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## PREPARATION AND CHARACTERIZATION OF QUATERNARY AMMONIUM SURFACTANTS ON MUSCOVITE MICA

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**Abstract:** *In order to reduce friction, lubricants are usually employed. We describe the possibility of self-assembled monolayers (SAMs) being used as lubricants. Our aim was to produce homogeneous monolayers of surfactants on substrate. Because the surfactant behavior in the solution can be changed in contact with a substrate, we considered the adsorption mechanisms of surfactant molecules at the solid-liquid interface to be important. SAMs were prepared by using different methods, and their stability and structure was studied, but a homogeneous hydrophobic monolayer was difficult to realize. It has been shown that the factors, such as the temperature during solution preparation, frequently neglected, can be very important in the process of surfactant adsorption from solution.*

**Keywords:** *adsorption, SAMs, stability, muscovite mica, contact angle*

### 1. INTRODUCTION

The tribological research involves the study of friction, wear and lubrication. These three components between materials in contact are of fundamental importance in many areas, such as aircraft engines, automobiles, gears or bearing. Practically, in all modern mechanical machines the major problems are friction and wear. The advanced technical applications and the invention of new characterization techniques, lead to the appearance of the new field of tribology, known as micro-tribology/nano-tribology, which involves the study of friction and wear at a very small length scales. Nanotribology part of particular importance is called nanolubrication, defined as the study of ultra-thin lubricant films. The application of nanolubrication is important in a device which needs a lubricant layer of few nanometers, to reduce friction and wear. Therefore, research and testing of nano-lubricants, needed for microelectromechanical systems (MEMS) components, is a big challenge.

An attractive model system that can be used for studies in wetting, adhesion and friction of surfaces is the system of self-assembled organic monolayers (SAMs). The concept of self-assembly was invoked by Zisman, more than 50 years ago. At that time,

the potential of self-assembly was not recognized, but the field of self-assembled monolayers has considerably developed in the past 30 years. Due to possibility of controlling the physical and chemical properties of these systems in a systematic way, and in order to solve many practical friction connected problems by SAMs, the interest in their study significantly increases [1,2]. The interest in the general area of self-assembly, specifically in SAMs, comes from their observed importance in science and technology.

One example of the general phenomena of self-assembly is the formation of monolayers, by self-assembly of surfactant molecules at surfaces. Self-assembled monolayers can be prepared using different types of molecules and different substrates, by very simple process, which makes SAMs manufacturable and thus technologically attractive in surface engineering [3]. Surfactant adsorption from solution can produce various SAM morphologies. It has been shown that surfactants can form monolayers, bilayers [4], or aggregates of various shapes and sizes [5]. Commonly studied factors during SAMs formation are properties of the surfactant concentration - above the cmc [6] and below the cmc [7] different chain length and head group structure [4] or types of solid surfaces (oxide

surfaces, graphite, gold, silica or mica [8]. A significant part of work has been done at a concentration above the cmc [6], in order to clarify the structure of the adsorbed layers, especially the aggregates on the surface. The properties of the adsorbed films on the solid surface seem to be dependent on experimental parameters, such as concentration, pH, temperature and humidity, rarely described in the literature.

Adsorbed surfactants have been characterized using various techniques, such as x-ray photoelectron spectroscopy (XPS) [9], contact angle measurements [10], ellipsometry [11]. The AFM was first used to image surfactant aggregates on the surface by Manne et al. [12]. This technique indeed offers a convenient method for the imaging of molecular assemblies, i.e. *in situ* [13] or rarely in *ex situ*. In order to test the stability and measure the thickness of SAMs on mica, a scratch test can be used [14]. Due to the small thickness of SAMs (~nm), the development of AFM gives a powerful tool to the visualization of the adsorbed surfactant on solid substrates and facilitates the study of the adsorption mechanism at the molecular level. It can identify defects on the sample and detect the structure of formed layers on the substrate. Over the last 20 years experiments performed with the atomic force microscope or with the other measuring techniques, have provided new insights into the physics of contact between single asperities, friction, wear and lubrication on a molecular level.

Many authors have aimed at investigating the adsorption of cationic surfactants from aqueous solution onto a variety of solid surfaces, including graphite [12], silica [15] and mica [16]. Cationic surfactants have been the most studied ones, using the technique of the direct surface forces measurements, particularly with the surfaces forces apparatus [17]. Most of the surface force work was directed towards studying the interaction between surfactant coated surfaces, for better understanding of hydrophobic forces [18]. The surface force technique has been used to probe the lubrication properties of aqueous surfactant solutions [19]. Due to the possibility to simultaneous measuring of the thickness and the intermolecular forces of surfactant films, this technique has been used as an effective tool in the study of surfactant model system.

