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Case study

Molecular Modeling of Lubricant Additives

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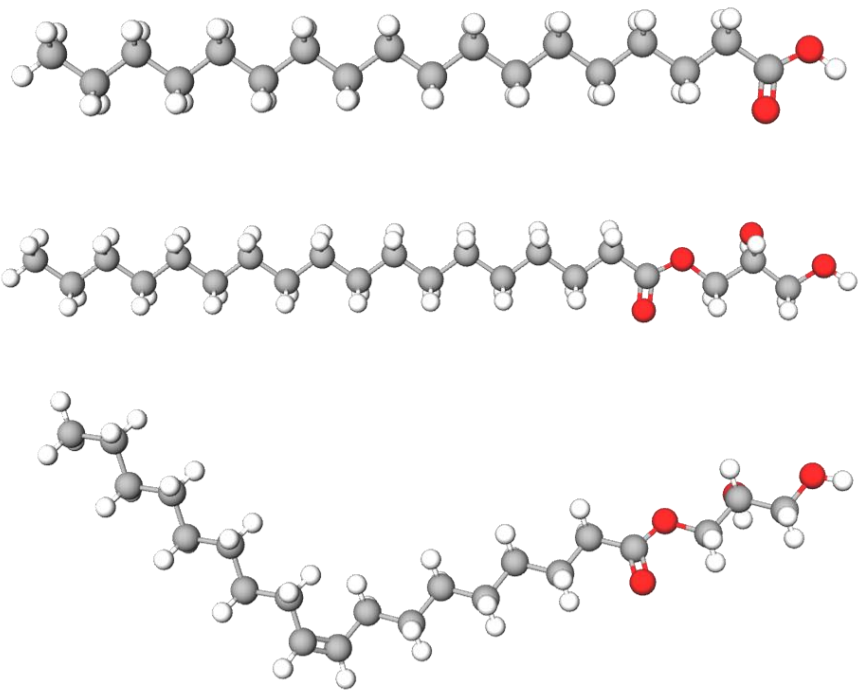
The Challenge

Modern lubricant formulations are a mixture of a base oil and additives that impart or enhance properties of the lubricant. Lubricants are crucial to control friction and wear, to clean, to cool and to avoid oxidation in contacts between surfaces in engines and equipment. Thus, they prolong the lifetime of machines and improve energy efficiency. In particular, new efficiency and environmental regulations are leading to a growing use of additives that reduce friction in boundary lubrication conditions, a lubrication regime in which the lubricated surfaces come into contact through asperities and friction increases. Among these additives, organic friction modifiers (OFM) are of particular interest because they are not environmentally harmful and do not reduce the efficiency of after-exhaust catalysts. Some OFMs used in modern formulations are shown below.



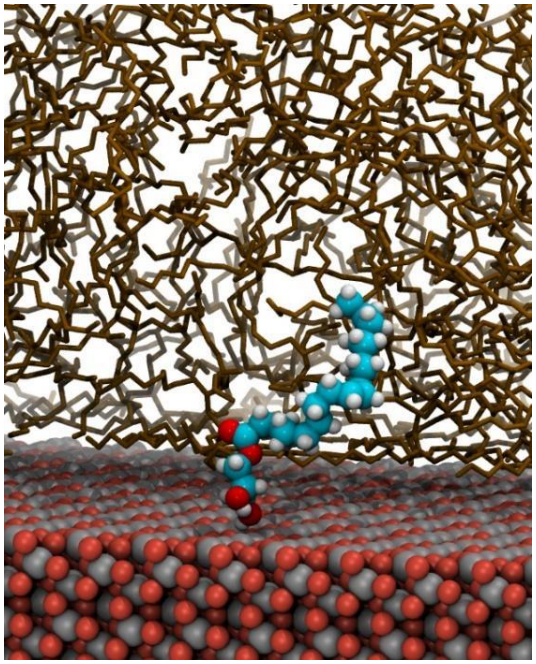
These OFM are surfactants that adsorb on the lubricated surfaces and form a monolayer film that reduces friction and wear. Developing an efficient methodology to study in silico the adsorption and friction reduction of these additives for a given set of conditions would accelerate the design of new lubricant additives.

The Approach

In this joint project between Nextmol and Repsol Technology Lab, we have used a two-step methodology to study the adsorption and subsequent friction reduction of three model OFMs: Glycerol monooleate (GMO), glycerol monoostearate (GMS) and stearic acid (SA). Both adsorption and macroscopic friction are determined by processes at the smallest (atomic) scale, thus molecular simulations can be used to study them via a systematic approach that can also be applied beyond OFM adsorption.

The present methodology is based on state-of-the-art techniques reported in the literature and has two main components, namely the simulations at the atomic scale and the theoretical model that takes as input the results of the simulations.

