**Surface Charge Characterization
of Solid-Liquid Interfaces
using Atomic Force Microscopy**

Naveen Kumar

**SURFACE CHARGE CHARACTERISATION OF SOLID-LIQUID
INTERFACES USING ATOMIC FORCE MICROSCOPY**

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INTERFACES USING ATOMIC FORCE MICROSCOPY**

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CHAPTER 1

INTRODUCTION

ABSTRACT

The main motivation of the research project is to understand the scientific challenges in enhanced oil recovery (EOR) processes. The increasing oil demand, while natural oil reservoirs are limited, requires new technologies for EOR [1]. One such method is “low salinity water flooding”, where oil recovery is increased by flooding the reservoir with low salinity water. However, the microscopic origin of the “low salinity water flooding” still remains unclear due to the lack of understanding of fluid-rock interactions. One aspect is surface charge, which is known to play an important role in such interactions and vary a lot under various brine solutions.

In this thesis, we characterise the surface charge on rock/clay material under different brine solutions and we study the adsorption desorption of ions and model oil components on these surfaces. In this chapter, I briefly discuss the motivation for undertaking this study and outline the problems in (the study of) EOR processes. Also, an outline of the chapters ahead is presented.

1.1. MOTIVATION: ENHANCED OIL RECOVERY

Globally, the fraction of oil that is recovered from oil reservoirs, i.e. the so-called recovery factor, is only between the 20%- 40% [2]. So a large amount of oil is left behind. Since, it is becoming increasingly difficult to discover new oil fields, there is a need to improve the recovery factor for better utilization of the known oil resources. This is the main driving force behind studying enhanced oil recovery (EOR) mechanisms and to design new technologies to enhance its efficiency. In this thesis, the main research questions are motivated by the quest for more efficient recovery methods of the global oil reserves. Before formulating my scientific research questions, I briefly describe the formation and composition of oil reservoirs and present some insights into the oil recovery process.

1.1.1. Oil reservoir:

Oil reservoirs are merely porous rock formations in which oil has been accumulated. Material remains of plants and animals are settled into seas and large inland lakes along with sand and silt, layer by layer. Over a span of millions of years, high temperature and high pressure transforms the sand and silt into solid rocks (also known as source rock) and the organic material trapped in these rocks slowly turns into liquid (crude oil) or gaseous hydrocarbons. The crude oil further migrates out of the shale source rock because of buoyancy force via cracks and fissures into porous and permeable rocks, known as reservoir rocks. The pore sizes can vary from the sub-micron to sub-millimeter range, and the porosity of the reservoir rock can vary from 10-35% [3]. These reservoir rocks consist usually of sandstone or carbonate containing silica, alumina, feldspar etc., and are capped by an impermeable layer. Due to the nature of these reservoir rocks, they act as a sponge holding significant amounts of oil within the pore volume. A schematic of a model oil reservoir is shown in Figure 1.1. The figure shows the oil (black) trapped between the rock grains (yellow) and clay particles (brown) (Figure 1.1.a). In this thesis, we focus on the situations where the oil is directly bounded to the rock or clay particles.

Both rock and clay materials acquire surface charge in aqueous salt solutions or under sea water conditions. Also the oil contains some polar organic compounds containing nitrogen, oxygen, sulphur etc. as head groups. In particular, these polar head groups can interact with rock/clay material and control the wettability of rock reservoir. Adsorption of oil components on the rock surface makes it more oil-wetting. Making the rock more water-wetting favours the oil release, which

increases the oil recovery. Self-assembled monolayer of various amphiphilic molecules have long been used as model systems for the hydrophobization and wettability alteration studies as depicted in Figure 1.1b.

Figure 1.1: A schematic of model oil reservoir illustrating (a) oil trapment between rock/clay surfaces (b) binding of polar head group to a positively charged clay surface.

1.1.2. Oil Recovery

Oil recovery is referred as a process by which hydrocarbons are extracted from the oil reservoirs. Due to the complex interactions between crude oil, rock and brine in the reservoirs, there exists a considerable number of methods for oil recovery. These methods can be categorised according to the phase at which they are applied during the recovery process; primary, secondary and tertiary/enhanced.

Some oil wells flow naturally due to the natural reservoir conditions such as gas drive, ground water drive or gravity drainage, which move oil to the well and up to the surface. This method of oil recovery is termed as primary recovery. It accounts for only 5-15% of the oil in the reservoir to be extracted.

Further, to recover more oil from reservoirs, secondary recovery methods are exploited. These methods consist of creating pressure gradients in the reservoir by injecting water (water flooding) or gas (gas flooding) through injection wells. The injected water partially displaces the oil and drives it to a production wellbore resulting in the recovery of up to 30-50% (see Figure 1.2) of the oil in the reservoir. However, even after these conventional methods 50-70% of the oil is still left in the reservoir. The amount of oil trapped, is determined by the properties of the oil and the characteristics of the reservoir rock such as spatial distribution of

pores, wettability, and heterogeneity in rock permeability (number, size and connectivity of the pores) [2].

To recover this significant amount of trapped oil, tertiary recovery methods, also known as enhanced oil recovery processes need to be engaged [4]. The traditional methods include thermal recovery, and injection of gases [5] or surfactants (chemical injection) [1, 2, 6, 7]. In recent years, another method known as low salinity water flooding (LSWF) has gained popularity. The primary principle of this method is the alteration of the reservoir wettability [2]. As shown in Figure 1.2, using enhanced oil recovery methods, additionally 5-20% or more of the reservoirs oil can be extracted. For optimal implementation of such EOR methods at industrial scale, it is important to understand the underlying mechanisms.

Figure 1.2: A schematic to highlight the increase in oil recovery during low salinity water flooding. Figure adapted from Webb et al. [8].

1.1.3. Low salinity water flooding mechanisms:

LSWF is an emerging promising technique which uses low saline water i.e. water with substantially lower salt concentrations than sea water, injected in the reservoirs for EOR[1]. Several independent studies have confirmed that oil recovery can be enhanced (with an average increase of 15%) by using LSWF [9-13]. These studies suggest that wettability alteration is one of the main phenomena

leading to EOR. Polar organic components in the crude oil play a crucial role in the wettability of reservoir rock. It has been proposed that a change of the surface charge on the rock affects the binding of polar organic components onto these surfaces, thereby changing their wettability [14]. LSWF causes the previously oil-wetting rock to become water-wetting, by a mechanism which is still unclear.

Many mechanisms have been proposed to explain it. One explanation is that wettability alteration occurs due to pH increase of brine because carbonate dissolves from it [15, 16]. It is understood that pH increase results into a reduction of the oil-water interfacial tension [17], which increases the water wettability of the rock and thus increasing oil recovery. Fine (small clay particles) migration is also one of the proposed mechanisms [9]. When exposed to low salinity solutions, fine particles would detach from the rock surface and move the retained oil. Later, Lager et al.[15] concluded that it was not fine migration, but multi-component ion exchange between the charged clay particles and the injected brine, which is responsible for the wettability alteration. The pore walls become oil wetting as divalent cations like Mg^{2+} and Ca^{2+} bind between the negatively charged oil components and the also negatively charged mineral/clay surfaces (see Figure 1.3). Low saline brine which has a low concentration of these ions, facilitates the removal of ion-bound oil from rock/clay surfaces [18, 19], due to the drive of the divalent cations towards the bulk phase. This increases the water wettability of the surface and thus improves the EOR. Despite these many propositions, a general consensus about the dominant mechanism for LSWF is still missing. LSWF does in principle work for both sandstone and carbonate reservoir rocks. However, the underlying mechanisms are different for different reservoir rocks. In this thesis, we only focus on the sandstone reservoir.

Figure 1.3: Various interaction mechanisms between polar organic components of oil and negatively charged rock/clay surface in presence of sea water ions. Figure adapted from Lager et al. [15].

1.2. SCIENTIFIC CHALLENGES AND THESIS SCOPE

It is quite evident that macroscopic experiments will not provide any nanometre scale explanation of the low salinity mechanism. But understanding of the microscopic mechanisms in LSWF is necessary for further improvement of enhanced oil recovery. As illustrated in Figure 1.1b and 1.3, the charging behaviour of rock/clay-liquid interfaces plays an important role in the binding/unbinding of oil components to these surfaces. Therefore, researchers have studied this topic extensively in past few decades [15, 20-22]. Key questions, answers of which can provide us better understanding of the EOR mechanisms, especially LSWF are:

- How is the rock/clay-liquid interface charged in aqueous conditions? Is the surface charge homogenously distributed or heterogeneously?
- What is the effect of pH and salt concentration on the surface charge?
- Do divalent ions adsorb on charged rock/clay materials?
- What happens to polar oil components at the rock/clay-liquid interface as solution conditions change (i.e. pH, salt ion, concentration)? Is it possible to desorb them more efficiently in absence of divalent ions?

This thesis is dedicated to answer these questions. Aside from oil recovery, charging behavior and ion adsorption at solid-liquid interfaces play a crucial role in wide range of fields like colloid science, self-assembly, wetting, electrochemistry, and molecular biology [23, 24]. Thus, molecular characterization of solid-liquid interfaces is gaining more and more attention from the researchers. Many experimental techniques are routinely used for the same, such as x-ray or neutron reflectivity, ellipsometry, sum frequency generation, surface plasmon resonance. But unfortunately, most of the available experimental techniques have not been able to capture the complex structure of solid-liquid interfaces with resolution at nano-meter scale. They also tend to miss the intrinsic heterogeneity of the system by averaging out the interfacial properties.

Recent advancements in Atomic force microscopy (AFM) have equipped us to study solid-liquid interface with unprecedented resolution. We use AFM force spectroscopy to characterise the charging behaviour of rock/clay surfaces. Silica is used as representative of sandstone rock. Kaolinite, being the dominant clay mineral in sandstone reservoirs, is also studied extensively. We have also investigated the charging behaviour of mica as it is representative for many 2:1 layer type clay minerals. Furthermore, we demonstrate the role of divalent ions in binding/unbinding polar oil components to silica surfaces. Stearic acid molecules are used in this study as a representative for the polar organic components in the oil.

1.3. THESIS OUTLINE

In this research project we investigate various aspects related to the charging behaviour of rock/clay surfaces under different aqueous solutions and we further examine the role of surface charge on adsorption/desorption of oil components in a reservoir. This study will elucidate the role of surface charge in oil recovery mechanisms. Further, it would explain adsorption desorption of oil components via cation bridging mechanisms, which would explain wettability in low salinity water flooding.

Chapter 2 discusses the materials, methods and techniques used in the study. Firstly, clays in terms of their morphology and charge characteristics have been discussed. Secondly, the techniques used to characterise the rock/clay-water interface i.e. AFM, contact angle goniometry and Langmuir trough have been explained. Additionally, a detailed description is presented of the theoretical model

used to calculate the surface charge of these clay particles using DLVO theory with charge regulation boundary conditions.

After a brief description of the basic concepts used in the study, in **Chapter 3** we determine the distribution of surface charge on kaolinite, since it is the most abundant clay material. The surface charge density is extracted from the measured force distance curves using DLVO theory. The results of these experiments suggest that simple surface complexation models of clays that attribute a unique surface chemistry and hence homogeneous surface charge densities to basal planes may miss some important aspects of real clay surfaces, in particular surface chemistry and surface charge. With these results, we also validate the methods and techniques for surface charge calculation.

In Chapter 3 we discuss only a single case: one concentration and a fixed pH, although oil reservoirs are much more complicated. Therefore, in **Chapter 4**, using the same methods and techniques, we determine the surface charge on kaolinite in presence of mono- and divalent ions and under variable pH solutions. The results highlighted that different salts with varying concentrations and variable pH have different significant effects on surface charge.

After surface charge characterisation of kaolinite particles, we focus in **Chapter 5** our attention on the charging behaviour of mica, which is a 2:1 type clay material. We determine the surface charge of mica for five different salt solutions (Li^+ , Na^+ , Cs^+ , Ca^{2+} and Mg^{2+}) and three different pH values (4, 6 and 9) of the solution. A substantial difference between the surface charge of monovalent and divalent salt ions is observed. Also, the effect of pH on the surface charge of mica is significant for pH values in the range of 4 to 6.

In **Chapter 6** we investigate the adsorption/desorption of oil molecules on these surfaces. Langmuir-Blodgett films of stearic acid (representative of polar organic components of oil) are deposited on silica in the presence of Ca^{2+} and/or Na^+ ions. Large differences in macroscopic wettability (contact angles) are observed between the monolayer prepared in Ca^{2+} and Na^+ ions sub-phases. The observations on varying the composition of the droplets corroborate the stabilizing effect of Ca^{2+} . We attribute these findings to the cation-bridging ability of Ca^{2+} ions, which can bind the negatively charged stearate groups to the negatively charged substrates. In Chapter 6 we conclude that Ca^{2+} induced stabilization implies a destabilization and easy removal of ionically bounded organic layers in the absence of divalent ions.

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Abstract

In this chapter, we discuss the materials and methods employed in this research. Firstly, a brief introduction of clay minerals and their classification is presented. Further, we describe the physical and chemical properties of clay, highlighting the importance of studying these properties. Next, the technique used to characterise the surface charge with AFM, as employed in Chapter 3, 4 and 5, is discussed. Furthermore, we describe the theoretical model to calculate the surface charge using DLVO theory with charge regulation boundary conditions. Lastly, contact angle goniometry and Langmuir trough experiments are explained. These are used to study adsorption/desorption of fatty acid molecules on model rock surfaces in chapter 6.

2.1. RESERVOIR ROCK

Reservoir rocks are predominantly sedimentary rocks which are porous and permeable. The three types of reservoirs rocks which are most commonly found in oil fields are shales, carbonates and sandstone. In this thesis, we will mainly focus on the sandstone reservoir rock. Sandstone reservoirs are mainly composed of sand minerals e.g. quartz, feldspar, iron oxides, and clay minerals such as kaolinite, illite, montmorillonite, muscovite, chlorite etc. A majority of sandstone reservoirs contain clay minerals. Thus, oil and water interact with both clay and sandstone materials. Figure 2.1 shows a scanning electron micrograph (SEM) image of a Sherwood sandstone (Slyne basin, west of Ireland) covered with some clay minerals. In this thesis, we study silica as model sandstone rock and kaolinite and mica as dominant clay minerals.

Figure 2.1 SEM image of a Sherwood sandstone (Slyne basin, west of Ireland) covered with clay minerals (image taken from [1]).

2.2. CLAYS AND CLAY MINERALS

Clays and clay minerals are layered silicates that are formed as a result of chemical weathering of a variety of minerals at the earth's surface. Being a natural part of the soil, they are abundantly available, inexpensive and are used as raw materials in hundreds of industrial processes. Their applications are found in ceramics, paper, ink and paint, medicine, aerospace, the automotive and chemical industry [2, 3]. Clay minerals, also abundantly present in oil reservoirs, play a significant role in petroleum industry as well [4-6].

Clay minerals are characterized by a layered structure composed of silicon oxide tetrahedra (T) linked into sheets of aluminium - or magnesium - hydroxide octahedra (O). They are classified into mainly two layer types, distinguished by the number of tetrahedral and octahedral sheets combined to form a layer [7].

2.2.1. 1:1 layer type:

The 1:1 layer type (T-O layer) consists of one tetrahedral sheet linked with one octahedral sheet. One side of the layer (unshared plane) consists entirely of oxygen atoms belonging to the tetrahedral sheet, while the other side is composed of hydroxyl groups (-OH) of the octahedral sheet (See Figure 2.2). Two T-O layers are bonded to each other by hydrogen bonds (involving oxygens of the T sheet and hydroxyls of the adjacent O sheet) and van der Waals forces. The thickness of each T-O layer is 0.7 nm. Few of such 1:1 layer type clay minerals are kaolinite, dickite, nacrite, lizardite, antigorite etc. An important characteristic of this layer type mineral is that they have both the tetrahedral and octahedral sheets exposed to an aqueous solution. Due to this nature, they can be selectively oriented by adsorbing them onto substrates of opposite surface charge. In this research, we study kaolinite in great detail as a representative of 1:1 layer type mineral.

Figure 2.2 Crystal structure of the 1:1 layer type clay minerals. (a) Side view of the crystal structure orthogonal to the basal plane, top view of the (b) silicon oxide tetrahedral, and (c) aluminium hydroxide octahedral sheet structure.

2.2.2. 1:2 layer type:

The 1:2 layer type is composed of one silica-tetrahedral sheet sandwiched between two alumina-octahedral sheets giving it a triple sheet structure (T-O-T). The top and bottom sheet of each layer consists of oxygen atoms (O) and the adjacent layers are only loosely bounded by very weak O-O or O-cation bonds (See Figure 2.3). The thickness of this triple sheet layer is 1.0 nm. Mica, biotite, illite, montmorillonite, nontronite etc. are examples of such layer type minerals. Mica has been studied in detail in chapter 5 as a representative of 1:2 layer type clay mineral.

Figure 2.3 Crystal structure of the 2:1 layer type clay minerals. (a) Side view of the crystal structure orthogonal to the basal plane (b) top view of the silicon oxide tetrahedral sheet structure. Note: the solid blue spheres represent the interstitial ions (e.g. K⁺, Na⁺).

2.3. CLAY PROPERTIES

Properties of clay minerals like surface morphology, surface charge, and surface chemistry are extremely important to study because they determine the physical and chemical characteristics which has consequences on the applicability and thus on the economic use of these clay minerals.

2.3.1. Morphology of clay minerals

The surface morphology of each clay minerals is unique. As observed from the SEM and AFM images in Figure 2.4, kaolinite displays a plate-like pseudo hexagonal shape [8], while montmorillonite and illite display a lath-like or fibrous morphology [9]. Also, the particle thickness of kaolinite varies from a few tens of nm to a few hundreds of nm, whereas montmorillonite and illite are quite thin, varying between 1-10 nm.

Figure 2.4 SEM and AFM topography images of several clay minerals: gibbsite, kaolinite, montmorillonite and mica/illite.

2.3.2. Surface charge of clay minerals

Clay minerals are very reactive in nature because they have a high surface to volume ratio and carry a significant amount of surface charge. Many of the physical and chemical properties of clay minerals are directly or indirectly controlled by the nature and amount of surface charge, e.g. cation exchange capacity[10, 11], transport of chemicals in soil and ground water[12-14], dispersion behaviour[15, 16], colloidal stability[17] etc. So, understanding the surface charging properties of clay minerals is essential for various industrial processes. An important example is found in oil industry, where, surface charge plays a significant role in the binding/unbinding of polar oil components on reservoir material which has consequences for the wettability of clays and rock materials as well [18-20]. In chapter 6, we study this aspect of surface charge in the context of EOR processes.

Clay minerals usually have two types of charge: permanent and pH dependent. The permanent charge usually arises from isomorphous substitutions of lattice cations or can be caused by structural imperfections. The pH dependent charge arises from protonation/deprotonation of surface hydroxyl groups. Traditionally, the basal plane of the mineral is believed to carry a permanent charge whereas the edges are known to carry a pH dependent charge [21-23]. However, recent research in this direction has shown that even basal planes may have a pH dependent charge [24-27]. Recent advances in the atomic force microscopy technique have made it possible to study the charging behaviour on basal planes as well as the edges of

clay mineral [26, 28, 29]. Chapter 3, 4 and 5 focusses on studying the surface charge of mica and kaolinite basal planes using high resolution AFM techniques. In the sequel of this chapter we discuss the experimental techniques used in this research.

2.4. EXPERIMENTAL TECHNIQUES

In this section, we describe the various techniques used in our experiments such as Atomic Force Microscopy, contact angle goniometry and Langmuir-Blodgett trough. We use dynamic force spectroscopy to characterise the surface charge of different rock/clay materials under aqueous conditions.

2.4.1. Dynamic force spectroscopy

In dynamic force spectroscopy, the cantilever is driven to oscillate near the sample surface in normal direction. The cantilever dynamics are often modelled as a simple harmonic oscillator (SHO) [30]. During the measurements, the deflection, amplitude, phase and frequency of the vibrating cantilever is acquired while it interacts with a sample at varying tip-sample separations. To analyze the obtained signals, we consider the equation of motion of the cantilever tip that can be written as:

$$m^* \ddot{z} + \gamma_c \dot{z} + k_c z = F_{drive} + F_{ts}(h + z, \dot{z}) \quad (1)$$

where, $z(t)$ is the displacement of the cantilever with respect to its equilibrium position, h the tip-sample separation in equilibrium, k_c the cantilever's spring constant, m^* the total effective mass, γ_c the viscous damping around/of the cantilever, F_{drive} the driving force and F_{ts} the tip-sample interaction force. During the measurements, we use a very small oscillation amplitude (less than 2 nm), which in general is smaller than the characteristic length of interaction force one tries to probe. Thus, the tip-sample interaction force can be linearized as

$$F_{ts}(h + z, \dot{z}) = F_{ts}(h, 0) - k_{int}z - \gamma_{int}\dot{z} \quad (2)$$

Where, k_{int} is the interaction stiffness, γ_{int} the interaction damping coefficient and $F_{ts}(h, 0)$ the equilibrium force. To obtain expressions for the tip-sample interaction stiffness and damping from Eqs. (1) and (2), we need to know the driving force (F_{drive}) as well as the cantilever parameters (k_c , m^* and γ_c). The resonance frequency ω_0 and the quality factor Q of the cantilever are defined

as $\omega_0 = \sqrt{k_c/m^*}$, and $= m^*\omega_0/\gamma_c$. The spring constant k_c is obtained from the thermal noise spectrum of the cantilever, when it is far away from the substrate, i.e. $h > 1\mu\text{m}$. The mass m^* and the damping coefficient γ_c are obtained from ω_0 and Q (for details, see ref. [31, 32]). Depending on the driving mechanism of the cantilever, F_{drive} can also be determined.

2.4.1.1. Amplitude Modulation (AM)-AFM

In AM-AFM mode, the cantilever is driven with a constant drive force i.e. with a fixed drive amplitude and drive frequency. The amplitude $A(h)$ and phase $\phi(h)$ response of the cantilever are recorded as a function of the z-piezo position by varying the mean tip-sample distance.

The AM-AFM force spectroscopy measurements are performed with a commercial Asylum Research Cypher ES with blue drive which provides photo thermal excitation. The cantilever is driven by locally heating it with a laser beam, using the so-called photo thermal drive principle [33]. Due to the oscillating temperature field over the cantilever, resulting from the heating process, the relation between F_{drive} and tip displacement z is given by:

$$F_{drive} = k_c(z - z_T) \quad (3)$$

Where, z_T is the zero-load deflection due to the temperature enhancement along the beam caused by the laser radiation with intensity I . Rectangular cantilevers (MikroMash NSC36/Cr-Au BS) with a gold coated backside are used. Aside from the actual measurements, the fast capture mode is used to record the power spectrum of the cantilever when it is situated in the electrolyte some 20 nm away from the substrate so that the interaction between substrate and cantilever can be neglected. From the power spectrum, the quality factor Q and resonance frequency ω_0 is obtained, which are used to determine the cantilever parameters.

