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RESEARCH

Dynamics of SAMs in Boundary Lubrication

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ABSTRACT

Surfactant molecules have some properties responsible for a number of remarkable phenomena, such as oriented adsorption of surfactants at surfaces and interfaces. The capability to self-assemble into well-defined structures is often seen as being more important than their surface activity. When a surfactant solution is in contact with a solid surface, the surfactant molecules adsorb onto the surface, ideally forming an adsorbed layer of high order, termed as self-assembled monolayer (SAM). Many surface properties are influenced by such a film, and therefore, SAMs offer the capability to form ordered organic surface coatings, suitable for various applications, such as wetting or corrosion protection. Due to the flexibility in choosing the molecular architecture, organic molecules have many interesting applications, such as biosensors, in photoelectronics, in controlling water adsorption or boundary lubricant coating. This paper focuses on cationic surfactants (quaternary ammonium surfactants), with some unique properties that are not present in other surfactants.

1. INTRODUCTION

A contact between two surfaces is of great importance in technology. At the interface of two materials, when they are brought together, separated or moved with respect to one another, contact formation, friction, wear or lubrication are the processes that occur [1]. Friction has long been the subject of research. All machined metal surfaces, as viewed through a microscope, have their own roughness, called asperity. Therefore, two surfaces touch at an extremely small number of points, and their true area of contact is a part of their apparent contacting area. In contact of two surfaces, the number of asperities increases due to plastic deformation of some of them. The consequence of this is the appearance of the removal of material from a surface in bearing under dynamic conditions, defined as wear [2]. In order to reduce wear, lubricants are employed between the surfaces. Friction, wear and lubrication are the center of consideration in many tribological and technological problems. Having in mind that a contact occurs in numerous asperities, the research of two contact surfaces, especially at the molecular level and the friction phenomenon at the nanometer scale, is studied by nanotribology, a branch of tribology.

In order to categorize the friction properties between two surfaces, the "Stribeck curve" was developed. Machine elements may experience several lubrication regimes, including full-film, mixed, and boundary lubrication. These regimes depend on the properties of a lubricant and operating conditions [3]. In the case where speeds are too low and loads are too high to permit establishing a hydrodynamic film, or when the distance between contact surfaces is a few nanometers or a few molecular layers, we can define boundary lubrication (Fig.1).

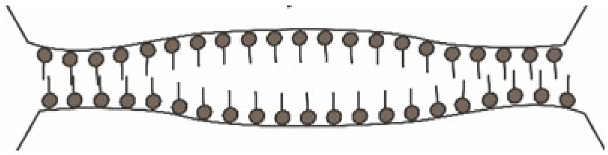


Fig. 1. Boundary lubrication.

The boundary films have been the subject of study for decades, since friction and wear phenomena are affected by these ultrathin films. Under friction, the dynamics of lubricants on surfaces is very important, especially the molecular behaviour of lubricants in boundary lubrication. The behaviour and dynamics of the boundary films, formed during sliding, becomes more complex due to change of some experimental parameters, such as temperature [4]. The computer simulation of processes during sliding contact, when several hundreds of atoms are involved, indicates that atomic processes cannot be neglected, when we describe nanotribology experiments [1,5]. For that purpose, several available methods can be included for research at a molecular level [6].

2. BOUNDARY LUBRICATION BY SAMS

Attractive model systems for boundary lubrication are organic self-assembled monolayers (SAMs). Preparing self-assembled monolayers is one of the most elegant ways to make ultrathin organic films of controlled thickness. The process of self-assembly is considered as a very important example of equilibrium structural organization on the molecular scale. Organic thin films are an emerging area of materials chemistry and are utilized in many application areas, such as electronic components, as well as in biomedical application [7]. There is also special interest in the possibility of manufacturing molecular layers with particular properties. Molecular self-assembly is recognized as a powerful strategy for the fabrication of nanoscale structures [8].

The interest in these systems has been further intensified in order to understand and solve friction, lubrication and related problems [9]. More recently, lubrication in a small-size system, such as the microelectromechanical system (MEMS) or nanoelectromechanical system (NEMS), is a big challenge in scientific work, especially in the study of new kind of lubricants. Different type of monolayers attached to sliding surfaces appears as a good candidate in MEMS lubrication. Therefore, the understanding of behaviour between monolayers films is of great importance in tribological and nanotribological experiments.

