Influence of Unsaturations on the Organization and Air Reactivity of Triglyceride Monolayers

Clara Azémard, Marie-Claude Fauré, Slavica Stankic, Stéphane Chenot, Helen Ibrahim, Lucie Laporte, Philippe Fontaine, Michel Goldmann, Laurence de Viguerie

▶ To cite this version:

Clara Azémard, Marie-Claude Fauré, Slavica Stankic, Stéphane Chenot, Helen Ibrahim, et al.. Influence of Unsaturations on the Organization and Air Reactivity of Triglyceride Monolayers. Langmuir, 2022, 38 (2), pp.711-718. 10.1021/acs.langmuir.1c02613 . hal-03521186

HAL Id: hal-03521186
https://hal.sorbonne-universite.fr/hal-03521186v1

Submitted on 11 Jan 2022

Influence of Unsaturations on the Organization and Air reactivity of Triglycerides Monolayers

C. Azémard[1], M.C. Fauré[2,4], S. Stankic[2], S. Chenot[2], H. Ibrahim[2], L. Laporte[1], P. Fontaine[3], M. Goldmann[2,3,4], L. de Viguerie[1*]

1. Sorbonne Université, CNRS UMR 8220, LAMS, 4 place Jussieu 75252 Paris cedex 05, France
2. Sorbonne Université, CNRS UMR 7588, Institut des NanoSciences de Paris INSP, 4 place Jussieu 75252 Paris cedex 05, France
3. Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin BP48, 91192 Gif-Sur-Yvette, France
4. UFR de Sciences Fondamentales et Biomédicales, Université de Paris, 45 rue des Saints-Pères 75006 Paris, France

corresponding author email : laurence.de_viguerie@sorbonne-universite.fr

Abstract

The behavior of Langmuir monolayers of saturated and unsaturated C18 triglycerides (TAGs) was studied as two-dimensional (2D) models for paint systems, at the air-water interface or transferred onto solid films. The organization of saturated tristearin (C18:0) monolayer was probed thanks to grazing incidence X-ray diffraction: one observes a hexagonal packing of the chains perpendicular to the air-water interface, in contrast to what is described in the literature. Conversely, the mono- and poly-unsaturated TAGs (triolein C18:1, trilinolein C18:2 and trilinolenin C18:3) monolayers do not present any organization at the air-water interface but do exhibit peculiar reactivity regarding the air atmosphere. The obtained results derived from the evolution of surface pressure - molecular area isotherms and monolayers compressibility under different atmospheres over time, combined with ultrahigh-vacuum infrared (UHV-FTIR) spectroscopy, showed the adsorption of O_2 molecules in the monolayer together with chemical reactions with hydrocarbon chains. The kinetic effect of lead ions, known to be efficient siccative agents in oil paints, was also assessed: the addition of Pb^{2+} in the subphase induces an increase of the O_2 adsorption.

Keywords

Siccative oils; surface pressure isotherms; grazing incidence X-ray diffraction; infrared spectroscopy

Introduction

Oils are present in many products: foods, cosmetics, lubricants, fuel or paints. They are mostly composed of fatty acids (FAs) and triglycerides (TAGs), the latter being composed of three FAs connected by a glyceride head. Natural oils used in paint, such as linseed, walnut or poppy seed oils, are said to be siccative i.e. displaying air-drying properties thanks to the presence of polyunsaturated fatty acids[1–5].

Fatty acids and triglycerides can form films at the air-water interface (Langmuir films) as they display hydrophilic head and hydrophobic carbon chains. A plethora of studies were carried out on saturated and unsaturated FAs Langmuir monolayers exploring their structure and behaviour depending on the length of the hydrocarbon chain, the presence of unsaturations and pH conditions[6-11]. In the dense phases, a hexagonal or rectangular packing of the chains can be observed. In the collapse, multilayer systems are obtained which present similar crystalline structure as in bulk, i.e. orthogonal, orthorhombic or triclinic forms. The presence of unsaturation(s) affects the surface pressure of the monolayer[12-14] in a similar way as shortening the alkyl chain length. Moreover at the same hydrocarbon chain length, unsaturation causes expansion of the monolayer as also shown in the bulk crystallization features of the unsaturated fatty acids which crystallize in a more difficult fashion than the corresponding saturated straight-chain fatty acids.

Although less studied, Langmuir monolayers of TAGs can also be formed with all chains pointing toward the same direction (in a so-called trident conformation)[15-17]; which enables the hydrophilic part of the molecule to be in contact with water while the hydrophobic chains point into the air. In the context of a broader research on TAGs in paint films (their interfacial behavior and drying process) we focused on saturated, mono- and poly-unsaturated C18 TAGs (tristearin, trioléin, trilinolein and trilinolenin). Among them, tristearin monolayer is the most studied one with various publications from Zdravkova and Eerden[15, 18]. Few studies have described unsaturated TAGs behavior: Michalski *et al.* [19] have shown thanks to AFM studies after transfer on glass substrates, that triolein collapsed in amorphous droplets, but as far as we are concerned no recent study has focused on unsaturated C18 TAGs monolayers, which are key components of historical oil paintings. The first aim of this study was to investigate the influence of unsaturation on the organization and stability of C18 TAGs monolayers and confirm the previous results concerning tristearin monolayer by combining surface pressure – molecular area isotherms measurements and grazing incidence X-ray diffraction experiments, to probe it directly at air-water interface. Then, considering the peculiar air-drying properties of unsaturated TAGs, we aimed at investigating the reactivity of their Langmuir monolayers, as 2D model systems of oil paint systems: the evolution of their surface pressure-area isotherms under different atmosphere, was monitored over time and further interpreted thanks to infrared spectroscopy after transfer on a silicon substrate. The effect of lead, used as a siccative agent in oil paints, [20-26] was also investigated, probing the influence of the addition of lead ions in the water subphase on the isotherms and compressibility modulus.

Materials and Methods

The standard molecules were purchased from Larodan®, France (Table 1). The tristearin (three C18:0 chains), triolein (C18:1 chains), trilinolein (C18:2 chains) and trilinolenin (C18:3 chains) were solubilized in chloroform to a concentration of ca. 1 mM. Milli-Q Millipore ultra-pure water (18.2 MΩ.cm) was used for the subphase.

