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Quartz crystal microbalance investigation of the structure of adsorbed soybean oil and methyl oleate onto steel surface ☆

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ABSTRACT

The adsorption behavior of soybean oil (SBO) and methyl oleate (MO) from hexadecane solvent onto a steel surface at room temperature was investigated using quartz crystal microbalance with dissipation (QCM-D). Adsorption of both SBO and MO in hexadecane increased with increasing concentration until a full surface coverage was attained. At full surface coverage, SBO and MO formed rigid films and achieved a concentration of 1.5 and 1.7×10^{-10} mol/cm^2, respectively. Analysis of the QCM-D data determined that each formed a thin, rigid film where the thicknesses were approximately 1.5 nm for SBO and 7 Å for MO. The thicknesses indicate that the SBO adsorbed nearly perpendicular to the surface where MO molecules adsorbed nearly parallel to the surface.

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1. Introduction

The use of vegetable oils as a renewable source of lubricants has increased in recent years [1–6] largely due to global environmental concerns and the limited supply of petroleum. Vegetable oils are also attractive because they are abundant [7] and biodegradable, giving them excellent environmental and safety properties.

Vegetable oils are typically liquid at room temperature and can serve as solvents for various applications. Most vegetable oils contain triacylglycerides (TAGs) as the major component. The amphiphilic nature of TAGs gives vegetable oils low volatility and a narrow range for changes of viscosity due to temperature. It is also the amphiphilic properties of the TAGs that affect the boundary lubrication ability of vegetable oils. For instance, the polar ester group typically found in TAGs gives them good adsorption properties to metal surfaces. Vegetable oils also can incorporate a variety of additives and be treated as functional fluids and therefore can be studied as lubricant formulations. However, to fully understand lubricant formulation requires understanding the fluid and boundary characteristics of vegetable oils.

When studying boundary lubrication characteristics of vegetable oils, consideration must be given to adsorption and reaction properties of the oils [7,8]. Adsorption, occurring mainly through functional groups of vegetable oil, can be monitored using the quartz crystal microbalance technique. In previous works [7,8], the chemical properties of a vegetable oil on its ΔG_{ads} on steel was studied using friction measurements to determine adsorption isotherms of soybean oil (SBO), jojoba, methyl oleate (MO), safflower oil, methyl palmitate, and methyl laurate. These studies, however, did not provide any information about the adsorption behavior of these oils onto the steel surface. Adsorption behavior determines the structure of the adsorbed films on the surface. Adsorbed molecules from the various oils could have different orientations on the surface and hence, provide different film thickness. The effect of chemical structure of vegetable oils on adsorption behavior has not been investigated. Thus, the objective of this work is to investigate the effect of chemical structure on the adsorption behavior of two previously studied oils, SBO and MO, on steel using the quartz crystal microbalance with dissipation monitoring.

Quartz crystal microbalance (QCM) explores film deposition and growth on surfaces using an oscillating quartz crystal. QCM is sensitive to nanogram quantities of the adsorbed material and has been commonly used in vacuum [9] and liquids [10]. QCM uses the piezoelectric property of quartz to measure mass adsorption. When an alternating voltage is applied across the quartz it experiences

☆ Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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induced expansions and contractions at a resonance frequency. As the material comes into contact with the quartz and adsorbs onto the surface, there is a change or shift in the resonance frequency (which is in the MHz range). Sauerbrey analysis has demonstrated, to a first approximation, the existence of a linear relationship between frequency shift and mass adsorbed [11]. The linear relationship between mass adsorbed and frequency shifts will hold true if three assumptions are made: 1) the adsorbed mass is small in relationship to the crystal; 2) the adsorbed mass is rigidly bound and does not slip; and 3) the adsorbed mass is evenly distributed over the surface.

QCM with dissipation monitoring simultaneously measures frequency shifts (Δf) in the resonating crystal and changes in the decay or dissipation of the oscillations (ΔD) [12]. This decay in the oscillation is because there are energy losses due to frictional interactions on the molecular level. Dissipation shifts are measured when the alternating voltage is temporarily disconnected and the decay of the resonance frequency is monitored. The decay of the resonance frequency is directly related to the viscoelastic properties of the adsorbed mass.

2. Experimental details

2.1. Materials

Soybean oil (SBO) was purchased from local supermarket and used as supplied. Methyl oleate (MO, ≥99% purity) and hexadecane (≥99% pure, anhydrous) were purchased from Sigma-Aldrich Chemical Company (St. Louis, MO). Hexadecane was further purified by passing down a column packed with silica beads. The purpose for further purification of hexadecane was to remove all trace amounts of impurities (≤1%) which were previously found to affect experimental results. Ethanol (200 proof) was purchased from VWR (Batavia, IL) and used for initial cleaning of crystals. Clear glass vials, methanol, Alconox, and chloroform were all purchased from Fisher Scientific (Suwannee, GA). Distilled and deionized water was further purified to a resistance of 18.2 MΩ and UV-treated on a Barnstead Nanopure Diamond water purification system (Model D11911; Thermo Fisher Scientific, Inc.; Waltham, MA). Sensor crystals (5 MHz) were purchased from Q-Sense AB (Västra Froölunda, Sweden) with a steel coating as the active layer. According to the supply brochure, the steel coating was prepared by sputtering onto gold-coated quartz crystals. High purity nitrogen and argon gases were purchased locally (Airgas, Inc.; East Peoria, IL). Hellmanex II cleaning solution was purchased from Hellma GmbH & Co. KG (Mülheim, Germany). Chemicals and supplies were used as supplied unless otherwise stated.