Due to very small thickness of monolayers (range of few nanometers), new tools are required for this nanotribological studies. Widely used are the following: surface-force apparatus (SFA), the scanning tunneling miscorscope (STM), the atomic force and friction-force microscopes (AFM and FFM). Developed more than 40 years ago, the SFA is usually applied to study properties of molecularly thin films, confined between two molecularly smooth macroscopic surfaces, with surface separations at the angstrom level and forces between them. A scanning tunneling microscope (STM) is an instrument for imaging surfaces at the atomic level [1]. With the development of a number of powerful techniques in surface analysis, as mentioned above, academic interest in SAMs has regained, because of the possibilities to investigate the growth and the structure of such layers on the nanometer scale [10,11].

3. SURFACTANTS SELF-ASSEMBLY

The word “surfactant”, does not always appear in dictionaries, because it is a contracted form of the phrase SURFace ACTive AgeNT. Surfactants are molecules essential to the chemical industry and in many products such as soaps, detergents, shampoos, softeners, pharmaceutical products, etc.

Surfactant molecules have amhiphilic properties because they consist of two distinct parts - one that has an affinity for the solvent, and the another one that does not. This dual structure is responsible for a number of remarkable phenomena, such as micelle formation in solution at a certain concentration, the so-called critical micelle concentration (cmc), and oriented adsorption of surfactants at surfaces and interfaces. Micelle formation has attracted a notable part of the surfactant research, in order to investigate the formation of micelles [12,13], their shape [14] or their interactions [15]. Systems below the cmc have not been widely studied [16].

The self-assembled monolayers can be prepared using different types of molecules and different substrates. A very often studied SAM model system comprises thiol molecules, adsorbed onto gold, silanes on an oxide surfaces, or alkanephosphate monolayers, which was in detail reviewed by Ulman [17]. The choice of the substrates, used in the self-assembling process, is dictated by the molecules and their interactions, as well as the final application.

Self-assembled monolayers form spontaneously, when certain classes of molecules adsorb onto a solid surface from solution. When a surfactant solution is in contact with a solid surface, the surfactant molecules adsorb onto the surface, ideally forming an adsorbed layer of high order, termed as self-assembled monolayer (Fig.2).

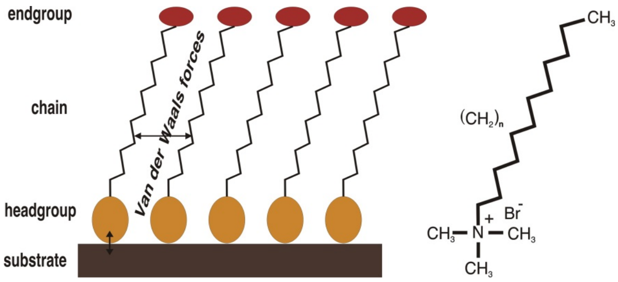


Fig. 2. a) An organized monolayer on a substrate; b) CTAB chain.

Many surface properties are influenced by such a film, e.g. the hydrophobicity or the wetting or electrostatics [18]. Due to the flexibility in choosing the molecular architecture, organic molecules have many interesting applications, such as biosensors, for lubrication or in controlling water adsorption. Therefore, in recent years, much attention has been directed to the study of SAMs. However, a discrepancy still exists between the theoretical understanding and the practical importance involved in the formation of such layers.

Cationic surfactants are a small subgroup with some unique properties that are not present in other surfactants. In order to help understanding of adsorption of cationic surfactants, adsorption of quaternary ammonium surfactants onto inorganic substrates, such as mica, has been widely studied [19-21]. The process of adsorption has been investigated by different techniques [22], such as x-ray photoelectron spectroscopy (XPS), the surface forces apparatus, (SFA) [16] or contact angle (CA) measurements [23]. This paper focuses on quaternary ammonium surfactants with a cationic head group, single-tailed hexadecyltrimethylammonium bromide, CTAB, with the molecular structure $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$ (Fig. 2b).

