

Mixed Lubrication with C18 Fatty Acids: Effect of Unsaturation

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Received: 28 August 2013 / Accepted: 21 November 2013 / Published online: 4 December 2013
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Abstract In this paper, the lubrication mechanism of fatty acids is revisited with a new approach combining experimental and computational chemistry studies. The lubricating properties of single and mixtures of stearic, oleic and linoleic acids in a synthetic Poly-Alpha-Olefin base oil (PAO4) on iron oxide surface are investigated under mixed boundary regime with temperatures from 50 °C up to 150 °C. Low friction coefficient (about 0.055) with no visible wear is reported in the presence of single stearic acid at high temperature. This lubricating behavior is inhibited in the presence of unsaturated fatty acids highlighting an anti-synergic effect of a saturated/unsaturated mixture, especially at 150 °C. To understand the anti-synergic effect and the adsorption mechanism of these molecules, molecular dynamic (MD) and quantum chemistry simulations are performed to evaluate their diffusion coefficient in PAO4 and their adsorption mechanism on iron oxide at different temperatures. MD simulation results show a faster diffusion toward the surface for unsaturated fatty acids than for saturated fatty acid at all the studied temperatures. This means that unsaturated molecules arrive and mainly adsorb before

stearic acid on the surface leading to a tribological behavior of the mixture characteristic of the unsaturated molecule. Computational chemistry suggests that all fatty acids (saturated and unsaturated) adsorption mechanism is due to the chemisorption of the carboxylic group on iron oxide surface with no desorption up to 150 °C.

Keywords Fatty acids · Mixed lubrication regime · High temperature · Computational chemistry

1 Introduction

Most of the traditional additives used in automotive lubrication, such as ZDDP and MoDTC, are considered as source of pollution and are accused to have a major contribution to environmental concerns. Nowadays, with the growing concern around the world on environment protection, these additives must be eliminated or progressively replaced with biodegradable molecules having the same efficiency while being friendly to the environment. In order to meet these requirements, automotive and oil industries are trying to develop new lubrication technologies based on biodegradable additives. Although they were largely used in the past in mineral oils and greases, fatty acids are now used as friction modifiers in fuels and synthetic lubricating oils and could be good candidates in mild wear conditions to meet the environmental concerns.

Over the years, many studies have proved the efficiency of fatty acids under certain operating conditions, and authors have proposed different lubrication models. In 1920, Well and Southcombe [1] have shown that the addition of a small amount of long-chain carboxylic acids to mineral base oils improves the boundary lubricating properties of a liquid lubricant. Few years later, Hardy [2]

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has proposed that boundary lubrication is favored by the adsorption of a close-packed monolayer of brush-like polar molecules of fatty acids on metal surfaces. He has shown that the friction is not only influenced by the chemical nature and the length of the molecule but also by the nature of the underlying surface. Nevertheless, Hardy model of boundary lubrication is very idealistic as the surface is never perfectly flat.

In the 40s, Bowden and Tabor [2] have proposed a new model where contacts between asperities were considered. They have suggested that the normal load is supported by the contact between the surface asperities and that the pressure generated by this contact disrupted the adsorbed monolayer.

Through the years, several authors have used different techniques and methods to validate their models by studying different parameters. In fact, the effectiveness of additives depends on their affinity toward the base oil as well as the properties of the material surfaces and the lubrication regime [3–14]. Among those parameters, several authors have showed the impact of the substrate material, especially the oxidation/hydroxylation sites of the surface [3–7]. In addition, the chemical structure of additives is a predominant factor that determines the attraction of molecules toward the surface. Regarding fatty acids, this includes the impact of the alkyl chain length [8, 9] and the influence of unsaturation [10–13]. It was shown that a minimum alkyl chain length is necessary to ensure the protection of the substrates against high friction and wear and that saturated fatty acids have better tribological behavior than unsaturated fatty acids [10–13]. For all types of fatty acids, the adsorption occurs through the acid group. It is of course necessary to take into account environmental conditions such as temperature, load and sliding speed [6, 13]. Recently, Simic and Kalin have proposed adsorption mechanisms of fatty acids molecules on steel surfaces by studying the effect of temperature, rubbing condition, exposure to air and moisture [14] as shown on Fig. 1. At initial state, the steel surface is partially covered by iron hydroxide and iron oxide. Depending on the activation sites, fatty acids can be physisorbed or chemisorbed on the surface through the acid group that can be mono-dentate or bi-dentate. The increase in the temperature up to 80 °C induces an increase in the surface coverage by chemisorbed and physisorbed fatty acids molecules. Only the dynamic effect induces the formation of stearate in addition to chemisorption.

Among fatty acids, stearic acid presents the best tribological behavior [10–13] but it is not soluble at room temperature in base oils often used in the formulation of lubricants. For this reason, it is interesting to pay attention to mixtures of both saturated and unsaturated fatty acids. Actually, mixtures of saturated and unsaturated fatty acids are present abundantly in many vegetable oils such as

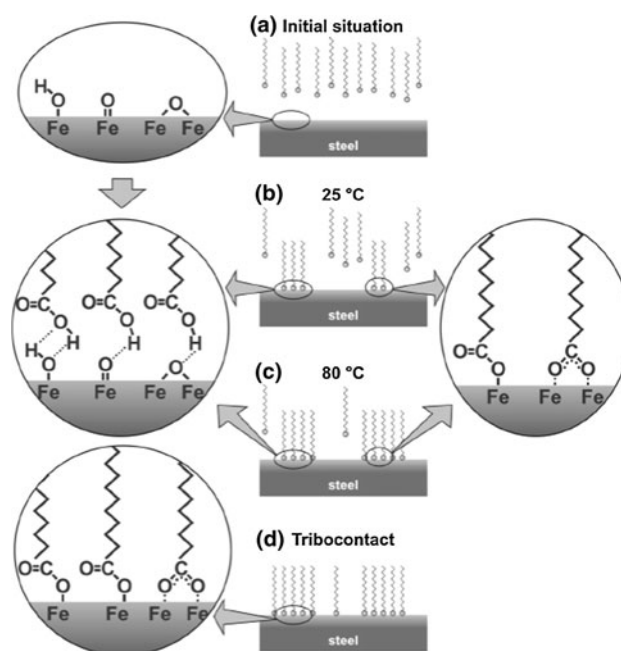


Fig. 1 Proposed mechanism of fatty acid molecules adsorption on steel surfaces. **a** The surface is partially covered by hydroxides and oxides. **b** Fatty acids are physisorbed and chemisorbed on the surface depending on the surface oxidation/hydroxylation. **c** Increasing the temperature increases the physisorption and the chemisorption through the acid group. **d** Rubbing induces chemisorption and the formation of iron carboxylate structures [14]

