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How Do Silanes Affect the Lubricating Properties of Cationic Double Chain Surfactant on Silica Surfaces ?

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ABSTRACT

The effect of an aminosilane on the lubricant properties of a C_{18} double-chained cationic surfactant has been investigated in the context of glass fiber forming process. The surfactant adsorption was studied on silica by Fourier Transform Infrared (FT-IR) spectroscopy in the Attenuated Total Reflexion (ATR) mode as a function of the aminosilane concentration in an organic water based formulation (sizing) used to coat the glass fibers during the process. A reciprocating ball-on-plate tribometer was used to compare friction properties of silica in contact with the aminosilane-surfactant mixture and in presence of each component of the sizing. Surface forces were measured between silica and an Atomic Force Microscope (AFM) silicon nitride tip in the sizing and in the pure cationic surfactant solution.

The aminosilane on its own has no lubricant property and reduces or even suppresses the cationic surfactant adsorption on silica. However, the silica-silica contact is lubricated even if the infrared spectroscopy does not detect any surfactant adsorption. The repeated contacts and shear due to the friction experiment itself induce accumulation, organization and compactness of surfactant bilayers.

KEYWORDS : Friction, lubrication, silica, cationic surfactant, aminosilane, coadsorption

Introduction

Many plastic and mineral materials are reinforced by glass fibers for industrial applications such as transportation (structural automotive components…), buildings and infrastructures (wall covering, lighting…) or electricity (supply boxes…) and electronics (printed circuits…). Glass fiber-reinforced composites combine low density with highly attractive chemical, thermal and mechanical properties such as corrosion resistance, insulating, shock and heat resistance. The mechanical performances of such composites depend both on the glass fiber toughness and on the fiber – matrix interaction levels in the final product. Both can be controlled through the application of an organic water based formulation or sizing on the fibers during the fiber forming process [1-3]. Indeed, the sizing contains a cationic or non ionic surfactant, an organofunctional silane and additives (anti-static, wetting and sticking agents, emulsifiers). The surfactant adsorbs on glass [4,5] and has a lubricating effect [6] which protects fibers from damage through sliding contacts between fibers and with the guiding elements of the process. Thus the good mechanical properties of glass fibers are kept. The organofunctional silane or coupling agent insures compatibility between the fiber and the matrix through covalent bonds with glass after the silane hydrolysis [7,8] and with the matrix.

A question then relates to the possible interaction between the silane and the surfactant, both able to adsorb on the glass surface. Investigations on friction properties of silica, glass or mica in presence of silane and surfactant mixture are not available in the literature. A few studies only concern mixtures containing a cationic surfactant mixed with a copolymer [9], an anionic surfactant [10] or an alcohol [11]. In this work, we focus on the surfactant lubricant effect in the context of competing silane adsorption for a better understanding on the mechanisms involved in the protecting effect of the sizing.

A model sizing containing the 3-aminopropyltriethoxysilane (aminosilane) and a cationic double-chained surfactant (1-methyl-2-noroleyl-3-oleic acid-aminoethyl-imidazolinium methosulfate or DOAIM) is chosen. These molecules could be potentially used in an industrial sizing formulation for the glass fibers coating. The surfactant adsorption is studied on silica (main component in glass fiber composition) and is followed by Attenuated Total Reflexion Fourier Transform Infrared spectroscopy as a function of the aminosilane concentration in the sizing. Friction properties of silica in contact with the sizing are investigated using a reciprocating ball-on-plate tribometer and are compared to the friction properties of silica in contact with each component of the sizing. The effect of coadsorption of the aminosilane and the cationic surfactant on surface forces is measured by Atomic Force Microscope (AFM) between silica and the AFM tip in a silica liquid cell. We show that the aminosilane reduces or even suppresses the surfactant adsorption. However, the absence of surfactant adsorption pointed out by infrared spectroscopy does not prevent its accumulation and organization which is induced by the contact itself and shear during the friction tests, leading to the lubrication of the silica – silica contact.

Experimental section

Materials and Methods

The cationic double-chained surfactant, 1-methyl-2-noroleyl-3-oleic acid-aminoethyl-imidazolinium methosulfate (DOAIM) is obtained from Goldschmidt GmbH & Co. It contains 25 wt % of isopropanol and it is used as received. The bulk critical micelle concentration (CMC) is 1.10^{-5} M, as measured by surface tension and the Krafft temperature determined by DSC is 46°C.