Adsorption of cationic surfactants, especially quaternary ammonium surfactants cetyltrimethylammonium bromide-CTAB, onto relatively simple inorganic substrates, such as mica, has been studied very often, as a good model system for boundary lubrication. Depending on the

conditions, it has been reported that CTAB adsorbs on mica as a compact monolayer [19], as a stable hydrophobic surface [20], as a bilayer [6], or forms aggregates [21]. For the preparation of CTAB self-assembled films on mica, numerous adsorption protocols have been proposed in the literature. The applied procedures include the variation of many parameters, such as different temperatures in SAM preparation, the immersion time or the post-adsorption sample treatment [10]. Different conclusions about adsorption theories and the existence of numerous mechanisms, underline this broadness [22]. On the other hand, the Krafft temperature is a very important quantity for CTAB/water solutions as previously reported [6]. Due to the important structural changes in CTAB solution, above the cmc at and above the Krafft temperature, this surfactant transition is still the area of research interest.

Our attention here will be directed toward modification of the mica surface by adsorption of quaternary ammonium surfactants, with the aim to produce hydrophobic and well-ordered homogeneous monolayers. Adsorbed layers were prepared on mica using different concentrations of surfactants in aqueous solution, below and above the critical micelle concentration, in order to check the hypothesis that the adsorption depends on the solution structure. The adsorbed layers were characterized by contact angle (CA) measurements and atomic force microscopy (AFM) imaging.

## 2. MATERIALS AND METHODS

The self-assembled monolayers of quaternary ammonium surfactants on mica, we made by single-tailed hexadecyltrimethylammonium bromide (CTAB), with the molecular structure  $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$ . CTAB was purchased from Fluka and for further purification was recrystallized from an ethanol/acetone mixture. As a solvent, ultra pure water of resistivity 18.3M $\Omega$ cm was prepared, using a Barnstead EASYpure™ batch-fed water purification system. In the process of sample rinsing we used water of the same quality before drying with a clean nitrogen stream.

To avoid any contamination, the glassware and bottles used in the experiments were consistently cleaned by piranha solution and then rinsed with purified water. All the employed tools were previously cleaned in order to minimize the occurrence of a molecular contamination, particularly on the high-energy mica surface.

## Mica samples preparation

For the adsorption experiments, we used muscovite mica purchased from Spruce Pine Mica Company Inc. (USA). Small mica samples of 1-1.5cm<sup>2</sup> size were cut by scissors and after that freshly cleaved on both sides and immersed into the surfactant solution. The adsorption was performed from the surfactant solution in a volume of 20ml.

## 3. EXPERIMENTAL PART

Several experiments, described in the literature, suggested that the transition through the three-phase boundary is an important step, with a significant influence on the surfactant film morphology. To distinguish effects due to adsorption at the solid-liquid interface and the deposition at the three-phase boundary (TPB), we have systematically varied the immersion/extraction protocol and defined four different experiments. All four adsorption protocols, separately described below, have been used with/without temperature control. The results observed under the temperature controlled conditions have been described.

Every experiment consists of four steps: adsorption, rinsing, drying and analysis (AFM and CA). Varying the immersion and extraction of mica sample into and out of the surfactant solution, we have defined four different adsorption protocols (figure 1).

The first option, called “CTAB in/CTAB out“, involves immersion and extraction from the surfactant solution at the nominal concentration.

The second adsorption type (“CTAB in/dilute out”) uses immersion into the nominal surfactant solution, a rest time and subsequent rapid (10seconds) dilution with pure water prior to extraction, in order to eliminate surfactant deposition during the transition through the TPB.