The amplitude and phase of the tip displacement, $z(\omega) = Ae^{j\phi}$, are measured as a function of the tip-sample distance, to probe the interaction of the tip with the substrate. Using F_{drive} and the cantilevers parameters, the interaction stiffness of the cantilever can be obtained as (see Ref. [32] for a detailed derivation):

$$k_{int} = k_c \left[1 - \left(\frac{\omega}{\omega_0} \right)^2 \right] \frac{A_\infty \cos(\phi - \phi_\infty) - A}{A} + \gamma_c \omega \frac{A_\infty \sin(\phi - \phi_\infty)}{A} \quad (4)$$

Here, A_∞ and Φ_∞ are the amplitude and phase, respectively, measured at distance far away from the substrate (~ 140 nm), where both k_{int} and γ_{int} are zero. Integrating Eq. (4) results into the tip-sample interaction force.

To measure the interaction force correctly, the tip-sample distance should be known precisely. This distance is defined by the piezo position relative to the substrate plus the cantilever deflection. The piezo position relative to zero is determined by analyzing the deflection approach curve, when the tip is in hard contact. We fit a straight line to the measured deflection vs. piezo position curve for high deflection values (typically above ~ 10 nm). Extrapolating this line to zero deflection gives us the piezo position (P_0) at which a non-deflected tip would just touch the substrate. Adding the cantilever deflection at this point to P_0 would give us the actual tip-sample distance.

2.4.1.2. Frequency Modulation (FM)-AFM

In FM-AFM mode, the cantilever is always self-driven at its actual resonance frequency [34]. There are two methods to drive the cantilever as a self-driven oscillator. In constant-amplitude (CA) mode, the oscillation amplitude is kept constant, while in constant excitation (CE) mode, the excitation amplitude is constant. The CE mode is well suited for force spectroscopy measurements as it allows for a quantitative determination of the tip-sample interactions in a straightforward way [34].

A Dimension Icon AFM (Bruker Corporation) equipped with a Nanoscope V controller is used for dynamic force spectroscopy measurements. Additional electronics (QFM-module, NanoAnalytics GmbH) is used to drive the cantilever in FM-mode at constant excitation (CE) [34-36]. Dynamic force-versus-distance experiments are conducted by recording the amplitude $A(h)$ and frequency shift $\Delta w(h) = \omega_a - \omega_0$ of the oscillating tip as a function of the z-piezo position by varying the mean tip-sample distance. Here, w_a represents the distance dependent actual frequency and the w_0 is the resonance frequency far away from the surface (see Figure 2.5). In case of FM-AFM the force acting on the tip due to the sample surface can be correlated with the frequency shift and oscillation amplitude using formulae developed by Ebeling and Holscher [37] and Sader and Jarvis [38] as:

$$F_{ts}(h) = -\frac{\partial}{\partial h} 2k_c \int_h^\infty \frac{\Delta w(z)}{w_0} \left[(z-h) + \sqrt{\frac{A(z)}{16\pi}} \sqrt{z-h} + \frac{A(z)^{3/2}}{\sqrt{2(z-h)}} \right] dz \quad (5)$$

Figure 2.5 Schematic illustration of the Frequency-modulation AFM force measurements showing attractive (blue) and repulsive (red) forces. (a, a') amplitude vs piezo displacement (b, b') frequency shift vs piezo displacement (c, c') tip sample interaction forces.

2.4.2. Atomic resolution imaging

Atomic resolution imaging experiments are carried out two AFMs, a Cypher Asylum research AFM and a Multimode8 AFM (Bruker Corporation) equipped with a Nanoscope V controller. Sharp tips (Bruker BBB, tip radius ~ 3 nm) are used in desired salt solutions by injecting liquid using the syringe. Tapping mode or AM mode is used throughout all the experiments with a free amplitude A_0 , typically less than 1 nm. The ratio of the imaging amplitude set point (A/A_0) is kept as high as possible (typically ≥ 0.9) to minimize the force of interaction between tip and the surface [28, 39, 40]. A very high scanning rate ~ 15 Hz is used with a scan resolution of 512 samples per line. Usually, it takes ~ 30 sec to capture one image. In case of Multimode, to minimise the thermal drift, the system is allowed to thermally equilibrate at room temperature for 20-60 min before acquiring any data. However, in case of Cypher, because of improved instrument design, the time required for thermal equilibration is far less (typically 5 min).

2.4.3. Langmuir-Blodgett trough

In chapter 6, we study the stability of stearic acid (SA) Langmuir Blodgett (LB) films under various aqueous salt solutions. The film deposition is performed using

a computer-controlled trough from Nima Technology. Prior to the experiment, the trough is rigorously cleaned with pure water, ethanol and chloroform. The system is assumed to be clean if the surface pressure of the bare subphase (i.e. prior to spreading the SA solution) varies by no more than 0.1 mN/m upon moving the barriers back and forth. Subsequently, a drop (50 μL) of the SA solution in chloroform is deposited on the subphase. During 30 min the solvent is allowed to evaporate and the SA layer is allowed to spread, before initiating the LB transfer. All LB transfers are performed at a constant surface pressure of 30 mN/m, just above the kink in the pressure-area isotherm. It indicates the apparition of a compact solidified layer. The pulling speed is 2 mm/min. Under these conditions, the transfer ratio for the monolayers is unity implying that the substrates become completely covered by the monolayers. Several parameters such as sub-phase composition, temperature, surface pressure during the deposition, deposition speed and the time for which the solid substrate is stored inside the sub-phase determine the quality of the deposition.

2.4.4. Contact angle goniometry

To study the macroscopic wettability of droplets on a sample substrate an optical contact angle goniometer with automated data analysis software (OCA 20L; Dataphysics) is used. The sample substrate contains LB films of stearic acid prepared under different sub-phase conditions. The static water contact angles of 5-10 μL droplets are determined with an accuracy of $\pm 0.5^\circ$. Droplets of pure water or saline solutions are placed on the substrates in air. 20 hours after the sample preparation, goniometry measurements are performed on at least at 3-4 different locations on each sample. For each given sample the contact angle values are reproducible within $\pm 3^\circ$, reflecting the quality of the deposited monolayer.

2.5. THEORETICAL BACKGROUND

In this section, we discuss the basic procedures for the conversion of measured forces to surface charges. These are described recently by Ebeling, et al. [41] and Siretanu, et al. [28]. A systematic account of the procedure to include charge regulation into the standard framework of DLVO theory was originally provided by Ninham and Parsegian [42] and was later refined by various authors. Its specific adaption to high resolution AFM spectroscopy is described in detail by Zhao, et al. [43]

2.5.1. DLVO theory

In DLVO theory, the disjoining pressure between two adjacent surfaces at a distance h is decomposed into contributions from van der Waals interactions Π_{vdW} and electrostatic double layer forces Π_{el} . Additional contributions due to short range interactions such as hydration forces only become important at tip-sample separations smaller than 1-2 nm, which are beyond the scope of our present study. The AFM tips used in our experiments are slightly flattened leading to a local parallel plate geometry[41]. For such case, the van der Waals contribution is written as

$$\Pi_{vdW}(h) = -\frac{A_H}{6\pi h^3} \quad (6)$$

where A_H is the Hamaker constant.

The electrostatic disjoining pressure (Π_{el}) consist of two contributions, one due to osmotic repulsion caused by local variations of the ion concentration and another due to direct electrostatic attraction (Maxwell stress). Π_{el} can be written as

$$\Pi_{el}(h) = k_B T \sum_i (c_i(z) - c_{i\infty}) - \frac{\varepsilon \varepsilon_0}{2} \left(\frac{\partial \psi}{\partial z} \right)^2 \quad (7)$$

for every value of z between d_s and $h-d_s$. Here k_B is the Boltzmann constant, T the temperature, $\varepsilon \varepsilon_0$ the dielectric permittivity of water, while i represents all ionic species in the system and $c_{i\infty}$ is the bulk number concentration of ions. $\psi(z)$ is the electrostatic potential in the electrolyte at an arbitrary position $d_s < z < h-d_s$ between the two solid surfaces, where d_s is the Stern layer thickness (see Figure. 2.5). The potential distribution $\psi(z)$ can be calculated by numerically solving the Poisson-Boltzmann (PB) equation

$$\frac{d^2}{dz^2} \psi(z) = -\frac{e}{\varepsilon \varepsilon_0} \sum_i Z_i c_{i\infty} \exp\left(-\frac{Z_i e \psi(z)}{k_B T}\right) \quad (8)$$

between the substrate and the tip using a fourth order Runge-Kutta algorithm. Here, e represents the elementary charge, and Z_i is the valency of corresponding ions. Eqs. (7) and (8) indicate that Π_{el} only depends on the potential and ion distribution in the diffuse layer. The surface chemistry that we are interested in enters the problem via the boundary conditions for Eqn (8). There are three ways to formulate the boundary conditions (i) constant charge (CC) (ii) constant potential (CP) (iii) charge regulation (CR). In the first case the surface charge density is kept constant during the whole approach, in the second case the surface potential is fixed. The real picture lies in between these two extreme cases (i.e. Charge regulation, see next section). The potentials $\psi(d_s)$ and $\psi(h-d_s)$ that are related to the net surface charge densities of tip (σ^I) and substrate (σ^{II}) via Gauss' law can

be specified to solve Eqn (8). Once $\psi(z)$ is known, we can calculate the total diffuse layer charge as

$$\sigma_d = \int_{d_s}^{h-d_s} \frac{e}{\varepsilon \varepsilon_0} \sum_i Z_i c_{i\infty} \exp\left(-\frac{Z_i e \psi(z)}{k_B T}\right) dz \quad (9)$$

Also, the measured forces on the tip can be calculated by integrating the total disjoining pressure over the tip surface as $F(h) = A_{tip}(\Pi_{el} + \Pi_{vdW})$, where A_{tip} is the area of the tip.

Figure 2.6 (a) A schematic representation of the electrical double layer (EDL) structure on the surface of an isolated plane showing potential variation with distance. (b) The EDL structure between two adjacent planes with overlapping diffuse layers.

2.5.2. Charge regulation

As the equations given above show, we need to solve the Poisson-Boltzmann equation and substitute the potential $\psi(z)$ in the equation (7) for Π_{el} in order to calculate the charge and the force between tip and substrate. Solving the PB equation requires a boundary condition on both substrate and tip. Frequently, either the charge or the potential is assumed to remain constant upon varying the tip-sample distance. In general, however, neither the surface charge density nor the potential remains constant as two surfaces come closer. Instead, when two charged surfaces approach each other, the diffuse layers start to overlap and some of the counter ions are forced to re-adsorb onto their original surface sites (as illustrated in Fig.2.6). Thus, as the tip sample separation changes, the surface charge density also changes, i.e. it becomes a function of the tip-substrate separation. This is known as charge regulation.

As mentioned above, the surface charge is controlled by adsorption and desorption of protons and salt ions from the solution to the interface and vice versa. As an example, we consider the charging of a surface site SH due to deprotonation of the surface group. This process is described by the chemical reaction

which has an equilibrium constant $K_{H1} = \frac{\{S^-\}[H^+]_s}{\{SH\}}$. The curly brackets denote a surface density in sites/nm² and the square brackets represent a volume density or concentration in mol/L. The deprotonated sites may be occupied again by counter-ions from the solution to form surface complexes. This is described by a second surface reaction:

with equilibrium constant $K_c = \frac{\{S^-\}[C^{Z_c}]_d}{\{SC\}}$, where Z_c is the valency of the cation C.

Due to these two reactions, three surface species are present on the surface: $\sim SH$, $\sim S^-$, $\sim SC^{Z_c-1}$. Because the total site density Γ must be conserved, we can write

$$\{S^-\} + \{SH\} + \{SC^{Z_c-1}\} = \Gamma \quad (12)$$

Eqs. (10)-(12) can be summarized in the following matrix equation:

$$\begin{pmatrix} 1 & 1 & 1 \\ [H^+]_s & -K_{H1} & 0 \\ [C^{Z_c}]_d & 0 & -K_c \end{pmatrix} \begin{pmatrix} \{S^-\} \\ \{SH\} \\ \{SC^{Z_c-1}\} \end{pmatrix} = \begin{pmatrix} \Gamma \\ 0 \\ 0 \end{pmatrix} \quad (13)$$

It should be noted that the $[H^+]_s$ and $[C^{Z_c}]_d$ are evaluated at the surface and the Stern plane, respectively, not in bulk. These concentrations are related to the bulk concentrations (indicated with subscript ∞) via the Boltzmann relation

$$[H^+]_s = [H^+]_\infty \exp\left(-e\psi_s/k_B T\right) \quad (14)$$

$$[C^{Z_c}]_d = [C^{Z_c-1}]_\infty \exp\left(-eZ_c\psi_d/k_B T\right). \quad (15)$$

Moreover, the surface potential is related to the potential at the Stern plane by the capacitance of the Stern layer: $C_s = \frac{\sigma}{\psi_s - \psi_d} = \frac{-e\{S^-\}}{\psi_s - \psi_d}$. Eventually, we have established the CR boundary condition as:

$$\begin{aligned} \sigma_s &= f(\psi_s; K_{H1}; K_c; \Gamma; [H^+]_\infty; [C^{Z_c-1}]_\infty; C_s) \\ &\equiv f(\psi_s, p) \end{aligned} \quad (16)$$

Where, p stands for all parameters. It is important to note that the extracted surface charge σ_s is essentially the net surface charge, i.e. the opposite of the diffuse charge (σ_d).

2.5.3. Solving Poisson-Boltzmann equation using point and shoot method:

In this section, we discuss the numerical approach to solve the PB equation using charge regulation boundary conditions. The electrostatic contribution of the disjoining pressure (Π_{el}) acting in between the two surfaces is a function of the potential distribution $\psi(z)$ and its slope or derivative $\frac{\partial\psi(z)}{\partial z}$. Thus, we can write:

$$\Pi_{el} = f\left(\psi(z); \frac{\partial\psi(z)}{\partial z}\right) \quad (17)$$

From the charge regulation boundary condition, we know the relation between the charge density and the slope of the potential:

$$\begin{cases} \left(\frac{\partial\psi}{\partial z}\right)_{d_s} = \frac{-1}{\varepsilon\varepsilon_0} \sigma^I = \frac{-1}{\varepsilon\varepsilon_0} f_1(\psi_{d_s}, p) \\ \left(\frac{\partial\psi}{\partial z}\right)_{h-d_s} = \frac{1}{\varepsilon\varepsilon_0} \sigma^{II} = \frac{1}{\varepsilon\varepsilon_0} f_2(\psi_{h-d_s}, p) \end{cases} \quad (18)$$

Now we use a ‘point and shoot method’ to obtain the numerical solution of the two-point boundary problem in the form of Eqs (17) and (18). The method uses an iterative scheme using the initial values $\psi(d_s)$ and $\left(\frac{\partial\psi}{\partial z}\right)_{d_s}$. The idea is to determine in a systematic way the initial value $\psi(d_s)$ (and its slope via Eqn (18)) for which the solution satisfies the remaining boundary condition on the other surface at $z = h - d_s$.

We first define a range for the initial potential ($+\psi_{limit}$ to $-\psi_{limit}$), from which we choose $\psi(d_s)$ with which we solve Eqn (18). We start with an initial value of $\psi_{max} = +\psi_{limit}/2$ or $\psi_{min} = -\psi_{limit}/2$ at $z = d_s$ and calculate the value $\psi(h-d_s)$ and slope ($S_{z=h-d_s,calc}$) at $z = h - d_s$. Next, we compare the calculated slope $S_{z=h-d_s,calc}$ with the slope from boundary condition ($S_{z=h-d_s,BC}$) at $z = h - d_s$. If $S_{z=h-d_s,BC} > S_{z=h-d_s,calc}$, we replace ψ_{max} by $\frac{\psi_{max}+\psi_{min}}{2}$, if $S_{z=h-d_s,BC} < S_{z=h-d_s,calc}$, we replace ψ_{min} by $\frac{\psi_{max}+\psi_{min}}{2}$ and repeat the above steps until $|S_{z=h-d_s,BC} - S_{z=h-d_s,calc}| < \epsilon$, where $\epsilon \cong 10^{-6}$. Figure 2.7 shows a schematic diagram of this shooting method. Case II and III corresponds to the situations just described. In the other two cases, indicated with I and IV, the solutions cross the upper (ψ_{max} is replaced by $\frac{\psi_{max}+\psi_{min}}{2}$) or lower (ψ_{min} is

replaced by $\frac{\psi_{max} + \psi_{min}}{2}$ boundary. Once ψ_{max} and ψ_{min} have converged to each other within $\epsilon \sim 10^{-6}$ to 10^{-8} , we know both ψ and $\frac{\partial\psi}{\partial z}$ at both boundaries. To speed up the calculations of $\psi(z)$, we use a limited number of grid points with a high density near the substrates and low density in the middle of the gap. Doing so, 20 grid points are sufficient to determine $\psi(z)$ with good accuracy.

Figure 2.7 schematic illustration of numerical solution of non-linear PB equation using charge regulation boundary conditions. The final solution is indicated with the green dotted curve.

2.5.4. Force fitting and linear interpolation procedure:

The force vs. distance curves, as calculated with the theoretical model depend on a number of parameters, including the area of the AFM tip A_{tip} , the Hamaker constant A_H , the site density Γ , and the equilibrium constants K_j of the surface speciation reactions. The last are the primary parameters of interest here. Therefore, we use reasonable estimates for the former ones based on literature value. Only the equilibrium constants K_j are used as fit parameters when fitting the calculated force curves to the experimental curves by minimizing the error function

$$S(K_1, \dots, K_m) = \sum_{j=1}^N (F_j - F_{calc}(z_j))^2 \quad (19)$$

where F_{calc} and F_j denote the calculated and experimental force values at various distances z_j .

Figure 2.8 Schematic illustration of experimental and theoretically calculated tip sample interaction force vs distance curve. Linear interpolation is used to determine the calculated force at distances z_j .

One of the challenges to calculate the theoretical force is the ‘calculation time’. Experimental curves normally consist of $N \sim 512$ or 1024 points (see Figure 2.8). Calculating the force curve for this number of points will cost a lot of calculation time. To circumvent this problem we calculate, for every iteration, the curve F_{calc} only on a few points z_n (typically 20) and determine $F_{calc}(z_j)$ from linear interpolation between $F_{calc}(z_n)$ and $F_{calc}(z_{n+1})$, where $z_n < z_j < z_{n+1}$, such that

$$F(z_j) = \frac{(z_j - z_n)}{(z_{n+1} - z_n)} F(z_{n+1}) + \frac{z_{n+1} - z_j}{z_{n+1} - z_n} F(z_n) \quad (20)$$

In this way we reduced the number of force evaluations from typically 512 to 20 speeding up the procedure by a factor of 25. This linear interpolation only works fine, if the force values are monotonic i.e. either increasing or decreasing in the region of interest. Therefore, if the total interaction force has a non-monotonic behaviour due to the vdW contribution, this procedure will not result in an optimal fit. In such case one should increase the number of points (z_j) or, even better, subtract the vdW contribution from the total force before fitting.

2.6. CONCLUDING REMARKS:

In this chapter, we have introduced the different types of clay minerals and indicated their importance in various industrial applications. We discussed the role of surface charge of these clay minerals in determining their physical and chemical properties. To investigate the rock surfaces and clay particles, we introduced various characterization techniques such as AFM, contact angle goniometry and LB trough. Because the determination of surface charge on clay particles is the central theme of this thesis, we explained in detail the calculation of the surface charge, using DLVO theory. We also discussed the implementation of the charge regulation concept and the force fitting procedures.

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CHARACTERIZATION OF THE SURFACE CHARGE DISTRIBUTION ON KAOLINITE PARTICLES USING HIGH RESOLUTION ATOMIC FORCE MICROSCOPY

Abstract

Most solid surfaces, in particular clay minerals and rock surfaces, acquire a surface charge upon exposure to an aqueous environment due to adsorption and/or desorption of ionic species. Macroscopic techniques such as titration and electrokinetic measurements are commonly used to determine the surface charge and ζ –potential of these surfaces. However, because of the macroscopic averaging character these techniques cannot do justice to the role of local heterogeneities on the surfaces. In this chapter, we use dynamic atomic force microscopy (AFM) to determine the distribution of surface charge on the two (gibbsite-like and silica-like) basal planes of kaolinite nanoparticles immersed in aqueous electrolyte with a lateral resolution of approximately 30 nm. The surface charge density is extracted from force-distance curves using DLVO theory in combination with surface complexation modeling. While the gibbsite-like and the silica-like facet display on average positive and negative surface charge values as expected, our measurements reveal lateral variations of more than a factor of two on seemingly atomically smooth terraces, even if high resolution AFM images clearly reveal the atomic lattice on the surface. These results suggest that simple surface complexation models of clays that attribute a unique surface chemistry and hence homogeneous surface charge densities to basal planes may miss important aspects of real clay surfaces.

3.1. INTRODUCTION

Clay minerals belong to a specific family of aluminosilicates, which are characterized by a layered structure composed of silicon oxide tetrahedra linked into sheets of aluminum- or magnesium-hydroxide octahedra. Clays and clay minerals, being a natural inorganic part of the soil, are abundantly available and inexpensive, and are used as raw materials in hundreds of industrial processes. They are utilized in agriculture, environmental remediation, engineering and construction applications, pharmaceuticals, food processing and many other applications [1, 2]. While only present in petroleum reservoirs in relatively small amounts by weight, clays are disproportionately important in oil recovery processes due to their large surface area and high reactivity. This holds especially for certain enhanced oil recovery (EOR) techniques [3-5]. EOR methods depend to a large extent on the amount and type of clays, and also by their response to the injected EOR brine composition [3-7].

The discovery of surface charge on clay minerals had quite an impact on both fundamental and applied research in clay science [8, 9]. Many physical and chemical properties of clays are directly or indirectly controlled by the nature and the amount of surface charge, i.e. dispersion behavior [10, 11], flocculation/deflocculation [12-14], coagulation [15, 16], colloidal stability [17], solubility [18, 19], adsorption and transport of nutrient ions, toxic heavy metals, organic molecules and pesticides [20-23] etc.

Today, there are excellent review papers and books that cover the entire field of clay materials research, including their surface charge [8, 24-27]. As the surface charge distribution on clays can be quite heterogeneous and complex, there are many discrepancies among the published data. Probably, one of the main reasons is a lack of insight into the fundamental physical and chemical processes of the clay surfaces on the atomic-scale.

Along with other clay minerals, kaolinite properties in aqueous solutions have been investigated extensively, as it is chemically very stable, has a low shrink–swell and a low cation-exchange capacity [8]. Kaolinite is one of the abundant components of the clay fraction in many sandstone formations. Therefore it has been studied intensively in the framework of EOR [28-30].