4. SAMS PREPARATION AND CHARACTERIZATION

A standard protocol, which can produce a well-defined and reproducible hydrophobic CTAB film on mica, does not exist. Namely, previous studies of CTAB adsorption on various substrates, suggested that the behaviour of CTAB is more complex than the behaviour of other cationic surfactants [23-25], but the reason for this singularity has not been clearly determined [18].

The original goal of these experiments was to produce self-assembled monolayers and use them as model systems to study boundary lubrication. But, there was a problem concerning the results being repeated, as well as the characterization of the adsorbed CTAB layers on muscovite mica in detail. The various SAM morphologies, found on mica by the use of different adsorption protocols, demonstrate the influence of a large number of experimental parameters on the adsorption process, such as concentration, pH, temperature and humidity. They are rarely described in the literature.

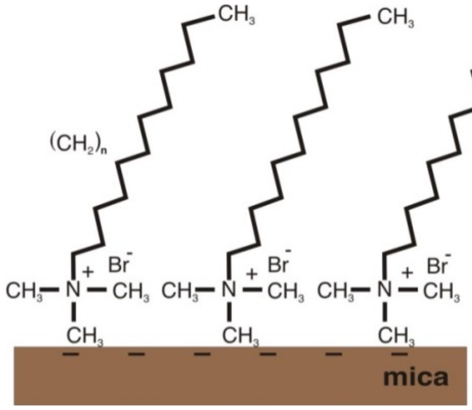


Fig. 3. CTAB layer on muscovite mica.

In order to characterize and determine the properties of SAMs, two techniques have been extensively used in this work, contact angle measurements [3] and the atomic force microscopy (AFM) [26]. For example, freshly cleaved mica has contact angle less than 10° and contact angle on the SAM produced by CTAB adsorption on mica can be 140° [23]. A contact angle greater than 90° is determined on hydrophobic surfaces.

In our experiments the contact angle measurements have been used in order to define the degree of hydrophobicity of the modified mica surface and molecular order after surfactant adsorption, performed by using ultra pure water.

All contact angle measurements were averaged over several samples.

5. EXPERIMENTAL PROCEDURE

We made self-assembled monolayers of quaternary ammonium surfactants on mica. Single-tailed hexadecyltrimethylammonium bromide, CTAB, with the molecular structure $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$, was purchased from Fluka. For further purification, CTAB was recrystallized from an ethanol/acetone mixture. As a solvent, ultra pure water of resistivity 18.3 MΩcm was prepared using a Barnstead EASYpure™ batch-fed water purification system. The same water quality was also used for the sample rinsing, before drying with a clean nitrogen stream.

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

Muscovite mica purchased from Spruce Pine Mica Company Inc. (USA) was used for the adsorption experiments. Small mica samples of 1-1.5 cm^2 size, were cut by scissors. Then, they were freshly cleaved on both sides before immersion into the surfactant solution. The adsorption was performed from the surfactant solution in a volume of 20 ml.

In our first adsorption series without temperature control, a 1000 ml stock solution of 10^{-2} M (~10 cmc) CTAB was prepared at room temperature. Since the solubility of CTAB in water was low at room temperature, the solution was heated to 30-35 °C. By dilution of this solution, prepared by adding the appropriate volume of ultra pure water, surfactant solution concentrations ranging from 10^{-3} M (~cmc) to 10^{-6} M (~cmc/1000) have been prepared. One option, called "CTAB in/CTAB out" (Fig. 4), involves immersion and extraction from the surfactant solution at the nominal concentration. In the water dipping step, the mica samples were dipped for 30 sec into 20 ml of ultra pure water to remove the excess solution and excess surfactant molecules.

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

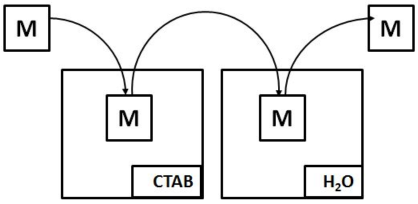


Fig. 4. "CTAB in CTAB out" experiment.