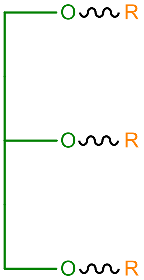
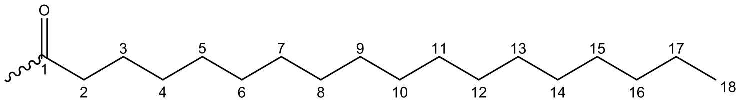
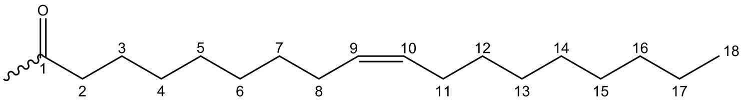
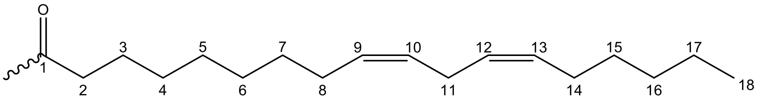
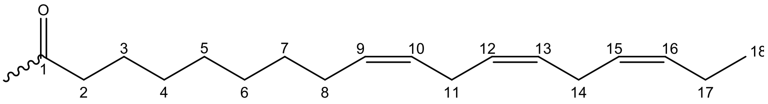
Glycerol residue	**Fatty acid chains**		
	R formula	***Abbreviation***	***Name***
		C 18 :0	Stearic
		C 18 :1 (n-9)	Oleic
		C 18 :2 (n-6 ; n-9)	Linoleic
		C 18 :3 (n-3 ; n-6 ; n-9)	Linolenic

Table 1: Structure of the FA chains of the studied triglycerides.

Thermodynamic measurements on Langmuir films were carried out on a homemade device with two movable barriers for film compression. The TAGs solutions were deposited drop by drop with a micro syringe (Hamilton) to reach an initial surface density around 2 nm^2/molecule and let 10 minutes before compression to enable the solvent evaporation and the equilibration of the monolayer before compression. The surface pressure was measured according to the Wilhelmy plate method. The temperature was regulated at 20 ± 0.5 °C using a circulating water bath. We performed the isotherms at least 3 times to check the reproducibility of the results. All isotherms were performed in a 193 cm^2 trough at a constant speed compression of 4.2 cm^2/min. For controlled atmosphere experiment, the trough was enclosed in a box with nitrogen flux. The compressibilities are extracted using the usual relation

$$\chi = -\frac{1}{A}\left(\frac{\partial A}{\partial \pi}\right)_{T,p,n}$$

with A being the area per molecule, π the surface pressure at constant temperature T, external pressure p, and number n of moles of material.

Grazing Incidence X-Ray Diffraction (GIXD) experiments were performed at the air-water interface at the SIRIUS beamline of the SOLEIL synchrotron source (France) with the usual setup described previously[27]. The energy of the incoming X-Ray beam was 8 keV (λ = 1.55 Å). The scattering intensity was recorded using a vertical PSD associated to a Sollers slit collimator with a resolution of 0.06°. The diffraction peaks were fitted with a Lorentzian functions and sloping background (the peak is considered as single when a fit using two Lorentzian functions does not lead to a better adjustment).

Fourier Transform Infrared Spectroscopy (FTIR) measurements were also carried out on trilinolenin films, deposited on a 300 μm thick Si intrinsic wafer, by the Langmuir Blodgett method. FTIR spectra were recorded by means of a Bruker Vertex 70 FTIR spectrometer equipped with a MCT detector with a resolution of 4 cm^{-1}, averaging 250 interferogram scans. We used a previously described Ultra High Vacuum (UHV) apparatus[28,29] which consists of the introduction, preparation and main chamber (i.e. the analysis chamber) – the latter two including working pressure in the 10^{-10} mbar range; the experiments were performed in the analysis chamber in the transmission mode (silicon being transparent in the frequency range of relevance), through ZnSe windows. Before introducing the two samples, the UHV system was backed and the P_{syst} was confirmed to be in the desired range ($< 10^{-10}$ mbar). Moreover, the background spectra were taken at t=0 and t=15 minutes and no changes were observed between them. The IR study on trilinolenin films deposited on Si-wafer were performed after the two precautions were applied.

Results and discussion

Organisation and stability of the C18 TAGs monolayers: effect of the unsaturation(s)

Thermodynamic study

Compression isotherms of tristearin, triolein, trilinolein and trilinolenin on water subphase were recorded at 20 °C (figure 1). The isotherm of tristearin, consistent with the literature[15], is quite different from the ones of unsaturated compounds. At large area it presents a coexistence plateau at almost zero surface pressure followed by a lift-off at around 0.6 nm^2/molecule from where the monolayer exhibits a low compressibility phase at ca. 2.7 m/N indicating a liquid condensed (LC) phase. This is in good agreement with the area of 0.2 nm^2/chain (cross-section of a typical hydrogenated chain). The collapse of the film is reached at about 50 mN/m and 0.5 nm^2/molecule.

Corresponding author : laurence.de_viguerie@sorbonne-universite.fr

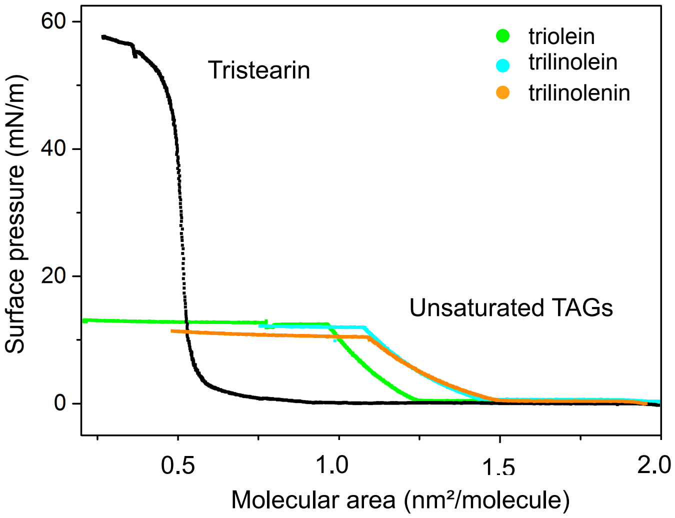


Figure 1: Surface pressure-molecular area isotherms of the four TAGs on pure water subphase at 20 °C (black: tristearin, green: triolein, blue: trilinolein and orange: trilinolenin).

