Table 3 Critical micelle concentration of carboxylic acids in aqueous solutions.

Carboxylic acid	Concentration used (mM)					
	Temp (°C)	CMC (mM)	0.05 wt.%	0.1 wt.%	0.5 wt.%	
C10 – Capric acid	27	24	2.9	5.8	29.0	No micelles
C12 – Lauric acid	27	12	2.5	5.0	25.0	
C14 – Myristic acid	27	13	2.2	4.4	21.9	Micelles
C16 – Palmitic acid	27	2.8	2.0	3.9	19.5	
C18 – Stearic acid	27	0.45	1.8	3.5	17.6	

The friction as a function of carboxylic acid concentration in polar lubricants is presented in Figure 6(a). When only the base lubricant (i.e. free of carboxylic acids) was used, the coefficient of friction was approximately 0.31. The frictional forces of the tribological system were efficiently reduced when introducing a small quantity of carboxylic acid with a chain length longer than 12 carbon atoms. Indeed, C10-capric acid only reduces friction at the highest carboxylic acid concentration (i.e. 0.5 wt.%). This trend is also found for the C12-lauric acid however, the lowest concentration still reduces friction although not as efficiently as for the longest chains. As the carboxylic acid chain length increases, a clear tendency of reducing the coefficient of friction is found for low concentrations (0.05 and 0.1 wt.%). This is not surprising given the fact that longer hydrocarbon chains resulted in the formation of a multilayer of carboxylic acids on the surface (Figure 4 (a)). For the highest concentration of carboxylic acids almost constant coefficient of friction was achieved for all of the carboxylic acids, being most relevant for the shorter carboxylic acids. This might be related to the fact that at 0.5 wt. % concentration we might be well above the CMC and therefore micelles of the carboxylic acids might be forming in the lubricant [33]. Interestingly, if micelles were created at the highest concentration, they would be beneficial for the frictional response. This could be attributed to the formation of macromolecules at the interface that would more efficiently separate the sliding surfaces.

The effect of carboxylic acid concentration on frictional behaviour in the non-polar lubricant is presented in Figure 6 (b). It is shown that the coefficient of friction of base lubricant (PAO) reaches a value of 0.35 exhibiting slightly poorer frictional performance as compared to unadditivated water-based lubricants (Figure 6 (a)). At the same time the coefficient of friction is significantly reduced by the addition of carboxylic acid almost independently of their concentration. However, slight better performance for C14-myristic and C16-palmitic at the lowest concentration (0.05 wt.%) was observed. Frictional reduction increased with carboxylic acid chain length and was most efficient for C18-stearic acid. This trend was similar to the results found for the polar lubricant. In addition, it was found that frictional performance of carboxylic acids in the non-polar lubricant is not as efficient as for the polar lubricant since friction is always higher for the PAO lubricant. A good example is C10-capric acid at the highest concentration, which for PAO only reduced the friction from 0.35 to 0.27, whereas for the aqueous lubricant the coefficient of friction was reduced from 0.31 to 0.14. For the water-based lubricant the lowest coefficient of friction was achieved by the C18-stearic acid and was in the range of 0.1 to 0.14 depending on the concentration. At the same time the lowest value of coefficient of friction for the non-polar lubricant was in the range of 0.15 to 0.17 for the same C18-carboxylic acid. These results might in fact confirm that the concentration dependency on the formation of multilayers or macromolecules (i.e. micelles) in the polar lubricant is an important parameter to take into account to adjust the good lubricating performance of water-based

lubricants. Therefore, although the surface coverage kinetics in the polar lubricant are slower or less efficient than in the less-polar lubricant this is not detrimental for the frictional performance since the thickness of the interfacial shear layer seems to be playing a more important role for reducing friction rather than the fast replenishment of the worn contact area. Indeed, the fast surface coverage kinetics in the less-polar lubricant are most relevant for the longest carboxylic acids and therefore C18-stearic acid is the optimal length for obtaining the best frictional performance in the less-polar lubricant.