Kaolinite is a structured aluminosilicate with the ideal formula $(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)$, consisting of alternating layers of aluminum hydroxide octahedral sheets (gibbsite

facet) and silicon oxide tetrahedral sheets (silica facet) [31]. These two layers are covalently bound together through common oxygen atoms, forming a repeating unit of the layered structure. Hydrogen bonds between hydroxyl sites on the gibbsite basal plane and the oxygen of the silica tetrahedral sheet hold the repeating units together. When kaolinite is cleaved along the [001] plane, the hydrogen bonds between the repeating units are broken, exposing the silicon oxide and aluminum hydroxide surfaces. The physicochemical properties of the resulting surfaces are determined by the crystal structure. The basal planes and edges of kaolinite have different surface structures and surface charges. The basal planes are generally believed to carry a constant negative charge, due to the isomorphous substitution of Al^{3+} ions for Si^{4+} in the silica tetrahedral layer and of Mg^{2+} or other divalent ions for Al^{3+} in the alumina octahedral layer. The surface charge derived from isomorphous substitution only depends on the type and degree of the substitution. Thus, it is largely independent of the pH and electrolyte composition of the solution. In contrast, the charge on the edges is pH-dependent, as it arises from protonation or deprotonation of aluminol (Al-OH) and silanol (Si-OH) groups at the exposed hydroxyl-terminated planes [32-37].

Several methods are routinely used to quantify the surface charge of various mineral surfaces including kaolinite particles, for example ion retention, potentiometric titration, electrokinetic techniques, salt titration, and the mineral addition technique [32, 37-44]. By measuring quantities such as net surface proton excess, zeta potential, it has been shown that kaolinite particles overall carry a negative surface charge. Even though these studies have made a valuable contribution to the understanding of the surface charge of kaolinite, they have important limitations in the characterization of these complex systems because the employed techniques only measure average values without revealing any information on the distribution of the charges. Indirect methods are usually invoked to estimate the relative contribution of edges and facets of the particles. Because the edges and facets display very different chemical behavior, the interpretation of such averaged properties and the identification of specific surface chemical reactions depend very strongly on the correct measurement of the relative areas of edge and facet sites. This, along with other uncertainties regarding the original composition of the sample, the purification procedure, the storage conditions, analytical conditions of titration (pH, ionic strength), side reactions such as complexation, dissolution, precipitation and re-adsorption result in huge discrepancies between the reported data [24, 25, 45, 46]. The situation also

hampers modeling. Because reliable experimental data sets for a wide range of fluid compositions are lacking, it is impossible to constrain the parameters and to identify the relevant surface reactions. It is clear that the primary disadvantage of these techniques is their inability to examine heterogeneity of clay surface charge. Hence, a non-invasive method, operating in liquid and providing information about the surface structure and surface charge (potential) with high lateral resolution is highly desired. Atomic force microscopy (AFM) is an excellent technique to probe the morphology and the charge characteristics of mineral and oxide particles [47-50]. This technique has been used already to characterize several clay particles such as, kaolinite [51], bentonite [52], hectorite [53], illite/smectite [54], and Montmorillonite [55]. Using AFM in contact mode, Gupta and Miller [51] have measured the surface charge individually on the two basal planes of a kaolinite particle and show for the first time that silica facets are negatively charged while gibbsite facets are positively charged. More recently, Siretanu, et al. [56] provided a more complete characterization of synthetic gibbsite nanoparticles adsorbed on silica surfaces. They used a combination of dynamic force spectroscopy to determine the distribution of the diffuse layer charge and high resolution AFM imaging to resolve the distribution of adsorbed divalent cations on the basal plane. Complemented by density functional theory, their results showed that the Ca^{2+} and Mg^{2+} ions in those experiments adsorbed in a hydrated fashion, with Cl^- ions co-adsorbing at higher concentrations. In contrast, monovalent cations (Na^+ and K^+) did not adsorb. The net surface charge, was extracted from the force-distance curves using DLVO theory with the classical constant charge (CC) or constant potential (CP) boundary conditions. Those measurements showed already that even on these rather well-defined synthetic gibbsite particles [57], the surface charge on the basal planes was much more heterogeneous than that on the adjacent silica surface.

In this work, we use small amplitude dynamic force microscopy measurements in FM-AFM mode to deduce the surface charge on kaolinite clay particles facets with high lateral resolution. Dynamic force spectroscopy with sharp AFM tips allows us to obtain the distribution of electrostatic interactions with a lateral resolution of the order of the tip radius (a few tens of nanometers), which outperforms the well-established methods like the colloidal probe technique [58] and the surface force apparatus [59] by orders of magnitude. By performing multiple force measurements along a scan line, two-dimensional force fields are recorded. Using DLVO theory we extract the surface charge values from each individual tip-sample

interaction force on both basal planes of kaolinite. Charge regulation (CR) effects, i.e. variations of the surface charge due to confinement-induced modification of surface chemistry (ion adsorption, (de)protonation of surface groups etc.), are taken into account in our extended DLVO model. The measurements reveal enormous lateral variations of surface charge on the seemingly very flat and homogeneous basal planes. High resolution images show the surface structure with true atomic resolution on both the gibbsite and the silica facet of kaolinite.

3.2. METHODS AND MATERIALS

3.2.1. Sample preparation

Kaolinite powder (KGa-1) was kindly provided by T. Hassenkam and S.L.S. Stipp (University of Copenhagen). A suspension of the powder (~1.5 mg/ml) was prepared using de-ionized water (Millipore Inc.). 20-30 μL of this suspension is drop casted onto sapphire or mica substrates. After a residence time of 2 min, the samples are gently dried with air and then rinsed with copious amounts of deionized water to remove loosely bound clay particles from the substrate. Before using, sapphire is cleaned by rinsing with isopropanol, ethanol and water and by subsequent plasma cleaning (PDC-32G-2, Harrick Plasma) for 20-25 min. Mica substrates are freshly cleaved prior to drop deposition. Sodium chloride (puriss, ACS reagent grade, Sigma Aldrich) solutions are prepared by dissolving the salt in deionized water. All experiments presented here are carried out at room temperature ($22\pm 1^\circ\text{C}$). The sample surface and the AFM cantilever are completely immersed in a 10 mM aqueous NaCl solution at near neutral pH (~5.8) in contact with ambient air.

3.2.2. Selective adsorption of kaolinite facets on mica and sapphire substrates

Kaolinite particles have two different basal planes or facets of which one is positively (gibbsite) and the other is negatively charged (silica) as shown by Gupta and Miller [51]. Thus, it should be possible to selectively orient kaolinite nanoparticles by adsorbing them onto substrates of opposite surface charge such as silica, glass and alumina as described by Alagha, et al. [60] and Gupta and Miller [51]. We expect kaolinite to adsorb with its negatively charged silica facet onto a positively charged surface such that the particle exposes its own positively charged gibbsite facet to the fluid. Conversely, we expect the particles to expose their negatively charged silica facets to the fluid if deposited onto negatively charged surfaces. In the present work, we managed to adsorb and immobilize kaolinite

particles with their silica facet up on negatively charge mica and with their gibbsite facet up on positively charged sapphire substrates. Attempts to immobilize the particles on silica were not successful. Preparation conditions at room temperature and near neutral pH (as in the case of mica and sapphire) resulted in very loosely adhered particles that were easily pushed around by the AFM, even under gentle imaging conditions. An alternative deposition procedure at elevated temperature (60-70°C) and elevated pH, as proposed by Alagha, et al. [60], resulted in better adhesion. Yet, all particles displayed an irregular roundish morphology without clear facets (Figure 3.A1) – very much in contrast to the particles deposited on freshly cleaved mica at room temperature and $\text{pH} \approx 6$. We suspect that the high pH treatment triggers partial dissolution of kaolinite as reported earlier [61, 62] and thereby rounds off the sharp edges and facets of the particles. To avoid this problem, mica used as a negatively charged substrate for studying the silica facet of kaolinite.

The height of the deposited KGa-1 kaolinite particles typically varies between 20 to 100 nm and their lateral dimension ranges from several tens to a few hundred nanometers, as illustrated in Figure 3.1c. The morphology of the particles displays a plate-like, pseudo-hexagonal shape with rather sharp corners (typically with angles of 60° or 120°) and flat facets as expected [63] for well-crystallized kaolinite particles (Figure 3.1b and 3.A3).

Figure 3.1 a) A schematic of the sample system consisting of kaolinite particles adsorbed on mica and sapphire substrate exposing both silica and gibbsite facets

respectively. Color code: red- negatively charged surface, blue- positively charged surface (different shades of red and blue colors show different magnitude of charges). b) Non-contact AFM topography images of kaolinite nanoparticles adsorbed on sapphire substrate under 10mM NaCl solution c) corresponding scan line showing height distribution of particles.

3.2.3. Frequency modulation AFM measurement

A Dimension Icon AFM (Bruker Corporation) equipped with a Nanoscope V controller is used for dynamic force spectroscopy measurements. Additional electronics (QFM-module, NanoAnalytics GmbH) are used to drive the cantilever in FM-mode at constant excitation (CE) [64-66]. Rectangular silicon cantilevers (MikroMasch, NSC36) are used. As usual, the silicon is covered by a 1-2nm thick native oxide layer with an amorphous silica-like structure. Prior to use, cantilevers are cleaned by rinsing with an ethanol/isopropanol mixture followed by plasma cleaning for 20-25 min. After this procedure, the tip is perfectly hydrophilic. Amplitude and phase of the response function of the cantilever in liquid are used to calculate its resonance frequency (ω_0) and quality factor (Q) from which the spring constant k is determined using Sader's method [67]. The length and width of the cantilever are used as provided by MikroMasch. The typical values of these constants are: $k \sim 8.7$ N/m, $\omega_0 \sim 84.1$ kHz, $Q \sim 6.97$. In FM-AFM mode, the cantilever is self-excited by feedback of the oscillation signal of the photodiode to the excitation piezo [65]. Dynamic force-versus-distance experiments are conducted by recording the amplitude and frequency shift of the oscillating tip as a function of the z-piezo position by varying the mean tip-sample distance. In constant excitation mode, the force acting between the tip and the sample surface can be correlated with the frequency shift and oscillation amplitude using formulae developed by Ebeling and Holscher [68] and Sader and Jarvis [69].

During imaging in CE-FM mode, the images of the frequency shift are recorded at a fixed distance close to the substrate. Each point or pixel in the image represents the change in the resonance frequency of the tip, caused due to its interaction with the substrate. As the tip-sample interaction forces are dominated by electrostatic forces [66, 70, 71], the frequency shift images provide information of lateral variations of the charge density on the sample surface. Positive frequency shifts correspond to repulsive tip-sample interaction forces; negative frequency shifts correspond to attractive forces.

3.2.4. Atomic resolution imaging

Atomic resolution imaging experiments are carried out with a Multimode8 AFM (Bruker Corporation) equipped with a Nanoscope V controller using an ultra-stable ‘A-scanner’. Sharp tips (Bruker BBB, tip radius ~ 3 nm) are mounted on a tapping mode tip holder (Bruker Corporation) adapted for operation in liquid [72]. After injecting liquid, the sample chamber is sealed externally and further allowed to thermally stabilize for 30 min before acquiring any data. The AFM is operated in standard tapping mode with a free amplitude A_0 , typically less than 1 nm, a high scan rate, ≈ 10 Hz is used, and the imaging amplitude set point is set as high as possible, typically $A/A_0 \geq 0.8$ [56, 73, 74].

3.3. THEORETICAL MODELING

The basic procedures for the conversion of measured forces to surface charges are described by Ebeling, et al. [75] and Siretanu, et al. [56]. A systematic account of the procedure to include charge regulation into the standard framework of DLVO theory was originally provided by Ninham and Parsegian [76] and refined by various authors since then. Its specific adaption to high resolution AFM spectroscopy is described in detail by Zhao, et al. [77].

3.3.1. DLVO theory

In DLVO theory the disjoining pressure between two adjacent surfaces at a distance h is decomposed into contributions from van der Waals interactions Π_{vdW} and electrostatic double layer forces Π_{el} . Additional contributions due to short range interactions such as short range hydration forces only become important at tip-sample separations ≤ 1 -2 nm, which are beyond the scope of our present study. Discarding short-range interactions in the model implies that we limit the analysis of our experimental data to values of $h > 2$ nm. For two locally parallel interfaces, the van der Waals contribution is written as

$$\Pi_{vdW}(h) = - \frac{A_H}{6\pi h^3} \quad (1)$$

where A_H is the Hamaker constant. For an atomically flat surface, the electrostatic contribution to the disjoining pressure for 1-1 electrolyte is given by

$$\Pi_{el}(h) = 4I_\infty k_B T \sinh^2 \left(\frac{e\psi}{2k_B T} \right) - \frac{\epsilon\epsilon_0}{2} \left(\frac{\partial\psi}{\partial z} \right)^2 \quad (2)$$

where $I_\infty = [Na^+]_\infty + [H^+]_\infty$ is the ionic strength in the bulk solution away from the substrates, k_B is the Boltzmann constant, T is temperature, e the

elementary charge, and $\varepsilon\varepsilon_0$ the dielectric permittivity of water. $\psi(z)$ is the electrostatic potential in the electrolyte at an arbitrary position $d_s < z < h-d_s$ between the two solid surfaces, where d_s is the Stern layer thickness. The potential distribution $\psi(z)$ is calculated by solving Poisson-Boltzmann (PB) equation

$$\frac{\partial^2}{\partial z^2} \left(\frac{e\psi}{k_B T} \right) = k^2 \sinh \left(\frac{e\psi}{k_B T} \right) \quad (3)$$

with appropriate boundary conditions at the two solid-liquid interfaces (see section

3.2 for a detailed discussion). Here $k = \sqrt{\frac{2e^2 I_\infty}{\varepsilon\varepsilon_0 k_B T}}$ is the reciprocal of Debye length.

The measured forces on the tip are calculated by integrating the disjoining pressure over the tip surface. In our experiments, the AFM tips are slightly flattened leading to a local parallel plate geometry with a rather small contribution from the adjacent cone [75]. We therefore approximate the total force by $F(h) = A_{tip}(\Pi_{el} + \Pi_{vdW})$, where A_{tip} is the area of the tip. For the large separation between the two surfaces, the surface potential (ψ) can be related to the surface charge density (σ) using the Grahame equation for a 1-1 electrolyte as

$$\sigma = \sqrt{8I_\infty k_B T \varepsilon\varepsilon_0} \sinh \left(\frac{e\psi}{2k_B T} \right) \quad (4)$$

3.3.2. Charge regulation

As the equations given above show, we need to solve the Poisson-Boltzmann equation and substitute the potential ψ in the equation for Π_{el} in order to calculate the force between two charged plates. Solving the PB equation requires a choice of boundary conditions. Frequently, either the charge or the potential are assumed to remain constant upon varying the tip-sample distance. In general, however, neither the surface charge density nor the potential remain constant as two surfaces come closer. Instead, when two charged surfaces approach each other, some of the counterions are forced to readsorb onto their original surface sites. Thus, as the tip-sample separation changes, the surface charge density also changes, i.e. it becomes a function of surface separation. This is known as charge regulation. The effect of charge regulation always reduces the effective repulsion with respect to the calculated one assuming constant surface charge that approaches infinity when double layers start to overlap.

A variety of methods has been proposed to incorporate the charge regulation concept into the problem of double layer interaction. Reiner and Radke [78] did it by construction of the grand free energy functional (variational approach). Alternatively, charge regulation can be viewed as balancing between the chemical affinity of ions and/or dissociation reactions occurring at the surface (i.e., surface

complexation) and the diffuse layer potential [76, 78-83]. These theoretical studies show that due to chemical reactions the surface acquires a charge density σ_s . This charge density depends on the concentration of the electrolytes near the substrate and so on the local electric potential ψ_s . This dependence is formally written as: $\sigma_s = f_s(\psi_s, c_1^\infty \dots c_n^\infty, \Gamma, K_1 \dots K_m)$ where c_i^∞ is the bulk concentration of the corresponding ions, Γ the site density on the substrate and K_m the equilibrium constant of the considered surface reactions. The latter, together with the associated site densities, are usually referred to as the surface ionization parameters. Hence, the boundary condition for the BP equation can be formulated as

$$-\varepsilon\varepsilon_0(\hat{n} \cdot \nabla \psi)_s = \sigma_s = f_s(\psi_s, c_1^\infty \dots c_n^\infty, \Gamma, K_1 \dots K_m) \quad (5)$$

where $\hat{n}$ is the normal to the substrate pointing inwards the electrolyte. In table 1, we list the supposed surface reactions from which the surface charge-surface potential relations (f_s) have been derived for a silica tip or substrate mica and sapphire substrates and the silica and gibbsite facets of a kaolinite particle.

For example, for silica surfaces (as described in various publications [84]), charging occurs due to deprotonation of the surface groups. This is described by the chemical reaction

which has an equilibrium constant $K_{H1} = \frac{\{S^-\}[H^+]_s}{\{SH\}}$. The curly brackets indicate a surface density in sites/nm² and the square brackets represent a volume density or concentration in mol/L. When salt ions are present in the solution, we should also account for the fact that deprotonated sites (S^-) can adsorb electrolyte cations to form surface complexes

with equilibrium constant $K_c = \frac{\{S^-\}[C^+]_s}{\{SC\}}$ (we consider only monovalent cations C^+ since in our experiments NaCl was used). Due to these two reactions, three surface species are present on the surface: $\sim SH$, $\sim S^-$, $\sim SC$. As the total site density Γ must be conserved, we can write

$$\{S^-\} + \{SH\} + \{SC\} = \Gamma \quad (8)$$

Using Eqs. (6)-(8), the densities of three surface species can be calculated by solving the following matrix equation:

$$\begin{pmatrix} 1 & 1 & 1 \\ [H^+]_s & -K_{H1} & 0 \\ [C^+]_s & 0 & -K_c \end{pmatrix} \begin{pmatrix} \{S^-\} \\ \{SH\} \\ \{SC\} \end{pmatrix} = \begin{pmatrix} \Gamma \\ 0 \\ 0 \end{pmatrix} \quad (9)$$

It should be noted that both $[H^+]_s$ and $[C^+]_s$ are evaluated at the surface and not in bulk. The bulk (indicated with subscript ∞) and near-surface (subscript s) concentrations are related via the Boltzmann relation, $[H^+]_s = [H^+]_\infty \exp(-e\psi_s/k_B T)$ and $[C^+]_s = [C^+]_\infty \exp(-e\psi_s/k_B T)$, respectively. The surface charge σ_s can be evaluated from the densities of the surface species. The final expression for the charge density (σ_s) as a function of the surface potential (ψ_s) has been shown in Table 1. Following a similar approach, we also derive the expressions for the charge density on sapphire, mica, and the gibbsite and silica facets of kaolinite, as noted in Table 1. In the case of mica, a deprotonation reaction was taken to represent the potassium release. A detailed description of the charge regulation for specific surfaces like silica and gibbsite has been given in a recent publication by Zhao, et al. [77].

3.3.3. Model Parameters for Force Fitting

The force vs. distance curves, as calculated with the theoretical model depend on a number of parameters, including the area of the AFM tip A_{tip} , the Hamaker constant A_H , the site density Γ , and the equilibrium constants K_j of the surface speciation reactions. The last are the primary parameters of interest here. Therefore, we use reasonable estimates for the former ones based on the literature values. The area of the measuring tips ($A_1=3850\pm10 \text{ nm}^2$ and $A_2=2650\pm10 \text{ nm}^2$) was obtained from SEM pictures. The Hamaker constant, A_H , was fixed at $0.65 \times 10^{-20} \text{ J}$ for the $[\text{SiO}_2\text{--water--SiO}_2]$ system and $1.2 \times 10^{-20} \text{ J}$ for both $[\text{SiO}_2\text{--water--mica}]$ and $[\text{SiO}_2\text{--water--AlOH}]$ systems [56, 75]. The site density for silica was set to 8 nm^{-2} [85], for mica to 1.8 nm^{-2} [86], for sapphire to 16 nm^{-2} [45] and for the silica and gibbsite facet of kaolinite to 1.55 and 0.75 nm^{-2} , respectively [87]. Only the equilibrium constants K_j are used as fit parameters when fitting the calculated force curves to the experimental curves by minimizing the error function

$$S(K_1, \dots, K_m) = \sum_{j=1}^N (F_{calc}(h_j) - F_{exp}(h_j))^2 \quad (10)$$

where F_{calc} and F_{exp} denote the calculated and experimental force values at distance h_j . The best fitting pK values are used to calculate the surface charge densities with the formulae mentioned in Table 1.

Table 1

Surface chemistry equation and final charge regulation condition for different substrates

	Mica/Silica/Silica facet	Sapphire/Gibbsite facet
Reaction s	$\sim SH \leftrightarrow \sim S^- + H^+ ; K_{H1}$	$\sim SH_2^+ \leftrightarrow \sim SH + H^+ ; K_{H2}$
	$\sim SC \leftrightarrow \sim S^- + C^+ ; K_c$	$\sim SH_2A \leftrightarrow \sim SH_2^+ + A^- ; K_a$
	$\Gamma = \{S^-\} + \{SH\} + \{SC\}$	$\Gamma = \{SH_2^+\} + \{SH\} + \{SH_2A\}$
charge	$\sigma_s = \frac{-e\Gamma}{1 + \left(\frac{[H^+]_\infty}{K_{H1}} + \frac{[C^+]_\infty}{K_c} \right) \exp(-e\psi_s/k_B T)}$	$\sigma_s = \frac{e\Gamma}{1 + \left(\frac{K_{H2}}{[H^+]_\infty} + \frac{[A^-]_\infty}{K_a} \right) \exp(e\psi_s/k_B T)}$

3.3.4. Surface charge calculation for an AFM tip

As discussed by Zhao, et al. [77], for an asymmetric system, for example silica-mica, we first characterize the surface reaction parameters for the silica AFM tip by performing a reference measurement on an equivalent silica substrate. Fitting the interaction force between the silica tip and the silica substrate (not shown here) yields a surface charge $\sigma \sim -0.05 \text{ e/nm}^2$ for both surfaces. This is in good agreement with values found in literature [56, 88]. Once the surface charge of the AFM tip is known, the surface charge on other substrates can be determined following the same procedure. This approach allows us to extract the surface charge density of all investigated substrates. However, the obtained pK values depend on the assumed set of surface reactions (surface complexation equations), and are not reliable. But, as explained by Zhao, et al. [77], the resulting surface charge turns out to be insensitive to the assumed set of surface reactions, because the double layer contribution of the measured interaction force is formally given by $F_{\text{edl}}(h) = fnc(\sigma_{\text{substrate}}(h, K_1, \dots, K_m), \sigma_{\text{silica}}(h), I_\infty, h)$, *i.e.* the force $F_{\text{edl}}(h)$ depends only indirectly via the charge density $\sigma_{\text{substrate}}$ on the fit parameters K_j .

3.4. RESULTS

The force spectroscopy measurements are performed in two steps: first, we capture height and frequency shift images of a single kaolinite particle and the substrate around the particle, using frequency modulation AFM (FM-AFM). Next, we record oscillation amplitude and frequency shift vs. distance curves along a horizontal

scan line over the previously imaged particle and the substrate. Subsequently, amplitude and frequency shift curves are used to calculate the tip-kaolinite facets interaction force vs. distance curves [68, 75] from which the surface charge is extracted using DLVO theory.