The behaviour of unsaturated triglyceride monolayers is different (figure 1): the lift off is shifted to higher molecular area (between 1.25 nm^2/molecule and 1.5 nm^2/molecule), and the collapse surface pressure lowered to 10 - 13 mN/m. The compressibility of the single dense phase is 21, 26 and 31 m/N for the triolein, trilinolein and trilinolenin respectively, all corresponding to liquid expanded phases (LE). It is noticeable that the lift-off and collapse areas increase with an increase in the number of unsaturations (mostly observable between triolein and trilinolein or trilinolenin).

Isotherms performed at 30°C (not shown) are very similar indicating that the temperature has little influence in this range. Compression-expansion-compression cycles indicate a good stability of the studied saturated and unsaturated TAGs monolayers (figure S1).

Grazing Incidence X-ray Diffraction (GIXD) experiments

In order to probe the organisation of the studied C18 TAGs (and confirm the organisation of the LC phase of the tristearin monolayer[18]) GIXD experiments were carried out: tristearin (C18:0), triolein (C18:1) and trilinolenin (C18:3) monolayers were investigated on pure water subphase. In the case of triolein and trilinolenin, no diffraction peak was observed up to the collapse pressure. This result is expected in the case of LE phases, as observed here, and confirms the weak influence of the hydrophilic part on the inter-molecular interactions, already shown in the case of unsatured single fatty acids.[10] Conversely, one diffraction peak is observed in the LC phase of tristearin monolayer: the presence of unsaturation(s) prevents the organization of the monolayer.

The LC phase of the tristearin monolayer exhibits only one diffraction peak at $Q_{xy} = 15.1\ nm^{-1}$ (figure 2) at non zero pressure. This indicates a hexagonal packing of the chains with a lattice parameter a of:

$a = 2\pi / (q_{10} \sin 120°) = 0.480$ nm.

Corresponding author : laurence.de_viguerie@sorbonne-universite.fr

Increasing the surface pressure led to a slight shift of the peak to higher Q_{xy} associated with a broadening of the peak (as seen on Figure S2a and b). The unit cell area can be computed ($A_m = a^2 \sin 120°$), and from its evolution with surface pressure, a microscopic compressibility can be calculated. Its value is about 0.35 m/N, much lower than the macroscopic compressibility, calculated from the surface pressure – area isotherm (2.7 m/N as mentioned above). Such a value indicates a very close packed crystalline structure. Conversely, the largest value of the FWHM corresponds to a low coherence length (2/FWHM) of about 15 nm probably due to a constraint in the intermolecular chain organisation induced by the geometrical packing of the glycerol group [30].

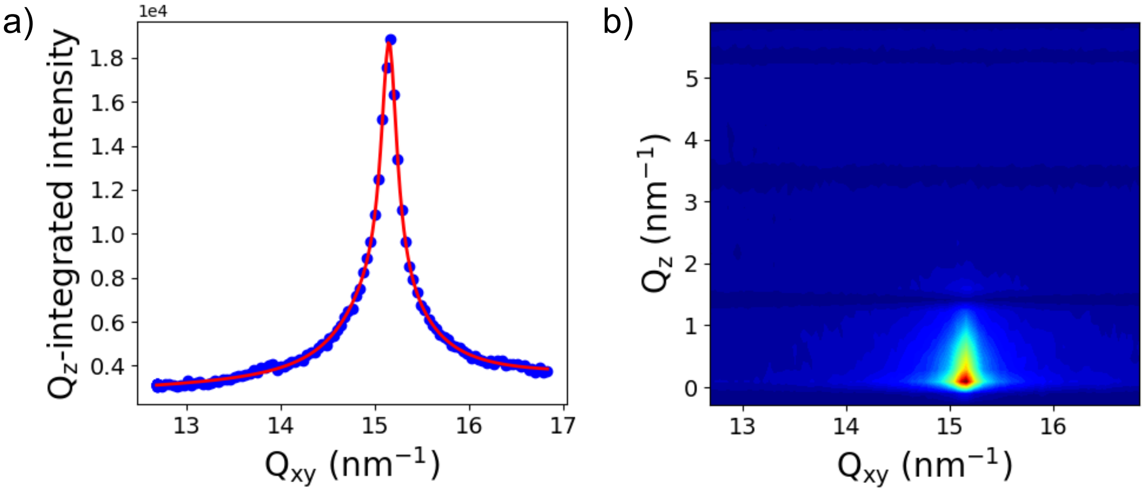


Figure 2: a) Qz integrated x-ray scattered intensity spectrum versus Q_{xy} obtained on a tristearin monolayer at a pressure of 10 mN/m, b) Corresponding Q_{xy}-Q_z GIXD pattern.

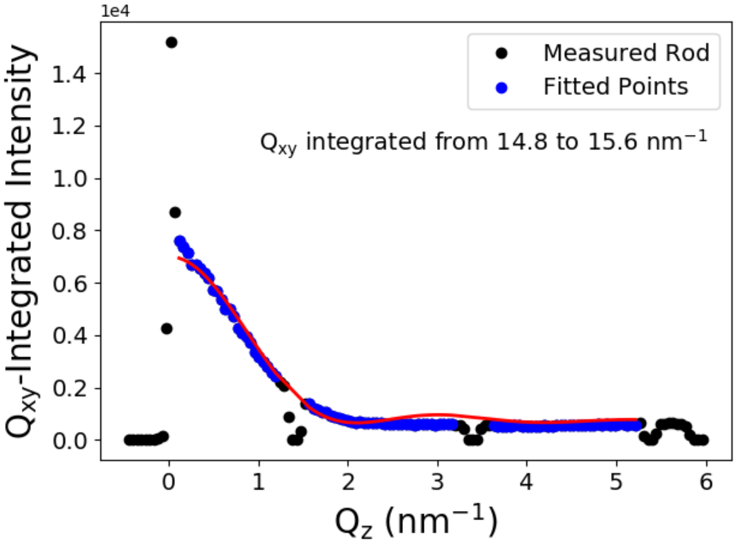


Figure 3: Rod scan analysis of the diffraction spectrum of figure 3. Only the points that correspond to the form factor of the molecule were kept. The rod scan is fitted (red line) by the form factor of a cylinder of length L and radius R (the product of a Bessel function of Q_{xy} and R that can be considered as a constant here, and a sinus cardinal function of Q_z.L/2).