soybean oil (15 % saturated fatty acids, 22 % monosaturated fatty acids and 62 % polysaturated fatty acids) or sunflower oil (10 % saturated fatty acids, 30 % monosaturated fatty acids and 60 % polysaturated fatty acids) [15–17]. Vegetable oils have already shown good tribological properties [15–17], especially soybean oil. It is known that the stearic acid has the most significant influence on wear and friction reduction [17]. In vegetable oils, stearic acid is soluble in the oil thanks to a mixture of other fatty acids. It is probable that stearic acid molecules could associate with unsaturated ones in micellar structures above the critical micelle concentration (CMC). Soybean and sunflower oils have similar amount of stearic acid. Differences in their unsaturated fatty acid may have been a controlling factor to induce lower friction and wear in soybean oils. It is not straightforward whether the stearic acid in the mixtures has the same efficiency as when it is alone. In fact, the chemical structure of fatty acids affects their diffusion toward the surface, and, therefore, all the additives present in the base oil compete for the active surface sites. The final adsorption state depends on the different species initially present in the formulation.

In this paper, the study of fatty acid lubricant mechanism is revisited with a new approach by combining experimental and computational chemistry works. The friction and wear behavior of stearic, oleic and linoleic acids in PAO4 on iron

oxide surface is investigated by tribological tests. The lubricant is composed of a PAO4 synthetic base oil containing a single fatty acid as an additive. Mixtures of saturated/unsaturated fatty acids are also studied to detect synergic or anti-synergic effects. Different temperatures are used to mimic the behavior of the thermal engine: from 50 °C up to 150 °C. To complete the experimental studies, molecular dynamic (MD) simulations are performed to evaluate the diffusion coefficient of those additives in PAO4 at different temperatures. Both adsorption and desorption effects related to the temperature increase are studied by quantum chemistry (QC) calculations.

2 Experimental and Simulation Methods

2.1 Friction Test Experiments

Tribological tests were performed using a reciprocating cylinder-on-flat tribometer. The cylinder and flat were made of AISI 52100 steel and had a mirror surface finish (Ra equal to 2 nm). The friction counterparts were completely immersed in a solution of lubricant prior to the friction test. The lubricant used was a Poly-Alpha-Olefin base oil (PAO4 supplied by TOTAL) additivated with 1 %w of a single fatty acid or with 2 %w (1:1) of a mixture of saturated and unsaturated fatty acids. Three pure fatty acids from Sigma-Aldrich containing 18 carbon atoms were studied: stearic acid (C18:0), oleic acid (C18:1) and linoleic acid (C18:2). First, the tribological behavior of steel samples in the presence of PAO4 + 1 %w of each single fatty acid is studied. Afterward, the synergic or anti-synergic effect of two mixtures: stearic and oleic acids and stearic and linoleic acids blended in PAO4 is investigated. The experiments were run for 4,000 cycles respectively at 50, 100 and 150 °C with a stroke length of 4 mm at 7 Hz corresponding to a sinusoidal movement (the maximum sliding speed was 56 mm/s at the middle of the stroke). The applied normal load was 50 N resulting in a maximum Hertzian pressure of 320 MPa. All tests were repeated three times to check their reproducibility. Considering the test conditions, the lubrication regime used in this study is mostly the mixed regime.

2.2 Numerical Simulation Approach

2.2.1 Molecular Dynamics (MD) Simulation

MD simulations are performed using NEW-RYUDO program [18, 19] in order to evaluate the diffusion coefficient of C18 fatty acids in PAO4 and to study qualitatively the adsorption of self-assembled monolayer (SAM) of C18 fatty acid on iron oxide surface. The Verlet algorithm is used to solve the equation of motion [20]. In this study, the potential

function in Eq. 1 is employed to consider the Van der Waals, ionic and covalent interactions among atoms [19, 21].

$$U = \sum_i \sum_{j>i} \left[\frac{Z_i Z_j e^2}{r_{ij}} + f_0 (b_i + b_j) \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) + \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} \right] + \sum_i \sum_{j>i} D_{ij} \{ \exp[-2\beta_{ij}(r_{ij} - r_0)] - 2 \exp[-\beta_{ij}(r_{ij} - r_0)] \} + \sum_\theta H_\theta (\theta - \theta_0)^2 + \sum_\varphi H_\varphi [1 + \cos(n\varphi - \varphi_0)] \quad (1)$$

The first term corresponds to the Coulomb potential ($Z =$ charge, $e =$ elementary electric charge), the second term corresponds to the short-range exchange-repulsion potential ($f_0 =$ constant for unit adjustment, $a =$ size of the surface, $b =$ stiffness of the surface), which gives a good account of the repulsive interactions arising from the overlap of electronic clouds and the third term represents the Lennard-Jones type potential ($A_{ij} = (A_i A_j)^{1/2}$, $B_{ij} = (B_i B_j)^{1/2}$, $r_{ij} =$ bond length). The term with the inverse 6th power is the attractive term that is predominant at long distance (Van der Waals interactions). The term with the inverse 12th power is the repulsive term based on the Pauli exclusion principle. The fourth, fifth and sixth terms in Eq. 1, respectively, correspond to the Morse-type potential ($D_{ij} =$ bond energy, $\beta_{ij} =$ form factor, $r_0 =$ bond length at minimum energy), angle potential ($H_\theta =$ force constant, $\theta =$ bending angle and $\theta_0 =$ bending angle at minimum energy) and torsion potential ($H_\varphi =$ force constant, $n =$ order of rotation axis, $\varphi =$ torsion angle and $\varphi_0 =$ torsion angle at minimum energy), which all represents covalent interactions.