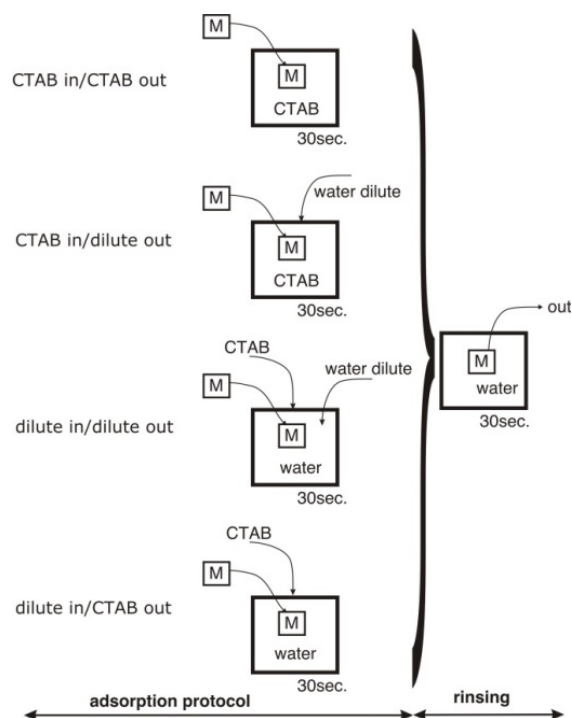
The third option (“dilute in /dilute out”) prevents surfactant deposition at the TPB in both steps, immersion into solution and extraction from it. In this case, CTAB is added to the solution after the sample is submerged.

The fourth option (“dilute in/CTAB out”) allows deposition at the TPB during extraction only.

In the water dipping step, the mica samples were dipped into 20ml of ultra pure water to remove the excess surfactant molecules.

The same set of adsorption experiments shown in figure 1 has been repeated at controlled temperature in the laboratory, at 18°C (below the Krafft temperature) and 30°C (above the Krafft temperature). A stock solution, 250ml of 10<sup>-3</sup>M CTAB, has been prepared at controlled temperature

of 18°C or 30°C. It is important to emphasize that all the used chemicals, tools and substrates were equilibrated at the defined temperature before the adsorption experiments.



**Figure 1.** Schematic representation of four different adsorption protocols used to discriminate different deposition mechanisms at the three-phase boundary. All samples were dipped into ultra pure water to strip off possible excess CTAB (e.g. incomplete second layer)

After the post-rinsing step, the modified mica surface was gently blown dry with nitrogen before the AFM imaging or contact angle measurements. Each type of protocol (at different concentrations) was repeated several times to also assess the reproducibility.

The samples were imaged with an Atomic Force Microscope (Digital Instruments, Nanoscope IIIa), which was operated under ambient conditions. The images were systematically collected for different scan sizes (i.e. 10µm×10µm, 5µm×5µm and 1µm×1µm, and again 10µm×10µm) and they were repeated by scanning several different areas on a given sample. At least two samples of each preparation protocol were analyzed.

The contact angle is the angle conventionally measured through the liquid, where a liquid/vapor interface meets a solid surface. It quantifies the wettability of a solid surface by a liquid. On every sample advancing (maximal) contact angle and the receding (minimal) contact angle are measured. A water contact angle greater than 90° is determined on hydrophobic surfaces. For example, freshly cleaved mica has a contact angle less than 10°, and a contact angle on the SAM produced by CTAB adsorption on mica can be 140°.

For water contact angle measurements, after the placing the droplet on the surface, the advancing contact angle was measured,  $\theta_a$ , after which the droplet was retracted, and the receding contact angle,  $\theta_r$ , recorded. The times for both contact angle measurements, were similar, in the range of a few seconds duration for each.

Using hexadecane as the probing liquid, we can define a well-ordered monolayer on a substrate and the expected CA of ordered surfactant layers are around or larger than  $40^\circ$ . A high contact angle suggests a high degree of order and “tails-up” molecules orientation in the layer. With hexadecane only a static contact angle has been measured by placing  $1\mu\text{L}$  drop on the sample. Measurements were performed at room temperature conditions and humidity. The contact angle values were detected with accuracy  $\pm 1\text{-}2^\circ$ .

#### 4. RESULTS

The influence of the temperature on the surfactant solution properties and the resulting SAM morphology, spurred us to control the temperature during the solution preparation, as well as during adsorption. Two distinct temperatures have been chosen—one below ( $18^\circ\text{C}$ ) and one above ( $30^\circ\text{C}$ ) the Krafft temperature of CTAB.