The 3-aminopropyltriethoxysilane (aminosilane) is supplied by Aldrich. The formula of the two molecules is given in figure 1.

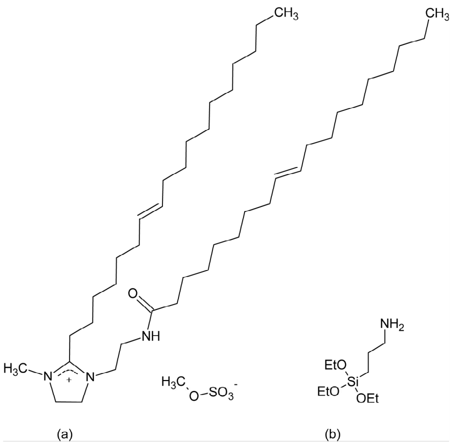

Figure 1. (a) DOAIM (b) aminosilane.

Preparation of solutions

All experiments were performed at pH and ionic strength of the mixture (respectively 4.5 and $2.2.10^{-2}$M) at ambient temperature. Such ionic strength and pH conditions are typical for sizing formulations. Water was produced by a Millipore filtration system having an internal specific resistance of 18.2 MΩ. The solutions of DOAIM, aminosilane and the surfactant-silane mixtures were prepared as follows. To obtain a 5.10^{-4} M DOAIM in acetic acid, 1 mM DOAIM in milli-Q water solution was prepared and left under stirring one day before the experiment. pH, ionic strength and the final surfactant concentration of the solution were adjusted by acetic acid (10 wt %), NaOH (1M) and water addition. Final concentrations of NaOH and acetic acid in the surfactant solution were respectively 25 mM and 80 mM. To obtain the 0.02 M and 0.04 M aminosilane in acetic acid, the aminosilane (0.5 wt % and 1 wt %) was hydrolysed in water (natural pH of 10.6) for an hour under stirring before pH adjustment by 10 wt % acetic acid addition. The DOAIM-aminosilane mixtures were prepared at a constant DOAIM concentration and increasing silane concentration while keeping pH and ionic strength constant. The aminosilane (0.1 wt %, 0.5 wt % and 1 wt %) was first hydrolysed in a 160 mM acetic acid - NaOH solution (NaOH concentration adjustment according to the aminosilane wt %) for one hour. It was then added to an equivolume of a 1 mM DOAIM in milli-Q water solution. For some experiments, the mixture was also prepared from equivolumes of a $4.5.10^{-2}$ M aminosilane in acetic acid solution and a 1 mM DOAIM in milli-Q water solution. The concentration of DOAIM in all prepared solutions is above its CMC. The surfactant associates in multilamellar vesicles with a cell parameter of 3.3 nm as determined by Small-Angle X-ray Scattering.

FTIR/ATR experiments

Attenuated Total Reflexion Fourier Transform Infrared (ATR-FT-IR) spectroscopy was used to follow the DOAIM adsorption kinetics. Tests were conducted on a Nicolet Nexus 670 spectrometer equipped with an IR source, a KBr beamsplitter and a MCT-A detector. Spectra were taken at a resolution of 4 cm^{-1} for 8, 32 and 128 scans with unpolarized light. The internal reflection element was a 50 mm × 10 mm ×1 mm, 45° incident angle, trapezoidal germaniun wafer covered by a magnetron sputtered silica layer (~ 7 nm thick) on the larger side. Before use, the wafer was cleaned using a detergent-water-acetone-absolute ethanol sequence for 15 minutes in an ultrasonic bath and irradiated for one hour by a UV-Ozone flow. After cleaning, the wafer was placed in the internal multireflexion cell which was immediately assembled and aligned in the sample compartment of the spectrometer. A peristaltic pump and a three-way valve were used to circulate either the pure solvent or the organic solution through the flow cell. A first spectrum was taken to check on the presence of the silica layer and its cleanliness and a background spectrum was collected after introducing milli-Q water in the cell. Then, the organic solution was pumped into the cell and spectra were collected during the reaction until no change could be detected.