Figure 2 shows the stearic acid (C₁₈H₃₆O₂), oleic acid (C₁₈H₃₄O₂), linoleic acid (C₁₈H₃₂O₂) and the PAO4 (C₂₄H₅₀) molecules models used in the calculation. They are designed with Material Studio[®] V6. The geometry optimization of these molecules is performed with DMol3 [22] by using the Vosko, Wilk and Nusair as the local density approximation functional [23].

2.2.1.1 Evaluation of the Diffusion Coefficient One molecule of C18 fatty acid is placed in 42 molecules of PAO4 in order to reach a 1 %w of additives in the base oil. The model is presented on Fig. 3a. The cell size has a size of 27.4 × 40.3 × 35.3 Å³, so the density of the PAO4 is equal to 0.819 g/cm³. Periodic boundary conditions are imposed in all directions. To reduce the time-scale and length-scale gap between experimental and computational work, coarse-graining method is used [24]. Instead of representing every atoms of the system, we use “pseudo-atoms” to represent CH, CH₂ and CH₃ group of atoms for PAO4. The diffusion is carried out under atmospheric pressure. The time step and number of calculation step

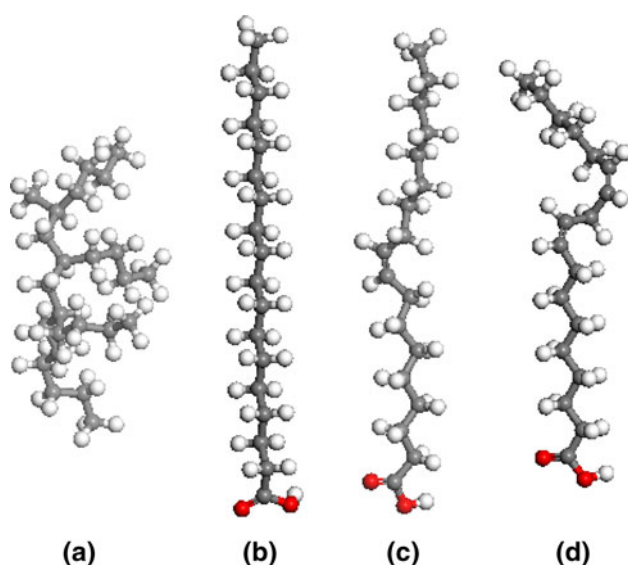
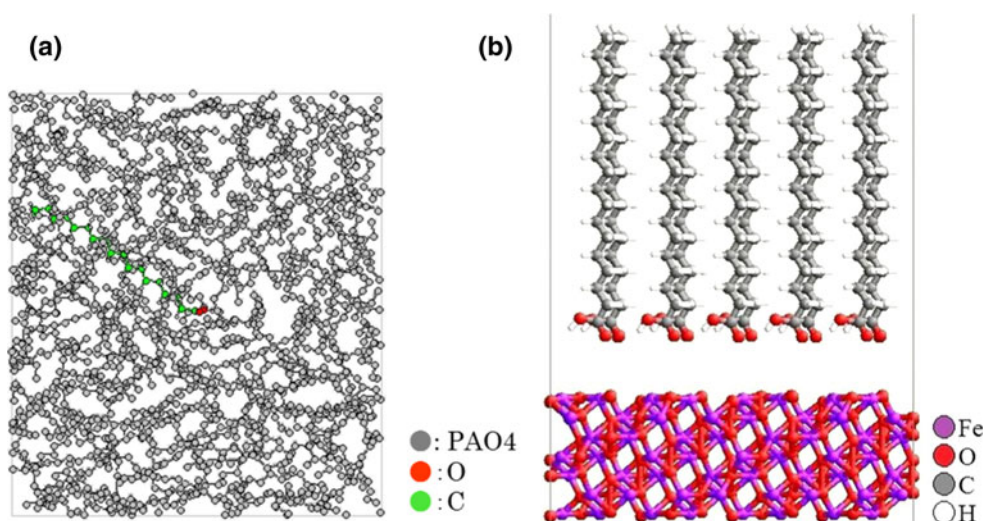


Fig. 2 Molecules designed with material studio V.6: **a** PAO4, **b** stearic acid, **c** oleic acid and **d** linoleic acid

were 0.1 fs and 10,000,000, respectively. Simulations are carried out under a constant volume and a temperature of 50, 100 and 150 °C for each fatty acid in the PAO4. Temperature is controlled by scaling the velocities of atoms in the system (Woodcock algorithm [25]). MD simulations can output mean square displacement (MSD) of each atom in x , y and z directions. The MSD in all directions for all C18 fatty acids atoms as a function of time is a linear curve where the slope divided by 6 (positive and negative x , y , z directions) is the diffusion coefficient.

2.2.1.2 Qualitative Adsorption of Molecule Fifteen molecules of fatty acids are placed at 7 Å above iron oxide surface $\alpha\text{Fe}_2\text{O}_3$ at SAM configuration as shown on Fig. 3b. The substrate system has a size of $27 \times 21 \times 100 \text{ \AA}^3$, and periodic boundary conditions are imposed in the x and y directions. The substrate is composed of 560 atoms (336

Fig. 3 MD simulations model: **a** 1 %w of stearic acid in PAO4, **b** SAM stearic acid 15 molecules on Fe_2O_3



oxygen atoms and 224 iron ones). The adsorption is carried out under atmospheric pressure. The time step and number of calculation step were 0.1 fs and 1,000,000, respectively. Simulations are carried out under a constant volume and a temperature of 50, 100 and 150 °C for each SAM of fatty acids in order to investigate potential desorption of molecules at high temperature.