3.4.1. Frequency modulation AFM imaging of kaolinite facets

Figure 3.2 and 3.3 show topography (a) and frequency shift (b) images of two typical kaolinite particles adsorbed, respectively, on sapphire and mica substrates along with corresponding cross sections. Both the gibbsite and the silica basal planes display large flat regions with a roughness below 1 nm, suggesting atomically smooth terraces. These regions are separated by occasional defects on the surface, such as steps and dislocations. Overall, the step density is slightly enhanced near the rim of the particles. While the topography follows the general expectation of largely homogeneous flat basal planes, the frequency shift images (reflecting the charge density on the surface) display much stronger heterogeneity. Substantial variations of the frequency shift are found not only at the locations of topographic defects, but also on the topographically flat parts of the surface. This observation applies to both the gibbsite and the silica facet of the particles. Note that the frequency shift in the images and the corresponding cross sections are plotted relative to the supporting surrounding substrate, *i.e.* relative to the positively charged sapphire surface in Figure 3.2 and relative to the negatively charged mica surface in Figure 3.3. Positive frequency shift in Figure 3.3b and 3d thus implies that the silica facet of the kaolinite particle is less charged than the mica substrate – and the image shows that the excess varies by more than a factor of two across the particle.

Figure 3.2 FM-AFM imaging of kaolinite particle adsorbed on sapphire under 10mM NaCl solution: (a) topography (b) frequency shift (c) height profile and (d) frequency shift profile corresponding to the scan lines shown in a) and b). (Tip parameters: $Q = 6.97$, $\omega_0 = 84.1$ KHz, $k = 8.7$ N/m, $R = 29$ nm).

Similar conclusions apply to the gibbsite facet as well. Particularly close to the edge (boundary) of the particle we consistently observe a wide band of few tens of nanometer of enhanced positive frequency shift (Figure 3.2d and 3d). This band is also visible as a bright rim in the frequency shift images (Figure 3.2b and 3b) suggesting a higher degree of charge heterogeneity at these locations. This band is very characteristic and it has been observed on many particles in many independent experiments with different AFM tips (Figure 3.A3). The frequency shift images thus directly suggest that the surface charge of both the silica-like and gibbsite-like facet of kaolinite displays very pronounced lateral variations. The only exception are sharp negative spikes right at the edge of the particle at $x \approx 280$ nm and $x \approx 620$ nm (Figure 3.3d), whose origin is not yet clear. These spikes persisted after repeated scans but are not visible on all the particles (Figure 3.2d). We tentatively attribute these spikes to artefacts due to the steep topographic step at the edge of the particle rather to change of the surface charge.

Figure 3.3 FM-AFM imaging of kaolinite particle adsorbed on mica under 10mM NaCl solution: (a) topography (b) frequency shift (c) height profile and (d) frequency shift profile corresponding to the scan lines shown in a) and b) (Tip parameters: $Q = 6.82$, $\omega_0 = 87$ KHz, $k = 8.95$ N/m, $R = 35$ nm).

3.4.2. 2D Force Field Measurements

To go beyond the qualitative characterization of the surface charge in terms of frequency shift images, frequency shift and oscillation amplitude vs. distance curves (Figure 3.A2a and b) are recorded along the same scan line as used for the topographic and frequency shift in Figure 3.2c,d and Figure 3.3c,d. Frequency shifts are converted to tip-sample interaction forces (Figure 3.A2) as described elsewhere [68, 69, 75]. Figure 3.4a and 4b depict the resulting 2D force field generated from 100 evenly distributed curves along the cross sections. Both the sapphire and the mica substrate next to the particles display a very homogeneous background with rather strong attractive (blue) and repulsive (red) forces upon approaching the surface. Because the forces are probed with a negatively charged silica tip, this implies that the sapphire surface is positively charged and the mica surface is negative, as expected. The forces on the kaolinite particles display the same sign as the surrounding substrates, confirming that the particles are indeed adsorbed with the gibbsite-like facet up on sapphire and the silica-like facet up on mica, in agreement with earlier reports by Gupta and Miller [51].

Figure 3.4 Color coded 2D force field generated from 100 tip-sample interaction curves recorded on (a) sapphire/gibbsite facet of Kaolinite under 10mM NaCl solution (b) mica/Silica facet (blue: attractive force; red: repulsive force; green: zero force; see scale bar). Surface charge values calculated by analyzing the tip-sample interaction forces with DLVO theory with charge regulation for (c) sapphire/gibbsite facet sample (d) mica/silica facet.

On average, the absolute value of the force on the gibbsite and silica facets of kaolinite is lower than on the mica and sapphire substrates (Figure 3.4). At the same time, compared to the adjacent substrates, there is a significant heterogeneity in force distribution on the both basal planes, as already anticipated based on the frequency shift images. Again, it should be noted that this holds not only for the particularly pronounced rim along the edge of the particles and along extended defects, but also on the topographically homogeneous terraces. This is particularly evident in the case of the silica facet, where the magnitude of the forces is prominently higher at the center compared to near the rim of the particle (Figure 3.4). The heterogeneous distribution of forces over the two facets indicates the presence of charge heterogeneity on the same basal planes due to a varying surface chemistry. To obtain a detailed quantitative information, we extract the surface charges for each of the force curves shown in the 2D force field from Figure 3.4 using the DLVO theory. The resulting surface charge profiles for the mica/silica facet and the sapphire/gibbsite facet are given in Figs. 4c, d.

3.4.3. Surface Charge Determination

As described in section 3, DLVO theory was used to determine the surface charge properties of kaolinite basal planes from the obtained AFM force profiles. Figure 3.5 shows the theoretically calculated force curves (dotted lines) and the experimental force curves acquired on mica, sapphire and the kaolinite particle adhering to these substrates (solid lines). The lower limit for fitting range is set to 2 nm to minimize the influence of short range forces such as hydration forces that are not included in the theoretical model, the upper boundary was set to 15 nm above which the interactions are negligible. The resulting surface charge profiles have been plotted in Figure 3.4c,d for mica/kaolinite silica facet and sapphire/kaolinite gibbsite facet, respectively. From the charge profiles, it is clear that both mica and kaolinite silica facet are negatively charged, while sapphire and kaolinite gibbsite facet are both positively charged. Mica and sapphire substrates have a homogeneous charge distribution of $\sigma = -0.048 \text{ e/nm}^2$ and $\sigma = 0.018 \text{ e/nm}^2$, while the two facets of kaolinite particle have heterogeneous charge distribution ranging between $+0.015$ to 0 e/nm^2 for gibbsite facet and 0 to -0.045 e/nm^2 for silica facet. In case of silica facet, the surface charge is highest $\sim -0.04 \text{ e/nm}^2$ at center of the particle. While near the boundary of the particle, the surface charge is very low (-0.001 e/nm^2). This is consistent with the very low magnitude of force curves observed near the boundary of silica facet (Figure 3.5). Such flat force curves are also observed on the gibbsite basal plane giving very small positive surface charges.

Figure 3.5 Tip-sample interaction forces on the silica facet, silica facet edge, gibbsite facet, mica and sapphire under 10 mM NaCl solution. Solid lines are the experimental curves and dotted lines are the theoretically fitted force curves with DLVO theory with charge regulation boundary condition.

3.4.4. Atomic resolution imaging of kaolinite basal planes

The above results show that kaolinite facets exhibit a high level of charge heterogeneity, however, its origin is not so obvious. Structural defects and atomic steps on basal planes, chemical imperfections, specific ions adsorption and surface contamination may act as a source of charge heterogeneity. As shown in recent publications, currently AFM is capable of probing the atomic structure of surfaces, the adsorption and reaction of ions, water molecules and other charged or organic species, which has direct relevance to clay minerals characterization [56, 89-91]. To clarify the role of the above mentioned factors, the kaolinite surface was also imaged with atomic scale resolution.

Figure 3.6 Amplitude modulation topography images of (a) gibbsite facet (b) silica facet of kaolinite particles under 10 mM NaCl solution revealing atomic resolution. Insets: two dimensional fast Fourier transform of image (bottom left); magnified

and Fourier-filtered view of topography image with superimposed crystallographic lattice in ab plane (bottom right). (c) Height profiles of silica facet in ab directions displaying periodicity of 0.51 nm and 0.90 nm.

Figure 3.6a and 6b show atomically resolved topographic images of the gibbsite and silica facets of kaolinite obtained using non-contact AM-AFM mode. It is encouraging that true atomic resolution images could be obtained for these natural clay surfaces that are more complex than synthetic ones [56]. The images also indicate that the basal planes of the investigated kaolinite particles are clean and are free of organic or non-organic pollutants. Hence the surface charge heterogeneity is not due to contamination. The lower insets of Figure 3.6a and 6b correspond to two-dimensional fast Fourier transform (2D-FFT) patterns of the height image. The top right insets show a magnified view of the FFT filtered image for a better visualization of the periodic structure suppressing the inevitable noise appearing in the original images [92]. The images reveal the hexagonal lattice structure of both facets of kaolinite. We extract the lattice parameters (a and b) by taking topographic cross sections along two axes of the hexagonal cell that are indicated as a and b axes in the images (Figure 3.6a and b). For the gibbsite facet we extract lattice spacings of $a = 0.49$ nm and $b = 0.93$ nm, and for silica facet $a = 0.51$ nm and $b = 0.90$ nm. These lattice parameters match very well with X-ray data (unit cell parameters $a = 0.5154$ nm, $b = 0.8942$ nm) [31, 93]. This is also visible in the top right insets where the experimentally captured images are superimposed on the X-ray resolved structures. Closer to the rim of the particle depicted in Figure 3.A5, we observe defects as lattice distortions and atomic steps (~ 0.7 nm). The presence of these atomic scale imperfections close to the edge of the particle certainly contributes to the charge heterogeneity on the particle. For our present results, we cannot directly correlate the presence of these atomic imperfections to heterogeneous charge distribution, since the two experiments (force spectroscopy and high resolution imaging) were performed with two different AFM devices and hence on different particles. However, all investigated clay particles display similar features and in all cases the surface is decorated with a high density of lattice imperfections and atomic steps close to the rim of the particle.

3.5. DISCUSSION

This work emphasizes two important aspects of charge characteristics of kaolinite particles. First, our results clearly indicate that kaolinite facets have a more heterogeneous charge distribution compared to their supporting substrates, mica and sapphire. The observed heterogeneous charge distribution on kaolinite basal planes shown in Figure 3.4 is characteristic for many investigated particles (Fig A3). The average value of the surface charge of silica facets quantitatively corresponds to the value obtained for oxidized silicon wafer [56, 88]. Similarly, average charge on the gibbsite facet is in agreement with values reported for basal plane of chemically synthesized gibbsite nano-particles [56, 94, 95]. It is also observed that both mica and sapphire substrates have a homogeneous charge distribution of $\sigma = -0.048 \text{ e/nm}^2$ and $\sigma = +0.018 \text{ e/nm}^2$, respectively. These values are also consistent with the reported literature values [96, 97]. Furthermore, upon approaching the edge of the particle a higher charge heterogeneity was observed as compared to flat terraces. Such increased heterogeneity might be caused by a different surface chemistry and higher density of the defects in this region, as suggested by high resolution images (Figure 3.A5).

Secondly, these results obtained with improved lateral resolution confirm the recently reported observation by Gupta and Miller [51] demonstrating the opposite charging of the kaolinite particle i.e. the silica facet is negatively charged and the gibbsite facet is positively charged. This implies that the measured charge of kaolinite facets is not derived only from isomorphous substitutions within the lattice, but can also arise from ionizable groups on the basal planes which are exposed to the electrolyte. This picture is in agreement with theoretical and experimental studies which also indicated that the ionization of edges alone cannot explain the magnitude of the charge variation with change of pH or salt concentration [8, 51, 62, 98, 99]. So it is assumed that hydroxyl groups at the facets also contribute to these charges. Such high resolution quantification of charge characteristics of kaolinite facets is a step forward towards the understanding of electrokinetic properties of kaolinite particles. This also helps to explain the non-reproducible and inconsistent data of electrokinetic and titration measurements, which is limited to average (global) intrinsic surface charge density [24, 25, 45].

In summary, both force spectroscopy and atomic resolution measurements highlight the complexity of individual kaolinite particles. The heterogeneous charge distribution of the kaolinite basal planes should be taken into account when one investigates processes like inter-particle interactions in suspensions as well as

the adsorption of ions and organic molecules onto the surfaces. Additional measurements at variable fluid composition are expected to provide more information on the specific surface chemistries and their lateral heterogeneity.

3.6. CONCLUSIONS

In the present work, we characterize the charge distribution on the basal planes of kaolinite particles with high lateral resolution using dynamic force microscopy. Force spectroscopy data show attractive and repulsive tip-sample interaction forces on the gibbsite and silica facets of kaolinite particles, respectively. From the force curves the surface charge was extracted using DLVO theory and charge regulation. We have found a significant heterogeneity of the surface charge values on both basal planes of kaolinite. This is expected to affect many processes such as ion adsorption, wettability alteration, the stability of colloidal systems and adsorption/desorption of oil components on such clay materials, which eventually have consequences in modern technologies for enhanced oil recovery.

Additionally, using non-contact AM-AFM, we resolve the atomic structure of the two facets of kaolinite and extract their lattice parameters. The combination of AFM spectroscopy and high resolution imaging offers a unique experimental capability to investigate charge characteristics of complex clay systems.

3.7. REFERENCES

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3.8. APPENDIX

A1. Effect of pH

Figure 3.A1 FM-AFM imaging of kaolinite particle adsorbed on silica under 10mM NaCl solution: (a) topography (b) frequency shift (c) height profile and (d) frequency shift profile corresponding to the scan lines shown in a) and b). The kaolinite particle adhere very loosely to silica wafer compared to mica and sapphire substrates. To stick them very nicely to silica surface, we prepare the kaolinite particle suspension in higher pH solution ($\sim$ pH 10). Also we deposit this suspension at elevated temperatures i.e. the silica substrates are heated at 60-70 $^{\circ}$ C before drop casting the kaolinite suspension.

A2. Tip-sample interaction force calculation

Figure 3.A2 FM-AFM measurements on kaolinite particle adsorbed on sapphire under 10 mM NaCl solution. (a) and (b) show the measured oscillation amplitude

and frequency shift as a function of piezo displacement. The corresponding tip-sample force vs. distance curves are depicted in (c). In red a represented forces measured on the supporting substrate and blue on the facet of kaolinite particles. Tip parameters: $Q = 6.97$, $\omega_0 = 84.1$ kHz, $K = 8.7$ N/m, $R = 29$ nm.

A3. Frequency modulation AFM imaging of kaolinite particles

Figure 3.A3 FM-AFM imaging of different kaolinite particles adsorbed on mica under 10 mM NaCl solution. (a) topography (b) frequency shift image. Height profiles (black) of three different kaolinite particle namely 1, 2, and 3 adsorbed on mica are shown in c, d, and e, respectively. The magnitude of surface charge values corresponding to the particle morphology is plotted in blue.

A4. Contour plot of the squared error (S):

Figure 3.A4 Contour plot of the of squared error (S) in the parameter space defined by pK values of surface reactions for deprotonation (pK_H) and cation adsorption (pK_c) for silica-silica case under 10mM NaCl solution. It shows that a whole range of combinations of fit parameters provides similar quality of fitting (similar values of S) depicted by the narrow white band.

A5. High resolution imaging near the rim (edge boundary) of kaolinite particle

Figure 3.A5 High resolution imaging near the rim (edge boundary) of a particularly thin kaolinite particle adsorbed on mica in 10 mM NaCl solution. (a) topography (b) phase image and (c) height profile showing atomic/molecular steps corresponding to the scan line in (a).

KAOLINITE BASAL PLANES CHARGE PROBED BY HIGH RESOLUTION ATOMIC FORCE MICROSCOPY

Abstract

In previous chapter, we presented that the surface charge on the basal plane of kaolinite particles is heterogeneously distributed. But we discuss only a single case: one salt concentration and a fixed pH, although oil reservoirs are much more complicated. Therefore, in this chapter, we use high resolution Atomic Force Microscopy to map the surface charge of the basal plane of kaolinite nanoparticles in an ambient solution of variable pH and CaCl_2 concentration. From the measured force distance curves we conclude that the basal planes of kaolinite do carry charge that varies with pH and salt concentration. The silica facet was found to be negatively charged at $\text{pH} \geq 4$, whereas the gibbsite facet is positively charged at $\text{pH} < 7$, and negatively charged at $\text{pH} > 7$. Investigations in CaCl_2 at pH 6 show that the surface charge of the gibbsite facet increases up to a concentration of 10 mM CaCl_2 and starts to decrease upon further increasing the salt concentration to 50 mM. The increase of surface charge at low concentration is explained by Ca^{2+} ion adsorption, while chloride ion adsorption at higher CaCl_2 concentrations partially neutralize the surface charge. Atomic scale imaging and DFT calculations show that hydrated Ca^{2+} ions can spontaneously form ordered structures at the gibbsite facet.

4.1. INTRODUCTION

Clays are naturally occurring aluminosilicate minerals that are widely used in industrial applications. Millions of tons are utilized annually in a large variety of applications. These applications cover the fields of geology, process industries, agriculture, environmental remediation and construction [1, 2]. Particularly, kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is often used because of its unique physical and chemical properties [2]. The shape, size, color, softness, and non-abrasiveness of the particle are important physical properties. Chemical properties, such as low cation exchange capacity, low shrink–swell capability, and relative insolubility are essential for many applications [3]. Moreover, the presence of clay minerals, i.e. kaolinite, is seen to be a key requirement for low-salinity Enhanced Oil Recovery (EOR) [4-9]. In above mentioned applications, the surface charge characteristics of kaolinite particles play an essential role. However, in spite of a few decades of studies, the charging properties and the adsorption mechanisms of ions on kaolinite and clay minerals, in general, remain largely elusive [10-12]. The published studies of kaolinite show a large variations in the measured surface charge [13, 14]. Several aspects can explain these differences. First, the complexity of the system, with its high degree of structural heterogeneity and facet-specific properties, makes a consistent interpretation of the experimental results rather difficult. Second, currently available experimental techniques do not allow for facet specific investigations at a molecular scale.

The kaolinite has a flat structure composed of two basal planes (Si-O tetrahedral (silica) and Al-O octahedral sheets (gibbsite)) and edges (i.e. broken surfaces). Two different charging mechanisms are proposed for edges and basal surfaces of kaolinite with respect to proton and ions interaction. On one side, based on the charge measured via conventional macroscopic techniques (i.e. electrokinetics, potentiometric titrations, etc.), it is proposed that basal surfaces of kaolinite exhibit permanent, negative charge arising from the isomorphic substitution of the central ions in the crystal lattice (Al^{3+} by Si^{4+} on silica facet and Mg^{2+} substituting Al^{3+} on gibbsite facet) and it is typically not expected to depend on the proton concentration; whereas the charge on the edges is due to the protonation/deprotonation of exposed hydroxyl groups and therefore depends on the pH of the solution [15-20]. The attribution of surface charge in kaolinites to isomorphous substitution is called the Constant Basal Surface Charge (CBSC) model [21, 22]. This view was originally presented by van Olphen[23] and supported by many other researchers in this field [19-21, 24, 25]. On the other

side, results of Gupta et al. [26] and Liu et al. [27] contradict with the CBSC model [26-29]. Using the colloidal probe AFM technique, they were able to determine separately the charge of the gibbsite and silica facet of the particle. They found that both, the gibbsite and the silica, basal planes exhibit pH-dependent charging behavior, suggesting proton uptake and/or release from the surface functional groups. Despite this first step forward in characterization of specific surface planes of distinct particles, more experimental evidence is required to come to a more profound conclusion.

Not only the influence of pH, but also ion adsorption/desorption on kaolinite has been addressed in various publications [30-34]. The adsorption of toxic metals cations, viz., As^{3+} , Cd^{2+} , Cr^{3+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Pb^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+} , etc., has been studied predominantly³⁰. Kaolinite and various modification of it, have drawn attention of the researchers as suitable absorbers for scavenging heavy toxic metal cations from water. The mechanism of binding of the cations to the kaolinite surface has not been worked out in great detail, but it is believed that the OHs groups on the basal planes have minimal chemical reactivity, while sites at the edges are expected to bond with cations and organics. However, this interpretation often fails to explain experimental observations, especially measurements in the presence of divalent cations. For instance, Yukselen et. al. [35], Hunter et. al. [36], and Tournassat et. al. [37] had to assume specific adsorption of hydrolyzed product $(\text{M}(\text{OH})_x^{(n-x)+})$ to the basal planes of kaolinite, in order to explain the non-monotonic behavior of the zeta potential of kaolinite as a function of pH in the presence of Co^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} and Ca^{2+} ions. However, these assumptions were never validated since the conventional macroscopic techniques (i.e. zeta potential, potentiometric titrations, etc.) cannot offer a microscopic mechanistic insight i.e. not infer a molecular picture of the adsorption mechanisms and to distinguish between specific sorption of cations on the edges or on basal plane surfaces.

Using recent advances in Atomic Force Microscopy we want to study the charge distribution on both basal planes of kaolinite particles. The two objectives of this research are formulated as follows: 1) determination of the pH dependence of the surface charge of the gibbsite facet and the silica facet; 2) determination of the CaCl_2 concentration dependence of the surface charge of the gibbsite facet of the individual kaolinite particle. The net effective surface charge densities, similar to those obtained by ζ -potential measurements, on single facet is extracted from the recorded force–distance curves, using DLVO theory with charge regulation

boundary conditions. Atomic scale images at much smaller distances, gives a direct view of lateral and perpendicular organization of ions within the Stern layer. In order to derive a complete molecular-level understanding of the charging mechanism and ion adsorption to the kaolinite facets, we also perform density functional theory calculations and compare our high-resolution images and AFM spectroscopy results with the DFT simulations.

4.2. MATERIALS AND METHOD

4.2.1. Sample preparation

Kaolinite powder (KGa-1) was provided by T. Hassenkam and S.L.S. Stipp (University of Copenhagen). A suspension of the powder (~ 1.5 mg/ml) is prepared using de-ionized water (Millipore Inc.). 20-30 μ L of this suspension is drop casted onto sapphire or mica substrates. After a residence time of 2 min, the samples are gently dried with air and then rinsed with copious amounts of deionized water to remove loosely bounded clay particles from the substrate. Before using, sapphire is cleaned with isopropanol, ethanol and water and by subsequent plasma cleaning (PDC-32G-2, Harrick Plasma) for 20-25 min. Mica substrates are freshly cleaved prior to drop deposition. Sodium chloride and calcium chloride (puriss, ACS reagent grade, Sigma Aldrich) solutions are prepared by dissolving the salt in deionized water. The pH is adjusted with HCl or NaOH solutions. All experiments are performed in fluid, in closed AFM fluid cell that allows solvent exchange and at a constant temperature of $22.7 \pm 0.5^\circ\text{C}$.