Following N.J. Harrick [12], the amount of surfactant adsorbed can be related to the absorbance of a characteristic stretching band of the molecule. In our case we have followed the evolution of the adsorption bands between 2800 and 3000 cm^{-1}. Absorbance of the vibration band $\nu_s(CH_2)$ at 2854 cm^{-1} is used to determine the amount adsorbed at each time of the kinetics. This band has been chosen because it is less affected by the baseline drift which is due to the strong band of water in the range 3200-3300 cm^{-1}. The adsorbed quantity Γ is calculated from the relation (1) [13]:

$$A = k\varepsilon\left[\frac{c_s d_p}{2} + \Gamma\right] \qquad (1)$$

Where $k = \frac{n_2 E_0^2}{n_1 \cos\vartheta} N$ and $d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2\vartheta - \left(\frac{n_2}{n_1}\right)^2}}$

d_p is the penetration length of the evanescent wave, λ the wavelength, N the number of internal reflexions, E_0 the electric field amplitude, n_1 and n_2 the refractive index of germanium and solution respectively, θ the incident angle, A and ε respectively the absorbance and molecular extinction coefficient of the vibration band considered, and c_s the concentration of the absorbing species in solution. Assumption is made that ε is not modified by the grafting. Practically, N and E_0 cannot easily be determined. k was then determined from relation (1) by a calibration with a non adsorbing compound of known ε. Tert-butanol was used.

Atomic Force Microscopy (AFM) in liquid cell

Surface force measurements were performed in a silica liquid cell of a Nanoscope III atomic force microscope (Digital Instruments, CA) using a silicon nitride tip in contact mode. Prior to the experiment, the AFM tip was cleaned by irradiation for 60 minutes in a UV-ozone flow to remove any organic contaminant. Each AFM experiment started with a control of the tip shape quality and silica surface cleanliness by measuring interaction forces between the tip and the silica surface in milli-Q water. Water was then removed from the cell and replaced by the organic solution. Surface forces were recorded every 3 minutes as a function of exposure time of the silica surface to the solution. The interaction forces are presented without normalizing by the radius of the tip. The zero of separation is not necessarily the contact between the silica surface and the tip because the zero of separation is not absolute but is defined as the point where the surfaces move at the same rate as the piezoelectric tube. The zero of separation can correspond to the contact between the tip and organic molecules if they are trapped in the contact.

Friction experiments

Friction tests were performed on a reciprocating ball - on plate tribometer (Plint T79) with a fused silica sphere as the ball specimen in organic solutions at ambient temperature. All experiments were carried out with an initial Hertzian mean pressure of between 320 and 340 MPa (for a normal load F_N of 2N and a diameter of the ball specimen close to 4 mm). Sliding velocity and length of sliding were fixed at 10 µm/s and 1mm respectively. The sliding speed considered in this study is much lower than the typical drawing high speed of several meters per second, but is in the range of the slow sliding velocities between glass filaments in contact within a fiber.

The silica flats were prepared by cutting a 40 mm x 30 mm piece out of a silica plate (WQS). The silica balls were made from silica rods (Won Ik Quartz): the extremity was melted with a blowtorch until a molten droplet of glass formed. Prior to friction tests, silica samples were cleaned using a detergent-water-absolute ethanol sequence for 15 minutes in an ultrasonic bath and irradiated for one hour by a UV-Ozone flow. At the beginning of each experiment, the friction force F_T between silica counterparts was measured in milli-Q water to control their cleanliness. The water was then removed from the liquid cell and replaced by the organic solution. Friction measurements started 5 min after silica surfaces exposure to the solution and friction force was recorded at regular intervals. Friction was not continuous, i.e. silica samples were only brought into contact every 5 minutes for a series of two cycles. Friction force was measured and averaged on the latter cycle. When separated, silica counterparts remained immersed in the solution until the next measurement. Mean values of the ratio F_T / F_N are reported as a function of silica exposure time to organic solutions and the first mean value corresponds to a silica - silica contact in pure water.

Results

Adsorption of the mixture on silica surfaces followed by FTIR-ATR

Figure 2 shows the adsorption kinetics of 5.10^{-4} M DOAIM on silica in acetic acid solution and in a range of aminosilane concentrations from 0.002 M to 0.02 M in the mixture. At zero aminosilane concentration, the adsorption kinetics of DOAIM is fast during the first minutes and the amount of adsorbed DOAIM on silica reaches a pseudo-saturation within 10 minutes which is close to 5 µmol / m^2. From surface tension measurements of DOAIM solutions, the quantity of adsorbed surfactants at the air-liquid interface is 2.1 ± 0.1 µmol / m^2. Assuming a monolayer adsorption, the area per molecule at the air-liquid interface is evaluated at 79 ± 5 $Å^2$. It is then concluded that the value of 5 µmol / m^2 obtained at pseudo-saturation is in agreement with a complete surface coverage by a bilayer of DOAIM molecules. Figure 2 also shows that the adsorption of the cationic surfactant after an adsorption time of 80 minutes decreases when the aminosilane concentration increases. The highest aminosilane concentration leads to a drastic reduction of adsorbed quantity by a factor close to 3. An even lower adsorption can be achieved by changing the preparation procedure of the solution, i.e. by aminosilane hydrolysis in pure water rather than in NaOH - acetic acid solution (see experimental section for details).