Adsorption



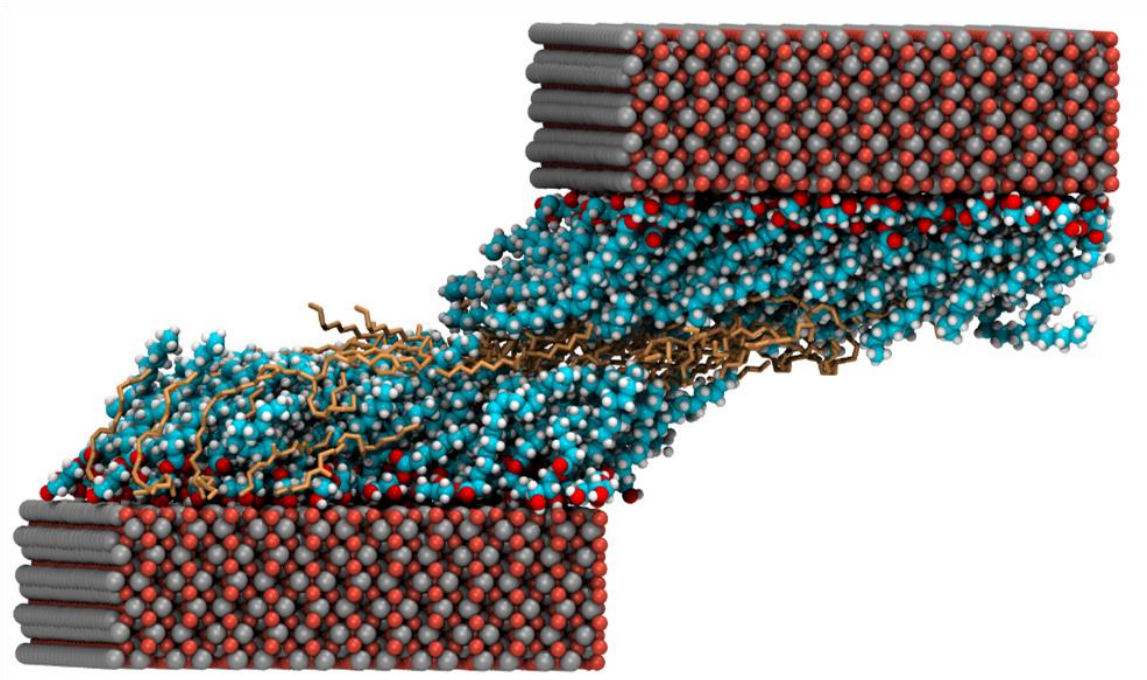
Adsorption of additives is quantified by determining the relation between the concentration in the base oil and the surface coverage, also known as adsorption isotherm. To determine the adsorption isotherm, a Molecular Thermodynamic Theory (MTT) model for surfactants is used together with Molecular Dynamics (MD) simulations. MD simulations calculate the adsorption energy and the area occupied by the molecule on the surface, which are the two main parameters of the MTT model that determines the adsorption isotherm. The simulations include OFM molecules dissolved in a base oil (PAO 4 in our case) in contact with an iron oxide surface.

In addition, the adsorption energy results are validated using experimental measures from a High Frequency Reciprocating Rig (HFRR) and a theoretical adsorption model for OFM monolayers in boundary lubrication regime.

The Approach

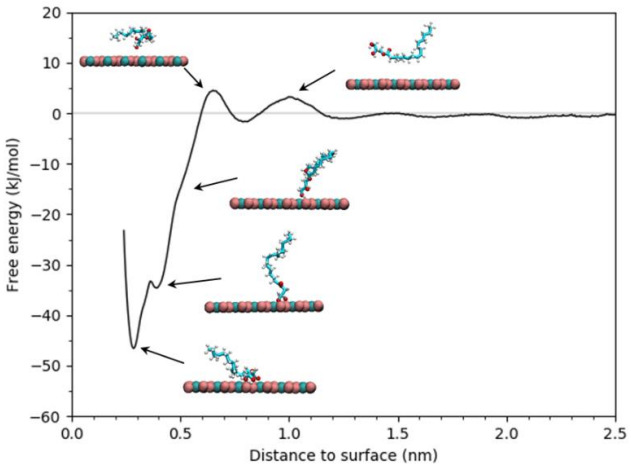
Friction

Once the adsorption isotherm is determined, we can predict the coverage of the surface for a given concentration of the OFM. This surface coverage is then used in another kind of MD simulations in which two surfaces of iron oxide enclosing the base oil are covered with OFMs and slid with respect to each other. As an external force is applied to move both surfaces, these simulations are known as Non-Equilibrium Molecular Dynamics (NEMD). The friction coefficient is calculated as a function of the sliding speed for a given coverage, temperature and pressure.

