



Interaction forces between silica surfaces in cationic surfactant solutions: An atomic force microscopy study

Liset A.C. Lüderitz, Regine v. Klitzing*

Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 124, D-10623 Berlin, Germany

ARTICLE INFO

Article history:

Received 13 July 2012

Accepted 5 November 2012

Available online 28 November 2012

Keywords:

Aggregates
Forces
Morphology
Nanobubbles
Silica
Surfactants

ABSTRACT

The interaction forces between silicon oxide surfaces in the presence of surfactant solutions were studied. Based on the qualitative and quantitative analysis of these interaction forces the correlation with the structure of the aggregates on the surfaces is analyzed. A colloidal probe atomic force microscope (AFM) was used to measure the forces between two colloidal silica particles and between a colloidal particle and a silicon wafer in the presence of hexadecyltrimethylammonium bromide (CTAB) at concentrations between 0.005 mM and 1.2 mM. Different interaction forces were obtained for the silica particle–silica particle system when compared to those for the silica particle–silicon wafer system for the same studied concentration. This indicates that the silica particles and the silicon wafer have different aggregate morphologies on their surfaces. The point of zero charge (pzc) was obtained at 0.05 mM CTAB concentration for the silica particles and at 0.3 mM for the silica particle–silicon wafer system. This indicates a higher charge at the silicon wafer than at the silica particles. The observed long range attractions are explained by nanobubbles present at the silicon oxide surfaces and/or by attractive electrostatic interactions between the surfaces, induced by oppositely charged patches at the opposing Si oxide surfaces.

© 2012 Published by Elsevier Inc.

1. Introduction

The morphologies, functions, and applications of surfactants are diverse. There are natural surfactants such as the phospholipid protein, a pulmonary surfactant [1] used to reduce the surface tension in the lung. In addition synthetic surfactants are used in industry, including textile, cleaning products, cosmetics, food, and others. Depending on the concentration the surfactant can act as a destabilizing or stabilizing agent. Therefore, it is important to understand the interaction forces between two surfaces in presence of the surfactant. Related to that, the morphology of the surfactant aggregates on the surfaces has a dominant effect. The morphology of the surfactant aggregates in the bulk depends on the critical packing parameter [2,3]. Therefore, different aggregate morphologies like spherical, cylindrical, globular, oblate micelles, single and multiwalled vesicles, microtubules, bilayers, lamellar phases, and inverted structures can be found depending on the size ratio between head group and hydrophobic tail of the surfactant [3]. It is known that hexadecyltrimethylammonium bromide (CTAB) forms spherical micelles in the bulk at the critical micelle concentration (CMC) [4–6]. Additional parameters, like surface charge, head groups and interaction between the hydrophobic tail, define the structure of the adsorbate on surfaces [4,7]. Several

studies of the adsorption of surfactant to a hydrophilic surface, like mica and silica, have been performed [6–9]. Tyrode et al. [8] mention the two limit cases for adsorbing charged ionic surfactant at an oppositely charged hydrophilic surface below the CMC. For low surface charge systems, where the electrostatic interaction between head groups and surface is weak, no monomer adsorption at low concentration takes place. At a certain concentration, the critical surfactant aggregation concentration (csac), aggregates start to adsorb to the surface. No monolayer formation is present in this system, since a monolayer with aliphatic chains facing towards the aqueous solution would be entropically unfavored. Due to hydrophobic interactions additional surfactant molecules (with the hydrophilic groups facing out to the water) will start to adsorb before monolayer coverage is reached. In case of high surface charge, monolayer formation is favoured due to strong electrostatic attraction between the surfactant head groups and the oppositely charged surface. Subramanian et al. [4] studied the effect of the counterion on the shape of the adsorbed aggregates on the silica surface with AFM and demonstrated that it is possible to change the morphology of the CTAB from spherical to cylindrical by changing the counterion. With Cl^- ions for example spherical micelles are obtained whereas with Br^- ions cylinder aggregates on the silica surface are reported. Velegol et al. [9] obtained similar results studying the adsorbed layer at concentrations from 0.9 mM to 10 mM. Other authors [10,11] reported the presence of micelles on the silica surface above the CMC studied with optical reflectom-

* Corresponding author. Fax: +49 30 31426602.

E-mail address: klitzing@mailbox.tu-berlin.de (R. v. Klitzing).

etry and surface force apparatus respectively. Stiernstedt et al. [2] measured the surface force between silica particles across tetradecyltrimethylammonium bromide (TTAB) with a bimorph surface force apparatus. The obtained adsorbed layer thickness is 4 nm. Rutland and Parker [11] could not conclude if a patchy bilayer or flattened micelles were present on the silica surface close to the CMC. They observed a strong dependency of the adsorption of CTAB molecules on the surface charge of the particles. Raman scattering and sum frequency spectroscopy showed that the thickness of the CTAB layer on silica particles is about 3 nm. Surface neutralization is obtained around 0.1 mM surfactant concentration. Neither of the two principal models mentioned in the literature (“The two step model” and “The four region model”) can explain the adsorption to the silica surface [8].