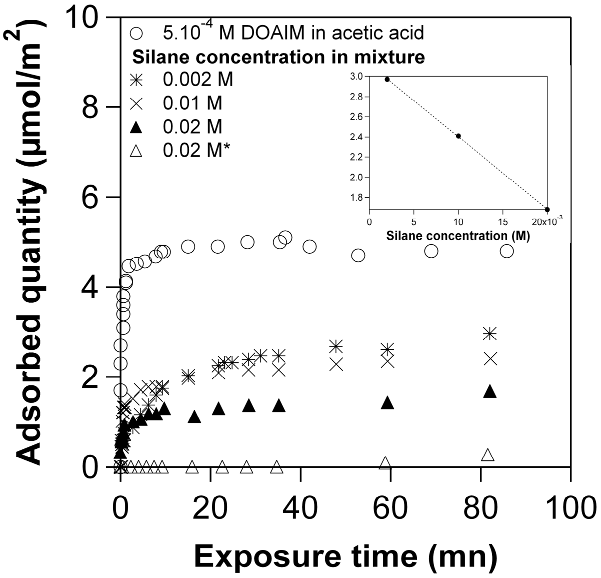

Figure 2. Adsorption kinetics of 5.10^{-4} M DOAIM on silica in acetic acid solution and at different aminosilane concentrations * denotes an alternative preparation procedure of the mixture (i.e. silane hydrolysis in pure water) - Inset: Adsorbed quantity of DOAIM after 80 minutes of exposure time as a function of aminosilane concentration in the mixture after silane hydrolysis in NaOH – acetic acid solution.

Friction

Results of adsorption kinetics in mixture solutions have shown a drastic reduction in adsorbed quantities of DOAIM after 80 minutes when the aminosilane concentration in the mixture is the highest. Friction properties of silica in presence of the mixture are then studied under conditions least favorable to surfactant adsorption (i.e. highest aminosilane concentration in the mixture with silane hydrolysis in pure water and in NaOH - acetic acid solution). Figure 3 compares the evolution of friction between silica surfaces with exposure time to the aminosilane, surfactant and mixture solutions. The aminosilane on its own has no lubricant property as compared to a silica - silica contact in pure water. In presence of the DOAIM, friction between surfaces gradually decreases except at the beginning of the test where a reproducible abrupt drop is observed and a low and stable friction value (F_T / F_N = 0.05) is reached at the end of the test. DOAIM has lubricant properties as compared to a silica - silica contact in pure water. When the aminosilane is mixed to the DOAIM, a progressive reduction in the friction towards a low and stable value is also observed with time and is equivalent whatever the aminosilane hydrolysis procedure (F_T / F_N = 0.07 - 0.08). The general trend of the decrease towards a stable regime of friction is close to the one of the cationic surfactant on its own except the abrupt drop which is not observed. It is interesting to emphasize that a lubricant effect can exist while FTIR experiment shows no surfactant adsorption within 60 minutes.

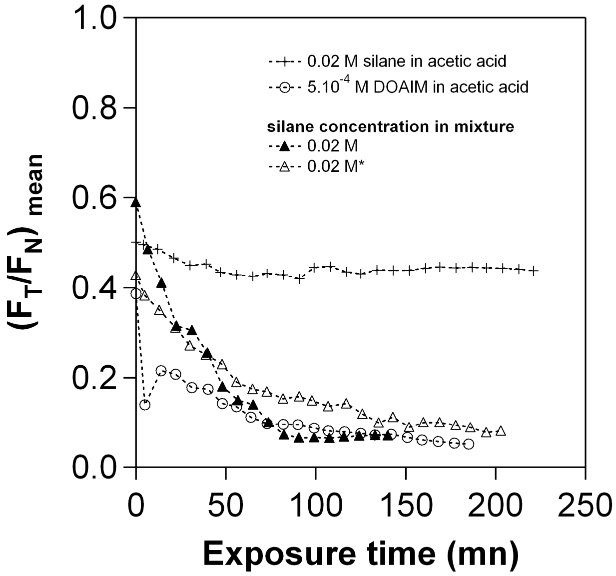

Figure 3. (F_T / F_N) mean evolution with exposure time of silica to: (o) 5.10^{-4} M DOAIM in acetic acid (+) 0.02 M aminosilane in acetic acid (△) 5.10^{-4} M DOAIM – 0.02 M* aminosilane mixture after the silane hydrolysis in pure water (▲) 5.10^{-4} M DOAIM – 0.02 M aminosilane mixture after the silane hydrolysis in NaOH- acetic acid solution.