The rod scan I(Qz) analysis presents a maximum at Q_z around 0, which implies that the hydrocarbon chains are perpendicular to the liquid surface (thus in trident conformation, figure 4) in agreement with the hexagonal structure deduced from the in-plane position of the diffraction peak. The diffraction rod, extracted by Qxy-Integration of the Qxy-Qz intensity distribution (figure 3), was fitted by the form factor of a cylinder, as classically in the case of hydrocarbon chains in a rotator phase. The best fit, given in figure 3, is obtained for the length of the molecule of 3.00 ± 0.05 nm. This value is slightly above the length of a C18 hydrocarbon chain, 2.4 nm, but not far from the one expected when taking into account the headgroup of the tristearin molecule.

In previous publications, Zdravkova and van der Eerden[18] have shown that the trident conformation is thermodynamically stable in the case of tristearin monolayers up to $\pi \approx 5$ mN/m, which is in accordance with our observations. However, they estimated the monolayer thickness at about 1.8 nm, with molecules tilted at 45 ± 2° (Figure 4). This discrepancy can be explained by the followed protocols: the monolayer thickness was estimated from AFM experiments on transferred monolayer on a mica substrate, whereas GIXD allowed to investigate the monolayers *in situ*, at air-water interface. It is thus reasonable to consider that transferring the film on a mica substrate induced a modification of the structure.

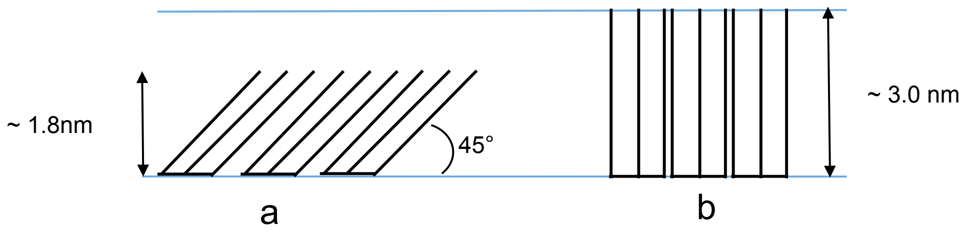


Figure 4: Proposed structures of the tristearin monolayer at air-water interface, in trident conformation: a) from Zdravkova et van der Eerden after deposition on mica substrates: the tilt angle was estimated from the measured thickness of the monolayer by AFM, compared to the extended alkane chain length; b) structure deduced from GIXD experiments in situ (at the air-water interface).

Reactivity with air of unsaturated TAGs monolayers

The presence of unsaturation(s) was shown to prevent from the organisation of the monolayer; it also influences strongly its reactivity with the atmosphere. As mentioned above, (poly-) unsaturated TAGs are major constituents of siccative oils used in historical paintings providing them with air-drying properties. The "drying" of siccative oils is a chemical process, taking place spontaneously when exposed to the air, following complex reaction paths of oxidation and radical polymerization. The use of metal driers (historically lead, but also zinc, manganese, cobalt…) became a common practice to accelerate this process and is still today. In order to investigate the air-drying properties of unsaturated TAGs, we have followed the evolution of their monolayer under different atmospheres over longer time (at short time scale, the monolayers are stable, as proven by the compression-expansion cycles, Figure S1).

The first experiment was carried out by recording at constant area the surface pressure evolution of a trilinolenin (C18:3) monolayer after compression in the dense phase. When exposed to the air atmosphere, one observes a continuous increase of the surface pressure, whereas under nitrogen atmosphere, the surface pressure remains almost constant (figure 5a). Therefore, it can be deduced that the observed pressure increase under air results from an interaction between the trilinolenin molecules and the atmospheric oxygen. In the case of trilinolein (figure 5b), the surface pressure slightly increases during 5h before saturation (we checked that the weak decreasing of the surface pressure observed at longer time is due to the water evaporation). Triolein, with only one unsaturation, does not present such a pressure increase (Figure 5b) but a relaxation process is clearly observed as for tristearin (figure S3). Such a pressure increase at constant area and in a single phase state of the trilinolenin monolayer indicates an increase of the average microscopic area per molecule. Two scenari can be then considered: (i) the oxygen is adsorbed on the chains increasing its average area. The double bonds induce a specific configuration to the chain which could lead to the oxygen physisorption. (ii) There is a chemical reaction between atmospheric oxygen and the double bonds of unsaturated chains. Finally, one could also consider that these two phenomena occur simultaneously or successively.

Since the number of possible oxidation sites of the TAGs is related to the number of unsaturations, trilinolenin provides more of such sites and presents a larger spatial growth. In the case of triolein, the effect of the reorganisation of the film prevails over that of the molecule structure modification.

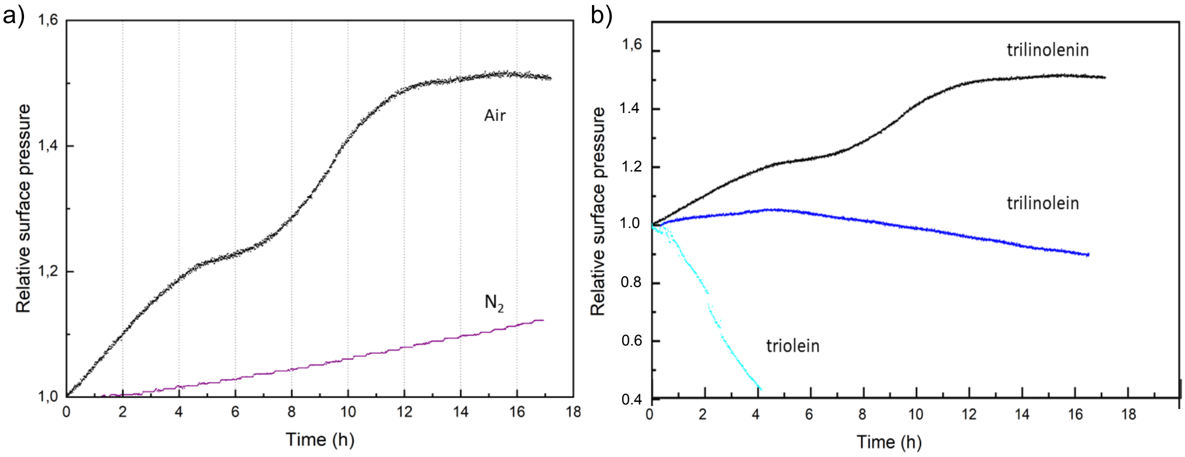


Figure 5: a) Evolution of the relative surface pressure (surface pressure at time t divided by the surface pressure at time t=0) during 17h at constant area under air atmosphere (black) and nitrogen atmosphere (pink) for trilinolenin; b) Comparison of the evolution of the relative surface pressure at constant area under air atmosphere for the 3 unsaturated TAGs.