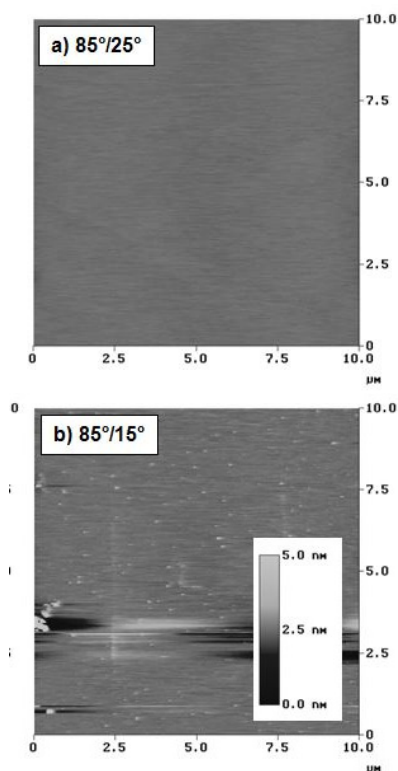
CTAB adsorption results on mica observed at low concentrations are illustrated in figure 2.a below the Krafft temperature (at  $18^\circ\text{C}$ ), and 2.b above the Krafft temperature (at  $30^\circ\text{C}$ ). The temperature dependence of the observed film morphology at  $18^\circ\text{C}$  and  $30^\circ\text{C}$  can be confirmed by contact angle measurements. Due to the variations determined in the different samples spots, both the results for water (advancing/receding) are given with errors.

In both groups of experiments, hydrophobic surfaces with advancing contact angles between  $75^\circ$  and  $90^\circ$  have been obtained. The significant hysteresis suggests a chemical heterogeneity or roughness in the surfactant film [24].

Considering the highest contact angles in both measurements with water and hexadecane, the most promising hydrophobic surfaces have been obtained at  $18^\circ\text{C}$ , using the protocol “CTAB in /CTAB out”, suggesting a significant surfactant adsorption at the three-phase boundary. Therefore, this adsorption protocol has been selected for all the following measurements at  $18^\circ\text{C}$ .

The temperature dependence of the observed film morphology at  $18^\circ\text{C}$  and  $30^\circ\text{C}$  can be confirmed by contact angle measurements. Contact angles for various preparation protocols are summarized in the tables below. Due to the variations determined in the different samples

spots, both the results for water (advancing/receding) and hexadecane are given with errors.



**Figure 2.** The comparison of AFM images of CTAB modified mica by the “CTAB in/CTAB out” protocol at controlled temperature: a) from saturated  $10^{-3}\text{M}$  solution (at  $18^\circ\text{C}$ ) b) from  $10^{-4}\text{M}$  solution (at  $30^\circ\text{C}$ )

**Table 1.** Contact angle of water and hexadecane on CTAB coated mica from the saturated  $10^{-3}\text{M}$  solution prepared at  $18^\circ\text{C}$

$18^\circ\text{C}$	hexadecane	water
CTAB in/CTAB out	$27\pm 2^\circ$	$85^\circ/35^\circ$
CTAB in/dilute out	$19\pm 2^\circ$	$79^\circ/25^\circ$

**Table 2.** Contact angle of water and hexadecane on CTAB coated mica at  $30^\circ\text{C}$  from  $10^{-4}\text{M}$  solution

$30^\circ\text{C}$	hexadecane	water
CTAB in/CTAB out	$17\pm 2^\circ$	$85^\circ/15^\circ$
dilute in/dilute out	$14^\circ$	$90^\circ/10^\circ$
dilute in/CTAB out	$12^\circ$	$79^\circ/12^\circ$
CTAB in/dilute out	$7^\circ$	$76^\circ/12^\circ$

#### 5. DISCUSSION

The structure and the stability of the adsorbed films are sensitive to the experimental conditions, primarily temperature.

According to the AFM results in figure 2.a, the adsorbed film can be the homogeneous SAM on the mica. Hysteresis in water CA indicates a hydrophobic but not homogeneous film. Similar contact angles have been reported in the literature. The decay in CA values with time shows instability of the formed layer, due to desorption of the adsorbed molecules into the water drop. A similar observation has been also made [24] and interpreted as water penetration into the monolayer, a phenomenon already known to Langmuir in 1938. The degree of water penetration can also be influenced by the local environment, e.g. relative humidity or temperature [24].

In all experiments hydrophobic surfaces with advancing contact angles between  $75^\circ$  and  $90^\circ$  have been obtained. The significant hysteresis suggests a chemical heterogeneity or roughness in the surfactant film. Measurements of hexadecane contact angle represent one of the most sensitive tools to determine the conformational order of hydrocarbon thin films. High hexadecane contact angles are observed on hydrocarbon SAMs only when the monolayers are densely packed. Using hexadecane we have observed lower values than the expected  $40^\circ$  for ideally ordered films.