AFM experiments

The most striking friction results are related to the development of silica – silica contact lubrication in the 5.10^{-4} M DOAIM – 0.02 M* aminosilane mixture (with the silane hydrolysis in pure water) whereas the surfactant is not adsorbed. To understand the lubrication effect in the absence of

DOAIM adsorption, this mixture solution was chosen for AFM experiments. Surface forces were also measured in the 5.10^{-4} M DOAIM solution in acetic acid for comparison. The evolution of surface forces on approach between the AFM tip and a silica surface in the mixture solution is reported in figure 4 for different exposure times.

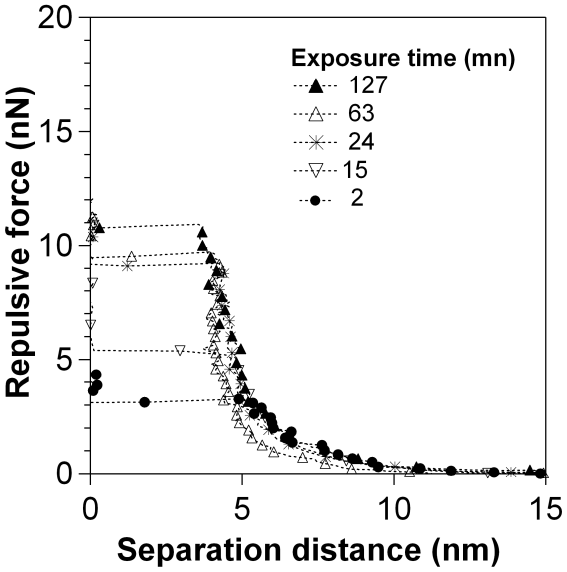

Figure 4. Measured interaction forces on approach between the AFM tip and a silica surface in a 5.10^{-4} M DOAIM – 0.02 M* aminosilane mixture (after silane hydrolysis in pure water) as a function of exposure time.

After a few minutes, a repulsive force between the two surfaces already exists at separation distances close to 10 nm. It is followed by a jump-in and contact of the tip with the surface at a separation distance of 3.5 nm – 4.5 nm. Furthermore, the maximum repulsive force or barrier height, defined by the force at which the tip jumps into contact with the surface, increases with time. A short-range repulsive force barrier also exists at 3.5 nm when the silica surface and the AFM tip are brought into contact after immersion in the pure DOAIM solution (not presented). This distance separation is close to the thickness of a DOAIM bilayer determined by SAXS measurements, indicating the presence of an adsorbed bilayer in the contact region as supported by FTIR results. Surfactant compression forces are also observed for systems such as C_{10-16}TAB cationic surfactant [14,15], C_{8-16}TAB/SDS mixtures [16] or double-chained lipids [17] and can be used to estimate the mechanical resistance of the adsorbed bilayers [15,16]. The surfactant compression force also increases with time. The evolution of the maximum repulsive force with time is detailed in figure 5 and is compared with that obtained under the conditions least favorable to surfactant adsorption (i.e. highest aminosilane concentration in the mixture with silane hydrolysis in pure water). The presence of the aminosilane in the mixture does not change the general trend of the barrier height, which increases with time.

