THE INFLUENCE OF TEMPERATURE ON THE ADSORPTION OF CATIONIC SURFACTANTS ON MUSCOVITE MICA

by

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The attention in this paper is directed toward the modification of the mica surface by adsorption of quaternary ammonium surfactants, and the influence of temperature on the adsorption process. The aim is to produce a very well-ordered hydrophobic surface. In order to produce adsorbed layers, we realized numerous experiments and applied the solutions of different surfactants concentrations, below and above the critical micelle concentration. The characterization of adsorbed layers was performed by contact angle measurements and atomic force microscopy imaging, and we observed films of variable morphology. The influence of many parameters is responsible for different results, such as solution concentration, and temperature, humidity in sample analysis, as well as substrate properties (muscovite mica). Special attention was paid to the influence of temperature on the solution properties and the stability of the deposited surfactants layers.

Key words: *adsorption, surfactants, self-assembled monolayers, muscovite mica, Krafft temperature*

Introduction

In many scientific fields, such as electronics [1], biomedical application [2] or material science [3-5] the production and application of organic thin films represent a very important area of research. For that purpose numerous organic compounds have been applied, since they have the ability to form films of very small thicknesses on an appropriate solid surface (substrate). Thin organic films of a defined or controlled thickness are usually described in the literature as self-assembled monolayers (SAM), and the process of self-assembly is described as an example of equilibrium structural organization on the molecular scale [6, 7]. Due to the possibility of changing the properties of a solid surface or defining their desired properties, there is a significant increase in the interest in SAM formation.

The process of self-assembly is a promising process and it is recognized as a powerful strategy for the fabrication of nanoscale structures [8]. With the development of nanotechnology, especially techniques that enable investigation and research at nanoscale, such as atomic force microscopy (AFM), X-ray photoelectron spectroscopy or tunneling microscopy, academic interest in SAM and surface science has increased, and it has become possible to conduct precise research into self-assembled layers on the nanometer scale [9-11]. This research at the nanoscale is very important because of the applications of SAM in many scientific fields, such as: organic chemistry [12, 13], surface properties in micro-electromechanical

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devices [14, 15], corrosion of surfaces [16, 17], production of nanoscale organic transistors [18, 19], or biology [20, 21].

The literature review indicates several very often studied SAM systems, such as thiol molecules adsorbed onto gold [9, 22], silanes on an oxide surfaces [23], alkanephosphate monolayers [24], and these systems have often been reviewed [25]. In our research we organized experiments of cationic surfactants adsorption onto the hydrophilic, negatively charged muscovite mica surface [26-29]. The investigation of the adsorption of cationic surfactants from aqueous solution onto the numerous substrates such as graphite [30, 31], silica [32] or mica [33, 34] was the subject of many studies, performed on the surfactants-concentration above the critical micelle concentration (CMC) [35-37] and below the CMC [38, 39]. The CMC is the surfactant concentration at which the surfactant molecules, monomers, start to form spherical structures called *micelles*. In order to characterize adsorbed surfactant films, various techniques have been applied, as described above [40-43].

The object of our research, the system muscovite mica and cetyltrimethylammonium bromide (CTAB), was very often investigated [44, 45]. A large number of adsorption experiments has been conducted at concentrations above the CMC, where CTAB molecules form bilayers on mica [37, 40]. The adsorption of CTAB on mica at surfactant concentration below the CMC has not been investigated often, although the obtained results show that the adsorption of surfactants onto mica does indeed take place below the CMC [46] and even aggregates can be formed on the surface under these conditions [38]. Numerous aspects of this adsorption of cationic surfactants onto mica have been studied in detail, but there are still open questions about the interactions between the mica surface and alkylammonium ions.

Studying the available literature it is possible to find numerous proposed adsorption protocols for CTAB adsorption on mica, and as a consequence, various SAM morphologies have been obtained on mica. The adsorption protocols are different in many steps or parameters, such as the sample-handling during adsorption, the adsorption time, the temperature of the surfactant solution or the temperature and humidity before and after the adsorption process itself [40, 47, 48]. After many conducted experiments, considering the obtained results of the adsorption process, we suggested new protocols appropriate to form homogeneous SAM [49], and only one is described here.