6. RESULTS OBTAINED WITHOUT TEMPERATURE CONTROL

The first two sets of experiments were realized without temperature control, in March and June 2003.

During the first experiments in March, the room temperature was in the range 21±2 °C, and a few months later, in June, the conditions in the laboratory were clearly different, 32±2 °C. As documented by the air temperature measured outside of our building, shown in Fig. 5, the temperature during the summer 2003 has been much higher than in spring. In several experiments the temperature was more than 30 °C.

Using the above described preparation protocols a significant number of samples have been prepared. The AFM images of two representative samples obtained by the "CTAB in/CTAB out" protocol at a concentration below the cmc are shown in Fig. 6. The AFM results observed at all solution concentrations below the cmc (from 10^{-4} M to 10^{-6} M), are very similar with the results presented in Fig. 6.

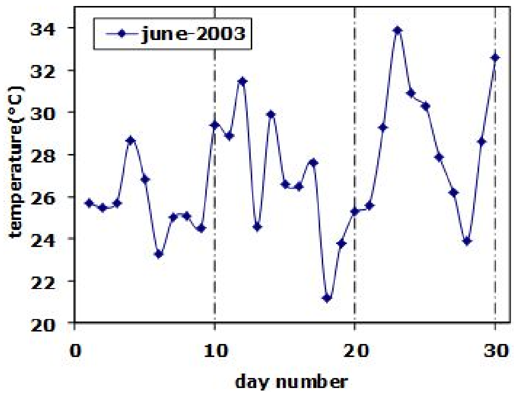


Fig. 5. Local temperature recorded in June 2003 (measured at 12:40 PM in Zürich-SwissMeteo data).

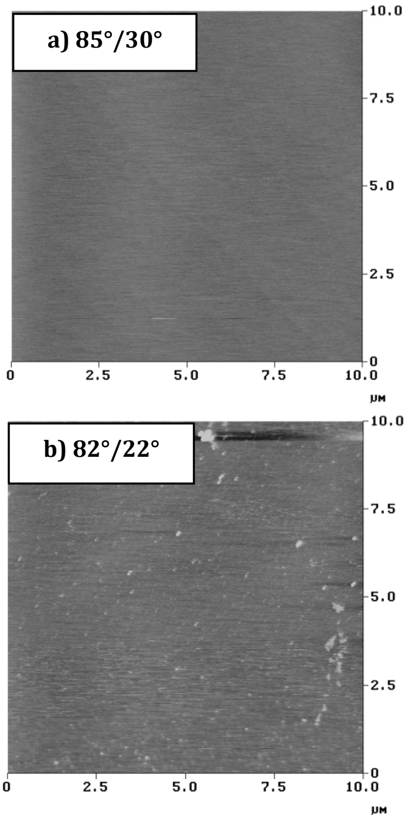


Fig. 6. AFM images of CTAB on mica obtained with the "CTAB in/CTAB out" protocol at a concentration of 10^{-4}M. Advancing and receding water contact angles are also shown: a) in March 2003 and b) in June 2003.

A clear seasonal influence on SAMs adsorption has been observed in all experiments realized without temperature control, regardless of the experimental protocols. On the sample prepared in June, where the air temperature outside of the laboratory building was higher than in March (Fig. 5), a significant number of clusters of height between 0.5 nm to 3.8 nm and the size around 250 nm size have been observed, according to the grey scale of the image, which represents a height range of 5 nm (cf. Fig. 6.b). The sample prepared in March, shown in Fig. 6.a, is more promising.

The advancing and receding water contact angle were measured on both samples exhibit hysteresis. Without temperature control, the reproducibility of those surfactant films was difficult to accomplish. Therefore, it was difficult to identify the most promising protocol for us.