2.2.2 Tight-Binding Quantum Chemistry (TB-QC) Simulations

After running adsorption of fatty acids on iron oxide surface by MD, one molecule from the SAM is isolated with the substrate and QC calculation is applied in order to confirm quantitatively the adsorption mechanism of each fatty acid at 50, 100 and 150 °C.

In the TB-QC, the electronic structure calculation is performed by solving the Schrödinger equation with diagonalization condition, as follows [26]:

$$HC = \varepsilon SC, \quad (2)$$

$$C^T SC = I. \quad (3)$$

(H = Hamiltonian matrix, C = eigenvector, S = overlap integral matrix, ε = eigen value, I = unit matrix).

In TB-QC, the double Slater-type basis set is employed, and the Ewald method [27] is used in order to compute long-range Coulombic interactions. To determine the off-diagonal elements of H , denoted H_{rs} , the corrected distance-dependent Wolfsberg-Helmholtz (W-H) [28] is used as shown in Eq. 4:

$$H_{rs} = \frac{K}{2} S_{rs} (H_{rr} + H_{ss}) \quad (4)$$

(K = distance-dependent W-H constant, S_{rs} = integral overlap matrix, H_{rr} , H_{ss} = diagonal terms of Hamiltonian matrix).

H and **S** in our TB-QC simulator needed to be set by evaluating exponents of a Slater-type ζ_r atomic orbital (AO) and valence-state ionization potentials (VSIP) for the valence shell of an AO of C, O, H and Fe atoms. ζ_r is used to calculate the **S** matrix and H_{rs} in Eq. 4. The VSIP parameter of AO number r and atom number i denoted I_r^i is linked to H_{rr} by Eq. 5:

$$H_{rr} = -I_r^i \tag{5}$$

This parameter is used to determine the diagonal element of **H** in Eq. 4. ζ_r , and H_{rr} are calculated by the polynomial function of atomic charges as described in Eqs. 6 and 7.

$$\zeta_r = a_0 + \sum_{k=1}^5 a_k (Z_i)^k \tag{6}$$

$$H_{rr} = b_0 + \sum_{k=1}^5 b_k (Z_i)^k \tag{7}$$

(Z_i = atomic charge of atom i)

All parameters ($a_0, \dots, a_5, b_0, \dots, b_5$) of AO s, p and d are adjusted to reproduce the binding energies and electronic structures of each reactant calculated by the first-principle parameterization.

In TB-QC method, the total energy is expressed as:

$$E = \sum_{i=1}^n \frac{1}{2} m_i v_i^2 + \sum_k \varepsilon_k + \sum_{i=1}^n \sum_{j=i+1}^n \frac{Z_i Z_j e^2}{R_{ij}} + \sum_{i=1}^n \sum_{j=i+1}^n E_{ij}^{\text{repul}}(R_{ij}) \tag{8}$$

where terms on the right side refer to the kinetic energy (m = the atomic mass, v = velocity of atom), the molecular orbitals energy ($\varepsilon_k = k$ -th eigen value, $n_k =$ number of electrons occupied in k -th molecular orbital, “occ” means summation for all occupied molecular orbitals), the long-range Coulombic interaction energy (Z = charge, e = elementary electric charge) and the exchange-repulsion energy (R_{ij} = interatomic distance), respectively. Each energy can be divided into the sum of mono-atomic contribution and di-atomic contribution to the binding energy as shown in Eq. 9 for molecular orbitals energy:

$$\sum_{k=1}^{\text{occ}} n_k \varepsilon_k = \sum_{k=1}^{\text{occ}} \sum_r n_k (C_{kr})^2 H_{rr} + \sum_{k=1}^{\text{occ}} \sum_r \sum_s n_k C_{kr} C_{ks} H_{rs} \tag{9}$$

3 Results and Discussions

3.1 Tribological Tests Results

Figure 4 summarizes friction results obtained at 50, 100 and 150 °C in the presence of PAO4 and 1 %w of stearic, oleic and

linoleic acids, respectively. The friction coefficient is recorded at the steady state value at the end of the test. First of all, results show that some fatty acids seem to be very efficient in reducing friction and wear in certain conditions (Fig. 5a–d) compared to PAO4. Results at 50 °C are compared with those obtained at 100 and 150 °C. It appears that the increase in temperature leads to a drastic increase in friction and wear for linoleic acid and oleic acid. While on the other hand, a drastic decrease in friction by a factor of 2 (μ is about 0.056) at 150 °C is observed in the presence of stearic acid associated with no visible wear. Comparing saturated versus unsaturated fatty acids, it seems that increasing the number of unsaturated bonds leads to a decrease in the lubricating properties of fatty acids at high temperature. Thus, stearic acid gives the best tribological performance at 150 °C. This result is quite surprising considering the fact that under the effect of heating, the physisorbed molecules should desorb. Therefore, this result strongly suggests that the friction reduction is not due to physical but due to chemical adsorption of stearic acid on 52100 steel surfaces.