4.2.2. AM-AFM force spectroscopy

The dynamic force spectroscopy measurements in AM-AFM mode are performed with a commercial Asylum Research Cypher ES with blue drive which provides thermal excitation. The cantilever is driven by locally heating it with a laser beam, using the so-called photo thermal drive principle [38]. The force spectroscopy measures are performed in following way: i) topography and phase image of a single kaolinite particle along with the surrounding substrate is captured ii) tip-sample interaction volume map is acquired for the same area using the Cypher MFP3D software. During the mapping, the amplitude and phase response of the cantilever are recorded as a function of z-piezo position by varying the mean tip-sample distance. These can be used to obtain the tip-sample interaction forces by modeling the cantilever dynamics as a simple harmonic oscillator (SHO) [39]. This

procedure is called the force inversion and is described in detail in ref. [40] and in section 2.4.1.1.

4.2.3. Atomic Resolution imaging

Atomic resolution imaging experiments are carried out with a Multimode8 AFM (Bruker Corporation) equipped with a Nanoscope V controller. Sharp tips (Bruker BBB, tip radius ~ 3 nm) are used in desired salt solutions by injecting liquid using the syringe. To minimise the thermal drift, the system is allowed to thermally equilibrate at room temperature for 20-60 min before acquiring any data. Tapping mode or AM mode is used throughout all the experiments with a free amplitude A_0 , typically less than 1 nm. The ratio of the imaging amplitude set point (A/A_0) is kept as high as possible (typically ≥ 0.9) to minimize the force of interaction between tip and the surface [41-43]. A very high scanning rate ~ 15 Hz is used with a scan resolution of 512 samples per line. Usually, it takes ~ 30 sec to capture one image.

4.2.4. Force fitting and charge calculation

In this section, we briefly discuss the basic procedures for the conversion of measured forces to surface charges. The detailed explanation for the same is given in chapter 2 and 3.

4.2.4.1. DLVO theory

In DLVO theory, the disjoining pressure (Π) between two adjacent surfaces at a distance h is decomposed into contributions from van der Waals interactions (Π_{vdW}) and electrostatic double layer forces (Π_{el}). The total force on the tip is calculated by integrating Π over the tip surface. Our AFM tips are slightly flattened (see chapter 3 for details) leading to a local parallel plate geometry. We therefore approximate the total force by $F(h) = A_{tip}(\Pi_{el} + \Pi_{vdW})$, where A_{tip} is the area of the tip. For two locally parallel interfaces, the van der Waals contribution is written as

$$\Pi_{vdW}(h) = -A_H / 6\pi h^3 \quad (1)$$

Where A_H is the Hamaker constant. For an atomically flat surface, the electrostatic contribution to the disjoining pressure can be written as

$$\Pi_{el}(h) = k_B T \sum_i (c_i(z) - c_{i\infty}) - \frac{\epsilon \epsilon_0}{2} \left(\frac{d\psi}{dz} \right)^2 \quad (2)$$

The first term in Π_{el} is osmotic repulsion caused by local variations of the ion concentration and a second one due to direct electrostatic attraction (Maxwell

stress). Here, k_B is the Boltzmann constant, T is temperature, $c_{i\infty}$ is the bulk number concentration and $\varepsilon\varepsilon_0$ the dielectric permittivity of water. Calculation of the osmotic and electrostatic contribution requires the solution of the electrostatic potential $\psi(z)$ in the electrolyte at an arbitrary position $d_s < z < h-d_s$ between the two solid surfaces, where d_s is the Stern layer thickness. This potential is governed by the Poisson-Boltzmann (PB) equation:

$$\frac{d^2}{dz^2} \psi(z) = -\frac{e}{\varepsilon\varepsilon_0} \sum_i Z_i c_{i\infty} \exp\left(-\frac{Z_i e \psi(z)}{k_B T}\right) \quad (3)$$

where, e represents the elementary charge and Z_i is the valency of the corresponding ions. As explained in chapter 2 and 3, by numerically solving the PB equation with charge regulation boundary conditions between substrate surface and tip, we can calculate the potential distribution $\psi(z)$.

4.2.4.2. Charge Regulation

As mentioned above, to solve Eqn.3, we need to formulate a boundary condition which takes charge regulation into account. Many theoretical studies have suggested that due to chemical reactions, the surface acquires a charge density σ_s [44-50]. This charge density depends on the concentration of the electrolytes near the substrate and so on the local electric potential ψ_s . this dependence is formally written as: $\sigma_s = f_s(\psi_s, c_1^\infty \dots c_n^\infty, \Gamma, K_1 \dots K_m)$, where c_i^∞ is the bulk concentration of the corresponding ions, Γ the site density on the substrate and K_m the equilibrium constant of the considered surface reactions. The latter, together with the associated site densities, are usually referred to as the surface ionization parameters. Hence, the boundary condition for the BP equation can be formulated as:

$$-\varepsilon\varepsilon_0(\hat{n} \cdot \nabla \psi)_s = \sigma_s = f_s(\psi_s, c_1^\infty \dots c_n^\infty, \Gamma, K_1 \dots K_m) \quad (4)$$

where $\hat{n}$ is the normal to the substrate pointing inwards the electrolyte. In table 1, we list the supposed surface reactions from which the surface charge-surface potential relations (f_s) have been derived for a silica tip or mica and sapphire substrates and the silica and gibbsite facets of a kaolinite particle. Detailed description to get the charge- surface potential is discussed in chapter 2 and 3.

Table 1

	Mica/Silica/Silica facet	Sapphire/Gibbsite facet
	$\sim SH \leftrightarrow \sim S^- + H^+ ; K_{H1}$	$\sim SH_2^+ \leftrightarrow \sim SH + H^+ ; K_{H2}$
Reaction	$\sim SC^{Z_c-1} \leftrightarrow \sim S^- + C^{Z_c} ; K_c$	$\sim SH_2A \leftrightarrow \sim SH_2^+ + A^- ; K_a$
^s	$\Gamma = \{S^-\} + \{SC^{Z_c-1}\} + \{SH\}$	$\Gamma = \{SH_2^+\} + \{SH\} + \{SH_2A\}$
charge	$\sigma_s = \frac{e\Gamma\{(Z_c - 1)\frac{[C^{Z_c}]_\infty}{K_c} \exp(-e\psi_s/k_B T) - 1\}}{1 + \left(\frac{[H^+]_\infty}{K_{H1}} + \frac{[C^{Z_c}]_\infty}{K_c}\right) \exp(-e\psi_s/k_B T)}$	$\sigma_s = \frac{e\Gamma}{1 + \left(\frac{K_{H2}}{[H^+]_\infty} + \frac{[A^-]_\infty}{K_a}\right) \exp(e\psi_s/k_B T)}$

The force distance curves, as calculated with the theoretical model depend on a number of parameters including the area of the tip A_{tip} , the Hamaker constant A_H , the site density Γ , and the equilibrium constants K_j (or pK_j) of the surface reactions. Other than the pK_j values, most of these parameters are more consistently reported in the literature [43, 51-55], as mentioned in chapter 3. The area of the tip is also known (obtained from SEM image, see Figure 4.A4). Therefore, we take pK_H and pK_c as the fit parameters for our case. For each pair of pK values we can theoretically calculate the interaction force $F_{calc}(h)$ as a function of tip sample distance and compare them with experimental force values $F_{exp}(h)$. The best fit values of the fit parameters are calculated by maximising the merit function Q defined as:

$$Q(K_1, \dots, K_m) = \frac{1}{\sum_{j=1}^N (F_{calc}(h_j) - F_{exp}(h_j))^2} \quad (5)$$

Very good fit between experimental and theoretically calculated forces is obtained after optimisation of the pK pairs. It is important to note that the best fitting pairs are not unique. Rather a whole range of combination of fit parameters provides similar fit quality and same surface charge. But, as explained by Zhao et al [56], the resulting surface charge turns out to be insensitive to the assumed set of surface reactions, because the double layer contribution of the measured interaction force $F_{edl}(h)$ depends only indirectly via the charge density $\sigma_{substate}$ substrate on the fit parameters K_j .

To calculate the surface charge for an asymmetric system, we first need to calculate the surface charge for the silica AFM tip as explained above by performing a reference measurement on an equivalent silica substrate. Once the surface charge of the AFM tip is known, the surface charge on the other substrate can be determined following the same procedure. There can be two source for the error in the charge calculation method, (i) an error in the estimation of tip area and (ii) an error in the zero calculation. We assume an error of $\pm 12.5 \text{ nm}^2$ in the area of the tip and $\pm 0.3 \text{ nm}$ in the zero calculation and calculate the respective charge values. By taking the average and standard deviation of all these values, we get the error bar for each measured condition.

4.2.5. Computational details

Periodic density functional theory (DFT) calculations are performed using the program DMol3 with the COSMO-RS implicit solvent [57], the PBE functional, the DNP basis set and a dispersion correction [58]. We use a 1x2 unit cell of kaolinite with lattice parameters (0.86840x 1.01560 nm) as determined by x-ray diffraction. We construct the simulation cell to be three molecular layers thick, perpendicular to the [001] face and the lowest molecular layer is frozen in bulk positions throughout all calculations. Because inner shell adsorption is found to be significantly less stable than the outer sphere adsorption for gibbsite [59], we only consider outer sphere adsorption for gibbsite face of kaolinite. The outer sphere geometries are created by placing two hydrated divalent cations per primitive cell above the surface and removing three protons from hydration water molecules pointing towards the surface and one proton from a hydration water above the plane of cations. If two hydration water molecules are judged to be too close to each other, one is removed, and the remaining water is left bridging two cations. The structures created in this way are charge neutral, which is a good assumption considering that the measured surface charge values correspond to much less than a single charge per unit cell.

Formation energy calculation of different ion structures on kaolinite in aqueous solutions (Ca^{2+} , Mg^{2+} , and Cl^-) are performed using the reaction panel in COSMOtherm [60], using the DMOL3_PBE_C30_1301 parameterization for the reactions below, where the (aq) state is removed for clarity:

Formation of zig-zag structure:

OH⁻ to Cl⁻ exchange:

The free energy contributions from the partition functions of translation and rotation for all non-surface species are included using standard expressions from a DMol3 frequency calculation for the molecules and ions exchanging with the surface ($Ca(H_2O)_6^{2+}$, $Mg(H_2O)_6^{2+}$, OH⁻, H₂O and Cl⁻). But the effect of vibrations are excluded for two reasons: i) the computational effort of calculating vibrational frequencies for the large periodic system would be considerably more expensive than the geometry optimization ii) the accuracy of including vibrational entropy and zero point energy for an adsorbed system as complex as this would need careful assessment. The free energy of formation for the zig-zag structure (Eqn. 6) was then divided by 4 to get the energy per Ca(OH)₂ unit and the free energy for OH⁻ to Cl⁻ exchange (Eqn. 7) was divided by 2 to get the exchange energy per OH⁻/Cl⁻ ion. Further, description of the theoretical details is provided in Siretanu et al. [43] and references therein.

4.3. RESULTS AND DISCUSSIONS

4.3.1. Macroscopic characterization of nanoparticle morphology

Kaolinite nanoparticles have two different facets, a negative charged silica facet and a positively charged gibbsite facet (at neutral pH) [61]. By adsorbing them on sapphire or mica, we can expose either the gibbsite or silica facet to the fluid. Preparation conditions were optimized to achieve a reasonable coverage of well adhering isolated particles, as described in the Materials and Methods section. Atomic force microscopy topography images are used to reveal the surface features and characteristics of individual particles. The particles display a plate-like pseudo-hexagonal morphology with rather sharp corners and flat areas on the basal planes as expected for well-crystallized kaolinite particles (KGa-1 kaolinite) [62] (Figure 4.1a and A1). The majority of the particles has a relatively high aspect ratio. The height varies between 10 and 50 nm while the lateral dimension ranges from several tens to a few hundred nanometers. The majority of the basal planes (gibbsite and silica) appears smooth across 20-200 nm regions (Figure 4.1a), but many particles display regions with defects and cascade-like growth structures forming steps with a height of 1-20 nm.

4.3.2. Interaction Forces at Kaolinite Faces

As described in our earlier publications [59, 61, 63], AM-AFM-based force spectroscopy was used to map the spatial distribution of surface charge on the silica facet and the gibbsite facet of kaolinite particles as a function of the solution pH. Quantitative surface charge measurements using AFM are based on forces produced from overlapping electrical double layers when a charged tip is brought near a charged sample surface. Therefore, force distance (FD) curves are used to examine the spatial distribution of charge. Figure 4.1c shows a representative tip-sample interaction force map on a kaolinite-sapphire system in a 10 mM NaCl, pH 4 solution. A complete overview of force maps over all electrolytes for silica and gibbsite basal plane can be found in the Supplementary Information. The data are presented as a 2D projection on the substrate of the force measured 1 nm above the particle/substrate, that are extracted from 3D force maps. The lateral distance between each FD curve is 10 nm. The colors red and blue represent repulsive and attractive interaction forces, respectively. Since it is known that the isoelectric point of the SiO_2 surface is around pH 3, it can be assumed that the tip is negatively charged above pH 3. This suggests that the gibbsite facet of the kaolinite particle and the sapphire substrate are positively charged at pH 4 and 6 and negatively charged at pH 9. The silica facet of the kaolinite particle and the mica substrate are negatively charged at all conditions (pH 4, 6 and 9). Our measurements reveal a significant heterogeneity in the force distribution on both basal planes (Figure 4.1 and A2). Substantial lateral variations are found not only at the locations of topographic defects, but also on the topographically flat parts of the surface (terraces). This heterogeneity in the force distribution over the two facets reflects the heterogeneity in surface charge due to a varying surface chemistry. While the exact conversion of the observed force into local surface charge close to the edge or near terrace steps on the particles is difficult, our raw data clearly show that the tip-sample force decreases upon approaching these regions, suggesting (in case of the gibbsite facet) a less positive if not negative charge density here. Our further discussion focuses on the forces and charge on the terraces of the basal planes.

Figure 4.1 (a) Topography image and height profile of kaolinite particle adsorbed on sapphire imaged in 10 mM NaCl solution imaged at pH 4. (c) Force map showing tip sample interaction forces on the kaolinite particle in 10 mM NaCl solution at pH 4. Note: The map is shown at 1 nm distance from the surface. (d) Surface charge map calculated by analysing the tip sample interaction forces with DLVO theory. Force vs. distance curves along with theoretical calculated forces (black lines) on (b) silica and (b') gibbsite facet in 10 mM NaCl solution at pH 4, 6 and 9. Note: representative force curves corresponding to each condition are taken from the area marked on the force maps at kaolinite particle. (Tip parameters for silica facet: $Q = 2.16$, $f_0 = 16.97$ kHz, $K = 0.367$ N/m, $A_{tip} = 531 \pm 12.5$ nm² and for gibbsite facet: $Q = 2.37$, $f_0 = 17.06$ kHz, $K = 0.448$ N/m, $A_{tip} = 1018 \pm 12.5$ nm²).

4.3.3. Surface Charge of at Kaolinite Faces: Effect of pH

The normalized average force-distance curves across a flat region (marked with black box on the force maps) in the center of the particle in 10 mM NaCl electrolyte solution at different pH values are shown in Figure 4.1b and b'. Figure 4.1b shows that rising the pH leads to an increase in the magnitude of the long range repulsive force between SiO₂ tip and silica facet of kaolinite. An increase of

the repulsive interaction with increasing pH implies that at least one of the two involved surfaces (tip or silica facet) becomes more negatively charged. On the gibbsite facet, the attractive interaction force only weakens with increasing pH from 4 to 6, and becomes repulsive at pH 9, indicating a negative charged gibbsite facet. The force curves on the gibbsite facet of kaolinite and the sapphire substrate are comparable, and of similar magnitude. The solid lines give the best fitting DLVO calculations including charge regulation boundary conditions. From these fits the diffuse surface charge (and surface potential) is extracted (see Methods and Material section for details). This procedure is applied to all force-distance curves. The resulting charge maps, with spatial resolution of 10 nm, show the dependence on pH for both kaolinite facets on an individual particle (Figure 4.1d and A2). The silica facet of kaolinite, mica substrate and the silica-tip surface are negatively charged under all probed pH conditions (Figure 4.2). The surface charge on the silica facet changes very little, from -0.016 to -0.023 e/nm^2 , when the pH varies from 4 to 6. The charge increases more strongly (-0.023 to -0.044 e/nm^2) when the pH of the solution is increased from 6 to 9 (Figure 4.2). The surface charge of the silicon tip varies from -0.025 to -0.125 e/nm^2 when the pH increases from 4 to 9. The gibbsite facets of the kaolinite particle are positively charged for pH 4 and 6 ($+0.018$ and $+0.004$ e/nm^2 , respectively) but become negative (-0.028 e/nm^2) at pH 9. Sapphire shows similar behavior, although for pH 4 and 6 the charge values are higher than on gibbsite facet (Figure 4.2). Interestingly, the gibbsite facet behaves more or less identical to the sapphire surface in terms of the surface charge dependence as function of pH, despite the difference in crystal structure. These results corroborate the work of Eng et al.[64]. Using X-ray diffraction they have shown that a sapphire surface in contact with water restructures because the aluminum atoms configuration resembles that of gibbsite more than bulk sapphire. Infrared (IR) spectra studies [65] and simulations [66-68] reveal the same surface reorganization.

The results discussed above show that the pH strongly affects the surface charge on the basal planes of the kaolinite particle. The gibbsite octahedral facet of kaolinite shows an isoelectric point at pH 6.5, whereas the silica tetrahedral facet of kaolinite shows an isoelectric point below pH 4. These findings contradict the early interpretation of titration data that attributed the pH responsive sites only to the edges. But they support the more recent view that supposes proton active sites on both basal planes of kaolinite. Because proton donor-acceptor reactions occur on

both the silica and Gibbsite facets the surface charge becomes pH-dependent in a similar way as on Al_2O_3 and amorphous SiO_2 , as Figure 4.2 shows.

Figure 4.2. Surface charge of mica, silica tip, sapphire and two facets of kaolinite particle as function of pH. Note: these surface charge values are calculated corresponding to the area marked on the force maps shown in Figure 4.1 and A1, A2.

4.3.4. Surface Charge of at gibbsite kaolinite facet: Effect of CaCl_2

An intriguing charging behavior is observed on the gibbsite facet of the kaolinite particles in the presence of CaCl_2 . As can be observed in Figure 4.3, initially, σ_{eff} increases with increasing salinity, reaching a maximum at 10 mM and then decreases as the concentration further increases to 50 mM. This strong non-monotonic charging behavior with a pronounced maximum near 10 mM CaCl_2 was observed on the sapphire substrate as well. Synthetic nanoparticles of gibbsite show a similar charging behavior [59]. This can be explained by the competition between specific adsorption of divalent cations and anions. This specific adsorption is observed in AFM images which are taken with atomic resolution.

Figure 4.3. (a) Topography image of kaolinite particle adsorbed on sapphire imaged under 10 mM CaCl_2 solution. (b,c,d) Surface charge maps for kaolinite particle adsorbed on sapphire under different (1,10, and 50mM) CaCl_2 concentrations. (e) Surface charge as a function of salt concentration for gibbsite face (blue line) and sapphire substrate (red line). Note: average surface charge corresponding to each condition has been taken from the areas marked with squares in (b,c,d). Tip parameters: $Q = 2.94$, $f_0 = 22,67$ kHz, $K = 0.71$ N/m, $A_{tip} = 314 \pm 12.5$ nm².

4.3.5. Atomic resolution imaging of gibbsite kaolinite basal plane

To reveal the periodic ordered structures that are formed by Ca^{2+} and Cl^- ions at the gibbsite facet of the kaolinite particles, we image the gibbsite facet at atomic resolution in CaCl_2 solutions. Recently, we reported that the gibbsite basal plane of kaolinite displays a pseudo hexagonal pattern (surface unit cell, $a = 0.49$ nm and $b = 0.93$ nm) upon imaging in deionized water and various concentrations of monovalent salts [69]. The gibbsite facet appearance changes dramatically when imaged in 10 mM CaCl_2 . Instead of the hexagonal pattern, the surface displays an array of parallel double rows of protrusions aligned along the b direction of the lattice (Figure 4.4a). Within each double row, the protrusions are arranged in a zig-zag fashion. Averaging over several periods of the surface, we find periodicities of

$a = 0.96$ nm and $b = 0.49$ nm perpendicular and parallel to the double rows, respectively, in good agreement with the crystallographic lattice of the kaolinite gibbsite basal plane (see Figure 4.4b for a typical topographic cross sections). It makes sense to assume that these protrusions represent adsorbed ions from the solution. At first glance, one might think that the bumps in the double row structure represent Cl^- anions, since the positive charge of the surface should lead to a repulsion of the Ca^{2+} cations. Yet, this would be incompatible with the simultaneous increase of the positive surface charge. Therefore, we suppose that these protrusions are Ca^{2+} ions; two per unit cell. With surface charge densities as small as shown in Figure 4.3, the average distance between two adjacent discrete positive charges on the surface is of order 5 nm or more. At low concentrations, cations from the solution can therefore easily approach the neutral parts of the surface ‘in between’ adjacent repulsive charges thereby avoiding the electrostatic repulsion. Ca^{2+} ions are strongly hydrated. Several AFM [59, 70] and X-ray studies [71, 72] as well as DFT and MD simulation [73-76] show that dispersion forces between hydrated divalent ions and well hydrated substrates can strongly promote Ca^{2+} adsorption on the hydroxyl sites in the basal planes of kaolinite, gibbsite, silica or mica. For instance, calculations of Parsons and Ninham [77] predict for Ca^{2+} a contribution of $4.4 k_{\text{B}}T$ per ion of dispersion forces to the binding energy. This amount is approximately twice less for Na^+ ($2.6 k_{\text{B}}T$).

Figure 4.4 Atomic resolution topographic images of the gibbsite facet of kaolinite imaged in (a) 10 mM CaCl_2 solution showing double row structure and (d) in 100 mM CaCl_2 showing single row structure. Height profiles in (b) and (e) display periodicities of $a = 0.96$ nm and $b = 0.49$ nm; $a = 1.07$ and $b = 0.48$, respectively. (c, f) Equilibrium structure of adsorbed Ca^{2+} (blue) and Cl^- (yellow) on the gibbsite facet of kaolinite in aqueous solution predicted by DFT calculations. Top and side view of the optimized geometry for outer shell adsorption of (c) Ca^{2+} and (e) Cl^- for high salt concentration.

As we increase the CaCl_2 concentration to 100 mM, we observe a change in the appearance of the surface. The original double row structure transforms into two inequivalent parallel rows of brighter and fainter protrusions, (Figure 4.4d). The periodicities both along and perpendicular to the rows agree closely with the dimensions of the surface unit cell, $a = 1.07$ nm and $b = 0.48$ (Figure 4.4e). This transition from a double row structure to single rows of bumps coincides with the decrease in surface charge observed at 50 mM in Figure 4.3. Such a decrease in surface charge could be caused by desorption of the initially adsorbed Ca^{2+} cations or by co-adsorption of Cl^- anions. Adsorption of Cl^- ions is most likely, because increase of the Ca^{2+} concentration should promote adsorption and not desorption. The anion adsorption can be facilitated by an increase of the initially not-so-high positive surface charge due to the adsorbed cations. Recent numerical simulations of smectite in contact with CaCl_2 and NaCl suggest that Cl^- ions do form ion pair complexes with adsorbed Ca^{2+} ions at sufficiently high concentrations [78]. Also optical reflectivity measurements and MC simulations indicate an enhancement of the Cl^- density on silica near the pre-adsorbed divalent ions [79]. A question that arises from these observations is: do Ca^{2+} ions form inner-sphere or outer-sphere complexes with the surface?