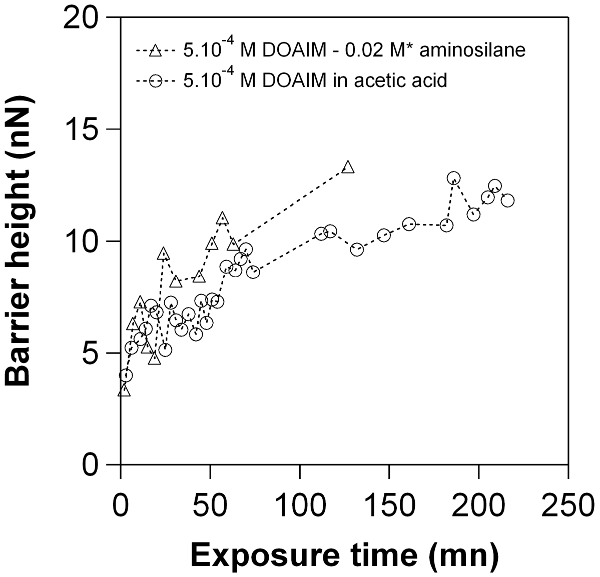

Figure 5. Surfactant compression forces evolution with exposure time of silica to (Δ) 5.10^{-4} M DOAIM – 0.02 M* aminosilane mixture (silane hydrolysis in pure water) and to (o) 5.10^{-4} M DOAIM in acetic acid.

Discussion

DOAIM adsorption, organization and the lubricated steady-state

a. The lubricated steady-state

When silica surfaces are fully immersed in aminosilane or DOAIM aqueous solutions, the friction between surfaces only decreases in presence of the surfactant (figure 3). A lubricated steady - state characterized by a low and stable friction value (F_T / F_N = 0.05) is reached after a progressive reduction in friction with exposure time. This value is one order of magnitude higher than friction coefficients reported for friction between two adsorbed bilayers of trimeric or gemini surfactants [18,19]. From surface forces measurements by SFA between supported bilayers of double-chained lipids, hemifusion thresholds of defect-free bilayers are several 10 MPa [20] but significantly lower than the mean normal pressure in the contact used here (320 - 340 MPa). This induces hemifusion of the two adsorbed bilayers (one on each silica conterface) into one bilayer, i.e. the outer monolayer of each adsorbed bilayer is expelled from the contact zone. The low and stable value of friction is then attributed to the friction between hydrocarbon terminated monolayers of DOAIM, resulting from the hemifusion of two defect-free bilayers.

b. Organization during adsorption

Defect-free bilayers of DOAIM resulting in the lubricated steady-state are not formed immediately after the fully immersion of silica surfaces in the pure DOAIM solution, as evidenced by the large initial value of F_T / F_N close to 0.4 (figure 3). Packing mismatches and local defects in the adsorbed bilayers can be explained by a difference in the structure of surfactant aggregates in the bulk solution and after adsorption. Indeed, the structure of adsorbed aggregates results from a compromise between the critical packing parameter of aggregates in the bulk and the constraints imposed by surfactant-surface interactions [21,22]. In the case of DOAIM, interactions with silica are strong: the positively charged headgroups of DOAIM in the bulk solution are electrostatically attracted by silica whose surface charge is negative at the sizing formulation pH of 4.5 (point of zero charge achieved for a pH value of 2-3 [23,24] and silanol dissociation constant pKa = 5-7 [25,26]). As a result, the initial adsorption of charged vesicles is fast with a complete surface coverage by the DOAIM within 10 minutes (figure 2). Aggregates adsorb in a disordered way. The density of electrostatically bound surfactant headgroups which is imposed by the solution pH, determines the structure of adsorbed aggregates of DOAIM and in particular the spacing between neighbouring aggregates within the bilayer [21,22]. Organization of adsorbed aggregates is then required before a defect-free bilayer is formed [27] and results in new adsorption sites for further adsorption of charged vesicles from the bulk. However, rearrangements are slow under the Krafft temperature, as also noticed for single-chained C_{18} cationic surfactants [28,29].