After studying the effect of each fatty acid in PAO4, the competition toward the steel surface of a mixture of saturated and unsaturated fatty acids is investigated. For this reason, mixtures of stearic with oleic acid and stearic with linoleic acids were prepared, respectively, in PAO4 up to 2 % with an equal (1:1) ratio. Figures 6 and 7 summarize friction results obtained at 50, 100 and 150 °C with these different mixtures. At the lowest temperature, the mixtures give almost the same range of friction and wear (Fig. 5e, f) as the fatty acids alone. However, at 100 °C, the mixtures give an intermediate friction and wear between the stearic acid and the unsaturated fatty acids, especially in the presence of linoleic acid. This result can be due to the fact that a strong competition occurs between the saturated and unsaturated fatty acids at 100 °C, and it is likely that both of them adsorb on the surface. At the highest temperature, the mixtures give similar

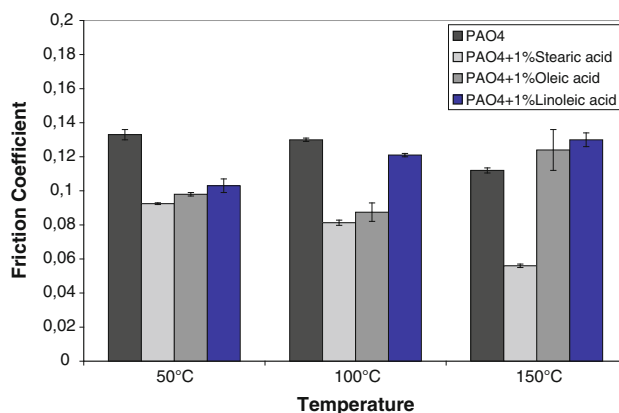


Fig. 4 Steady-state friction coefficient versus lubricant mixtures composed of PAO4 + 1 %w of single fatty acids of an AISI 52100 steel couple at 50, 100 and 150 °C

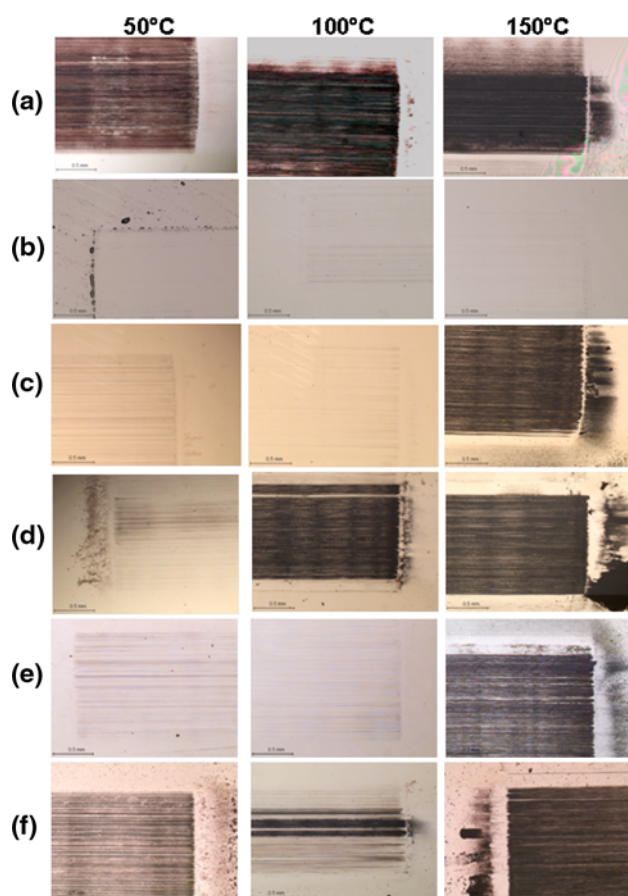


Fig. 5 Optical micrographs of AISI 52100 steel flat wear scars lubricated at 50, 100 and 150 °C in the presence of: **a** PAO4, **b** PAO4 + 1 %w stearic acid, **c** PAO4 + 1 %w oleic acid, **d** PAO4 + 1 %w linoleic acid, **e** PAO4 + 2 %w (1:1) stearic and oleic acids and **f** PAO4 + 2 %w (1:1) stearic and linoleic acids

friction and wear as the unsaturated fatty acid. This suggests that the presence of unsaturation made the molecules to reach the steel surface more quickly. In order to study the diffusion of these fatty acids in the presence of PAO4, we had recourse to computer simulations methods.

3.2 Simulation Results

3.2.1 Evaluation of Diffusion Coefficient

Figure 8 gathers the diffusion coefficient obtained at 50, 100 and 150 °C in the presence of PAO4 and 1 %w of stearic, oleic and linoleic acids, respectively. The diffusion coefficient is calculated as the MSD value of the sum of all atoms of the C18 fatty acid in x, y and z directions. Results show that at each temperature, stearic acid diffuses slower than oleic acid, which diffuses slower than linoleic acid. Values of diffusion coefficient are at the same range as those find in the literature [29–31]. The increase in temperature leads to an increase in the diffusion coefficient of stearic, oleic and linoleic acid, respectively. The

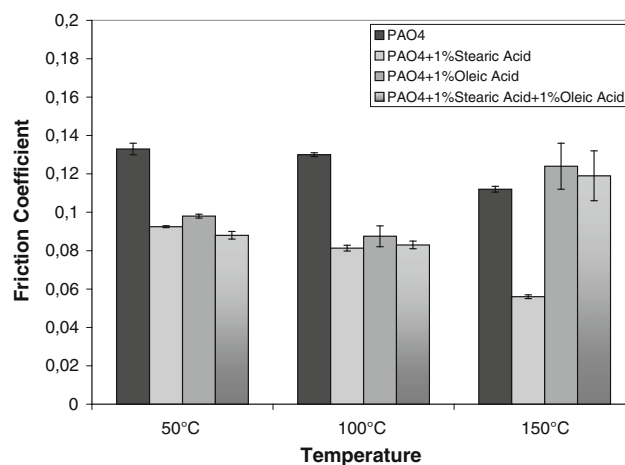


Fig. 6 Steady-state friction coefficient versus lubricant mixtures composed of PAO4 + 2 %w (1:1) of stearic and oleic acids of an AISI 52100 steel couple at 50, 100 and 150 °C