The surface forces in the presence of surfactants have been investigated by several authors. Parker et al. [12] studied the interactions between glass particles with a surface force apparatus across CTAB solutions of different concentrations. They observed attractive interactions between two silica surfaces for distances at about 20 nm. The attractive forces could not be explained by van der Waals forces and they were present after the charge reversal and at higher concentrations. Several researchers try to explain the long range attraction observed between hydrophobic surfaces. Craig et al. [13] reported long range hydrophobic attraction of about 40 nm for cetylpyridinium chloride (CPC) in 100 mM NaCl adsorbed to silica surfaces. Carambassis et al. [14] associate the long range attraction between hydrophobic surfaces with the presence of bubbles. In a further work Craig et al. [15] obtained a slightly less attractive hydrophobic force for adsorbed CPC layers on the silica surface in 100 mM NaCl when the surfactant solution was degassed. Although the influence of dissolved gas on the hydrophobic interaction was suspected, they could not prove that nanobubbles may be responsible for the observed attractions. Kekicheff and Spalla [16] reported the correlation between the prefactor of the long range hydrophobic interaction for silica particles in CTAB solutions and the ionic strength of the solutions, supporting the hypothesis that the long range attraction between hydrophobic surfaces may have electrostatic origin. In the work of Yaminski et al. [17] microcavitation between the adsorbed patches of CTAB on the surface is considered to explain the large range hydrophobic interactions. Pashley et al. [18] studied the phenomenon of cavitation in CTAB monolayer. No evidence of cavitation was observed for this system since the contact angle was less than 90°.

So far, no systematic study of the interaction forces in the presence of cetyltrimethylammonium bromide (CTAB) has been carried out using AFM and still the mechanism for the long range hydrophobic attraction present in those systems is debated. In this work the interaction forces between a pair of silica particles (system I) and between a silica particle and a silicon wafer (system II) in CTAB solutions were measured over a large range, from well below the CMC to concentrations above the CMC. A prediction of the aggregates structure on the silicon oxide surfaces in dependence on surfactant concentration is established based on the qualitative and quantitative analysis of the interaction curves.

2. Experimental section

2.1. Materials

A suspension of silica particles of 4.63 μm in mean diameter (10% solid content) was purchased from Bangs Laboratories. Solutions of cetyltrimethylammonium bromide (CTAB, analytic grade, Aldrich) were prepared in a concentration range from 0.005 mM to 1.2 mM in pure water (Milli-Q). CTAB was water soluble up to

1.2 mM at room temperature. Clear solutions were obtained at all concentrations, which shows that the experiments were performed above the Krafft temperature.

2.2. Methods

A colloidal silica particle was glued to the end of a tip-less AFM cantilever (CSC12, $\mu\text{-mach}$, Lithonia) with a nominal spring constant of 0.03 N/m. Another particle was glued to a glass slide (Menzel-Gläser, Germany) using an optical microscope and a micromanipulator. The colloidal probes and the glass slides with attached particles were cleaned with ethanol and water and placed in an air plasma cleaner for 20 min (Diener electronic, Femto timer). The silicon wafers (type-P) Wacker Siltronic Burghausen were cut and cleaned in piranha solution $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4:50/50$ for 30 min. Thereafter, they were washed with milli-Q water and then immediately used for the experiments. This method allows the creation of an oxide layer on the silicon wafer surface and renders the surface highly hydrophilic.

The force measurements between the two silica particles [19] were performed using a MFP-3D Asylum Research atomic force microscope mounted on an inverted optical microscope (Olympus IX71). This technique is well described elsewhere [20–22]. In brief, a cantilever with the colloidal probe is fixed at the AFM head and the glass slide with the attached particle is placed on the scanner. The two opposing particles are optically aligned. A laser is pointed at the end of the cantilever. The cantilever moves in the z-direction and the deflection of the cantilever while approaching the surfaces is registered by a photosensitive detector. The spring constant is determined using the thermal noise method. In the following only approach curves are shown. At least 50 repetitions were done. After each measurement an optical microscope was used to check, if the particle was still attached to the cantilever. For the particle-particle system this check was performed during the measurements using an inverse microscope placed in the AFM. The measurements performed with one pair of spheres are reported. The velocity of the approach was 600 nm/s. The measurements with MFP-3D were obtained at room temperature at 1 atm.

The zeta potentials were measured using a Malvern Zetasizer Nano ZS with a HeNe laser. Different solutions of CTAB from 0.005 to 1.2 mM containing 0.1% silica particles were prepared. These suspensions were placed in a clear disposable zeta cell (DTS1060C) and equilibrated for 2 min at 25 °C in the equipment before starting measurements [23]. The average of 10 zeta potential measurements of the same sample was taken as the zeta potential value.

2.3. Simulations

The simulations are based on the DLVO theory. The DLVO theory only takes two kinds of forces into account to explain the stability of colloids in a suspension: electrostatic double layer and van der Waals forces. The electrostatic interactions are calculated solving numerically the non-linear Poisson–Boltzmann equation for two parallel plates using two boundary conditions, constant charge and constant potential. The van der Waals forces are the sum of the interactions between atomic and molecular dipoles in the particles or between different particles [24]. According to Borkovec et al. [25] the Derjaguin approximation is still valid for a particle size around of 4.63 μm . The algorithm used was proposed by Chan et al. [26]. The software used was written by McKee [27] based on the algorithm of Chan [26]. In the algorithm the electrostatic interactions are computed across symmetrical electrolytes. The planar Poisson Boltzmann equation is integrated to obtain a differential equation, and using the two boundary conditions, the electrostatic free energy of interaction is calculated for each distance

Download English Version:

<https://daneshyari.com/en/article/6999557>

Download Persian Version:

<https://daneshyari.com/article/6999557>

[Daneshyari.com](https://daneshyari.com)