However, the influence and importance of temperature on the adsorption process and the results of the adsorption are often neglected. It is very interesting that several authors have suggested adsorption at 5 °C (in the refrigerator) [40], many more have organized experiments at temperatures of around 25 °C or *at room temperature* [46, 50], while in a significant number of adsorption protocols, below and above the CMC temperature as a parameter, has been not measured [47, 51]. This paper investigates and shows the importance of temperature in the process of CTAB self-assembly on muscovite mica.

Materials and methods

In order to determine the properties of SAM we applied contact angle (CA) measurements and the AFM. These techniques are very well described [51]. The preparation of the mica samples (substrate) and the surfactant solutions are described in more details.

Geometrically, CA is defined as the angle formed at the three-phase boundary, where the liquid, the gas and the solid meet. This technique is applied to determine the hydrophobicity of CTAB adsorbed layer. If CA is less than 30° the surface is hydrophilic, and on hydrophobic surfaces the CA is around or greater than 90°. For example, freshly cleaved mica has the CA of less than 10° (it is already known that muscovite mica is a hydrophilic surface)

and the CA on the SAM produced by CTAB adsorption on mica can be 140° measured by some researchers [52].

The CA measurements, advancing and receding, were obtained with a CA goniometer (Rame Hart model 100, Rame Hart Inc., USA). All CA measurements were averaged over several samples. For water CA measurements, after placing the droplet on the surface, the advancing CA was measured, θ_a, after which the droplet was retracted and the receding CA, θ_r, recorded.

The order of molecules in the surfactant layer can be detected by hexadecane CA measurements. With hexadecane only static CA were measured by placing 1 μL drop on the sample, performed in laboratory conditions. The CA values were detected with accuracy ±1-2°. These measurements were carried out only on some samples.

The surfactant covered samples were imaged with an AFM (Digital Instruments, NanoscopeIIIa) under laboratory conditions using the constant force mode [39]. The images were created for different scan sizes (*i. e.* 10 μm × 10 μm, 5 μm × 5 μm, and 1 μm × 1 μm). The scanning was conducted in few different sample areas. With this technique (AFM) it is possible to estimate the stability and the thickness of the self-assemble surfactant film, with a simple scratch test under defined conditions [35].

Solution preparation. The SAM were prepared on mica by quaternary ammonium surfactants, single-tailed hexadecyltrimethylammonium bromide, CTAB ($CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$). For further purification, CTAB was recrystallized from an ethanol/acetone mixture. Ultra-pure water of resistivity 18.3 MΩcm was prepared as a solvent using a Barnstead EASY-pure™ batch-fed water purification system. The same water quality was also used for sample rinsing.

All the employed tools were previously cleaned to minimize any molecular contamination. The glassware used in the experiments was cleaned by the piranha solution and then rinsed with purified water to avoid any organic contamination.
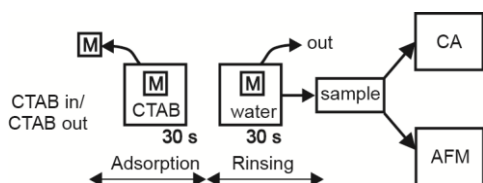
Mica samples preparation. Muscovite mica, used as the substrate, was purchased from Spruce Pine Mica Company Inc., USA. Very small mica samples ($\approx$1 cm^2 size) were cut by scissors, cleaved on both sides and immersed into the surfactant solution of appropriate concentration. The adsorption was performed from the surfactant solution in a volume of 20 mL, rinsed in ultra-pure water, and after rinsing the sample was dried with a clean nitrogen stream. Then the sample was ready for the CA measurement and the AFM imaging.

Experimental part

In this paper the greatest attention will be devoted to the influence of temperature on the surfactant thin film morphology. The adsorption protocols, separately described below, were used with/without temperature control and the observed results are described separately.

Solution preparation. In the first set of adsorption experiments, a 1000 mL stock solution of 10^{-2} M (~10 CMC) CTAB was prepared at current room temperature (temperature was not measured in the laboratory). Due to very low solubility of CTAB in water at that temperature, the surfactant solution was heated in order to dissolve all present crystals in the solution. This solution and ultra-pure water were used to prepare the surfactant solutions of few different concentrations, ranging from ~CMC (10^{-3} M) to ~CMC/1000 (10^{-6}M).

With thus prepared solution, we began the adsorption process. Adsorption, rinsing, drying and analysis (AFM and CA) are four experimental steps of every adsorption experiment, fig. 1.