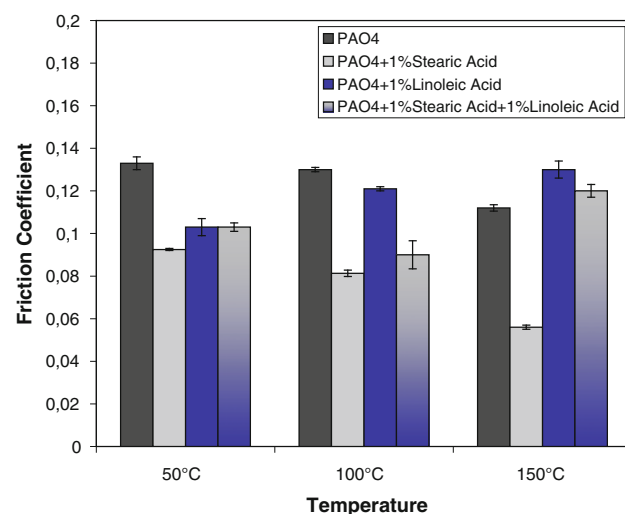


Fig. 7 Steady-state friction coefficient versus lubricant mixtures composed of PAO4 + 2 %w (1:1) of stearic and linoleic acids of an AISI 52100 steel couple at 50, 100 and 150 °C

difference between the diffusion coefficient of saturated and unsaturated molecules increases with the temperature. Comparing saturated versus unsaturated fatty acids, it seems that the double carbon bond induces bending of the molecule that facilitates the movement in the PAO4. These results suggest that when a mixture of stearic, oleic and linoleic acids is added in PAO4, linoleic acid will reach the surface at first, followed by oleic acid and finally stearic acid. So there will be a depletion of stearic acid molecules in the adsorbed film.

3.2.2 Qualitative Adsorption of Fatty Acid SAM on Iron Oxide

After moving in the PAO4, fatty acids reach the surface and get adsorbed. In this computer study, the SAM model

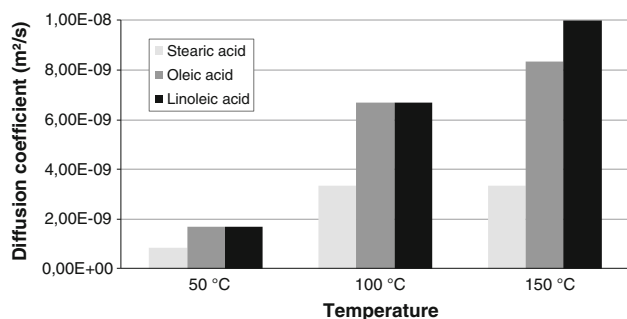


Fig. 8 Diffusion coefficient of stearic, oleic and linoleic acids in PAO4 at 50, 100 and 150 °C by MD simulation

of fatty acids is chosen. The density of the molecule on the substrate is equivalent to a liquid-like thermal film. Figure 9 shows snapshots after 100 ps of MD simulations at 50, 100 and 150 °C. It is observed that once the film has reached the surface, it stays on the surface. It seems that the thermal film is adsorbed on the surface through interactions with the acid group. Increasing the temperature does not change the formation of the thermal film. No molecule is desorbed at high temperature. This means that the thermal film is strongly adsorbed on the surface. Same simulations were run for oleic and linoleic acids at 50, 100 and 150 °C.

Figure 10 represents snapshots after 100 ps of MD simulations at 50 °C for the SAM model of 15 molecules of stearic, oleic and linoleic acids, respectively, above iron oxide surface. At 100 and 150 °C, adsorbed films of oleic and linoleic acid are the same as the one at 50 °C. It is concluded as for the stearic acid thermal film that no desorption occurred at 150 °C. It is noticed that, like stearic acid, adsorption of oleic acid SAM and linoleic acid SAM occurs through the acid group. It is noted that the adsorbed film is more disordered when the number of double bonds in the backbone increases. In fact, steric effect becomes

important with double carbon bonds, and this prevents the formation of a close-packed monolayer.

3.2.3 Adsorption Mechanism of C18 Fatty Acids

One molecule is extracted from the SAM to investigate quantitatively the adsorption mechanism of C18 fatty acid SAM model on iron oxide surface. Tight-binding quantum chemical simulations are run for single stearic, oleic and linoleic acids, respectively, extracted from the SAM while the substrate is kept for QC calculations. Interactions between the fatty acid carboxylic group and the iron from the substrate are investigated at 50 °C. Table 1 gathers the bond population which is equal to 0 when there is no interaction in the considered pair and positive when electrons are present in the considered pair. Therefore, chemical bond can be created. Table 1 also gathers the total energy that can also be called the binding energy of the considered pair. It is the sum of interatomic interactions caused by molecular orbitals, coulomb interactions and atomic core repulsions. The considered pairs are (a) (i) oxygen from the carboxyl group of the molecule and (ii) iron from the iron oxide surface, (b) (i) oxygen from the hydroxyl group of the molecule and (ii) iron from the iron oxide surface and eventually (c) (i) hydrogen of the hydroxyl group and (ii) oxygen from the iron oxide surface. The values of bond population as well as the energy of pair (a) both suggest that stearic, oleic and linoleic acids bond at the surface through the carboxyl group. The bond population is 0.45 ± 0.01 for the three fatty acids. The binding energy is similar for the three considered fatty acids, that is, between -85.4 and -87.7 kcal/mol. At this level of energy, it can be concluded that the adsorption is chemisorption, and therefore, the thermal film is strongly adsorbed on the surface through the acid group. Bond