We focused then on the most reactive monolayer, i.e. trilinolenin one, and recorded their surface pressure – molecular area isotherms for different waiting times (between the molecules deposition and the film compression). Figure 6 shows isotherms recorded for waiting time of 10 minutes, 3 hours or 10 hours after molecules deposition. Two effects can be observed as the waiting times increases: 1) the

Corresponding author : laurence.de_viguerie@sorbonne-universite.fr

lift-off associated to the LE phase is shifted to larger molecular area, indicating a lower surface density of the LE phase, 2) the monolayer collapse occurs at the same surface density but at higher surface pressure. Besides, for waiting times of 3 h and 10 h, the surface pressure after the beginning of the collapse is not constant anymore but increases under compression. These changes imply an increase of the macroscopic compressibility of the LE phase which varies from 31 to 60 m/N for waiting times ranging from 10 min to 10 h. Such a compressibility increase can be interpreted as induced by the desorption of remaining O_2 (and N_2) molecules that were adsorbed in the film submitted to the air atmosphere. One can then propose a two-step process. In the first one, the air molecules get adsorbed in the monolayer. The lower surface density of the disorganized LE phase with respect to the close packed LC one justifies why such effect is not observed on the dense phase of the tristearin monolayer. Then, in the second step, only a part of the adsorbed O_2 molecules react with the double bounds whereas some air molecules (O_2 and N_2) which did not react but remain adsorbed in the film and can be thus expulsed under compression.

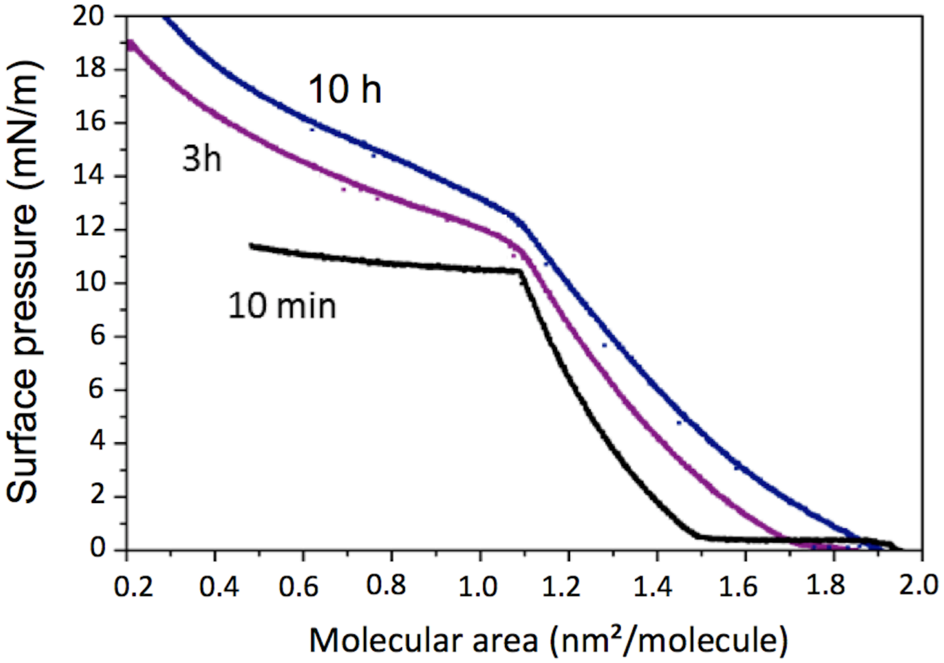


Figure 6: Compression isotherm of trilinolenin monolayer obtained for break time of 10 min, 3h, and overnight (10h) after molecule deposition.

To validate the hypothesis according to which a chemical reaction occurs between O_2 and the unsaturated chains we performed ultra-high vacuum infrared spectroscopy (UHV-FTIR) experiments on monolayers transferred on solid substrate. We compared the monolayer exposed to air over 24h before transfer to the one transferred just after deposition at the air/water interface. Figure 7a and b shows the obtained FTIR spectra: we monitored the markers of isomerisation and oxidation processes [24,25,31] according to the literature describing the drying mechanisms of siccative oils at the air. The band at 3010 cm^{-1} (cis υ(C-H) in C=C-H bands) disappears overnight (figure 7a) while a new one pops up at 1699 cm^{-1} (figure 7b). The appearance of this band in the spectrum recorded on the

Corresponding author : laurence.de_viguerie@sorbonne-universite.fr

monolayer exposed to air, is indicative of new carbonyl species (usually only noticed by the broadening of the ester band with the maximum at 1742 cm^{-1}) resulting from the oxidation and the appearance of ketones and acids. The UHV chamber connected to the FTIR spectrometer, a system that is typically used in surface science studies, allows for the majority of physisorbed species from the air to be removed (the pressure in the analysis chamber is below 10^{-9} mbar) which results in better resolution of the spectra and the identification of new species that otherwise, may undergo broadening and remain masked. This is shown here through the appearance of new peaks in the close environment of the ester band, which usually overlap and hide within other carbonyl bands. These findings are coherent with the opening of the double bonds and oxidation processes and, thus, they confirm the chemical reaction between unsaturated TAGs and oxygen from air.