4.3.6. Density Functional Theory Calculations

To explain our experimental findings from an atomistic point of view, we performed density functional theory (DFT) calculations to examine the adsorption of Ca^{2+} and Cl^- onto the gibbsite facet of kaolinite. We used the COSMO-RS implicit solvent model with periodic boundary conditions to calculate the equilibrium structure of the adsorbed ions on the gibbsite facet of kaolinite. We scrutinize our models not only on their stability, but also on the ability to reproduce and confirm our experimental findings. Figure 4.4c shows the optimized geometry in case of cation adsorption. The cations form indeed a zig-zag row structure, which reproduces the features observed with atomic resolution AFM (Figure 4.4). The DFT/COSMO-RS formation energies for the divalent ion structures were -127 kJ/mol/ $\text{Ca}(\text{OH})_2$. These formation energies predict that the zig-zag structure should begin to form already at ~ 0.01 mM and pH 6 based on the equilibrium defined by Eqn. 6, which is lower than the observed concentration of 10 mM. The difference in concentration threshold for zig-zag structure formation corresponds to a difference in formation energy of ~ 20 kJ/mol, which is within standard DFT uncertainties.

The DFT calculations suggest that all the cations are located at virtually the same height above the kaolinite surface, which is in agreement with the experiments (Figure 4.4c). The OH^- ion that is located down the plane of Ca^{2+} ions, bridging two Ca^{2+} ions, is responsible for the positive surface charge via partial protonation. We have previously predicted the pKa for the water to OH^- deprotonation for the similar structure on the gibbsite surface, where it was found to be ~ 5 for the Mg structure and ~ 10 for the Ca structure [59]. These values are significantly lower than for the hydration of the free cations in the solution, and partial OH^- to water protonation on the surface leads to a weak positive surface charge, consistent with experiments (Figure 4.3). The OH^- can furthermore be exchanged by a Cl^- ion if the CaCl_2 concentration is increased, as suggested by previous DFT calculations for the gibbsite system [59]. The Cl^- ion, on the other hand, is larger and for kaolinite, it adsorbs in quasi-threefold hollow sites on the cation zig-zag structure further away from the surface compared to the plane formed by the cations (Figure 4.4f). The predicted structure agrees with the single rows observed with the AFM at higher salt concentrations, although DFT predicts a single zig-zag row with a very small angle, which is not distinguishable from a single straight row in the AFM experiments. The vertical position of the Cl^- ions is $1\text{--}1.5 \text{ \AA}$ above the Ca^{2+} plane. The OH^- to Cl^- ion exchange disables OH^- protonation and with it the mechanism for positive surface charge generation. Upon Cl^- exchange, the surface structure becomes neutral, which explains the decrease in σ_{eff} at high salinity. The OH^- vs. Cl^- exchange energies predicted from DFT are 76 kJ/mol for the Ca structure. This is close to what was observed on the basal plane of synthetic gibbsite nanoparticles, but according to the DFT calculations the OH^- to Cl^- exchange is less favorable on kaolinite, probably because DFT overestimates the stability of the $\text{Ca}(\text{OH})_2$ structure. The DFT calculations predict the Cl^- structure to form at concentrations $>10 \text{ M}$. For complex structures, such as the zig-zag structure formed by the divalent cations Ca^{2+} on gibbsite and kaolinite, the DFT calculations provide a very useful support for the interpretation of the experiments, but the high accuracies required for quantitative predictions could not be obtained, partly because of uncertainties in the chosen method, the DFT functional itself, partially due to the approximations used to obtain the free energies.

Preliminary DFT calculations on the formation of a similar zig-zag structure on the silica facet suggest that the lack of hydrogen bonding to the surface results in a much more compact structure which has a significantly lower formation energy of about $-90 \text{ kJ/mol/Ca}(\text{OH})_2$. This suggests that the formation of a zig-zag row on the

silica facet would only form for concentrations of about 1-10 M, which is a 5-6 orders of magnitude higher concentration than for the gibbsite facet. Thus, qualitatively the DFT calculations suggest a quite different adsorption behavior for the two basal planes of kaolinite in the presence of CaCl_2 .

In summary, we have demonstrated that the two facets of kaolinite – the silica facet and the gibbsite facet – differ significantly in their surface chemistry characteristics. At pH 6 the silica-like basal plane displayed on average a negative surface charge density of -0.05 e/nm^2 and the gibbsite facet a weak positive charge density of approximately $+0.025 \text{ e/nm}^2$, corresponding roughly to one charge per 20-40 surface unit cells. This contradicts the assumption that both facets of kaolinite carry a permanent negative charge due to isomorphous substitution. Secondly, based on force measurements, we find that the basal planes of kaolinite does carry charge that varies with pH and salt concentration. The silica facet was found to be negatively charged above pH 4, whereas the alumina facet was found to be positively charged below pH 7, and negatively charged above pH 7. Compared to macroscopic studies that reveal charge values averaged over the total particle surface, *i.e.* edges and basal planes, our measurements are more specific without the need for assumptions regarding the relative weight of edge vs. basal plane sites. Gupta et al. observed a similar pH dependency of the basal planes of kaolinite using colloidal probe AFM spectroscopy[20, 26]. Our 2D charge mapping also reveal that the surface charge of the particles displays lateral variations that correlate with the presence of topographic defects such as steps. Charge heterogeneity is present even on topographically rather smooth terraces of facets. Therefore, we believe that our extracted average charge vales (Figure 4.2) from specific smooth terraces may be less affected by the contributions from defects (e.g. steps) of lower charge density that are unavoidably included in the wide lateral average of the colloidal probe technique. Regions with defects, depending on their surface chemistry, may dominate the apparent surface charge measured in a colloidal probe AFM measurement and thereby suggest a different surface chemistry of the basal plane than the true intrinsic one. In light of the significant similarity between the gibbsite basal planes of kaolinite with basal plane of sapphire (IEP near pH 7) we believe that, as predicted by Bickmore and Jodin [80, 81] for sapphire surfaces, the doubly coordinated surface hydroxyl groups ($\equiv\text{Al-OH}_2\text{OH}$) on the basal plane that have pK_a values around 5, are responsible for the pH-dependent surface charge of gibbsite facet. On silica basal plane, similar to

amorphous SiO₂ surface, the ≡Si-OH groups with pK_a value around 6.9 would reproduce our experimentally measured values.

AFM measurements performed in CaCl₂ (pH 6) solutions show a clear and unequivocal preferential adsorption of divalent ions on the gibbsite facet of kaolinite. Atomic resolution imaging demonstrates that the Ca²⁺ and Cl⁻ ions do not adsorb randomly at the gibbsite facet but form preferentially ordered structures such as zig-zag rows or linear rows due to ion–substrate attractive interactions controlled by the water at the interface. DFT calculations show that two conditions should be fulfilled for this ordering to take place: i) the ion's hydration energy has to dominate over ion–substrate electrostatic interactions, The position and orientation of hydroxyl groups and the location of the hydrogen bonded water impose a set distribution and distance between adjacent bounded Ca²⁺ ions. The weakly charged gibbsite facet of kaolinite provides an appropriate hydration landscape that allows for the formation of Ca²⁺ ionic structures stable enough to be observed by AFM imaging. In contrast, highly mobile Na⁺ cations on the surface and the loose hydration state prevent a structural organization of these ions on the surface.

This additional piece of information justifies the yearly assumption of Yukselen et al., Hunter and James, and Tournassat et al. that based on macroscopic titration and zeta potential measurements [35-37] alluded that hydrolysible divalent ions, i.e. Co²⁺, Cu²⁺, Cd²⁺, Pb²⁺ and Ca²⁺ have strong affinity for the surface of kaolinite. AFM data and DFT show that divalent Ca²⁺ can adsorb on kaolinite facet and more explicitly at gibbsite facet and not only at the edges of the particles as was assumed earlier. Moreover, DFT calculation also show that indeed the Ca₄(H₂O)₁₂(OH)₈ and not bare Ca²⁺ ion adsorb on gibbsite facet, as also suggested in works of Yukselen et al., Hunter and James, and Tournassat et al. Our work presents, to the best of our knowledge, the first direct observation of atomic resolution image of divalent cation–anion 3D structure at gibbsite facet of kaolinite. By providing the direct visualization of surface charge distribution, we make a significant step forward for the understanding of electrical surface property on the kaolinite nanoparticles, which plays a vital role on various applications and on the oil recovery.

4.4. CONCLUSIONS

In the present work, we characterize the charge distribution on the basal planes of kaolinite particles under variable pH and salt concentrations using dynamic force microscopy. The surface charge of the silica facet is always negative and increases in magnitude with increasing pH. While for the gibbsite facet, the surface charge is positive for $4 < \text{pH} < 6$, and becomes negative for higher pH ~ 9 . The surface charge of the gibbsite facet at pH 6 increases up to a concentration of 10 mM CaCl_2 and starts to decrease upon further increasing the salt concentration to 50mM. The increase in surface charge is explained in context of Ca^{2+} ion adsorption, while chloride ion adsorption at higher CaCl_2 concentrations makes the surface charge neutral. Our conclusions are well supported by the atomic scale imaging as well as the DFT calculations.

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4.6. APPENDIX

Effect of pH: force and charge maps on gibbsite facet

Figure 4.A1 (a) Force maps showing tip-sample interaction forces on kaolinite particle adsorbed on sapphire under 10mM NaCl solution at pH 6 and 9. Note: The maps are shown at 1 nm distance from the surface. (b) Surface charge maps calculated by analysing the tip sample interaction forces with DLVO theory. (Tip parameters: $Q = 2.37$, $f_0 = 17.06$ KHz, $K = 0.448$ N/m, $A_{tip} = 1018 \pm 12.5$ nm²)

Effect of pH: force and charge maps on gibbsite facet

Figure 4.A2 (a) Force maps showing tip sample interaction forces on kaolinite particle adsorbed on mica under 10mM NaCl solution at pH 4, 6 and 9. Note: The maps are shown at 1 nm distance from the surface. (b) Surface charge maps calculated by analysing the tip sample interaction forces with DLVO theory. (Tip parameters: $Q = 2.16$, $f_0 = 16.97$ Khz, $K = 0.367$ N/m, $A_{tip} = 531 \pm 12.5$ nm²).

Effect of CaCl₂ solutions: force and charge maps on gibbsite facet

Figure 4.A3 (a) Force maps showing tip sample interaction forces on kaolinite particle adsorbed on sapphire under different (0.5, 5, and 30mM) CaCl₂ salt concentrations. Note: The maps are shown at 1 nm distance from the surface. (b) Surface charge maps calculated by analysing the interaction force curves with

DLVO theory. (Tip parameters: $Q = 2.94$, $f_0 = 22,67$ Khz, $K = 0.71$ N/m, $A_{tip} = 314 \pm 12.5$ nm²)

SEM Images of AFM tips

Figure 4.A4 SEM images of the AFM tips used for different experiments. (a) $A_{tip} = 531 \pm 12.5$ nm² for silica facet (b) $A_{tip} = 1018 \pm 12.5$ nm² for gibbsite facet and (c) $A_{tip} = 314 \pm 12.5$ nm² for gibbsite facet in presence of CaCl₂ ions.

Figure 4.A5 Equilibrium structure of adsorbed Ca²⁺ (blue), Mg²⁺ (violet) and Cl⁻ (yellow) on the gibbsite facet of kaolinite in aqueous solution predicted by DFT

calculations. Top and side view of the optimized geometry for outer shell adsorption of (a) Ca^{2+} and Cl^- and (b) Mg^{2+} and Cl^- for high salt concentration. In case of MgCl_2 , the Cl^- ions form completely straight rows.

CHARGING BEHAVIOUR OF MICA BASAL PLANES IN PRESENCE OF ALKALI AND ALKALINE EARTH METAL IONS

Abstract

So far in chapter 3 and 4, we have studied the surface charge of a 1:1 layer type clay mineral (kaolinite) under various electrolyte conditions. In this chapter, we study the charging behaviour of 2:1 layer type clay mineral (mica surface) in presence of alkali and alkaline earth metal ions. We use dynamic atomic force microscopy (AFM) to determine the surface charge of mica in five different salt solutions (Li^+ , Na^+ , Cs^+ , Ca^{2+} , Mg^{2+}). Moreover, the surface charge is measured for three different pH (4, 6 and 9) solutions of fixed LiCl concentration.

We observed that the mica remains negatively charged in presence of all the monovalent ion solutions, while charge reversal occurs above 20 mM of divalent salt concentrations. The charge screening capacities of these ions are in order of $\text{Li}^+ < \text{Na}^+ < \text{Cs}^+ < \text{Ca}^{2+} \approx \text{Mg}^{2+}$. High resolution images show the surface structure with true atomic resolution on mica basal plane. In presence of pure water and NaCl solutions, the hexagonal surface pattern is observed representing crystal lattice structure of mica, while it changes completely in the presence of CsCl and CaCl_2 solutions due to ion adsorption. Also, we observed pH dependent charging behaviour of the mica, similar to that of the silica surface.

5.1. INTRODUCTION

Most silicate minerals such as mica and other clays acquire surface charge in aqueous solutions due to the ionization of surface groups and/or dissociation of crystal lattice ions [1]. This surface charge is balanced by the counter ions present in the electric double layer (EDL). The adsorption strength of these ions at an interface and hence the interface charging is influenced by their size, valency and hydration structure [2-4]. The study of surface charging and ion adsorption on basal planes of clay minerals can provide fundamental insights to many processes, such as adsorption and transport of toxic heavy metals, nutrient ions, organic molecules and pesticides [5-7], flocculation/deflocculation [8], coagulation [9], and clay swelling, an important process for petroleum engineering and catalysis applications [10, 11].

Mica, $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$, is a 2:1 layer type phyllosilicate mineral and its basal planes are structurally similar to many dominant surfaces of clay minerals like kaolinite, illite and, montmorillonite [12]. Also, mica occurs in large platy crystals and it is easy to cleave them to produce molecularly smooth surfaces without any defects. Hence, the mica-water interface is highly studied, both with theoretical [13-17] and experimental approaches [3, 18-20]. Charging of the mica interface in aqueous solutions generally has contributions from the free lattice charge (due to potassium ion dissociation) and the hydrolysis of surface silicate species in water. The electrical properties of the mica-water interface are known to depend on electrolyte composition (pH, ionic strength, ion size, valency etc.) due to the adsorption/ structuring of free ions at the interface. Thus, the mica water interface can behave differently under these variable conditions.

For example, Bera et al. [21] studied the wetting alteration of the mica surface in ambient decane by divalent salt solution. The study reported that a transition from near zero contact angle to a finite contact angle occurs as monovalent ions (Na^+ , K^+) are replaced by divalent ions (Mg^{2+} , Ca^{2+}) in aqueous drops. With the help of numerical calculations [22], it was shown that the electrostatic interaction potential is particularly relevant in determining the wetting behaviour of the oil-water-mica system. In an another study [23], large differences in the interaction force between two mica sheets is shown, depending on the hydration structure of the ions [23, 24]. Strong repulsive forces were observed between mica surfaces at a few nm separation in a 0.1 M NaCl solution, while almost no repulsion was observed in a 0.1 M CsNO_3 solution. Pashely et al.[19] made similar observations in earlier

attempts in order to understand the correlation of the double-layer and hydration forces with surface charging or ion-exchange properties of mica with alkali and alkaline earth metal ions [4, 20, 25]. In addition to this, some studies [16, 26-28] also showed that in the presence of divalent ions these repulsive forces change sign and become attractive in nature due to charge reversal of the mica-water interface. Kekicheff et al.[27] measured the forces between two mica sheets using SFA and deduced the effective surface potential using Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. Ninham et al. [16] has observed similar trends of charge reversal by calculating surface potential using modified Poisson-Boltzmann approach. Despite these studies, there are still some open questions, such as the ion distribution at the mica-water interface and the charge reversal capabilities of monovalent ions.

Another aspect of the mica interface charging is its dependence on the pH. Usually, it is assumed that mica has a pH independent charge and therefore, a permanent surface charge. However, some studies have shown that the zeta potential of mica varies significantly when the pH changes from 4 to 6 and changes a little for increasing pH [28-30]. Using streaming potential measurements, Scales et al.[28] reported an increase in the zeta potential from -35 to -80 mV on varying the pH from 3 to 10 in a background of 1mM KCl. Nishimura et al.[31] and Shubin and Kekicheff [32], however reported zeta potential data ranging from -20 to -140 mV for a variation of pH from 3 to 10. Since, there is no consensus in the literature, it is important to investigate the effect of pH on the charging behaviour of mica.

Characterization of these aspects requires a surface sensitive experimental technique that can resolve presence of a single ion at a sub-nanometric scale. With the recent advancements in AFM, it has now become possible to record forces with high lateral resolution and extract the surface charge using DLVO theory [33-36]. Recently, it has been shown that using DLVO theory complemented with charge regulation, it is possible to extract the surface charge along with the equilibrium constants ($pK = -\log K$) for adsorption/desorption reactions [37, 38]. Also, by using sharp AFM tips, it is possible to visualize the ion adsorption on crystal lattices [39-41].

In this chapter, we use small amplitude dynamic force microscopy measurements in AM-AFM mode to extract the surface charge on mica in different salt solutions (Li^+ , Na^+ , Cs^+ , Ca^{2+} and Mg^{2+}) and three different pH (4, 6 and 9) conditions. Using DLVO theory, we extract the surface charge values from each individual tip-

sample interaction force on the basal plane of mica. Further, we extract equilibrium constants of surface speciation reactions using the full non-linear PB equation and charge regulation boundary condition. Also, high resolution images show the surface structure with true atomic resolution on the mica basal plane in pure water and NaCl solution while different ion structuring is observed in CsCl and CaCl₂ solutions. The surface charge values are discussed in the context of adsorbed amount of ions and their structuring at the crystal lattice.

5.2. MATERIALS AND METHOD

5.2.1. Sample preparation

1M stock solutions of NaCl, LiCl, CsCl, CaCl₂, MgCl₂ salts (pursis, ACS reagent grade, Sigma Aldrich) are prepared by dissolving the required amount of salts in deionized (Milli-Q) water. Freshly cleaved mica is used for both force spectroscopy and atomic resolution measurements. Silicon wafer substrates are cleaned by rinsing with isopropanol, ethanol and water and by subsequent plasma cleaning (PDC-32G-2, Harrick Plasma) for 20-25 min. All experiments presented here are carried out at room temperature ($22 \pm 1^\circ\text{C}$) and at near neutral pH (~ 5.8) unless mentioned otherwise.

5.2.2. AM-AFM force spectroscopy

Dynamic force spectroscopy measurements are performed using an Asylum Research Cypher ES AFM equipped with photo-thermal excitation (Blue drive) along with a sealed fluid cell. The AFM cantilever is immersed in a droplet of salt solution which is sandwiched between the sample and top surface of the cantilever holder. The salt solution is exchanged with a pair (inlet and outlet) of plastic syringes (lubricant free). To exchange liquids, a new solution (20 times the drop volume) is injected via the inlet while the mixed solution is sucked out with the outlet of the fluid cell. After exchanging the solution, we wait approximately 10 minutes to equilibrate the system before recording the data. Rectangular silicon cantilevers (MikroMash NSC36/Cr-Au BS) with a gold backside coating are used for the spectroscopy measurements. The silicon is covered by a 1-2 nm thick native oxide layer with an amorphous silica-like structure. Prior to use, cantilevers are cleaned by rinsing with an ethanol/isopropanol mixture followed by plasma cleaning for 20-25 min. Next, we calibrate the cantilever parameters spring constant (k_c), quality factor (Q) and resonance frequency (f_0) by measuring the

thermal noise spectrum[42] at a tip-sample distance of about 150 nm. Typical values are $k_c \sim 0.85$ N/m, $f_0 \sim 22$ kHz, $Q \sim 3.0$.

In amplitude modulation (AM) force spectroscopy, the amplitude and phase of the cantilever deflection is measured. We drive the bending of the cantilever by locally heating it with a laser beam, using the so-called photo-thermal drive principal [43, 44]. For tip-sample interaction measurements, the cantilever is driven at a fixed frequency (near its resonance frequency f_0) by an intensity modulated blue laser diode that is focused on the gold coated topside of the cantilever close to its base. The measured amplitude and phase distance curves can be used to obtain the tip-sample interaction forces by modeling the tip of the cantilever as a simple harmonic oscillator (SHO). This procedure is called the force inversion and is described in detail by Liu et. al.[45] for small amplitude modulation with piezo excitation. Here we use photo-thermal excitation, which prevents the excitation of the extra resonances usually observed with acoustic driving and hence simplifies the force inversion procedure [46].

5.2.3. High resolution atomic force microscopy

Atomic resolution imaging experiments are carried out with two AFMs, a Cypher Asylum research AFM and a Multimode8 AFM (Bruker corporation) equipped with Nanoscope V controller. Sharp tips (Arrow, NSC 36, MikroMasch ~ 4 -8 nm) are used in desired salt solutions by injecting liquid using the syringe. The AFM is operated in standard amplitude modulation mode with a typical free amplitude A_0 , typically less than 1 nm, and imaging amplitude set point as high as possible, typically $A/A_0 \geq 0.9$. A very high scanning rate ~ 15 Hz is used with a scan resolution of 512 samples per line. Usually, it takes ~ 30 sec to capture one image.

5.2.4. Theoretical modeling for charge calculation

The basic procedures for the conversion of measured force to surface charge are described in chapter 2 and also by Ebeling et al.[47], and Siretanu et al.[40]. A systematic account of the procedure to include charge regulation into the standard framework of DLVO theory was originally provided by Ninham et al.[48] and refined by various other authors since then. Its specific adaption to high resolution AFM spectroscopy is described in detail by Zhao et al.[37] and Kumar et al.[49].