c. Contact properties during organization

The adsorbed bilayer evolves slowly, as confirmed by the mechanical responses evolution with exposure time, i.e. a continuous increase in the barrier height and a gradual reduction in friction. These evolutions are not directly correlated to the surface excess (the adsorbed quantity of DOAIM) quantified by infrared spectroscopy: the lubricated steady-state would be expected as soon as the pseudo-saturation of the surface by the surfactant is achieved. In order to clarify the origin of the bilayer evolution, it is important to remind the friction procedure which does not consist in a continuous and alternated linear movement between silica counterparts. Surfaces are brought into contact every 5 minutes for a series of two cycles only and remain fully immersed in the surfactant solution for 5 minutes between each series. Contacts and shear are repeated until the lubricated steady-state is established. The friction properties of silica surfaces in presence of a pure solution of DOAIM have been reported elsewhere. It has been shown that the defect-free bilayers inducing the low and stable friction are achieved faster under repeated contacts and shear. Contacts and shear accelerate the organization kinetics of the adsorbed bilayers. As mentioned previously, organization of adsorbed aggregates leads to new adsorption sites for further adsorption which occurs during the rest of silica surfaces in the DOAIM solution. It can be stated that the bilayers become more densely packed and increasingly ordered as the test proceeds, resulting in an improvement of their stability under the applied external pressure. This conclusion is supported by surface force data in figure 5 which show an increase in the force required to push the molecules away from the contact region with time. Such an evolution of the mechanical response in compression has been also pointed out in SFA or AFM experiments with supported double-chained lipids or positively charged single-chained CTAB [20,30,31], due to the presence of defects or surface excess. Indeed, defects in adsorbed lipid or cationic bilayers lead to larger pull-out forces and smaller jump-in forces. C.A. Helm [20] suggests that defects act as fusion sites which induce an increase in adhesion due to long-range hydrophobic attraction between exposed hydrocarbon tails. Moreover, surface forces in CTAB solutions close to the CMC show an increase in the pull-out force with the bulk surfactant concentration [4,5,32,33]. The increase in adhesion is correlated to a rise of the adsorption density in the hydrophobic monolayer. A similar trend for the evolution of the surfactant compressive forces is observed when the adsorption density of lipids on silica rises [34]. A comparison of AFM and friction results reveals that the barrier height and friction time evolutions are tightly connected. As reported in the literature, defects in adsorbed lipid bilayers affect their frictional response [19,30]. In AFM friction measurements performed under different normal loads in lipid solutions, the lateral force is close to zero as long as the bilayer withstands the external pressure. However, a steep increase in the lateral force is recorded when defects are caused by the tip, as revealed by topographic images [30]. A strong effect of the molecular packing of cationic surfactant films on friction is also observed by K. Boschkova and al.[19]. For a series of adsorbed gemini surfactants 12-$(CH_2)_s$-12 on gold, there is a decrease in the friction force when the length of the polymethylene spacer $(CH_2)_s$ becomes shorter an hence when the molecular packing of adsorbed surfactants is higher. A similar trend of the friction evolution with the packing density of molecules is reported for lipid bilayers in AFM experiments [30]. It is then concluded that the friction force evolution is related to the progressive increase in the packing density and ordering of adsorbed bilayers (one on each silica counterpart). The packing density and ordering increase result from the slow rearrangement of molecules in the surfactant film which allows further adsorption of charged vesicles from bulk. The removal of some surfactant from the contact due to shear is not excluded but this effect is balanced by the fast adsorption of DOAIM on the surfaces when the contact is disrupted for 5 minutes.

Effect of Silane addition

a. DOAIM adsorption

Results of adsorption kinetics in mixture solutions (figure 2) have shown a strong effect of the aminosilane on the adsorbed quantity of DOAIM after 80 minutes. The cationic surfactant adsorption on silica is lowered in presence of the aminosilane. When the silane is hydrolysed in a NaOH - acetic acid solution, there is a decrease of the adsorbed quantity of DOAIM at equilibrium for an increase of the aminosilane concentration in the mixture from 0.002 M to 0.02 M as detailed in the inset of figure 2. A stronger reduction of adsorption after 80 minutes is obtained when the silane is hydrolyzed in pure water rather than in a NaOH - acetic acid solution, leading to less than a tenth of one adsorbed DOAIM bilayer. The adsorption reduction could be explained by the faster adsorption kinetics of aminosilane on silica. Aminosilane molecules condense with the dissociated surface silanol groups of silica to form siloxane Si-O-Si covalent bonds. According to A. Carre [35], the aminosilane-treated glass is positively charged for pH lower than 7.3 (point of zero charge), due to the contribution of protonated amine and free silanol groups. Repulsive electrostatic forces between the positive surface charge and positively charged head of DOAIM molecules may prevent their adsorption. Therefore, the dependence of adsorbed surfactant quantity to the aminosilane concentration in the mixture is ascribed to the increase in the adsorbed quantity of aminosilane and consequently to a silica surface charge becoming more and more positive. It can be noticed that the variation in the surface excess as a function of the aminosilane hydrolysis conditions may result from the difference in the hydrolysis kinetics of the aminosilane. This assumption is based on the pH dependence of silanes hydrolysis [36]. There is a slowdown in the kinetics at the acidic pH of 4.5 as compared to the hydrolysis at the natural pH of 10.6 in pure water. The induction time before the hydrolysis starts in the acidic solution is large enough to allow the DOAIM adsorption whose adsorption kinetics is fast. Therefore, the stronger reduction in the surface excess with the aminosilane hydrolysis at natural pH could be explained by a larger quantity of adsorbed aminosilane on silica, leading to a more positive silica surface.