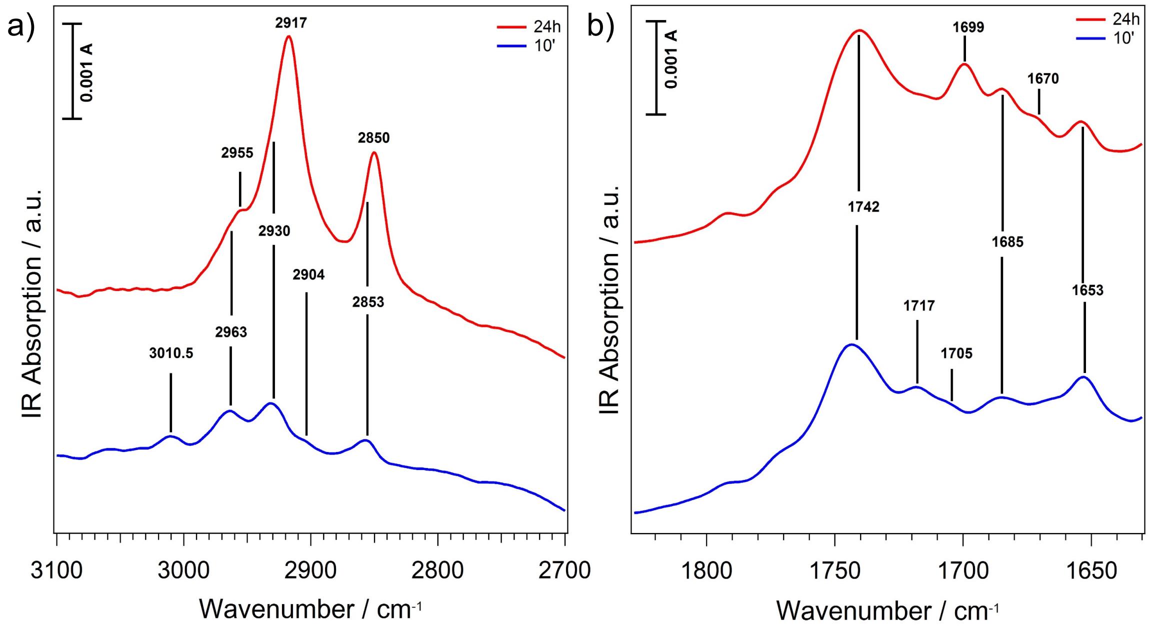


Figure 7. Evolution of trilinolenin FTIR bands a) between 3100 and 2700 cm^{-1}, and b) between 1830 and 1630 cm^{-1} after 24h at air (red) and after 10 minutes (blue) i.e. just after deposition (reference).

Effect of lead ions in the subphase: influence on the reactivity of TAGs monolayers

Carboxylic acid monolayers formed over dilute metal solutions have different properties from those formed over pure water[32,33]; among metals, lead has been singled out as having the greatest influence on the monolayer[34,35]. Divalent ions (such as lead or cadmium) induce an increase in the film rigidity with the appearance of organic-inorganic superlattices, with ions interacting strongly with the headgroups in the form of hydrated complexes or hydrolysis products.

With the aim of probing the effect of lead ions on TAGs monolayers, various experiments under air atmosphere were carried out adding $PbCl_2$ to the subphase. No influence on the isotherms carried out just after deposition of the different TAGs studied (tristearin and trilinolenin, figure S4) was found, with $PbCl_2$ dissolved at ca. 0.08 mM and 0.81 mM. Indeed, the Pb interaction with the hydrophilic head group of the TAG remains rather weak with respect to the interaction between the chains (three per headgroup in this case).

We then considered the interaction with air atmosphere, investigating the influence of lead on unsaturated TAGs and particularly trilinolenin monolayers. Indeed, lead compounds have been commonly used for centuries to enhance the siccativity of oils; this implies that the addition of lead should have an influence on the TAGs interacting with air. We compared the isotherms of trilinolenin monolayers when compressing the film 3h after deposition on pure water or on $PbCl_2$ solution (Figure 8). Adding lead in the subphase induces mainly a shift of the lift-off to larger molecular area from 1.7 nm^2/molecule to 2.0 nm^2/molecule, although the collapse area and surface pressure remain unchanged. Therefore, the compressibility of the LE phase, mainly defined by the chains interaction, has been increased by the presence of Pb^{2+} in the subphase. Such a shift and increase of the compressibility indicate that the reaction between the chain unsaturations and the air atmosphere is accelerated thanks to the presence of Pb^{2+}. Then, although the ions are usually considered to interact mainly with the hydrophilic headgroup, it appears that they have an effective influence on the chain reactivity in this case. It is noticeable that the isotherms for both subphases are identical after the collapse.

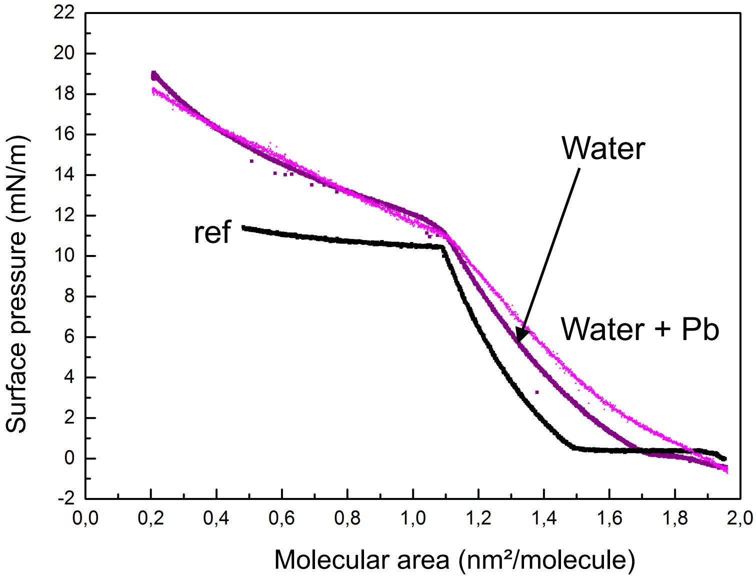


Figure 8. Isotherm of trilinolenin monolayers recorded 3h after deposition on pure water (purple) or on $PbCl_2$ aqueous solution (fuschia) and comparison with the reference isotherm corresponding to a compression after 10 min waiting time on a water subphase.

Conclusions

This study shows that the unsaturations of the hydrophobic chains have a strong influence on the properties of TAGs monolayers. Tristearin monolayer, with only saturated chains, presents at room temperature a direct transition from a Gas to a LC phase. In this last phase, the film is dense with close packed vertical chains organized on a hexagonal 2D lattice, conversely to what has been described in the literature. Unsaturated TAGs present a very different condensed phase behavior at room

Corresponding author : laurence.de_viguerie@sorbonne-universite.fr

temperature with only a Gas-LE transition. Compressing this LE phase, the collapse of the film occurs at rather large surface density, about twice the chain cross section, as observed for unsaturated fatty acid monolayer (i.e. linoleic acid[10]), preventing a dense structure of the chain layer. Consequently, the TAGs interaction with the atmosphere is strongly depending on the presence of unsaturation. In the LC phase of saturated chains, the surface density prevents any adsorption of O_2 molecules from the air atmosphere. For unsaturated TAG, the lower density of the monolayer, about a factor two, allows the adsorption of O_2 molecules. Some of the O_2 molecules do react chemically with the chains unsaturation while the others can be desorbed during the film compression. The adsorption process appears to be enhanced by the presence of Pb in the subphase. The oils with more unsaturated TAGs dry more quickly since the reaction with the air is favored and, represent, thus the painters' favorites (linseed oil, walnut oil).