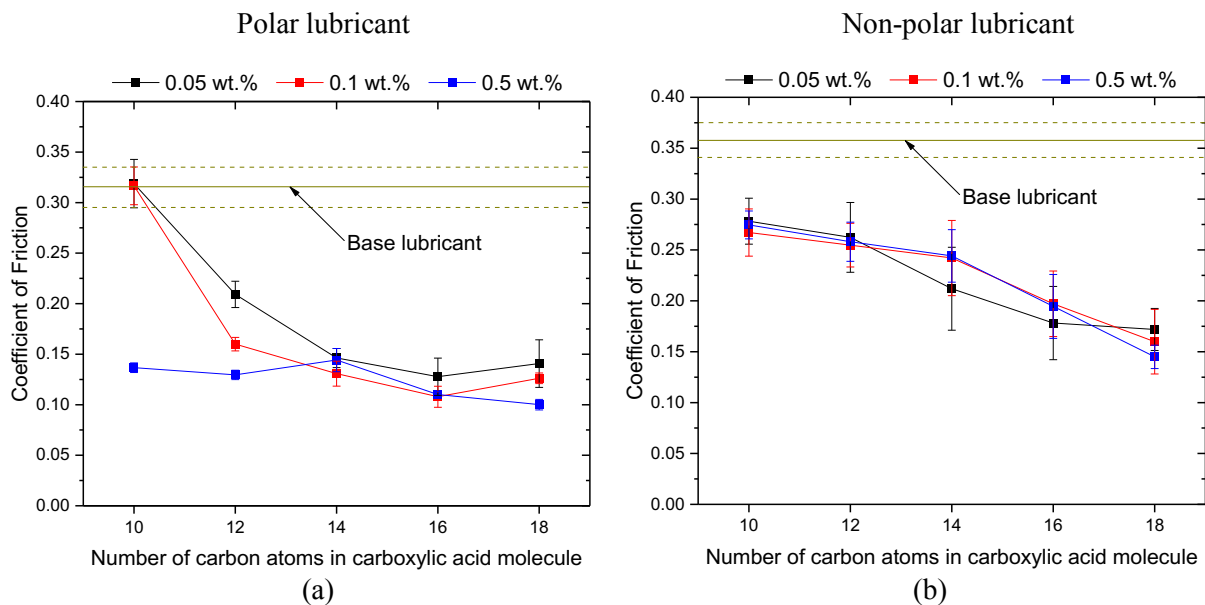


Figure 6 The influence of various carboxylic acids and their concentration on the coefficient of friction of water based lubricant (a) and PAO lubricant (b). Tests performed under 2 GPa contact pressure, 2.62 cm/s sliding velocity and room temperature.

4 Discussion

4.1 Solubility of carboxylic acids

As mentioned above, during the formulation of the water-base lubricant it was observed that as the hydrocarbon chain length increased, the solubility of the carboxylic acid decreased (i.e. increase of the hydrophobicity) therefore, cloudy lubricants were obtained when using C16-palmitic and C18-stearic acids, especially at the highest concentration (0.5 wt.%). The solubility of carboxylic acid in both polar and non-polar media can be explained as a result of the competition between the polar head and non-polar hydrocarbon tail. While the polar carboxylic acid group (head) is mainly responsible for good solubility of the carboxylic acid in aqueous media, its non-polar hydrocarbon chain impedes its solubility in that media. Therefore, the longer the hydrocarbon chain, the more dominant is the non-polar behaviour of the carboxylic acid molecule and thus the lower the solubility in water media (Figure 7). This phenomenon was not observed when preparing the non-polar lubricant (PAO) since carboxylic acids are fully soluble in that media. In addition, the concentration is also a factor to take into account in the solubility of additives in polar lubricants. Therefore, the concentration of the carboxylic acids needs to be carefully chosen since too low concentration will not allow the carboxylic acid to replenish the friction-damaged zone on time but, on

the other side, a too high concentration will cause the carboxylic acid not to dissolve completely in the base lubricant.

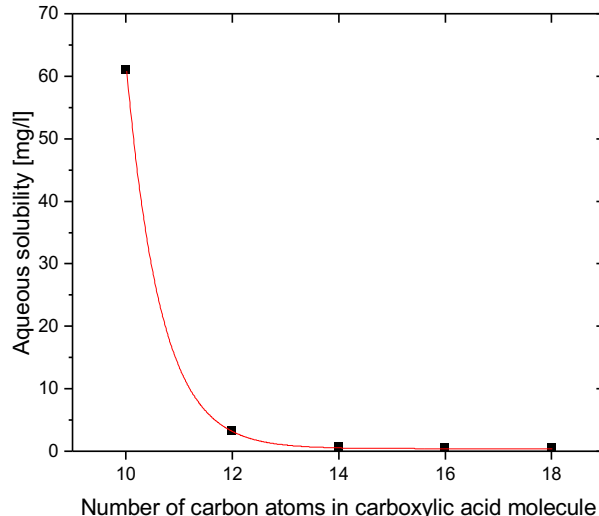


Figure 7 Aqueous solubility of carboxylic acids. Figure adapted from [32].