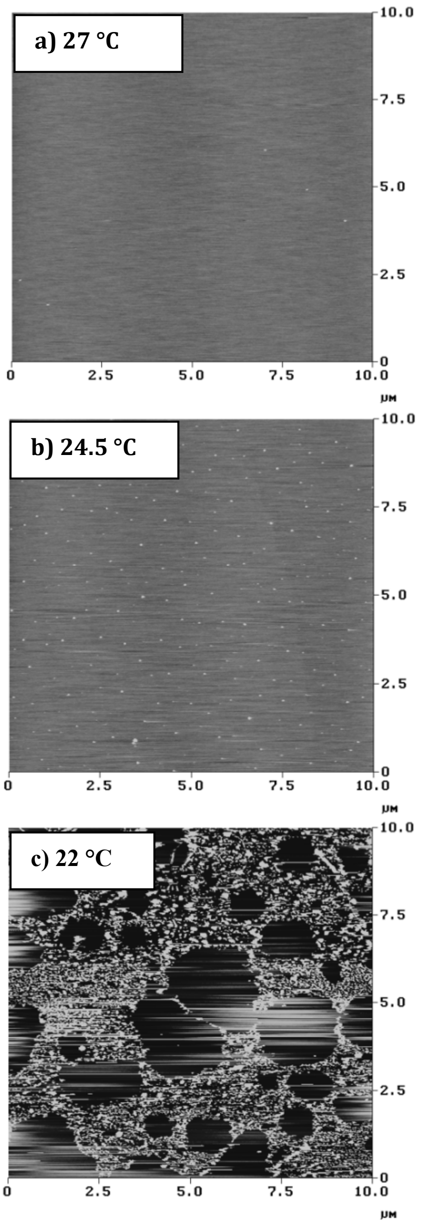


Fig. 7. Series of AFM images showing the surface morphology of CTAB coated mica by the protocol "CTAB in/CTAB out" at 10^{-2} M solution at temperatures: a) 27 °C, b) 24.5 °C and c) 22 °C.

We have performed a significant number of experiments at 10^{-2} M CTAB (i.e.10xcmc) solutions by the protocol "CTAB in/CTAB out", which nicely document the crucial role of the temperature. The results are summarized in Fig. 7.

Figure 7.a is representative of the sample prepared at 27 °C and is qualitatively different from the samples prepared at the lower temperatures. The bright spots observed in Fig. 7.b represent small islands on mica with a height between 0.5-1.3 nm. In Fig. 7.c we detect clusters of a height in order of 23 nm.

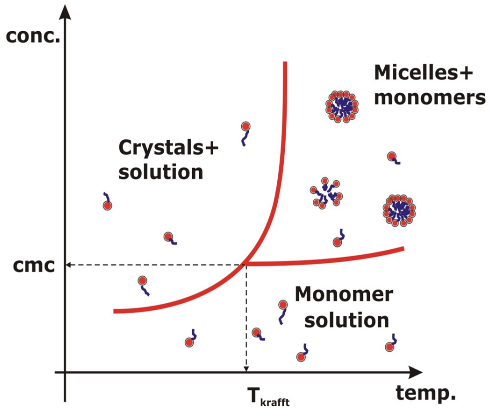
7. DISCUSSION

Our adsorption results have shown that the morphology, the structure and the stability of the adsorbed films are sensitive to the experimental conditions, primarily temperature.

One very important concept of surfactant solution is the Krafft temperature, whose effect is of great importance in SAMs formation. The Krafft temperature is the minimum temperature at which surfactants form micelles. Below the Krafft temperature micelles cannot form. The Krafft temperature is a point of phase change below which the surfactant remains in crystalline form, even in aqueous solution (Fig. 8). Around the Krafft temperature, Tk, many physical properties of the surfactant solution reflect this transition. The transition in CTAB solution around Tk clearly occurs over a range of temperatures. Although the Krafft temperature is a well-established concept, reported values of Tk for CTAB in water vary considerably, from 20 °C [18] to 25 °C [15]. Krafft temperatures, close to room temperature, significantly complicate the explanation of experimental results.

According to the AFM images, the sample obtained in March 2003 (Fig. 6.a) revealed a homogeneous CTAB film, in contrast to the sample performed in June (Fig. 6.b). The reason for such a difference must be related to changes in the solution structure.

Namely, solution used in the both experiments (10^{-4}M) has been prepared by dilution of a 10^{-2} M stock solution. The room temperature in March (21±2 °C) was slightly below the Krafft temperature of CTAB and we could expect that this stock solution mainly consisted of monomers. The same argument applies, of course, also to the diluted solution (10^{-4} M).