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Figure 1. Schematic representation of four steps; adsorption, rinsing, drying, and analysis (AFM and CA), in adsorption protocols used to produce surfactant films on mica, named "CTAB in/CTAB out"

It is also possible to change some of these steps, which resulted in new adsorption protocols [49]. The experimental procedure named *CTAB in/CTAB out* involved immersion and extraction from the surfactant solution at the nominal concentration. After adsorption (30 seconds), every mica sample was rinsed by dipping into 20 mL of ultra-pure water for 30 seconds (to strip off possible excess CTAB, *e. g.* the incomplete second layer), dried with nitrogen and subsequently analyzed by CA and AFM measurements.

The same adsorption experiment (described in fig. 1) was repeated at controlled temperature conditions in the laboratory, at 18 °C and 30 °C. It is important to emphasize that the temperature was controlled from the process of solution preparation to the end of adsorption protocols, and all used chemicals (water, ethanol, chloroform, *etc.*), tools and substrates were equilibrated at the defined temperature before the adsorption experiments.

As described previously, after the post-rinsing step, the modified mica surface was gently blown dry with nitrogen before the sample analysis. The measurements (CA and AFM) were observed in another laboratory where the equipment was located without the temperature controlled conditions. Every adsorption protocol was repeated several times in order to estimate the reproducibility.

Results

Our attention here is directed toward the investigation of SAM produced by the surfactant − certain classes of molecules that adsorb onto a solid surface from a solution. Surfactant molecules have two important parts, the hydrophilic headgroup that usually has an attractive interaction with the substrate surface, and the hydrophobic tail of the molecule, which does not have a strong interaction with the substrate. The adsorption is usually influenced by many experimental parameters, such as surfactant concentration [53], or solution temperature [38, 54]. The environmental conditions of the adsorption process, ambient temperature and humidity, also show a great influence on surfactant adsorption [49], what our results suggest.

In the first group of measurements the adsorption have been realised without temperature control (temperature was not measured). The laboratory conditions during the adsorption process at the room temperature around 23 °C for the first set of adsorption experiments, and at around 30 °C in the second set of experiments, were significantly different, and mostly influenced by the atmospheric conditions. Temperature around 23 °C and around 30 °C is approximately assumed by the air temperature measured outside of our building (measured in Zurich-SwissMeteo data, not shown here). After the numerous repeated measurements, we have observed the problem with the reproducibility of the results, what indicated that the detected different experimental conditions could be the reason for this. In the sets of adsorption experiments a significant number of samples were prepared using the described preparation *CTAB in/CTAB out* protocol. At a concentration below the CMC, the samples were imaged by the AFM, water CA was measured, and two representative samples were shown to indicate the previously mentioned differences.
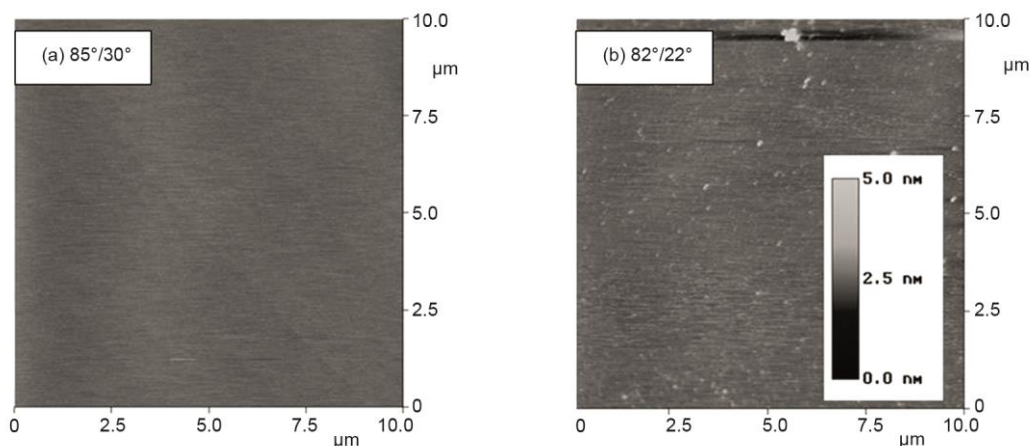
Figure 2. The AFM images of CTAB on mica obtained with the *CTAB in/CTAB out* protocol at laboratory temperature (a) around 23 °C, (b) around 30 °C, at a concentration of 10^{-4} M, with measured advancing and receding water contact angles on the samples, (a) 85°/30° and (b) 82°/22°
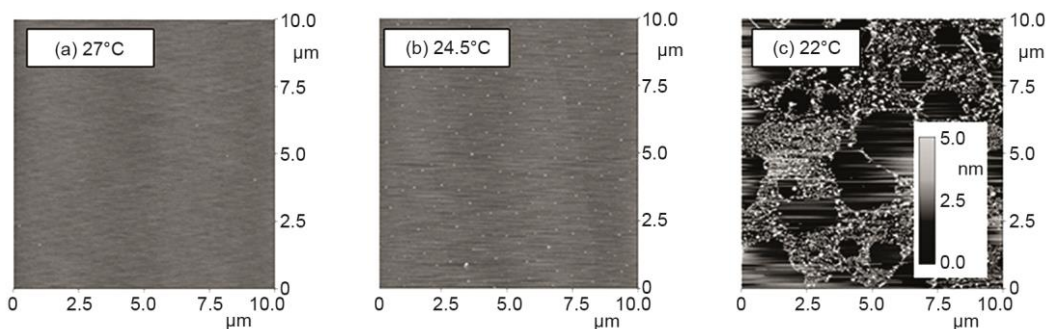*(for color image see journal web site)*