4.2 Adsorption mechanisms of carboxylic acids in polar and less-polar media

Carboxylic acids used as friction modifiers are suitable additives for boundary lubrication, due to their high mobility and affinity to the steel surface [35]. Depending on the sliding conditions they might physisorb or chemisorb to the surface forming very dense brush-like-structures that reduce friction between two mating counterparts. According to literature [35][24][26][36][37], adsorption of carboxylic acids to metal surfaces can be explained by the following mechanisms:

1. Carboxylic acid molecules surrounding the steel surface migrate to the surface-active sites by forming hydrogen bonds with the oxide or hydroxides present on the metal surface. Moreover, due to the dissociation of the carboxylic acid into a carboxylate anion and a proton, a chemical reaction of the surface metal atom (typically positively charged) and the carboxylate anion is possible. This would therefore cause the formation of the metal carboxylate in a monodentate form [24].
2. Another possibility is the formation of a bidentate configuration when a carboxylate head group is attached to the surface with both oxygen atoms [26].

This is mostly true when carboxylic acids are used in non-polar media. However, in this paper it has been found that changing the polarity of the media, affects the adsorption mechanisms of carboxylic acids and therefore influences frictional response of the system. The results obtained by the spread-coating technique in the AFM for different carboxylic acids on mica substrate in both polar and less-polar solvents showed a tendency of the acids to adsorb to the mica surface by forming islands (Figure 1 and 2). Since the mica surface is hydrophilic [36], it was tentatively assumed that all of the studied carboxylic acids adsorbed to the surface with its hydrophilic carboxyl group (head), thus stretching the hydrophobic chain outwards. Due to the amphiphilic nature of the carboxylic acid it can be assumed that a multilayer structure can be formed by facing together hydrophobic tail-hydrophobic tail or hydrophilic head-hydrophilic head of adjacent carboxylic acid molecules (Figure 8). Similar results were obtained by Yonghai et al. [30] who also showed that hexadecanoic acid formed multilayer assemblies while spread-coating to mica surface from ethanol. In addition, Terry A. [37] reported that the longer the hydrocarbon chain, the higher the degree of the hydrophobicity thus, the higher the affinity of the carboxylic acids to form multilayer arrangements. Interestingly, in this paper it has been observed that this behaviour is stronger in polar solvents as compared to less-polar ones. This might be attributed to the lower solubility of the hydrocarbon chains in the polar

solvent promoting a tail-to-tail interaction. In the case of the non-polar solvents the surface coverage is promoted since the hydrocarbon chains do not find an obstacle interacting with the base lubricant.

Indeed one need to keep in mind that the morphology of film obtained with a spread coating technique might vary from the adsorbed film in the fully formulated lubricant. This might be due to the different polarity of ethanol and acetone as compared to water and PAO, the possibility of micelles formation in aqueous fluids and external factors such as applied load and shearing forces [38].

Additionally, in the case of polar solvents, the pH was increased by the addition of amines (higher than pH 9). Knowing that the acid dissociation constant (pKa) of the carboxylic acids is equal or higher than 4.8 [39] and the fact that the pH of the lubricant exceeds 9, most of the carboxylic acids will dissociate in aqueous solution to form a carboxylate anion and therefore increasing the chance of carboxylates to chemisorb to the surface. Indeed, the composition of water-based and PAO lubricants was different, since the water-based fluid was additivated with corrosion inhibitor, glycols, and thickener. However, no effect of thickener nor amines was seen on the frictional performance of the fluid. However, some effect on the friction was seen when changing the glycol type for the lubricant formulation. Nevertheless, since in all formulated lubricants of this work the same ethylene-based glycol was used, this effect has been neglected. Therefore, the mechanisms for friction reduction in these two solvents/lubricants should be related to surface coverage and thickness of the carboxylic acid multilayers as function of carboxylic acid concentration, solubility and pH.