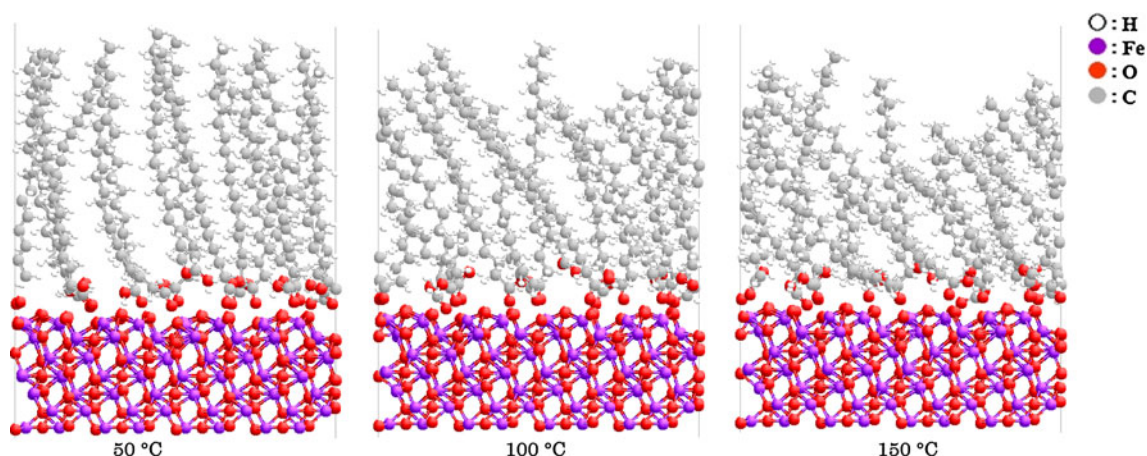


Fig. 9 Snapshots after 100 ps of MD simulations at 50, 100 and 150 °C of a SAM containing 15 molecules of stearic acid (liquid like) above an iron oxide surface

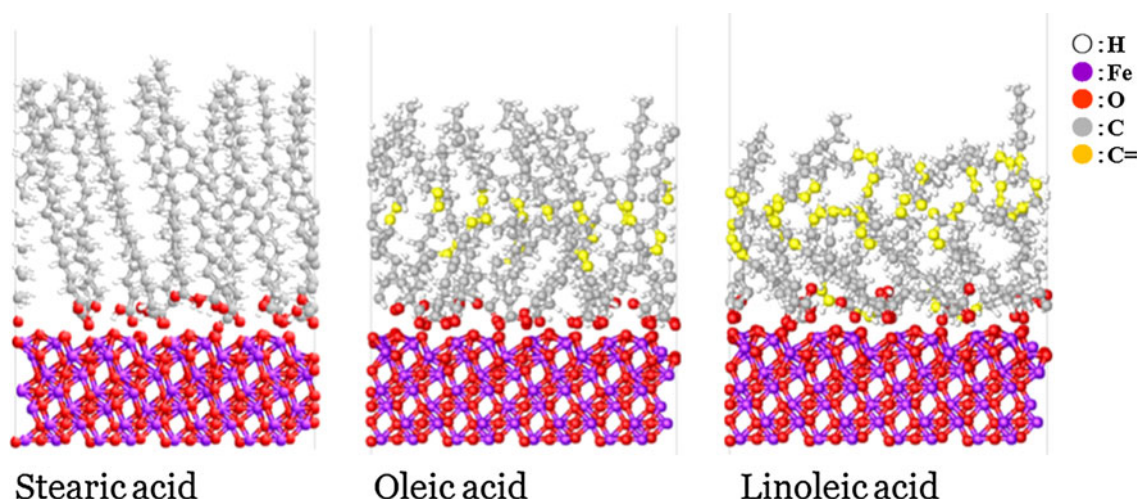


Fig. 10 Snapshots after 100 ps of MD simulations at 50 °C for a SAM of 15 molecules of stearic, oleic and linoleic acid, respectively

Table 1 Bond population and total energy (sum of interatomic energies caused by molecular orbitals, coulomb interactions and atomic core repulsions) calculated by QC for the oxygen and hydrogen from acid group—iron oxide substrate pairs (a) =O–Fe pair, (b) –O–Fe pair, (c) –H–O pair at 50 °C for an isolated molecule extracted from SAM after MD simulations of stearic, oleic and linoleic acids

	Pair	Bond population	E_{total} (kcal/mol)
<i>a</i>			
Stearic acid	=O–Fe	0.45	–86.5
Oleic acid	=O–Fe	0.45	–85.4
Linoleic acid	=O–Fe	0.46	–87.7
<i>b</i>			
Stearic acid	–O–Fe	0.00	–5.45
Oleic acid	–O–Fe	0.00	–5.09
Linoleic acid	–O–Fe	0.00	–7.29
<i>c</i>			
Stearic acid	–H–O	0.00	–8.96
Oleic acid	–H–O	0.00	–6.52
Linoleic acid	–H–O	0.00	–6.07

populations of pair (b) and (c) are 0, and adsorption energy of pair (b) and (c) is below –10 kcal/mol for the three fatty acids suggesting that there is no hydrogen dissociation in the hydroxyl group and that fatty acids are physisorbed through the hydroxyl group. Eventually, the main adsorption mechanism of SAMs of fatty acids on iron oxide surface is chemisorption through the carboxyl group.

In addition to energy calculation, carboxyl carbon/oxygen bond length has been measured before and after adsorption, as shown in Fig. 11. After geometry optimization, i.e., before adsorption, of an isolated stearic acid molecule, the C–O bond length of the carboxyl group is 1.210 Å. After adsorption, the C–O bond length increases significantly to 1.295 Å and the O–Fe bond length is

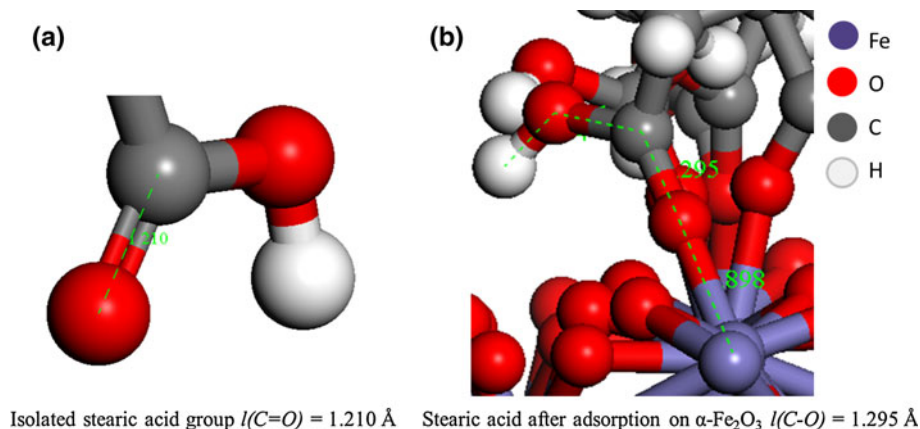
1.898 Å. The increase in the C–O bond length confirms that the original C=O double bond is modified and forms the C–O–Fe function by delocalization of probably π electrons inducing strong adsorption of the fatty acid molecule.