In the sample prepared at the laboratory temperature of around 30 °C, we observed numerous clusters (of 250 nm width and height between 0.5 nm to 4 nm), according to the grey scale of the image, which represents a height range of 5 nm, fig. 2(b). The samples prepared under lower laboratory temperature (certainly lower than 25 °C), were more promising because they looked homogeneous, fig. 2(a).

In these adsorption experiments, it is especially important to pay attention to the existence of the Krafft temperature. In fact, the Krafft temperature, T_k, is defined as a temperature at which dissolved molecules in the surfactant solution start to form micelles and change the surfactant solution structure. The Krafft temperature of CTAB/water solution in the literature is often considered as 25 °C [55]. As it is evident from the adsorption results, fig. 1, it seems that the temperature is of crucial importance for the results of adsorption experiment. Based on a large number of samples prepared on concentrations below the CMC (at least five samples at each selected concentration), there is evidence that very similar results were observed as the results shown in fig. 2. On the basis of the obtained results, two additional observations should be noted: hysteresis was detected in the advancing and receding water contact angle measurements on both samples regardless of experimental conditions, and it was difficult to reproduce those CTAB films on mica.

The next group of experiments were performed at concentrations higher than CMC, $10 \times$ CMC (*i. e.*10^{-2} M CTAB) by the protocol *CTAB in/CTAB out*, at different measured temperature. These results, summarized in fig. 3, confirmed the importance of temperature in adsorption experiments.

Figure 3 is representative of the sample prepared at 27 °C and is qualitatively different from the samples prepared at lower temperatures. The bright spots observed in fig. 3(b) represent small islands on the mica surface with a height between 0.5-1.3 nm. Figure 3(c) shows clusters with a height in order of 23 nm.

Adsorption experiments under temperature controlled conditions. After numerous experiments conducted under uncontrolled conditions in the laboratory, we chose two temperatures for adsorption protocols, one below (18 °C) and one above (30 °C) the Krafft tempera-

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Figure 3. Series of AFM images showing the surface morphology of CTAB coated mica by the protocol *CTAB in/CTAB out* at 10^{-2} M solution at temperatures: (a) 27 °C, (b) 24.5 °C, and (c) 22 °C
(for color image see journal web site)