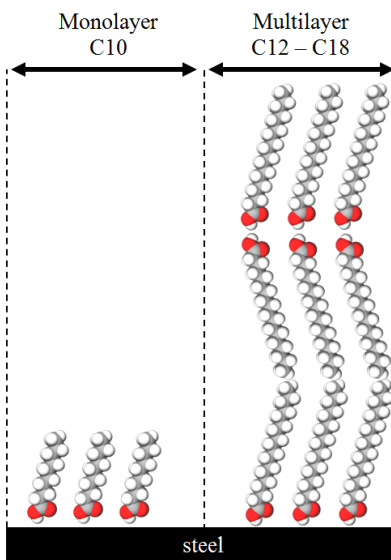


Figure 8 Schematic diagram showing mono or multi-layer formation of carboxylic acids.

Nevertheless, the mechanisms of adsorption were different for the polar and less-polar solvent. The monotonous increase in the surface coverage by longer carboxylic acids seen for both polar and less-polar solvents and the differences in the island height (Figure 4) indicate that besides the higher affinity of longer carboxylic acids to form multilayer structure they are also more reactive when binding with surface active sites depending on the media they are dissolved (polar or less-polar). In the case of water-based lubricant, carboxylic acids deprotonate and appear in the solution as carboxylate anions ($R-COO^-$), promoting chemisorption by the formation of iron carboxylates in a monodentate form. Whereas for the PAO lubricant, the carboxylic acids physisorb by forming hydrogen bonds with the metal surface atoms. Interestingly, the AFM adsorption study was performed with the same weight concentration for all carboxylic acids, meaning that the number of C10-capric acid molecules present in the lubricant was almost 40% higher than C18-stearic acid. However, a higher amount of C10-capric acid molecules did not improve its ability to adsorb to the surface nor to form a multilayer structure in the case of the polar lubricant at low concentrations (Figure 1).

4.3 Effect of carboxylic acid concentration on friction

During the testing of polar (water-based) lubricant, it was observed that the reduction of friction started to be visible for all of the lubricants where the concentration of carboxylic acids was exceeding 0.1 wt.%, while 0.05 wt.% was not satisfactory. Indeed, there was a significant difference in the number of molecules available in the solution for the same concentrations (weight %) of the different carboxylic acids, however this can be neglected since the concentration was only playing a role for very short carboxylic acids (C10, C12). This phenomenon is in fact related to the micelle formation in the polar lubricant, which is most relevant for shorter carboxylic chains at a constant concentration (see section 3.2). It is believed that to form a sufficient adsorbate film layer under lubricated sliding conditions in a polar lubricant, a minimum concentration of carboxylic acids is required due to their poorer solubility. Within a given concentration, a re-adsorption of surface active molecules (carboxylic acids) occurs between the successive sliding cycles thus reducing frictional forces [40]. Since the concentration of carboxylic acid necessary to reduce friction is decreasing for carboxylic acids with longer hydrocarbon tail, the frictional reduction was only seen for longer carboxylic acids (C14, C16 and C18) at all concentrations (Figure 6). For short carboxylic acids (C10), which at 0.1 wt.% concentration showed monolayer formation, concentrations above 0.5 wt.% were required to effectively reduce friction in the tribocontact region (Figure 6). However, this is in disagreement with what is found in literature of non-polar lubricants, since it is typically reported that a single monolayer of longer carboxylic acids (C18-stearic acid) can cause a substantial reduction in friction until the monolayer is removed [41]. A possible explanation for this phenomenon might be found in the AFM surface coverage results (Figure 4), where the longer carboxylic acids covered the surface more rapidly in the less-polar lubricant due to the low affinity of the base lubricant with the carboxylic acid polar group. At the same time for carboxylic acids with short hydrocarbon tail (i.e. highest solubility in aqueous media), the adsorption to steel surface in polar lubricants might be impeded due to the preferred dissolution of the carboxylic acid group as compared to their adsorption. In situations where low concentrations of carboxylic acids are used, a continuous adsorption-desorption process might take place, reducing the tribo-performance of the lubricant. In addition, at the highest concentration (0.5 wt.%) of carboxylic acids, the better frictional performance of the polar lubricant might be caused by the micelle formation. At this concentration, the CMC of the carboxylic acids might be well exceeded [32] and, in addition to the already adsorbed free carboxylic acids on the metal surface, adsorption of collapsed micelles might happen. Consequently, the thicker carboxylic acid film consisting of chemisorbed single molecules and micelles on the metal surface contributes to the better frictional characteristic of the lubricant at higher carboxylic acid concentration.