2.2. Sample preparation

SBO, MO and hexadecane were degassed by stirring them under a vacuum for at least 1 h. Clear glass vials were cleaned using a four-step wash that consisted of rinsing with the following: 1) diluted Alconox detergent, 2) nanopure water, 3) methanol, and 4) chloroform. Appropriate amounts of degassed SBO (density of 920 g/l) or MO (density of 874 g/l) were extracted with a glass syringe and placed into a cleaned glass vial. Degassed hexadecane was then added to the vial to give a final volume of 8 mL. Samples were then mixed until homogeneity. MO samples were protected from light throughout all measurements.

2.3. Quartz crystal microbalance with dissipation monitoring (QCM-D) instrument

A Q-Sense D300 system with an axial flow sample chamber (Q-Sense, Inc., Glen Burnie, MD) was used to record adsorption of SBO and MO onto stainless steel Q-Sense crystals. Data were recorded using Q-Soft 301 software and analyzed using Q-Tools software (all softwares were supplied with the Q-Sense system; Glen Burnie, MD).

2.4. QCM-D principle

The QCM-D technique is based on the principle that a vibrating quartz crystal will oscillate at fundamental resonance frequency. The change in resonance frequency for the crystal depends totally on the oscillating mass (solvent included) that attaches to the crystal. The fundamental frequency will decrease as mass adsorbs to the quartz crystal surface. The more mass adsorbs onto the steel coating, the larger the decrease in resonance frequency becomes. For rigid, thin films that form on the crystal, the frequency shift can be related to adsorbed mass by the Sauerbrey equation [11,13]:

$$\Delta m = \frac{C * \Delta f}{n}, \tag{1}$$

where C is the mass sensitivity constant (17.7 ng cm^{-2} Hz^{-1} for the 5 MHz fundamental mode AT-cut sensor crystals used here) and n is the frequency number (fundamental — n = 1; 3rd overtone — n = 3; 5th overtone — n = 5; 7th overtone — n = 7, etc.). The mass sensed and the frequency shift includes all material coupled to oscillating crystal, including any trapped or absorbed molecules of the solution.

Dissipation changes (ΔD) were monitored simultaneously as the frequency changes. ΔD is defined as the ratio of dissipated energy to stored energy during one period of oscillation in the system. By definition, ΔD is affected by processes that cause energy loss. Therefore, any coupling between the bulk medium and crystal will affect dissipation. This coupling in turn will affect the viscoelastic properties of the layer adsorbed to the surface. Dissipation changes, measured as $\Delta D \times 10^{-6}$, are typically less than 1×10^{-6} for rigidly adsorbed layers. Dissipation changes $> 1 \times 10^{-6}$ indicate a highly viscoelastic system.

2.5. QCM-D procedure

The system was allowed to stabilize in hexadecane prior to measurements. All experiments were conducted at 25 ± 0.05 °C. Frequency (as well dissipation) shifts were recorded for four frequencies (the fundamental frequency of 5 MHz and the 3rd, 5th and 7th overtones at 15, 25 and 35 MHz, respectively). Stainless steel crystals purchased from Q-Sense were cleaned first by rinsing them in water and ethanol. The crystals were then dried under a gentle nitrogen stream and placed into an UV/Ozone chamber (Bioforce Nanosciences, Ames, IA) for 10 min [14]. Following the UV/ozone treatment, the crystals were submerged in 4% (v/v) Hellmanex for an hour. The crystals were put through a final set of rinses with water and ethanol, followed by a final UV/ozone treatment. Crystals were kept under argon until used in an experiment.

Experimental measurements consisted of first initializing the system in air and allowing the QCM-D to equilibrate for several minutes. During this time, hexadecane was added to the syringe connected to the loop and flowed excess hexadecane (≥3 mL) through a preheated loop and allowing the hexadecane to thermally equilibrate while acquiring frequency and dissipation changes in air. After the signal remained stable for several minutes (Δf < 2 Hz) in air, 0.5 mL of hexadecane was flowed over the sensor crystal. The frequency and shifts were allowed to equilibrate again before hexadecane was introduced over the sensor. This process was repeated at least three times to ensure that all air bubbles were forced out of the crystal chamber and the frequency shifts remained ± 1 Hz. Again, the system was allowed to equilibrate and maintain a stable signal for several minutes. Once a stable baseline was obtained, the measurements of Δf and ΔD during adsorption were performed (approximately 0.5 mL of temperature-stable sample liquid being

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