5.2.4.1. DLVO theory

Here, we briefly describe the DLVO force analysis adapted from chapter 2 and Ref. [37]. In DLVO theory the disjoining pressure (Π) between two adjacent

surfaces at a distance h is decomposed into contributions from van der Waals interactions (Π_{vdW}) and electrostatic double layer forces (Π_{el}). The total force on the tip is calculated by integrating Π over the tip surface. Our AFM tips are slightly flattened (see chapter 3 for details) leading to a local parallel plate geometry. We therefore approximate the total force by $F(h) = \pi R^2 \Pi(h)$. For two locally parallel interfaces, the van der Waals contribution is written as

$$\Pi_{vdW}(h) = -A_H / 6\pi h^3, \quad (5.1)$$

Where A_H is the Hamaker constant. For an atomically flat surface, the electrostatic contribution to the disjoining pressure can be written as

$$\Pi_{el}(h) = k_B T \sum_i (c_i(z) - c_{i\infty}) - \frac{\varepsilon \varepsilon_0}{2} \left(\frac{d\psi}{dz} \right)^2 \quad (5.2)$$

The first term in Π_{el} is osmotic repulsion caused by local variations of the ion concentration and a second one due to direct electrostatic attraction (Maxwell stress). Here k_B is the Boltzmann constant, T is temperature, $c_{i\infty}$ is the bulk number concentration and $\varepsilon \varepsilon_0$ the dielectric permittivity of water. Calculation of the osmotic and electrostatic contribution requires the solution of the electrostatic potential $\psi(z)$ in the electrolyte at an arbitrary position $d_s < z < h - d_s$ between the two solid surfaces, where d_s is the Stern layer thickness. This potential is governed by the Poisson-Boltzmann equation:

$$\frac{d^2}{dz^2} \psi(z) = -\frac{e}{\varepsilon \varepsilon_0} \sum_i Z_i c_{i\infty} \exp\left(-\frac{Z_i e \psi(z)}{k_B T}\right), \quad (5.3)$$

Where e represents the elementary charge and Z_i is the valency of the corresponding ions. Equation 5.3 is conventionally solved by assuming either constant potential or constant charge on the tip and substrate. But these assumptions are only justified for a weakly interacting system (larger tip-sample separation) and usually fail in the regime of smaller tip-sample distance ($\kappa h <$

10 , where $\kappa = \left(e^2 \sum_i Z_i^2 c_{i\infty} / \varepsilon \varepsilon_0 k_B T \right)^{1/2}$ is the reciprocal of Debye length) [37].

In such a regime, both the surface charge density and the potential vary with the separation h to compensate the confinement induced modification of the surface chemistry. This is known as charge regulation.

Figure 5.1(a) Schematic of the experimental set up, the cantilever is excited photo-thermally with a blue laser and the deflection of the cantilever is detected by reflecting a red laser onto a photodiode. The AFM tip is slightly blunted (in contact mode) leading to a local parallel plate geometry having tip radius of $R \sim 28$ nm. (b) tip-sample interaction force between silica tip and silica substrate in a 10 mM LiCl solution recorded with AM-AFM mode. Correlation of fit parameters pK_H and pK_C : (c) contour plots of the merit function Q in parameter space defined by pK_H , and pK_C . (d) contour plots of surface charge corresponding to the pK pairs. Note: the color bar in (d) is over saturated for clear visualization of constant charge white line matching the maximum of the merit curve in (c). Any pK pairs, falling on the white thick solid line produce a same diffuse layer charge density of -0.094 e/nm² and thus results in the same calculated force in (b). Tip parameters: $R = 28 \pm 2$ nm, $k_c \sim 1.29$ N/m, $f_0 \sim 29.8$ kHz, $Q \sim 3.5$.

5.2.4.2. Charge regulation

As mentioned above, to solve Equation 5.3, we need to formulate a boundary condition which takes charge regulation into account. Mica and silica are the two interacting surfaces here. Generally, the surface charge is controlled by the adsorption and desorption equilibrium of protons and salt ions at the interface. In case of mica, the surface charge arises due to the dissociation of potassium ions but we represent this reaction also as a deprotonation reaction similar as deprotonation of silanol groups for silica surface [28]. Therefore, we consider two reactions, deprotonation and adsorption of cations on the deprotonated site in our surface chemistry model:

with equilibrium constants

$$K_H = 10^{-pk_H} = \frac{\{S^-\}[H^+]_s}{\{SH\}} \quad (5.5)$$

and

$$K_c = 10^{-pk_c} = \frac{\{S^-\}[C^{Z_c+}]_d}{\{SC^{Z_c-1}\}} \quad (5.6)$$

respectively. The curly brackets indicate a surface density in sites/nm² and the square brackets represent a volume density in mol/L. Here the index s indicates the surface while d represents the boundary between the stern layer and the diffuse part of the double layer. It should be noted that the distributions of H^+ and C^{Z_c+} ions is governed by the Boltzmann relation, and their concentrations near the tip and substrate differ from the bulk. As the total site density is finite and given by:

$$\Gamma = \{S^-\} + \{SH\} + \{SC^{Z_c-1}\} \quad (5.7)$$

Eqs. (5.4) – (5.7) can be summarized in the following matrix equation:

$$\begin{pmatrix} 1 & 1 & 1 \\ [H^+]_s & -K_H & 0 \\ [C^{Z_c+}]_d & 0 & -K_c \end{pmatrix} \begin{pmatrix} \{S^-\} \\ \{SH\} \\ \{SC^{Z_c-1}\} \end{pmatrix} = \begin{pmatrix} \Gamma \\ 0 \\ 0 \end{pmatrix} \quad (5.8)$$

The surface potential ψ_s is related to the diffuse layer potential ψ_d via the stern layer capacitance:

$$C_s = \varepsilon\varepsilon_0/d_s = \sigma/(\psi_s - \psi_d), \quad (5.9)$$

Where d_s is stern layer thickness. Using Eqs. (5.8) and (5.9), the surface charge $\sigma = -e\{S^-\} + e(Z_c - 1)\{SC^{Z_c-1}\}$ can be evaluated as:

$$\sigma(\psi_s) = \frac{e\Gamma \left([C^{Z_c+}]_\infty e^{\frac{e\sigma d_s}{\varepsilon\varepsilon_0 k_B T} \frac{e\psi_s}{k_B T}} / K_c^{-1} \right)}{1 + \left(\frac{[H^+]_\infty}{K_H} + e^{\frac{e\sigma d_s}{\varepsilon\varepsilon_0 k_B T} \frac{[C^{Z_c+}]_\infty}{K_c}} \right) e^{-\frac{e\psi_s}{k_B T}}}, \quad (5.10)$$

where $[H^+]_\infty$ and $[C^{Z_c+}]_\infty$ are the bulk concentration of proton and cations, respectively. Note that the surface charge is essentially 0-plane charge plus stern layer charge, i.e. equal to diffuse layer charge in magnitude.

5.2.4.3. Force fitting and extracting the surface charge:

The force distance curves, as calculated with the theoretical model depend on a number of parameters including the tip radius R , the Hamaker constant A_H , the site density Γ , stern layer capacitance C_s , and the equilibrium constants K_j (or pK_j) of the surface reactions. Other than the pK_j values, most of these parameters are more consistently reported in the literature[37, 49] and same values are used as mentioned earlier in chapter 3. The Tip radius is also known (obtained from a SEM image, see appendix figure A.3). Therefore, we take pK_H and pK_c as the fit parameters for our case. For each pair of pK values we can theoretically calculate the interaction force $F_{calc}(h)$ as a function of tip-sample distance and compare them with experimental force values $F_{exp}(h)$. The best fit values of the fit parameters are calculated by maximising the merit function Q defined as:

$$Q(K_1, \dots, K_m) = \frac{1}{\sum_{j=1}^N (F_{calc}(h_j) - F_{exp}(h_j))^2} \quad (5.11)$$

To explain the procedure of surface charge calculation, as an example we choose a Silica-Silica interacting system in a 10 mM LiCl solution. Figure 5.1(b) shows that a good fit between experimental and theoretically calculated forces is obtained after optimising the pK pairs. During the fitting, we fit our forces between 1.5 nm to 15 nm. The minimum separation of 1.5 nm is chosen to minimize the influence of short range forces such as hydration forces that are not included in our DLVO model and the maximum value of 15 nm is based on the rapid decay of forces beyond that distance. It is important to note that the best fitting pairs are not

unique. Rather a whole range of combination of fit parameters provides similar fit quality and same surface charge. But, as explained by Zhao et al.[37], the resulting surface charge turns out to be insensitive to the assumed set of surface reactions, because the double layer contribution of the measured interaction force $F_{\text{edl}}(h)$ depends only indirectly via the charge density $\sigma_{\text{substrate}}$ on the fit parameters K_j .

To calculate the surface charge for an asymmetric system, for example silica-mica, we first need to calculate the surface charge for the silica AFM tip as explained above by performing a reference measurement on an equivalent silica substrate. Once the surface charge of the AFM tip is known, the surface charge on the other substrate can be determined following the same procedure. There can be two sources of the error in the charge calculation method, (i) an error in the tip radius estimation or (ii) an error in the zero calculation. We assume an error of ± 2 nm in the tip radius and ± 0.3 nm in the zero calculation and calculate the respective charge values. By taking the average and standard deviation of all these values, we get the error bar for each measured condition.

5.3. RESULTS

In this section, we first discuss the interaction force between the silica tip and the mica surface measured for five different salt solutions (Li^+ , Na^+ , Cs^+ , Ca^{2+} and Mg^{2+}) and variable pH (4, 6 and 9) for a fixed 10mM LiCl concentration. Subsequently, we calculate the surface charge of mica corresponding to each salt type and concentration using DLVO theory with charge regulation.

5.3.1. Effect of salt type and salt concentration on the surface charge of mica:

Figure 5.2 shows the total interaction force along with only the electrostatic contribution measured between the SiO_2 tip and mica in NaCl, CsCl and MgCl_2 salt solutions of variable concentration. Results for LiCl and CaCl_2 are shown in appendix Figure A1. All shown force curves are an average of 10-15 overlapping curves recorded on the same location. The black star lines are the calculated forces using DLVO theory corresponding to each condition.

In case of NaCl and LiCl (Figure 5.2 a, a' and Appendix A1), we observe that both the electrostatic and the total interaction force is repulsive for all salt concentrations. The qualitative trends in case of NaCl and LiCl follow standard electrostatic screening. The repulsive interaction length decreases from ~ 20 to ~ 7 nm as the electrolyte concentration increases from 10 to 100 mM. For CsCl, the total interaction force changes from repulsive to attractive for concentrations

higher than 50 mM, whereas the electrostatic interactions are still repulsive for all salt concentrations. This implies that for higher salt concentrations the van der Waals interaction dominates over the electrostatic force to make the total interaction force attractive.

Forces recorded in MgCl_2 and CaCl_2 solutions show different behavior. The total interaction force is attractive for salt concentrations higher than 1 mM. While, the electrostatic contribution to the total force is repulsive for concentrations lower than 10 mM, and attractive for concentrations higher than 30 mM (Figure 5.2 c'). A similar behavior is noted for CaCl_2 solutions as well (see Appendix A1). This indicates that for concentrations higher than 10 mM, the surface charge reverses for either of the two interacting surfaces. To explore in detail which of the two interacting surfaces contributes to the charge reversal, we calculate the surface charge individually for each surface as discussed below.

Figure 5.2 Tip-sample interaction force measurements using AM-AFM mode on mica in (a) NaCl (b) CsCl (c) MgCl₂ solutions with variable concentration. The black dotted curves in a, b, and c show the theoretically calculated force using DLVO theory a'), b'), and c') show only electrostatic part of the interaction force for the corresponding salt solutions. Note: Tip parameters used for Na⁺ ions: $R = 40 \pm 2$ nm, $k_c \sim 1.25$ N/m, $f_0 \sim 29.9$ kHz, $Q \sim 3.5$ and for Cs⁺ and Mg²⁺: $R = 20 \pm 2$ nm, $k_c \sim 0.463$ N/m, $f_0 \sim 17$ kHz, $Q \sim 2.4$. both the tips are treated similarly to achieve stable tip geometry as explained in section 5.2.4.1.

The surface charge of mica and the SiO_2 AFM tip is calculated by fitting the tip-sample interaction forces with theoretically calculated curves using DLVO theory as discussed in section 5.2.4.3. Surface forces between SiO_2 - SiO_2 surface are repulsive for salt types and concentrations. Appendix Figure A2 shows that the SiO_2 surface is negatively charged for all measured CsCl and MgCl_2 salt solutions.

Figure 5.3 shows that the surface charge of mica for monovalent ions Li^+ , Na^+ and Cs^+ is negative for all measured concentrations. Furthermore, the magnitude of the surface charge depends on salt concentration and salt (ion) type. Mica has the highest negative charge value in the case of LiCl and it is slightly lower in case of NaCl and even lower for CsCl . It should be noted that for CsCl the charge magnitude reaches close to zero for concentrations higher than 50 mM, but does not change its sign and it still remains negative. This charging behaviour clearly indicates different affinity of the ions towards the mica interface. It shows that Cs^+ has a strong affinity and hence could almost compensate for the negative surface charge of the mica interface.

Figure 5.3 Surface charge values calculated for mica surface by analyzing the tip-sample interaction forces with DLVO theory with charge regulation under five different salt solutions.

In the case of divalent ions, the charge behaviour of mica is different as seen in Fig. 5.3. With increasing salt concentration, the surface charge of mica increases, reaches zero and becomes positive for concentrations above 20 mM. The charge

values in case of Mg^{2+} is slightly higher than Ca^{2+} , but both still lie within the error bar. The larger error bar for the charge values at higher salt concentrations reflects that the method used for the charge calculation is less sensitive at these conditions. This is because the electrostatic forces in the force fitting range (1.5 to 15 nm) have a very small magnitude.

To further understand the effect of ion adsorption on the surface charge, we need to know the best fitted equilibrium constant values for the surface speciation reaction considered. Therefore, we obtain the merit function Q for mica for every salt condition, as explained in section 5.2.4.3 and Figure 5.1c. We superimpose the merit functions to obtain a unique pK_H , and pK_c pair for each salt type. Figure 5.4 shows the contour plots obtained for all the five salt solutions. For a given pK_H value ~ 4 , the pK_c values corresponding to maxima regions are ~ 1.8 for Li^+ and Na^+ and ~ 3 for Cs^+ ions. The higher pK_c values indicate higher adsorption of Cs^+ ions. This could explain the lower surface charge for Cs^+ ions due to the improved screening effect, as compared to Na^+ and Li^+ . Further, in the case of Ca^{2+} and Mg^{2+} ions, the pK_H and pK_c values corresponding to maxima regions are 6.8 ± 0.5 and 1.8 ± 0.1 , respectively. For both the divalent ions, the pK_c values are comparable (at any given pK_H), which is also reflected in the similar surface charge values for the two.

As the equilibrium constants (pK_H , pK_c) are independent of ionic strength variation, we expect to obtain one unique pK pair for all the superimposed conditions. But as we see in Figure 5.4, we get a broad maximum for almost all the investigated salt types. Thus we conclude that the actual surface chemistry is much more complex than a single pK pair, as considered in our surface complexation model. This is also suggested by some other studies [37, 40]. However, the surface charge values calculated using our complexation model are still accurate as discussed earlier in section 5.2.4.

Figure 5.4 Contour plots of the merit function Q in parameter space defined by pK_H , and pK_C for mica in (a) LiCl (b) NaCl (c) CsCl (d) $CaCl_2$ (e) $MgCl_2$ salt solutions. Note: unit of scale bar is nN^{-2} .

5.3.2. Effect pH on the surface force and surface charge measurements:

To explore the effect of pH on the mica surface charge, we record interaction forces between a SiO_2 tip and mica for three different pH (4, 6 and 9) solution at a fixed LiCl concentration (10 mM). The measured force and the corresponding theoretically calculated forces (black solid lines) are shown in Figure 5.4. We observe that the nature of these forces in both cases (SiO_2 - SiO_2 and SiO_2 -mica) is repulsive. The interaction force magnitude increases with increasing pH. Also, a slight bend is observed at pH 4 for mica in the total interaction force. At these short range distances the Van der Waals interaction forces start to dominate over the electrostatic forces.

Figure 5.5 Tip-sample interaction force measurements using AM-AFM mode in 10 mM LiCl with three different pH (4, 6 and 9) solutions for (a) silica-silica surfaces (b) silica-mica surfaces. The black dotted curves in a, and b show the theoretically calculated force using DLVO theory. Tip parameters: $R= 28 \pm 2$ nm, $k_c \sim 1.29$ N/m, $f_0 \sim 29.8$ kHz, $Q \sim 3.5$.

We also calculate the surface charge for both mica and silica surfaces using DLVO theory (Figure 5.6). Both the surfaces are negatively charged over the entire investigated pH range. The surface charge of both mica and silica increases with increasing pH and has a tendency to flatten between pH 6 and 9. The surface charge of mica increases significantly from ~ -0.03 to ~ -0.10 e/nm² between pH 4 and 6 and increases slightly from -0.10 to -0.12 e/nm² between pH 6 and 9. The similarities in the shape of the curves for mica and silica is quite striking and will be discussed further in section 5.4.2.

Figure 5.6: Surface charge values calculated for mica and silica surfaces by analyzing the tip-sample interaction forces with DLVO theory with charge regulation in three different pH (4, 6 and 9) solution with a fixed LiCl concentration (10 mM).

5.3.3. Atomic scale imaging:

To further understand the nature of specific ion adsorption of the five salt ions Li^+ , Na^+ , Cs^+ , Ca^{2+} , and Mg^{2+} on the mica surface we perform atomic scale imaging. Figure 5.7 shows atomically resolved topography images showing the crystal lattice of mica basal planes in different solutions. We begin to establish a reference by atomic scale imaging of mica in pure water. We obtain the hexagonal crystal lattice structure of mica. The crystal lattice parameters (a , $b = 0.51, 0.91$ nm) obtained from the AFM images, are consistent with the reported literature values [50, 51]. Next, the effect of different type of salts solutions on mica surface is probed. In presence of NaCl solution, no change is observed, i.e. we observe the similar hexagonal pattern as observed in water (Figure 5.7 a). Atomic scale images of mica in CsCl (1mM) solution display some domain formations on the basal plane of mica. This is attributed to the ion adsorption on the surface. The behaviour indicates that Cs^+ ions have more affinity for mica compared to Na^+ ions. This is also in line with our previous observations (Figure 5.3), where the surface charge of mica decreases more in case of Cs^+ as compared to Na^+ for similar concentrations.

Figure 5.7: Amplitude modulation topography images of mica showing (a) mica crystal lattice in presence of pure water and Na⁺ ions (b) adsorption of Cs⁺ ions (c) adsorption of Ca²⁺ ions with rectangular symmetry. Insets: phase images corresponding to each height image. Height profiles in a (red) and b (blue) directions in presence of (d) pure water and Na⁺ (e) Cs⁺, and (f) Ca²⁺ ions. The lattice parameters (0.51 and 0.91 nm) are obtained in presence of pure water and Na⁺ ions.

Further, in a CaCl₂ solution a stark difference in the surface pattern is observed. Rather than a hexagonal pattern we see the rectangular symmetry in 100 mM CaCl₂ solution, which covers the complete mica surface. This is caused by (presumably hydrated) adsorbed Ca²⁺ ions. The complete coverage of mica explains the charge reversal at the higher CaCl₂ concentrations, as observed in Figure 5.3.

5.4. DISCUSSION

The present work emphasizes two aspects of mica surface charging- i) the effect of salt type and concentration and ii) the effect of pH. By making use of charge regulation boundary conditions in the DLVO theory framework, we can accurately calculate the surface charge of mica in different salt types using the surface speciation reactions.

5.4.1. Ion adsorption and charge reversal

Figure 5.3 shows the surface charge of mica in five (Li^+ , Na^+ , Cs^+ , Ca^{2+} , and Mg^{2+}) salt solutions as calculated based on the surface speciation reactions with optimized pK values for individual solid-liquid interface, i.e. extrapolated to infinite tip-sample separation. It is observed that the surface charge of mica decreases with increasing monovalent salt concentration. As we go to a bigger monovalent cation radius ($\text{Li}^+ < \text{Na}^+ < \text{Cs}^+$), the decrease in surface charge is more pronounced. From the surface charge values and extracted pK values of cation adsorptions, we observe that the ion affinity order for mica is $\text{Li}^+ < \text{Na}^+ < \text{Cs}^+ < \text{Ca}^{2+} \approx \text{Mg}^{2+}$. For monovalent ions, this order is consistent with the idea that larger cations are more polarizable and hence experience a stronger affinity due to a somewhat stronger dispersion attraction towards the surface [52]. Simultaneously, the hydration shell of larger ions is somewhat less strongly bound. This may lead to weaker repulsion between the hydrated ion and the hydrated mica surface. The Li^+ ion is more strongly hydrated and smaller than Cs^+ ion. Therefore, it has much less affinity towards mica compared to Cs^+ ion.

The divalent ions adsorb strongly to the mica surface. Both Ca^{2+} and Mg^{2+} have a greater capacity to adsorb in both the tetrahedral and octahedral interstitial sites of the mica crystal lattice [31]. This leads to the charge reversal of the mica surface as observed in Fig 5.3. The monovalent ions, having an equivalent diameter to the hexagonal layer sites of the mica basal plane, are weakly adsorbed. Therefore, they are removed or washout relatively easily. This is also evident from our atomic scale imaging of mica in presence of Na^+ , Cs^+ and Ca^{2+} ions (Fig. 5.7). For Na^+ ions, the surface pattern of mica does not change, while Cs^+ ions adsorb on mica surface in a hexagonal pattern. In the case of Ca^{2+} , the hexagonal pattern changes to a rectangular pattern, due to Ca^{2+} adsorption in the tetrahedral and octahedral cavities. This observation strongly agrees with the previous studies of mica charge reversal with divalent ions [16, 26, 27].

5.4.2. Effect of pH

The surface charge on mica arises mainly due to the dissociation of potassium ions. Hence, it should remain largely independent of the pH of the solution. However, our results show that the surface charge of mica significantly changes when the pH is increased from 4 to 6. While it does not change much with further increasing pH.

A similar pH dependence is reported in some other studies of surface potentials of mica, using techniques like streaming potential [28, 53], surface force apparatus [54] and colloidal probe AFM [33, 34, 36, 55]. The reported surface potential values are scattered in the range of a few millivolts (± 20 mV) for respective pH conditions as summarized in ref. [33]. These differences may arise due to the different experimental method, type of mica, and the storage conditions [56-58].

The mechanisms responsible for charge generation at mica are quite different from those for silica, but on the basis of results shown in Figure 5.6, the two surfaces show similar charging behaviour in the pH range of 4 to 9. This is unexpected, as mica is expected to have a constant and pH independent charge due to K^+ dissociation. Silica, however, should have a pH dependent charge due to ionisable silanol groups. Nishimura et al. [31] and Scales et al. [28] observed similar behaviour. They speculated that this behaviour originates from the formation of ionizable silanol groups as a result of the hydrolysis of the Si-O-Si at the mica basal plane. However, this particular interpretation has not been confirmed experimentally yet.

5.5. CONCLUSIONS

In this chapter, we studied the charging behaviour of mica in presence of alkali and alkaline earth metal ions. We observe a stark difference between the monovalent and divalent ions. The surface charge of mica is negative in presence of monovalent ions, while it becomes positive in the presence of high concentrations of divalent ions. It is observed that the effect of pH on the surface charge of mica is significant in the range of 4 to 6. However, charge changes slightly with further increasing the pH from 6 to 9.

On further inspection with atomic scale imaging, we resolve the crystal structure of the mica lattice. We observe hexagonal crystal lattice structures in pure water and NaCl solutions, while domain formations are observed in presence of CsCl solutions. However, Ca^{2+} ions adsorb strongly on mica, covering its surface completely and changing the surface pattern to a rectangular symmetry.

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5.7. APPENDIX

Figure 5.A1. Tip-sample interaction force measurements using AM-AFM mode on mica basal planes under (a) LiCl (b) CaCl₂ salt solutions with variable concentration. The black dotted curves in a, and b show the theoretically calculated force using DLVO theory. a'), and b') show only electrostatic part of interaction force for the corresponding salt solutions.