In less-polar solvents, the adsorption is quickly promoted due to the low affinity of the base lubricant with the polar head of the carboxylic acid molecule, causing an immediate replenishment of carboxylic acids on the damaged surface. Indeed, there was no effect of carboxylic acid concentration on friction for the non-polar solvent (Figure 6). This correlates with the much faster adsorption kinetics of the carboxylic acids in the less-polar lubricant and the thinner carboxylic acid film on the surface.

4.4 Friction mechanism by carboxylic acids in polar lubricants vs. non-polar lubricants

Carboxylic acids display an amphiphilic nature, making their frictional response dependent on the base lubricant (i.e. how they arrange on the surface of the metal). It was found in this work that the solubility of the carboxylic acids played an important role in their surface arrangement and also in the time needed for the surface to be covered in polar and less-polar base lubricants. Indeed, the results obtained in this study for the polar (water-based) lubricant show an improved frictional performance of carboxylic acids as compared to the non-polar (PAO) lubricant (Figure 6). This can be attributed to the fact that thicker multilayer arrangements (or micelle formation) are achieved in the water-based lubricant when carboxylic acid chains longer than 12 carbon atoms are used (Figure 5). Whereas in the case of the PAO, the predominant mechanism is based on a much more efficient surface coverage promoted by the high solubility of the hydrocarbon chains of the carboxylic acids in the lubricant (Figure 4). Interestingly, a study

performed by Bowden and Tabor [42], demonstrated the effect of different multilayer arrangements of C18-stearic acid on the frictional response in a non-polar lubricant. They found that the thickest multilayer film made of C18-stearic acid was more capable of maintaining low coefficient of friction for a longer number of sliding cycles than the monolayer arrangement (Figure 9). Therefore, the formation of a thick and homogeneous film should play a much predominant role on the frictional reduction than the surface coverage. Indeed, it was found in the present work that the shortest carboxylic acid chain (C10-capric acid) generated a monolayer of carboxylic acid on the surface (Figure 1) giving the highest frictional forces (Figure 6).

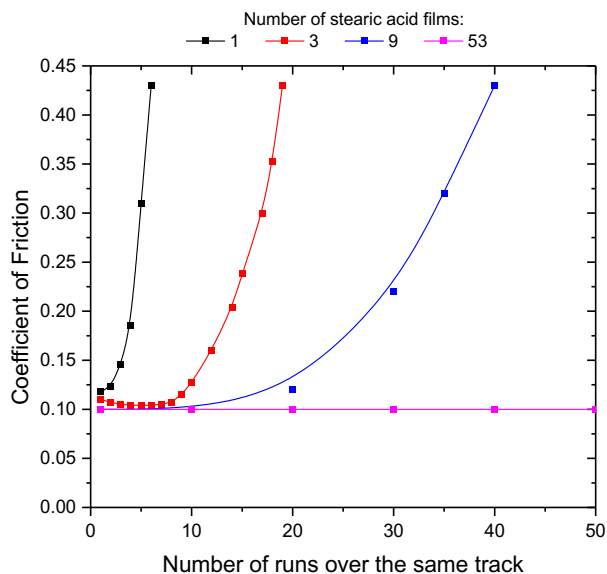


Figure 9 Frictional behavior of C18-stearic acid films deposited on stainless steel surface. Figure adapted from [42].

The reason why the surface coverage is much more efficient in the less-polar lubricant has been explained in previous sections. Main differences between the polar and the less-polar lubricants has been found in the generation a stronger adsorption of the carboxylic head to the metal surface allowing for a more efficient multilayer formation, rather than promoting surface coverage. In turn, the thicker-easy shear layer of carboxylic acids seen for polar lubricants results in better frictional reduction than thin layer seen for non-polar lubricants. The model depicted in the schematic of Figure 10 summarises the frictional mechanisms by carboxylic acids in polar (water-based) and non-polar (PAO) lubricants studied in this work. Worth noticing is the differences in the formation of the easy-shear layer of carboxylic acids when changing the concentration in the polar lubricant.