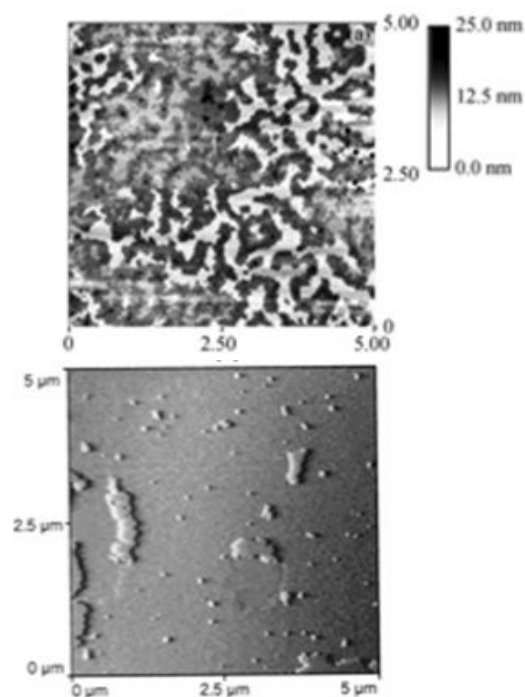
In order to relate our SAM preparation protocols to previous work, we have compared our results with those described in the literature. Much work has been devoted to the study of the adsorption of CTAB on mica using a variety of adsorption protocols and measurement techniques. For both solution concentrations, below and above the cmc, the picture shown in the literature demonstrates a high degree of variability.

The protocol proposed by Zhao [25] was reported to produce cylinder aggregates on the mica surface at a solution concentration of  $2\text{cmc}$  (figure 3.a). Due to the measured height of  $\sim 6\text{nm}$  of the features, the layer has been described as consisting of two bilayers.

At the CTAB concentration  $10^{-5}\text{M}$  monolayers and bilayers have been observed [22], using a similar adsorption protocol at room temperature (around  $25^\circ\text{C}$ ), as shown in figure 3.b. The AFM was operated in the surfactant solution.

We can conclude that the literature confirms that even small differences in the SAM adsorption protocol can significantly affect the surfactant film morphology on mica, especially above the cmc and the Krafft temperature. These observations are confirmed by our experimental results and there is the need to explain these variations by structural changes of the surfactant solution [26]. There are significant structural changes around the Krafft temperature. Below the bulk cmc and below the Krafft temperature, an equilibrated solution is

expected to be free of micelles. At the Krafft temperature, the solubility becomes equal to the cmc and micelles will form in the solution and this temperature is very often described in the literature. But, reported values of  $T_k$  for CTAB in water vary considerably (from  $20^\circ\text{C}$  to  $25^\circ\text{C}$ ), which is very close to a room temperature and complicates the explanation of experimental results.



**Figure 3.** a) AFM topographic image of a mica surface prepared unspecified temperature conditions, using “CTAB in/CTAB out” protocol (immersion time-1min), at  $2\text{cmc}$ , without rinsing after removal from the solution, dried with nitrogen before AFM imaging [25]; b) AFM image of a CTAB adsorbed layer on mica in a  $10^{-5}\text{M}$  solution at  $25^\circ\text{C}$  for 25min immersion time, observed in the surfactant solution [22].

It is important to note that most of the experiments described in the literature do not mention the problem of temperature control, and it is not possible to reconstruct this important parameter from the information provided. We have a clear evidence that temperature is the key factor determining SAM morphology. Therefore, we have systematically studied temperature effects by rigorously controlling the temperature during all procedures.

## 6. CONCLUSION

The concept of self-assembly on surfaces has been treated in this research and the experiments have revisited the adsorption of CTAB onto a muscovite mica. These results demonstrate the influence of a large number of parameters on the adsorption process, as well as the morphology and



the molecular order of SAMs. The molecular structure of the solution seems to be a key element. It is chiefly controlled by the temperature and concentration of the solution. The fact that the Krafft temperature range of CTAB is around room temperature (~25°C), makes this system particularly complex.

We have systematically studied the transfer across the three-phase boundary, under different experimental conditions and different adsorption protocols. The surfactant films on mica, formed according to different experimental protocols, were characterized by contact angle measurements and by AFM. It has been observed that the transition through the three-phase boundary during sample extraction can be a step of significant influence on the SAM morphology.

A high stability of the adsorbed films is very rarely detected. The problem of reproducibility in SAMs formation can be observed by controlling the temperature during all steps, or, working below the cmc. A reproducible stability of the resulting films, however, remains an issue.

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