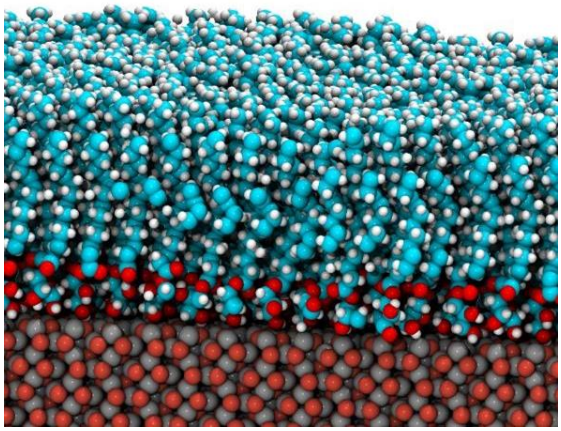


The Results

The parameters of the MTT model were calculated from the MD simulations. This included the adsorption potential of mean force (PMF) and the area occupied by each molecule on the surface, which on their own represent useful insights for the design of surfactant molecules. The PMF and, thus, the adsorption energy, can be related to the characteristics of each surfactant, gaining real understanding of the physics that drive adsorption in each particular case. Here, these parameters were used to determine the adsorption isotherm for every OFM.



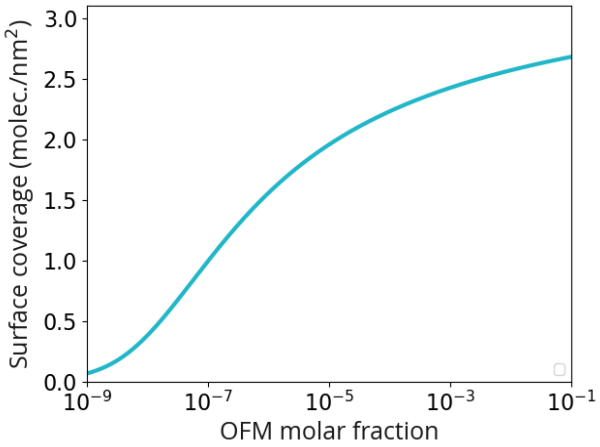
Adsorption potential of mean force for GMO



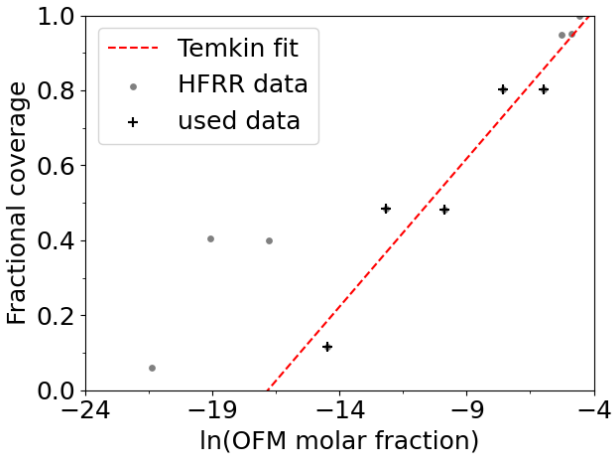
Calculation of the area occupied by each molecule on the surface

This computational approach was validated with the HFRR friction measurements done at Repsol Technology Lab. First, a theoretical model developed by Jahanmir et al. was used to transform the friction coefficient at each concentration into fractional coverage. Then, the fractional coverage was fitted to the Temkin adsorption isotherm model to obtain an estimation of the adsorption energy. This experimentally-derived value for the adsorption energy was in very good agreement with the one obtained from MD simulations.

The Results



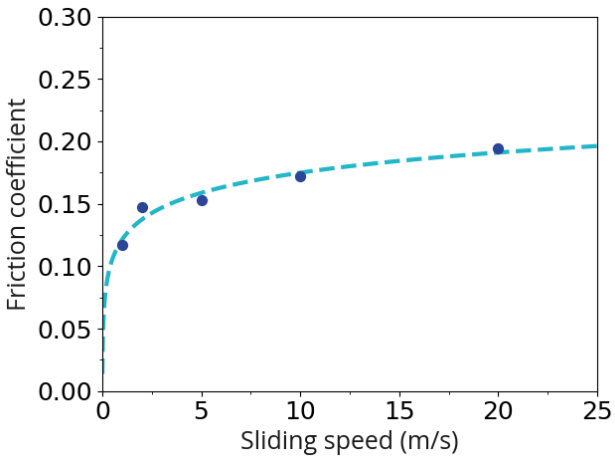
Adsorption isotherm



Experimental and simulation results for GMO

Once the coverage of the surface for a given concentration is known, the collective behavior of the OFM monolayer at a certain coverage of interest is studied.

Specifically, here we measured friction reduction through NEMD simulations. Our results are in good agreement with previous NEMD simulations from the literature (Ewen et al.).



In this way, the performance of each OFM is evaluated in terms of a balance between two properties: their efficiency, i.e. how easily the OFM adsorbs on the surface (quantified through the adsorption isotherm), and their effectiveness, i.e. the relation between coverage of the surface and friction reduction. This approach can be readily extended to other surfactant applications, such as anti-agglomerants, corrosion inhibitors, anti-foaming agents, emulsifiers, etc.

As a result, we conclude that molecular modeling using computer simulations is a promising tool for the development of new OFMs and other surfactants.

References of interest

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