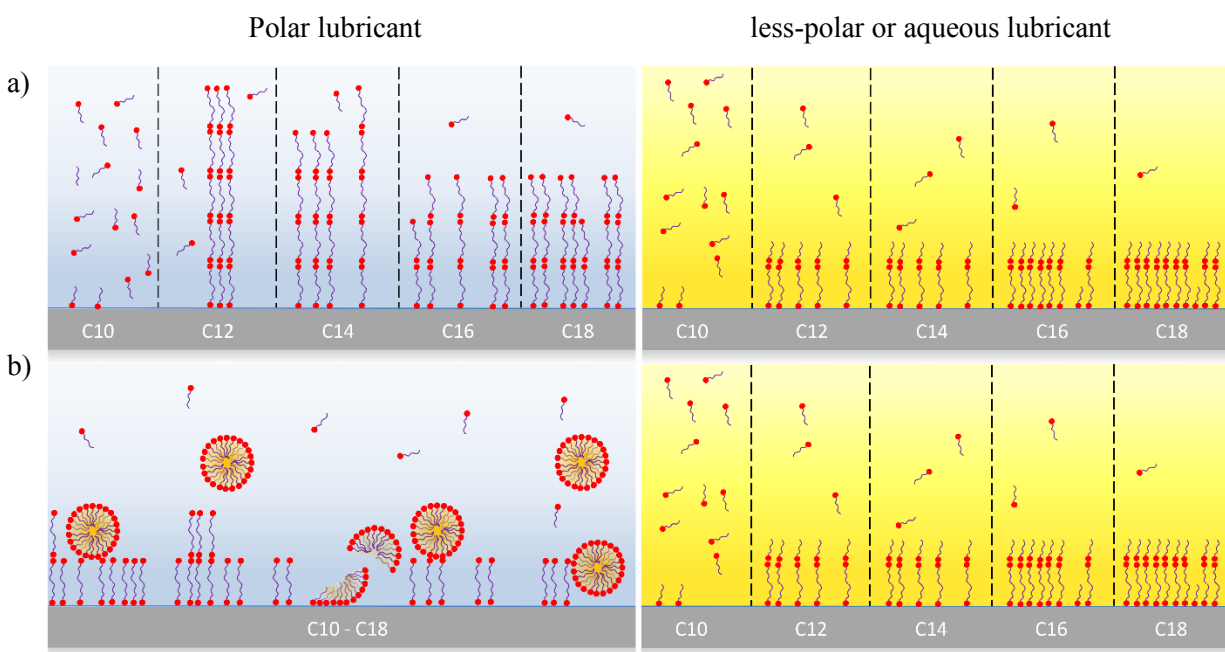


Figure 10 Molecular assemblies of carboxylic acids in polar and less-polar or aqueous lubricants at a) concentrations below the CMC and b) at concentrations exceeding the CMC for all carboxylic acids.

5 Conclusions

Saturated carboxylic acids with various chain lengths were dissolved in both polar (aqueous media) and non-polar lubricants (PAO). Their adsorption behaviour was studied with the use of AFM while frictional performance was studied using a pin-on-disc tribometer. The following conclusions can be drawn from this work:

1. Tapping mode AFM can be employed to study the adsorption ability of carboxylic acids with different chain lengths. It was observed that for both polar and less-polar solvents, surface coverage of carboxylic acids increases with longer hydrocarbon tail. In less-polar solvents, surface coverage is the predominant mechanism, whereas in polar solvents very dense multi-layered formation or even micelle (cluster) formation is promoted depending on the concentration of the carboxylic acid.
2. Adsorption of carboxylic acids of short hydrocarbon tail with high solubility in aqueous media is impeded due to the preferred dissolution of the carboxylic acid group as compared to their adsorption. In order to improve their tribo-performance a higher concentration should be used.
3. For the less-polar solvents, the adsorption and surface coverage of carboxylic acids on the surface are promoted over multilayer formation. In order to improve their frictional performance, carboxylic acids with long hydrocarbon tails (C16, C18) should be used.
4. Friction reduction achieved with the use of carboxylic acids in the non-polar lubricant was not as efficient as in the case of the polar lubricant. This is explained by the more important role of the thickness of the adsorbed species as compared to the surface coverage in the polar lubricant.
5. This study also showed that a minimum concentration is required to reduce friction in aqueous lubricants, which is dependent on the carboxylic acid chain length. Friction reduction activation is seen at a concentration as low as 0.05 wt.% for C14-C18 while at least 0.5 wt.% and 0.1 wt.% is needed for C10 and C12 respectively. Better frictional performance of carboxylic acids at the highest concentration (0.5 wt.%) might be also due to the contribution of carboxylic acids micelles/cluster formation.

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