Because they have the same reactivity toward the surface and no desorption occurred at high temperature, competition of additives depends on the rate at which they arrive on the surface among other factors: once an additive gets at the surface, its chemisorption occurs.

3.3 Discussions

Among all the studied fatty acids, stearic acid alone exhibits the best tribological behavior, even at 150 °C. This fact is confirmed by the computer simulation study that show no desorption at 150 °C for stearic acid, as well as for the other studied fatty acids. The good tribological behavior of saturated acid was already shown by other authors at room temperature and 50 °C [11, 15] but recently by Campen et al. [13] at 35 and 100 °C when she compared friction coefficient versus sliding speed for stearic and oleic acid. On the other hand, Bowden and Tabor predicted desorption of fatty acids at high temperature such as 150 °C [2]. In fact, as the temperature is raised, there is an increase in the thermal agitation of the molecules until a temperature where molecules are disoriented and they fade out all together. The desorption temperature was shown to be highly dependent on the substrate material. Therefore, it is likely that 150 °C is not yet the transition temperature of fatty acids on iron oxide surface. Our data show that friction reduction is not due to physical adsorption of stearic acid on steel surface, but to its chemical reaction. This is valid when each fatty acid is studied separately.

Fig. 11 Snapshots: **a** isolated stearic acid after geometry optimized with C=O length, **b** zoomed adsorption configuration of stearic acid in SAM configuration on iron oxide surface with new C–O length



When the mixture of unsaturated and saturated fatty acids is investigated by experimental analysis, anti-synergic effect is observed, e.g., the good tribological behavior of stearic acid is inhibited by the presence of oleic and linoleic acids at high temperature. Simulations clearly depicted that, for each temperature, unsaturated molecules diffuse faster than stearic acid in PAO4. In more practical words, in the mixture, linoleic acid and oleic acid molecules win the competition by reaching the surface before stearic acid molecules. The gap between the diffusion coefficient of unsaturated and saturated fatty acids increases with the temperature which suggest that the diffusion of molecules is an important factor at high temperature. Vegetable oils contained a mixture of saturated/unsaturated fatty acids and have been studied as lubricant. Among those studies, it was shown that stearic acid is the most effective fatty acid additive in sunflower oil and that it reduces both friction and wear [15] but when the temperature was raised up to 150 °C, the sunflower base oil failed to protect the surface. This is in agreement with our result where higher friction and wear is observed at 150 °C for the mixture of saturated/unsaturated fatty acid. However, this is not observed for only stearic acid content in the base oil at 150 °C.

The study of adsorption mechanism of fatty acids by computer simulation showed the same trend for the adsorption mechanism, e.g., chemisorption through the acid group with the same reactivity toward the surface ($\sim -86 \text{ kcal/mol}$). The three fatty acids have the same reactivity toward the iron oxide surface which means that once a molecule reaches the surface and is chemisorbed, it stays definitely on the surface. Moreover, no desorption is observed at 150 °C. The adsorption mechanism quantitatively derived from our computer simulation gives strong evidence to the one schematically and qualitatively proposed by Simic and Kalin at 25 and 80 °C, which is symmetric or asymmetric adsorption through the acid group [14]. In the presence of rubbing, they suggest a

friction-induced formation of a stearate [14]. The formation of stearate is not observed in our quantum chemical calculations, but the computational work was only performed on the formation of the adsorbed film, without friction. It will be interesting in future work to confirm the formation of stearate by computational study under friction conditions.

4 Conclusion

In this paper, fatty acid lubrication mechanism has been revisited by a new approach combining experimental analysis, e.g., friction tests and computational chemistry, e.g., TB-QC and MD simulations. The PAO4 was used as a solvent and iron oxide as the substrate. Temperatures of 50, 100 and 150 °C were tested. Stearic, oleic and linoleic acids friction behavior and adsorption mechanism on iron oxide surfaces were studied first separately and in a mixture of saturated/unsaturated fatty acid. The following conclusions can be drawn:

- OFMs adsorb on iron oxide surface through the acid group with the same reactivity whatever the acid.
- No desorption is observed at 150 °C.
- Stearic acid shows the best tribological behavior, even at 150 °C.
- The presence of unsaturated molecules mixed with stearic acid has an antagonist effect, especially at 150 °C.
- MD simulations show that unsaturated fatty acids diffuse faster than stearic acid in PAO4 and these at all temperatures.

In the presence of the three acids, it is proposed that oleic and linoleic acids reach the surface first before stearic acid and adsorb on iron oxide surface at high temperature. In such case (mixture sample), the diffusion coefficient of molecule in the PAO4 is an important factor to consider as

it determines which molecule arrives first at the surface. Once the molecules arrive on the surface, it adsorbs chemically. In the case of stearic acid alone, molecules form close-packed monolayer, which leads to low friction coefficient, especially at 150 °C. In the case of mixture, mainly oleic and linoleic acid adsorb on the surface and prevent the formation of a close-packed monolayer due to steric effects, which induce high friction coefficient, especially at 150 °C. This explains why the good tribological property of stearic acid is inhibited by unsaturated molecules.

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