Supporting Information

Trilinolenin isotherm stability test; Results from Gi-SAXS measurements: Evolution of the position of the peak maximum and of the FWHM of the organized layer deduced from the rod scan analysis as a function of the surface pressure; Surface pressure in a tristearin film at constant area during 20h under air atmosphere; Compression isotherms of trilinolenin on water and water + $PbCl_2$ subphases.

Acknowledgements

The authors thank the synchrotron SOLEIL for beamtime provision (Sirius beamline), and the *Maison de la Chimie* (Paris) for funding the post-doctoral fellowship of Clara Azemard.

Bibliography

(1) Soucek, M. D.; Khattab, T.; Wu, J. Review of Autoxidation and Driers. *Prog. Org. Coat.* **2012**, *73* (4), 435–454. https://doi.org/10.1016/j.porgcoat.2011.08.021.

(2) Klebsattel, C. A. Driers. *Journal of the American Oil Chemist's Society* **1950**, *27* (11), 500–504. https://doi.org/10.1007/BF02637770.

(3) Stenberg, C.; Svensson, M.; Johansson, M. A Study of the Drying of Linseed Oils with Different Fatty Acid Patterns Using RTIR-Spectroscopy and Chemiluminescence (CL). *Industrial Crops and Products* **2005**, *21* (2), 263–272. https://doi.org/10.1016/j.indcrop.2004.04.002.

(4) Tumosa, C. S.; Mecklenburg, M. F. The Influence of Lead Ions on the Drying of Oils. *Reviews in Conservation* **2005**, *6*, 39-47.

(5) van Gorkum, R.; Bouwman, E. The Oxidative Drying of Alkyd Paint Catalysed by Metal Complexes. *Coord. Chem. Rev.* **2005**, *249* (17), 1709–1728. https://doi.org/10.1016/j.ccr.2005.02.002.

(6) Roberts, G. *Langmuir-Blodgett Films*; Plenum Press: New York, 1990.

(7) Peng, J. B.; Barnes, G. T.; Gentle, I. R. The Structures of Langmuir–Blodgett Films of Fatty Acids and Their Salts. *Adv. Colloid Interface Sci.* **2001**, *91* (2), 163–219. https://doi.org/10.1016/S0001-8686(99)00031-7.

(8) Buhaenko, M. R.; Grundy, M. J.; Richardson, R. M.; Roser, S. J. Structure and Temperature Dependence of Fatty Acid Langmuir-Blodgett Films Studied by Neutron and X-Ray Scattering. *Thin Solid Films* **1988**, *159* (1), 253–265. https://doi.org/10.1016/0040-6090(88)90637-2.

(9) Vollhardt, D. Effect of Unsaturation in Fatty Acids on the Main Characteristics of Langmuir Monolayers. *J. Phys. Chem. C* **2007**, *111* (18), 6805–6812. https://doi.org/10.1021/jp0704822.

(10) Fidalgo Rodríguez, J. L.; Dynarowicz-Latka, P.; Miñones Conde, J. Structure of Unsaturated Fatty Acids in 2D System. *Colloids Surf. B* **2017**, *158*, 634–642. https://doi.org/10.1016/j.colsurfb.2017.07.016.

(11) Dopierała, K.; Krajewska, M.; Prochaska, K. Study on pH-Dependent interactions of linoleic acid with α-lactalbumin. *Food Hydrocolloids* **2021**, *111*, 106217.

(12) Langmuir, I. The constitution and fundamental properties of solids and liquids. II. Liquids *J. Am. Chem. Soc.* **1917**, *39*, 1848-1906.

(13) Adam, N. K. The properties and molecular structure of thin films. Part III. Expanded films. *Proc. R. Soc. London* **1922**, *A101*, 516.

(14) Welles, H. L.; Zografi, G.; Scrimgeour, C. M.; Gunstone, F. D. In *Monolayers;* Goddard, E. D, Ed; American Chemical Society: Washington, DC, 1975.

(15) Zdravkova, A. N.; van der Eerden, J. P. J. M. Structure and Stability of Triglyceride Monolayers on Water and Mica Surfaces. *Cryst. Growth Des.* **2007**, *7* (12), 2778–2787. https://doi.org/10.1021/cg060701t.

(16) Mayama, H. Blooming Theory of Tristearin. *Soft Matter* **2009**, *5* (4), 856–859. https://doi.org/10.1039/B815005B.

(17) Bursh, T.; Larsson, K.; Lundquist, M. Polymorphism in Monomolecular Triglyceride Films on Water and Formation of Multimolecular Films. *Chem. Phys. Lipids* **1968**, *2* (1), 102–113. https://doi.org/10.1016/0009-3084(68)90036-4.

(18) Zdravkova, A. N.; van der Eerden, J. P. J. M. Structure and Dynamics of Langmuir–Blodgett Tristearin Films: Atomic Force Microscopy and Theoretical Analysis. *J. Cryst. Growth* **2006**, *293* (2), 528–540. https://doi.org/10.1016/j.jcrysgro.2006.05.070.

(19) Michalski, M.-C.; Brogueira, P.; Silva, A. G. da; Saramago, B. Topography of Collapsed Triglyceride Monolayers on Glass. *Eur. J. Lipid Sci. Technol.* **2001**, *103* (10), 677–682. https://doi.org/10.1002/1438-9312(200110)103:10<677::AID-EJLT677>3.0.CO;2-H.

(20) Tripier-Deveaux, A. M. *Traité théorique et pratique sur l'art de faire les vernis*; L. Mathias, 1845.

(21) Cameron, J. *Oils and Varnishes*; J. & A. Churchill: London, 1886.

(22) McIntosh, J. G. *The Manufacture of Varnishes and Kindred Industries Based on and Including the "Drying Oils and Varnishes";* Scott, Greenwood & Son: London, 1908.

(23) Merrifield, M. P. *Medieval and Renaissance Treatises on the Arts of Painting: Original Texts with English Translations*; J. Murray: London, 1849.

(24) de Viguerie, L.; Payard, P. A.; Portero, E.; Walter, Ph.; Cotte, M. The Drying of Linseed Oil Investigated by Fourier Transform Infrared Spectroscopy: Historical Recipes and Influence of Lead Compounds. *Prog. Org. Coat.* **2016**, *93*, 46–60. https://doi.org/10.1016/j.porgcoat.2015.12.010.