Krafft temperature

Fig. 8. The structural changes in the CTAB solution in the performed experiments, such as heating/cooling cycle of solution (marked as hysteresis) and the dilution of the solution, both above the cmc.

In June, however, a significant daily temperature variation, with temperatures clearly above the Krafft temperature, has been recorded, particularly in the days before the described adsorption experiment. It is to be expected that the solution structure of the stock solution is metastable and complex. The diluted solution may thus not be in thermodynamic equilibrium and consists of micelles and monomers. The clusters seen on the sample prepared under such conditions (Fig. 7.b) can be interpreted as micelle, adsorbed in different shapes and sizes.

The results shown in Figs. 6 and 7 clearly demonstrate the temperature influence on the surfactant films, morphology formed in different seasons of 2003. The variety of adsorbed film morphologies in uncontrolled conditions above the cmc can also be explained by structural changes in the stock solution. Namely, warming up the highly concentrated stock solution (10^{-2} M) to some 30 °C (above the Krafft temperature) will result in the formation of micelles. Since the film shown in Fig. 7.b. has been adsorbed at a temperature of 24.5 °C, which is near the Krafft temperature, we might expect the presence of some aggregates in the solution and also on the mica surface. Some of the micelles are expected to transform into surface-layers. The repetition of the same experiment one day later, at a room temperature of 22 °C, reveals a substantially different SAM as shown in Fig. 7.c. Upon cooling of micellar CTAB solution from the initial value ~30 °C to 22 °C, the solution then consists of crystals, monomers and micelles. As a consequence of such structural changes in the solution, the complex morphology (Fig. 7.c) is not surprising. A distinction between monolayer or bilayer formation is not readily possible from AFM images above (Fig. 7). The applied test, not described here, on the samples in several experiments, suggested bilayer formation even at concentration 10^{-4} M.

8. CONCLUSION

The performed experiments describe the adsorption of quaternary ammonium surfactants onto anionic, atomically smooth, muscovite mica. The surfactant films on mica, formed according to described experimental protocols, were characterized by contact angle measurements and by AFM. We have observed that SAMs can have completely different properties, depending on the meteorological conditions, influenced by temperature. These results suggested that temperature can influence all steps in adsorption procedure, from solution preparation to the rinsing step. The fact that the Krafft temperature range of CTAB (~25°) is around room temperature, makes this system appear particularly complex.

The dynamic CA experiments and AFM measurements have shown that the exact protocol of solution and self-assembled monolayer (SAM) preparation can substantially influence the stability of the hydrophobic layer, as well as the hydrophobicity. The results indicate that the morphology and the homogeneity of SAMs depend on many parameters, and the main reason for that is probably the molecular structure of the solution, controlled by the temperature and concentration of the solution.

In this model case of quaternary ammonium surfactants, the formation of homogeneous, well-ordered and reproducible monolayers is a very challenging task. In order to assess such complex systems, systematic variation of a great number of parameters was a necessary procedure.

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REFERENCES

[1] B. Bhushan, J.N. Israelachvili, U. Landman: *Nanotribology: friction, wear and lubrication at the atomic scale*, Nature, Vol. 374, pp. 607-616, 1994.

[2] NASA: *Lubrication, friction and wear*, 1971.

[3] J.H. Horng et al.: *Tribological study of biocompatible hybrid organic molecules film with Antibacterial effect,* Tribology in Industry, Vol. 35, No. 2, pp.128-133, 2013.

[4] Choa Sung-H. et al.: *A model of the dynamics of boundary film formation*, Wear, Vol. 177, No. 1, pp. 33-45, 1994.

[5] B. Bhushan: *Nanotribology and Nanomechanica II*, Springer, New Tork, 2011.

[6] K. Miyake, et al.: *Effects of surface chemical properties on the frictional properties of self-assembled monolayers lubricated with oleic acid,* Tribology Online, Vol. 7, No. 4, pp. 218-224, 2012.