b. Contact properties

Friction results in figure 3 highlight a lubrication of silica – silica contact as soon as surfaces are exposed to the 5.10^{-4} M DOAIM – 0.02 M* aminosilane mixture (with the silane hydrolysis in pure water), while FTIR results show no surfactant adsorption. In parallel, a short-range repulsive force barrier at 3.5 nm - 4.5 nm already exists after a few minutes of silica exposure to this mixture, as displayed by surface force data in figure 4. AFM results are similar when DOAIM molecules are adsorbed on the silica surface after its immersion in the pure DOAIM solution. The distance separation is close to the thickness of a DOAIM bilayer, indicating the presence of an adsorbed surfactant bilayer in the contact. Previous surface force measurements with a SFA between silica surfaces in a pure DOAIM solution clearly showed that repeated contacts induce the accumulation and a lamellar organization of surfactant molecules in the contact zone (not presented). It is then concluded that the DOAIM adsorption is induced by the contact itself. The adsorbed bilayer evolves during the experiment, as pointed out by the barrier height increase with time. The barrier height evolution is similar to the one observed without the aminosilane (figure 5). As argued for the DOAIM on its own, the evolution of this force which depends on the packing density and ordering of the layer indicates that the confined bilayer becomes more compact and ordered with time and increasingly able to sustain the compressive stress. The friction evolves following the same trend as that measured without the aminosilane and also obeys a time evolution similar to the barrier height. From the contact and shear effect on the accumulation of surfactant molecules in the contact zone, lamellar organization and organization acceleration observed in SFA and friction experiments, the quantity of organized surfactant molecules in the contact region increases with repeated contacts and shear at regular intervals during the friction test. This induces an improvement of the bilayers mechanical resistance to the compressive and shear stresses. Figure 6 is a schematics of the organization of the DOAIM molecules in the contact. The DOAIM molecules may displace the silane.

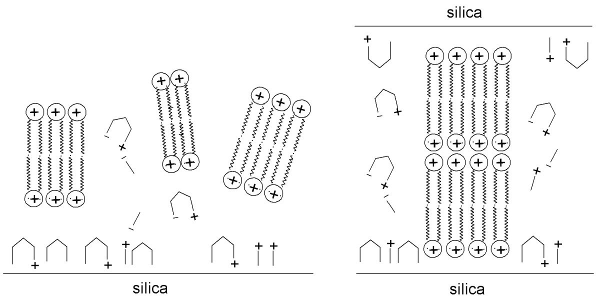

Figure 6. Schematic view of the organization of the DOAIM and aminosilane molecules in the acetic acid solution in the contact.

The final low and stable friction indicates that the bilayers are defect-free. The steady state low friction value is very close to the one observed at the end of the test when silica surfaces are immersed in the pure DOAIM solution. It is concluded that the low friction between silica surfaces in the mixture is due to the friction between hydrocarbon terminated monolayers resulting from the hemifusion of two dense and well organized surfactant bilayers.

Conclusion

This study details for the first time the strong impact of the competitive adsorption on silica surfaces of an aminosilane and a cationic double-chained surfactant (DOAIM) on the surfactant lubricant effect, in the context of glass fiber forming process. The adsorption kinetics of DOAIM - aminosilane mixtures followed by FTIR-ATR have shown a lowering or even a suppression of the cationic surfactant adsorption on silica in presence of the aminosilane, resulting from the faster adsorption kinetics of aminosilane on silica. The aminosilane adsorption blocks the surfactant adsorption. While the surfactant adsorption is suppressed and in spite of the non lubricant property of the aminosilane, the remarkable finding is that the lubrication of silica surfaces is possible. The aminosilane does not prevent the build up of a DOAIM bilayer at the interfaces**.** The build up of the bilayers is induced by the contact itself. The packing density and the ordering of the bilayers become higher with repeated contacts and shear during the friction test, due to the accumulation of surfactant molecules in the contact region which rearrange. This leads to an improvement of the bilayers mechanical resistance to the compressive and shear stresses and therefore to the gradual transition from an initial high friction to the lubricated steady-state characterized by a low and stable friction. The final lubricated steady-state is ascribed to the friction between hydrocarbon terminated monolayers resulting from the hemifusion of two dense and well organized surfactant bilayers (one on each silica counterface).

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