ture of CTAB. The influence and importance of the Krafft temperature has already been indicated. CTAB adsorption results on mica observed at selected temperatures are illustrated in fig. 4.
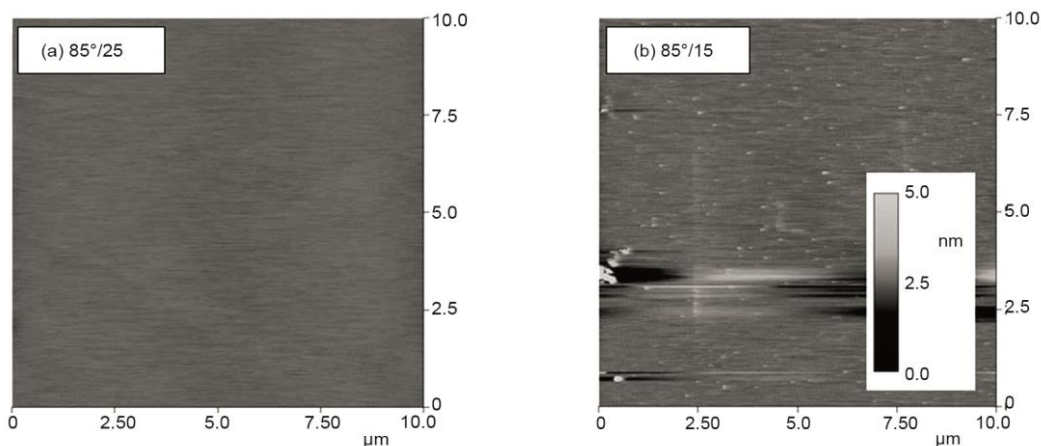
Figure 4. The comparison of AFM images of CTAB modified mica by the *CTAB in/CTAB out* protocol at controlled temperature (a) from saturated 10^{-3} M solution (at 18 °C), (b) from 10^{-4} M solution (at 30 °C); measured advancing and receding water CA on the samples are (a) 85°/25° and (b) 85°/15°
(for color image see journal web site)

In the observed film morphology at 18 °C and 30 °C, the quality of adsorption results can be confirmed by CA measurements, with water and hexadecane. Due to the variations determined in different samples spots, both results, for water (advancing/receding) and hexadecane, are given with errors. The CA of hexadecane (27±2°) and water (85°/35°) on CTAB coated mica from the saturated 10^{-3} M solution prepared at 18 °C were detected. In the experiments realized at 30 °C CA of hexadecane (17±2°) and water (85°/15°) on CTAB coated mica at 30 °C from 10^{-4} M solution have been measured.

In both groups of experiments, fig. 4, hydrophobic surfaces with advancing CA between 75° and 90° were obtained. The hysteresis in CA measurements suggests a chemical heterogeneity in the CTAB surfactant film [46]. For well-ordered films the expected hexadecane CA is around 40°, which is characteristic of the densely packed monolayers,

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and in our experiments the recorded CA values were lower. Comparing the achieved results, the most promising hydrophobic surface was obtained at 18 °C using the protocol *CTAB in/CTAB out*.

Discussion

After numerous experiments, we found that the adsorption results are influenced by many parameters. The greatest attention in the results description was paid to the effect of temperature change on the adsorption protocol.

According to the AFM images obtained in the laboratory below the Krafft temperature and above the Krafft temperature, figs. 2(a) and 2(b), one can see the implication of dramatic changes in SAM formation on mica due to temperature changes. The impossibility to achieve the repeatability of some results was another observation that indicates the complexity of the adsorption process CTAB on mica. The reason for such a difference in the homogeneous CTAB film, fig. 2(a) and very complex adsorption results presented in fig. 2(b), must be connected to changes in the solution structure. The solution used in both experiments (10^{-4} M) was prepared by diluting a 10^{-2} M stock solution. Since the room temperature in several groups of experiments was around 23 °C (20±3 °C), what is slightly below the Krafft temperature of CTAB (usually defined as 25 °C), it was expected that this stock solution mainly consisted of monomers, was similar to the diluted solution (10^{-4} M).

On the other hand, the temperature in a particular group of measurements was above the Krafft temperature (around 30 °C or higher), and we can expect very complex surfactant stock solution structure even during a single day. The diluted solution might thus not be in thermodynamic equilibrium and consist of micelles and monomers. Due to this great complexity, the clusters detected on the sample, fig. 2(b) can be described as micelles of different shapes and sizes adsorbed on the mica sample.

The adsorbed film, according to the AFM results shown in fig. 2(a), can be considered as the homogeneous SAM on the mica. But, hysteresis in water CA (85°/30°) indicates a hydrophobic but not homogeneous film, which is similar to the results reported in the literature [56]. The observed decrease in CA values with time shows the instability of the formed surfactant layer, and can be interpreted as water penetration into the monolayer [40, 47]. This phenomenon can also be influenced by the relative humidity or temperature in the laboratory [47], making CTAB adsorption on mica much more complex to study.

In order to relate our SAM preparation protocol and adsorbed films to previous work, we compared our results with those described in the literature. This was not an easy task, because for both adsorption CTAB solution concentrations, below and above the CMC, the picture drawn in the literature demonstrates a high degree of variability. From the experiments described in [27, 52], we can conclude that some researchers confirms that even small differences in the SAM adsorption protocol can significantly affect the morphology of surfactant films on mica, especially above the CMC and the Krafft temperature. These observations are also visible in our experimental results. 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. Our experimental results and experience explain these variations by structural changes of the surfactant solution.