[7] Jerome D. Swalen et al.: *Molecular monolayers and films. A panel report for the Materials Sciences Division of the Department of Energy*, Langmuir, Vol. 3, No. 6, pp. 932-950, 1987.

[8] J.A.M. Mellott: *Supercritical self-assembled monolayer growth*, Journal of the American Chemical Society, Vol. 126, No. 30, pp. 9369-9373, 2004.

[9] M.K. Chaudhury: *Adhesion and friction of self-assembled organic monolayers*, Current opinion in colloid & interface science, Vol. 2, No. 1, pp. 65-69, 1997.

[10] R.W. Carpick, M. Salmeron: *Scratching the Surface: Fundamental investigations of tribology with atomic force microscopy*, Chemical Reviews, Vol. 97, No. 4, pp. 1163-1194, 1997.

[11] D.K. Schwartz: *Mechanisms and kinetics of self-assembled monolayer formation*, Annual Review of Physical Chemistry, Vol. 52, pp. 107-137, 2001.

[12] J. Oremusova et al.: *Thermodynamics of micellization of hexadecylpyridinium bromide in aqueous and alcoholic (C-1-C-4) solutions*, Collection of Czechoslovak Chemical Communications, Vol. 65, pp. 1419-1437, 2000.

[13] K.K. Ghosh: *Thermodynamics of micelle formation of some cationic surfactants as a function of temperature and solvents*, Indian Journal of Chemistry, Sec. B. 37B, pp. 875-880, 1998.

[14] K. Boschkova et al.: *Lubrication in aqueous solutions using cationic surfactants - a study of static and dynamic forces*, Langmuir, Vol. 18, No. 5, pp. 1680-1687, 2002.

[15] P.S. Goyal, V.K Aswal: *Micellar structure and inter-micelle interactions in micellar solutions: Results of small angle neutron scattering studies*, Current Science, Vol. 80, No. 8, pp. 972-979, 2001.

[16] Y.a.J.I.N. Chen: *Effects of Ambient Conditions on Adsorbed Surfactant and Polymer Monolayers*, Journal of Physical Chemistry, Vol. 96, No. 19, pp. 7752-7760, 1992.

[17] A. Ulman: *An introduction to ultrathin organic films: from Langmuir-Blodgett to self assembly*, ed. Academic Press, Boston, 1991.

[18] I. Grosse, K. Estel: *Thin surfactant layers at the solid interface,* Colloid and Polymer Science, Vol. 278, No. 10, pp. 1000-1006, 2000.

[19] F. Zhao et al.: *Adsorption behavior of hexadecyltrimethylammonium bromida (CTAB) to mica substrates as observed by atomic force microscopy*, Science in China Ser. B Chemistry, Vol. 48, No. 2, pp. 101-106, 2005.

[20] S. Perkin et al.: *Stability of self-assembled hydrophobic surfactant layers in water*, Journal of Physical Chemistry, Vol. 109, No. 9, pp. 3832-3837, 2005.

[21] JM Mellott et al.: *Kinetics of octadecyltrimethylammonium bromide self-assembled monolayer growth at mica from an aqueous solution,* Langmuir, Vol. 20, No. 6, pp. 2341-2348, 2004.

[22] B.Y. Li et al.: *Time dependent anchoring of adsorbed cationic surfactant molecules at mice/solution interface*, Journal of Colloid and Interface Science, Vol. 209, No. 1, pp. 25-30, 1999.

[23] B.G. Sharma et al.: *Characterization of adsorbed ionic surfactants on a mica substrate*, Langmuir, Vol. 12, No. 26, pp. 6506-6512, 1996.

[24] W.A. Ducker, E.J. Wanless: *Adsorption of hexadecyltrimethylammonium bromide to mica: Nanometer-scale study of binding-site competition effects*, Langmuir, Vol. 15, No. 1, pp. 160-168, 1999.

[25] S. Manne, H. Gaub: *Molecular-Organization of Surfactants at Solid-Liquid Interfaces*, Science, Vol. 270, No. 5241, pp. 1480-1482, 1995.

[26] A.A. Minewitsch: *Some developments in trianalysis of coated machine components*, Tribology in Industry, Vol. 33, No. 4, 2011.