(25) Mallégol, J.; Lemaire, J.; Gardette, J.-L. Drier Influence on the Curing of Linseed Oil. *Prog. Org. Coat.* **2000**, *39* (2), 107–113. https://doi.org/10.1016/S0300-9440(00)00126-0.

(26) van den Berg, J. D. J.; Vermist, N. D.; Carlyle, L.; Holčapek, M.; Boon, J. J. Effects of Traditional Processing Methods of Linseed Oil on the Composition of Its Triacylglycerols. *J. Sep. Sci.* **2004**, *27* (3), 181–199. https://doi.org/10.1002/jssc.200301610.

(27) Ciatto, G.; Chu, M. H.; Fontaine, P.; Aubert, N.; Renevier, H.; Deschanvres, J. L. SIRIUS: A New Beamline for in Situ X-Ray Diffraction and Spectroscopy Studies of Advanced Materials and Nanostructures at the SOLEIL Synchrotron. *Thin Solid Films* **2016**, *617*, 48–54. https://doi.org/10.1016/j.tsf.2016.03.069.

(28) Haque, F.; Chenot, S.; Viñes, F.; Illas, F.; Stankic, S.; Jupille, J. ZnO Powders as Multi-Facet Single Crystals. *Phys. Chem. Chem. Phys.* **2017**, *19* (16), 10622–10628. https://doi.org/10.1039/C7CP01635B.

(29) Haque, F.; Finocchi, F.; Chenot, S.; Jupille, J.; Stankic, S. Interplay between Single and Cooperative H2 Adsorption in the Saturation of Defect Sites at MgO Nanocubes. *J. Phys. Chem. C* **2018**, *122* (31), 17738–17747. https://doi.org/10.1021/acs.jpcc.8b03192.

(30) Kaganer, V. M.; Möhwald, H.; Dutta, P. Structure and Phase Transitions in Langmuir Monolayers. *Rev. Mod. Phys.* **1999**, *71* (3), 779–819. https://doi.org/10.1103/RevModPhys.71.779.

(31) Derrick, M. R.; Stulik, D.; Landry, J. M. *Infrared Spectroscopy in Conservation Science*; The Getty Conservation Institute: Los Angeles, 1999.

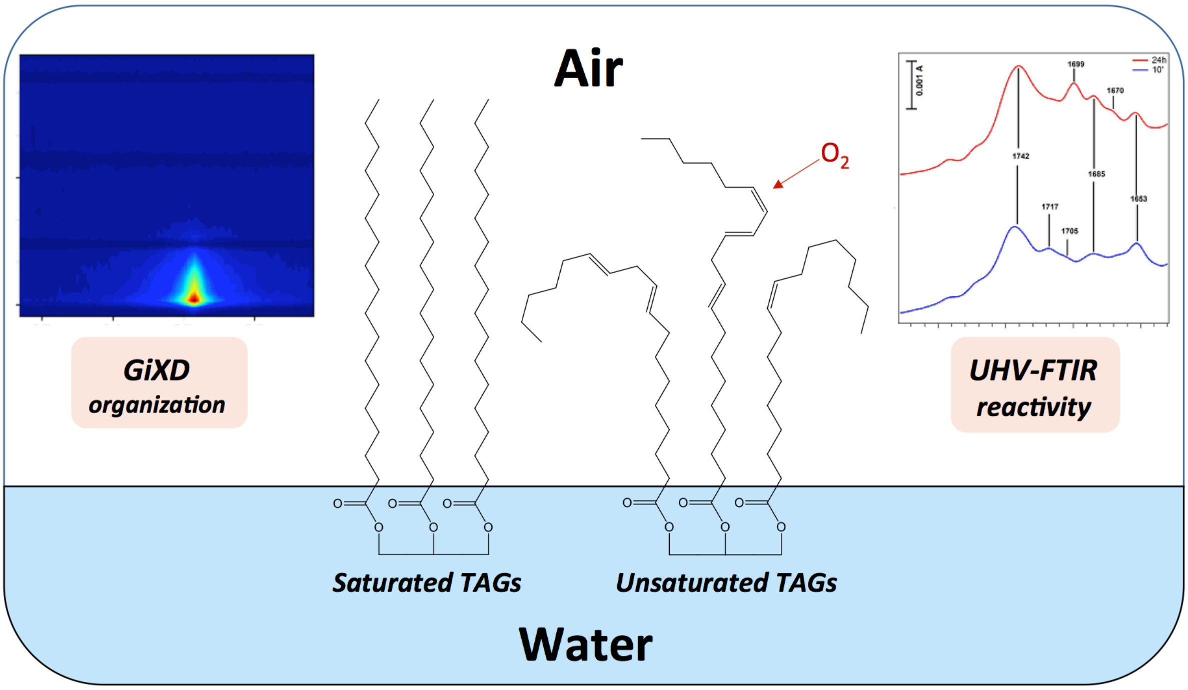
(32) Kmetko, J.; Datta, A.; Evmenenko, G.; Dutta, P. The Effects of Divalent Ions on Langmuir Monolayer and Subphase Structure: A Grazing-Incidence Diffraction and Bragg Rod Study. *J. Phys. Chem. B* **2001**, *105* (44), 10818–10825. https://doi.org/10.1021/jp0122169.

(33) Cantin, S.; Fauré, M.-C.; Perrot, F.; Goldmann, M. Structure and Kinetics of Fatty Acid Langmuir Monolayers on Zinc Salt Solutions. *J. Phys. Chem. B* **2013**, *117* (50), 16275–16282. https://doi.org/10.1021/jp407047a.

(34) Boyanov, M. I.; Kmetko, J.; Shibata, T.; Datta, A.; Dutta, P.; Bunker, B. A. Mechanism of Pb Adsorption to Fatty Acid Langmuir Monolayers Studied by X-Ray Absorption Fine Structure Spectroscopy. *J. Phys. Chem. B* **2003**, *107* (36), 9780–9788. https://doi.org/10.1021/jp0341772.

(35) Gericke, A.; Hühnerfuss, H. The Effect of Cations on the Order of Saturated Fatty Acid Monolayers at the Air-Water Interface as Determined by Infrared Reflection-Absorption Spectrometry. *Thin Solid Films* **1994**, *245* (1), 74–82. https://doi.org/10.1016/0040-6090(94)90880-X.

TOC Graphic



Corresponding author : laurence.de_viguerie@sorbonne-universite.fr