A comparison of reviewed results from the literature on this topic, points to an important fact that most of the described experiments do not mention the problem of temperature control and it is not possible to reconstruct this important parameter from the information provided. From our results and after more than 300 prepared and analyzed samples of CTAB

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adsorption on mica, there is clear evidence that temperature is the key factor in determining SAM morphology.

Therefore, the temperature effects were carefully studied in precisely controlled laboratory and experimental conditions, and the experiments were organized at 18 °C and 30 °C. The most promising contact angles were observed at 18 °C in the *CTAB in/CTAB out* protocol.

Besides the contact angle measurements and the characterization using AFM, the most promising samples were also further characterized with a *scratch test* to estimate the thickness and to determine the stability of the adsorbed CTAB film. A chosen example of a surface strongly modified by scratching is shown in fig. 5.
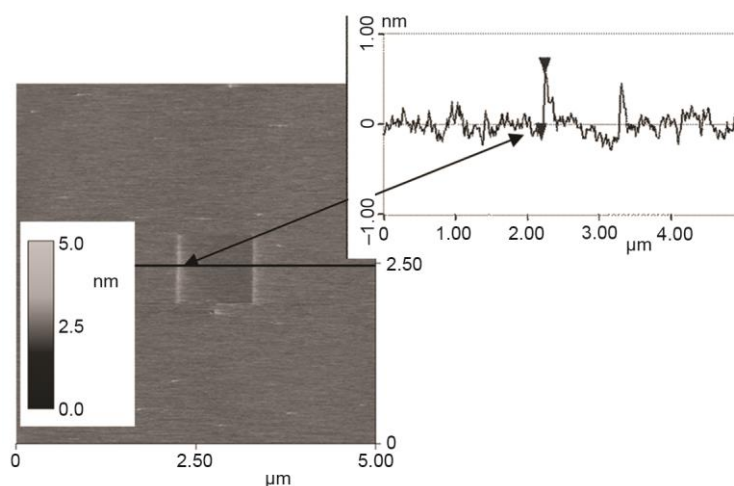
Figure 5. Topographic image of a CTAB film on a mica surface after the scratch test (at applied force of 100 nN); the scan (scratch) direction lies in the *x*-direction, where the molecules seem to accumulate, as shown by the vertical distance between the markers (~ 0.7 nm)

Applying the high load (L~100 nN) in a small scan area (1×1 μm) we have realized a square test area, which could then be imaged at lower load over a larger scan area (5×5 μm). There is a height difference of 0.7 nm in passing from the scratched to unscratched area. The notable accumulation of material at the edges of the scratched region indicates that CTAB moieties were forced by the probe tip to the edges of the probed zone.

Conclusions

The paper described the adsorption of quaternary ammonium surfactants onto an atomically smooth muscovite mica surface. It was observed that the morphology and the molecular order of SAM depend on many parameters, and a special attention was dedicated to the effect of temperature. We systematically studied this parameter and organized adsorption experiments under uncontrolled and controlled temperature conditions, with the same adsorption protocol, starting from the solution preparation process. The formed surfactant films on mica were characterized by contact angle measurements and by AFM.

One very important observation is that the Krafft temperature of CTAB around 25 °C (treated as *a room temperature* by numerous researchers) makes this system appear particularly complex. We have confirmed by the AFM results that even diluted micellar solutions

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may contain aggregates for relevant periods. These results suggest that the surfactant solution structure is dependent on the concentration and temperature of the solution.

The stability in adsorbed films is very rarely detected and it was very difficult to achieve. In order to provide the reproducibility in SAM formation we may conclude that it can be done by controlling the temperature during all experimental steps, or, working below the CMC. However, the stability of the resulting films is a problem that requires further and more detailed analysis of the studied system.

In this system of quaternary ammonium surfactants-mica, the formation of homogeneous, well-ordered and reproducibly monolayers is a very challenging task. In order to estimate such complex systems, there is a need to consider a large number of parameters, and not only temperature, which proved to be one of the key elements of the studied adsorption. The remarkable variety of film morphologies observed here, spurred us to go back even one more step and to study the properties of CTAB solutions.

Acknowledgment

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