Figure 5.A2. Tip-sample interaction force measurements using AM-AFM mode on silicon dioxide surface under (a) CsCl (b) MgCl₂ salt solutions with variable concentration. (c) Corresponding surface charge values calculated by analyzing the tip-sample interaction forces with DLVO theory with charge regulation. Tip parameter: $R = 20 \pm 2$ nm, $k_c \sim 0.463$ N/m, $f_0 \sim 17$ kHz, $Q \sim 2.4$.

Figure 5.A3. SEM image of the AFM tip used tip-sample interaction force measurements for (a) Li⁺, Na⁺ (b) Cs⁺, Mg²⁺ ions and (c) for pH measurements.

SALT DEPENDENT STABILITY OF STEARIC ACID LANGMUIR-BLODGETT FILMS EXPOSED TO AQUEOUS ELECTROLYTES

ABSTRACT

In this chapter, we study the adsorption/desorption of model oil on the model rock surface. We studied the stability of Langmuir-Blodgett (LB) films of stearic acid (representative of polar organic components of oil) deposited on silica (model rock) in presence of Ca^{2+} and/or Na^+ ions. The influences of Ca^{2+} and Na^+ ions are compared by varying their concentrations, both in the subphase before the LB transfer, and in the droplets to which the dried LB layers are exposed. Ca^{2+} ions in the subphase are found to enhance the stability, leading to contact angles up to 100 degrees, as compared to less than 5 degrees for Na^+ . Consistent with the macroscopic wettability, AFM images show almost intact films with few holes exposing bare substrate when prepared in presence of Ca^{2+} while subphases containing Na^+ result in large areas of bare substrate after exposure to aqueous drops. The observations on varying the composition of the droplets corroborate the stabilizing effect of Ca^{2+} . We attribute these findings to the cation-bridging ability of Ca^{2+} ions, which can bind the negatively charged stearate groups to the negatively charged substrates. We discuss the relevance of our findings in the context of enhanced oil recovery.

6.1. INTRODUCTION

The interaction of organic matter with solid surfaces in an ambient aqueous environment plays a key role in many processes and phenomena in nature, science, and technology including ground water-soil interaction, water purification, lubrication, corrosion inhibition, colloidal stability, Langmuir Blodgett (LB) films, (membrane) fouling, and enhanced oil recovery [1-5]. Two processes are crucial: the binding of the amphiphilic molecules to the substrate, and their assembly into an interfacial layer.

Since most solid surfaces, including in particular mineral and glass surfaces, assume a finite surface charge in water, usually electrostatic effects contribute strongly to the inter-actions with polar and/or charged organic molecules. Divalent ions as well as higher multi-valent ions are known to be particularly efficient ‘glues’ that stick organic molecules to solid surfaces [5, 6]. For instance, biophysicists make extensive use of this mechanism to immobilize DNA and proteins onto solid surfaces, for example to enable their visualization by Atomic Force Microscopy [7]. Monovalent ions, in contrast, are unable to provide such strong immobilization.

Additionally, organic films can also undergo rearrangements in three dimensions when they are exposed to aqueous solutions of multivalent ions. It has been reported that mobile counter-ions [8-10] embedded into layers of fatty acids can trigger structural rearrangements of molecules. A particularly dramatic example involves a so called ‘flip-over’, in which the molecules form a bilayer which exposes the polar head groups to the substrate and to the aqueous phase [11, 12].

Both (un)binding events and rearrangements can have a tremendous influence on the chemical affinity of the surface that is exposed to the aqueous liquid: the difference between hydrophilic and charged (for bare substrate), and hydrophobic (for coated substrates) gives rise to a completely different water wettability. Also the interactions between two such surfaces immersed in water change: from DLVO-type for the bare surfaces, to long-range attractive in case of some hydrophobized surfaces [11, 13-16]. In the present study we focus on the question, how the wettability of an adsorbed organic layer can be changed via exposure to aqueous solutions with different overall salinity and ionic compositions. While this is of interest for many applications (as indicated), the present paper is inspired in particular by recent observations in the field of enhanced oil recovery (EOR).

In traditional (i.e. secondary) oil recovery, highly saline seawater is pumped into the ground to expel oil from pores in the rock [5, 17]. However this process is not very efficient. Evidence has been growing that reducing the overall salinity (and in particular the concentration of divalent ions) of the injected water can substantially increase the oil recovery rate [5, 17]. A possible explanation of this observation assumes that over geological time scales, the intrinsically hydrophilic rock was turned into hydrophobic via the adsorption of polar components from the crude oil. In this picture, the hydrophobic layers become bound (at least partly) via electrostatic interactions. In particular multivalent ions like Ca^{2+} and Mg^{2+} are supposed to play a role, since these can bind acid groups from the oil to negatively charged sites on the surface via an ion bridging mechanism.

The effectiveness of using low salinity water then lies in weakening the bonding between the hydrophobic layers and the rock. As a consequence, the organic layers can be (partially) released. This renders the rock more hydrophilic, and facilitates the expulsion of oil from the narrow pores via a reduction in the required Laplace pressure. Ultimately this would explain the increased efficiency of the oil recovery process. Since the characteristic flow rates in oil recovery are of order one foot per day, corresponding to approximately $1\text{ }\mu\text{m/s}$, the decomposition of the hydrophobic layers should take place on much shorter time scales that are much more accessible in the laboratory.

The purpose of the present study is to develop a model system and to test various aspects of the scenario described above. In particular, we want to correlate macroscopic variations of the wettability with the microscopic decomposition or rearrangement of the hydrophobic layers and elucidate the relevance of divalent ions in this process. To this end, we choose one of the best characterized model systems of thin organic layers, namely monolayers of stearic acid (SA) that we deposit onto solid surfaces using the Langmuir Blodgett (LB) technique. While the details of this deposition are of course very different compared to the gradual adsorption from crude oil, LB transfer offers unique control of the physicochemical parameters that govern the stability of the resulting film.

Monolayers of SA and other fatty acids have been investigated in great detail in the past, both as Langmuir layers at the air-water interface [18-20] and as LB films deposited onto solid surfaces [12, 21] dating back all the way to the original work of Blodgett [22] and Langmuir [23]. It is well known that both the physical and chemical properties of such layers depend very much on pH and on the ion content

of an adjacent aqueous phase [24, 25]. A summary of early work based to an important extent on surface potential measurements has been summarized by Goddard [26]. At low pH, the carboxylic acid groups and solid surfaces like silica remain protonated and the affinity to ions (and interfaces) is weak. In contrast, at high pH, they are deprotonated and interact strongly with the ions [8, 25, 27, 28]. This affects amongst other things the transferability of Langmuir monolayers in the LB process [10, 29] and the stability of the layers [25]. More recently, Graber et al. [30] studied the consequences of these ideas for the macroscopic water-repellency of soils hydrophobized by fatty acids upon exposure to water of variable pH and salt contents. They demonstrated that such soils indeed resist the penetration of water drops more efficiently upon increasing the pH and calcium concentration. The mechanisms invoked to explain these observations are very similar to the proposed mechanism of enhanced oil recovery by low salinity water flooding. All these previous observations suggest that SA is a suitable model compound for our purpose.

In this work, we study the influence of Ca^{2+} and Na^+ ions on the stability and wettability of stearic acid monolayers. The layers are deposited onto oxidized silicon wafers mimicking silica surfaces using LB transfer. Subsequently we expose the surfaces to drops of variable salinity. Occasionally, mica is used as an alternative substrate representing clays. We investigate the effect of ions on the film stability in two complementary ways. First, we vary the ion contents of the subphase during LB transfer. Second, we vary the ion contents of the aqueous phase to which the LB films are exposed after the transfer. In both cases we focus on Na^+ and Ca^{2+} ions representing the prevalent mono- and divalent cations of sea water, respectively. Macroscopic contact angle goniometry, imaging ellipsometry, and Atomic Force Microscopy (AFM) consistently show that Ca^{2+} has a pronounced stabilizing effect on the SA films exposed to water. Microscopic AFM images demonstrate the partial decomposition of the LB films upon exposure to water. In the absence of multilayer formation, the contact angle of sessile drops on partially decomposed LB films is found to agree with the expectations based on the AFM data using Cassie's equation.

6.2. MATERIALS AND METHODS

6.2.1. Chemicals and solutions

All solvents and reagents are obtained from Sigma-Aldrich and used without further purification. Solution of stearic acid (SA) (octadecanoic acid, $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$, grade 1, approx. 99%) is prepared in chloroform (CHCl_3 , ACS reagent) at a concentration of 1 mg/mL. Aqueous subphases for the LB-transfer are prepared by dissolving sodium chloride (NaCl) and/or calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) (both ACS reagent grade) in deionized water (Synergy UV, Millipore, resistance $18.2 \text{ M}\Omega \cdot \text{cm}$). Three different types of subphases are used containing 0.5 M NaCl , 0.01 M CaCl_2 , and a mixture of 0.5 M NaCl , and 0.01 M CaCl_2 , respectively. These values of concentrations are chosen to mimic typical concentrations in sea water as it is used in secondary oil recovery. In all cases, the pH of these subphases is adjusted to 9.5 ± 0.1 with 0.1 M standard solution of NaOH , to ensure that the carboxylic acid groups of stearic acid are largely deprotonated[24] and to prevent substantial dissolution of stearate molecules in the bulk water, which occurs for $\text{pH} > 10$ [28].

6.2.2. Substrate preparation and LB film deposition:

As substrates, we use commercial silicon (100) wafers with a thermally grown oxide layer of $\sim 35 \text{ nm}$ thickness. The wafers are cut into pieces of $1 \times 5 \text{ cm}^2$. The substrates are cleaned by the following procedure: firstly, samples were extensively rinsed with successively Millipore water, iso-propanol, and ethanol, then gently dried with N_2 gas; secondly, wafers were exposed to ambient air plasma (PDC-32G-2, Harrick plasma) for 30-40 min. This procedure assures good hydrophilicity of the substrate (water contact angle: $\theta < 5^\circ$). AFM is used to verify the smoothness of the substrate. The typical RMS (root means square) roughness is found to be $< 0.2 \text{ nm}$.

LB film deposition is performed using a computer-controlled trough from Nima Technology. Prior to the experiment, the trough is rigorously cleaned with pure water, ethanol and chloroform. The system is assumed to be clean if the surface pressure of the bare subphase (*i.e.* prior to spreading the SA solution) varies by no more than 0.1 mN/m upon moving the barriers back and forth. Subsequently, a drop (50 μL) of the SA solution in chloroform is deposited on the subphase. Around 30 min are allowed for the solvent to evaporate and for the SA layer to spread before initiating the LB transfer. All LB transfers are performed at a constant surface pressure of 30 mN/m, just above the kink in the pressure-area

isotherm that indicates the apparition of a compact solidified layer (see Figure 6.1). The pulling speed is 2 mm/min. Under these conditions, the transfer ratio for the monolayers is unity implying that the substrates become completely covered by the monolayers. Qualitatively similar results were obtained in a few test measurements at a somewhat higher transfer pressure (45 mN/m).

In the following, we denote the LB layers transferred with the three different types of subphases as SA-Na, SA-Ca, and SA-Ca+Na films, respectively, to indicate the type of cation present during the transfer. Before further characterization using contact angle goniometry, ellipsometry and AFM, the samples are stored in a glove box under a continuous flow of dry nitrogen for 20 hours. All experiments are performed within 2-3 days of preparation.

6.2.3. Contact angle measurements:

An optical contact angle goniometer with automated data analysis software (OCA 20L; Dataphysics) is used to assess the macroscopic wettability and to determine static water contact angles on the samples with measurement accuracy of $\pm 0.5^\circ$. Droplets of 5–10 μL of pure water or saline solutions are placed on the surfaces in ambient environment. Goniometry measurements are performed after 20 hours of sample preparation at least at 3-4 different locations on each sample. For any given sample the contact angle values are reproducible within $\pm 3^\circ$.

6.2.4. Ellipsometry imaging:

The morphology of the transferred monolayers is analyzed after drying using an imaging ellipsometer at a wavelength of 658 nm (EP3 Nanoscope, Accurion). Absolute thickness maps of the material are obtained by measuring the ellipsometric angles ψ and Δ as a function of the position on the substrate, and using the (complex) refractive indices n_i of both layer and substrate along with the Fresnel equations to translate (ψ, Δ) into a thickness d_i [31]. Fitting ψ and Δ for the bare substrate with a two-layer model (Si: $d \rightarrow \infty$, $n_{\text{Si}} = 3.96 - 0.02i$ and SiO_2 : $n_{\text{SiO}_2} = 1.5$) yields the exact value of the oxide thickness (with precision of 0.1 nm). The thickness of the transferred SA layers is then calculated using a three-layer model using the previously determined oxide thickness as a fixed input and assuming a refractive index of $n_{\text{SA}} = 1.43$ for SA.

6.2.5. AFM imaging:

The topography of treated and untreated SA layers on the nanometer scale is obtained under ambient conditions (unless otherwise noted) with a commercial

atomic force microscope (Dimension Icon AFM with Nanoscope V controller, Bruker AXS). All images are collected in tapping mode with ScanAsyst Air and ScanAsyst fluid silicon probes purchased from Bruker with sharp tips. Nominal cantilever and tip properties are as follows: tip radius <10 nm; tip height, $0.5 - 0.75$ μm ; cantilever spring constant 0.4 N/m. The AFM is operated under “gentle” conditions with small cantilever oscillation amplitudes (<10 nm) and weak damping (i.e. high amplitude setpoint values) to protect both tip and sample against damage. Around 3-4 topography and phase images are recorded at representative neighbouring locations on each surface. Image analysis is performed using Bruker’s standard Nanoscope Analysis 1.4 package.

6.2.6. Monolayer characterization:

Initial images of the SA layers after preparation and drying show a flat topography with both AFM and ellipsometry in ambient air under all preparation conditions. Inset Figure 6.1b shows a representative AFM image with a typical roughness of approximately 0.15 nm rms. The Figure 6.1c and 1d show the typical ellipsometry thickness map and profile. The observed average thickness of ~ 2 nm is consistent with the length of SA molecules and thus with the expected molecular structure as sketched in the inset Figure 6.1a’ [32]. Yet, the topography, thickness and roughness of these monolayers highly depend on details of sample cleaning, preparation and drying protocols. For the non-optimized conditions, the monolayer could also have some holes in it or dirt sticks to it just after the preparation (See Appendix Figure 6.A1). We have discarded all such monolayers from further analysis in the present study.

Figure 6.1 (a) Surface pressure versus area (π -A) isotherm of stearic acid with 0.5 M NaCl aqueous subphase. (a') Schematic illustration of deposited monolayer (b) AFM image (c) Ellipsometry thickness map and (d) corresponding profile of a SA-Na monolayer.

6.3. RESULTS

To study the stability of the SA monolayers, we expose all layers to drops of an aqueous “exposure” solution with variable concentrations of NaCl and CaCl_2 at pH ~ 6 . Drops with a volume of 10 μL are deposited onto the substrates and left there for a period of 10 min. During this period we continuously monitor the contact angle. Subsequently the drops are removed from the substrate and the samples are blown dry using dry nitrogen. AFM and ellipsometry images (not shown here) are recorded both in the center and at the edge of the region previously covered by the drops. We discuss first the influence of the composition of the subphase on the layer stability upon exposure to pure water and subsequently, the effect of various salts added to the drop destabilizing the film.

6.3.1. Influence of the subphase composition

The contact angle θ of the (pure) water drop is found to decrease from an initial value θ_0 to a significantly smaller equilibrium value θ_e within a few seconds. The latter value is stable for several minutes until it begins to decrease slowly due to evaporation. This qualitative behavior is similar for all samples. The absolute values of θ_0 are difficult to determine due to the limited time resolution of the data

acquisition and due to inertial effects that are known to affect the drop dynamics within the first fraction of a second of contact [33]. For the present study, however, the quantity of interest is the limiting contact angle θ_e at long time scales.

As shown in Figure 6.2, θ_e depends very strongly on the composition of the subphase and decreases from approximately 80° for SA-Ca layers to $\sim 30^\circ$ for SA-Ca+Na layers to $<5^\circ$ for SA-Na layers. This very strong dependence of the contact angle on the counter ion species is the key observation of the present study. Since the contact angles of water on stable self-assembled monolayers such as alkylsilane layers on glass and alkylthiol layers on Au with a comparable length of the alkyl chain are known to be close to 110° [34], these results clearly show that the LB films of SA in our experiments do not remain intact upon exposure to water but decompose at least partially. The large variation of θ_e for the three different subphases suggests that the degree of decomposition varies substantially depending on the specific cation present in the subphase: SA-Ca layers seem to remain largely intact, SA-Na layers seem to be largely removed, and SA-Ca+Na layers show an intermediate behavior.

Qualitatively similar results were obtained for a large number of samples, also including mica substrates instead of oxidized silicon wafers. The trends regarding the stabilizing effect of Ca^{2+} in the subphase on θ_e were consistently found (see Fig 2a). Yet, the absolute values of θ_e vary substantially depending on details of the sample cleaning, preparation, and drying protocol. Occasionally, θ_e could be as low as 30° even for SA-Ca monolayers (see appendix Figure 6.A2).

Figure 6.2 Macroscopic wettability of three monolayers: SA-Ca (green), SA-Ca+Na (blue), and SA-Na (red). (a) Time evolution of the contact angle and (b) snapshots of drops in the final state showing the equilibrium contact angles (θ_e). Note: the axis break in (a) showing the final equilibrium angle.

These wettability changes could originate from different processes at the microscopic level. For example they could be due to desorption of the SA molecules upon exposure of the layer to the aqueous drop. But alternatively they might also result from structural rearrangements within the layer, such that hydrophilic headgroups become exposed to the aqueous liquid. To distinguish between the different possible scenarios, we performed additional characterizations aimed at the surface morphology. Images of the layers (after removing the drop and drying the samples) obtained with AFM are shown in Figure 6.3.

For the SA-Ca and SA-Ca+Na samples, AFM images recorded in the central area of the original drop look similar. AFM imaging reveals the details of the decomposition process: the monolayers partially desorb from the substrate, leaving behind areas covered by the original SA film (bright in Figure 6.3a' and b') and holes (dark) exposing what seems to be the bare substrate. The phase image (Figure 6.4a) also reveals a clear contrast between the high and the low level, which discriminate between different types of materials, supporting the interpretation that the lower level is indeed the bare substrate. From histograms of

the height distribution (right part of Figure 6.3 a', b', and c') we extract the area fraction and the thickness of the residual film. The latter is approximately 2 nm, in agreement with the all-*trans* length of the SA molecules. Since the missing SA molecules are not found at the surface and they are insoluble in water at pH=6, we think that they migrated to the air-water interface and were washed away upon removal of the drop.

For the SA-Na samples, AFM images confirm the results of the ellipsometry measurements. Within the previous contact area of the drop, the samples are perfectly flat. As we image the edge of the contact area, a clear topographic step is found with a height of ~1.5 nm, as in the case of the holes in the layers on the SA-Ca and SA-Ca+Na samples. Again, the topographic step is accompanied by a jump in the phase images, confirming the idea of different material compositions.

Figure 6.3 AFM topography images of SA-Ca (a'), SA-Ca+Na (b') and SA-Na monolayer (c') after exposure to water. Inset images are height profiles corresponding to the white scan line (abscissa in μm ; ordinate in nm). Histograms

in a', b', and c' show the frequency and cumulative bearing area of the height levels.

These observations unequivocally demonstrate that our LB layers of SA partially decompose upon exposure to water. The somewhat reduced height (as compared to the all-*trans* length of the SA molecules) of the steps in the AFM images suggests that the molecules in the residual layer are either slightly tilted or that the 'bare' substrate in the holes is in fact still covered by a sub-monolayer of hydrocarbon chains oriented parallel to the substrate. The present data do not allow drawing a definite conclusion in this respect. Notwithstanding this uncertainty, all data clearly and consistently demonstrate that Ca^{2+} ions in the subphase have strong stabilizing effect on the SA layers, whereas Na^+ ions do not.

Figure 6.4 AFM height and phase images along with section profiles for (a) SA-Ca monolayer exposed to water and (b) SA-Ca+Na monolayer exposed to 0.01 M CaCl_2 solution. The different contrasts correspond to bare substrate, monolayer and multilayer.

6.3.2. Effects of salinity of exposure water on monolayer stability:

Having demonstrated the stabilizing effect of Ca^{2+} ions in the subphase during preparation of the LB layers, we now address the effects of ions in the exposure

solution. We focus again on Na^+ and Ca^{2+} ions. In addition to the pure water discussed in the previous section, 0.01 M and 0.1 M NaCl, as well as CaCl_2 are used as the exposure solutions.

Figure 6.5a shows the time evolution of the contact angle for the five different exposure solutions on SA-Ca monolayers. The data for pure water are the same as in Figure 6.2a. The other exposure solutions display the same qualitative behavior, yet it is clear that θ_e is larger for higher salt concentrations. The highest value of $\theta_e \sim 95^\circ$ is obtained for the 0.1 M CaCl_2 solution. The contact angle after 10 min (not shown) is only slightly smaller than after 30 s, like in Figure 6.2. Similar results are found for samples prepared with the two other subphase compositions. As summarized in Figure 6.5b, more ions in the exposure solution lead to larger contact angles on the SA layers in all cases. Again, Ca^{2+} ions are - by and large - more efficient than Na^+ ions at stabilizing the LB films. Note, however, that the overall effect of ions in the exposure solution is only of order 10° and thus much less pronounced than for ions in the subphase.

Figure 6.5 (a) Contact angle vs. time on SA-Ca monolayer for various compositions of exposure solution. (b) Equilibrium contact angles for all compositions of subphase and exposure solution (bars: experimental results from contact angle goniometry; symbols: values extracted from AFM images in combination with Cassie equation (see text for details)).

In Figure 6.6 we show an overview of AFM micrographs obtained for all combinations of the composition of subphase and exposure solution investigated in this study. Desorbed area fractions are calculated from histograms of the height

distribution as in Figure 6.3. Comparing the different subphases, it is clear that LB films prepared on the subphase containing CaCl_2 are the most stable. We find that for an exposure solution of 0.1 M CaCl_2 , as little as $A_{des} = 6\%$ of the SA-Ca film decomposes. This percentage increases for exposure solutions containing less Ca^{2+} or containing Na^+ . The depth of the holes remains close to 2 nm, with only very small area fractions of thicker films in the case of NaCl exposure solutions. The maximum desorbed area amounts to 38%, indicating a fairly good stability of the LB film upon contact with water. The value of 38% is reproducible within $\pm 3\%$ for at least 5 consecutive experiments.

For subphases containing 0.5 M NaCl (with or without additionally 0.01 M CaCl_2), a dramatically different picture is found. For exposure solutions containing NaCl, the LB films are decomposed more or less completely, indicated by desorption ratios A_{des} close to 100%. For exposure solutions containing CaCl_2 we also find large areas of bare substrate but still a finite amount covered by a layer. Interestingly, in this case the thickness of the residual layers largely exceeds the initial 2 nm. We attribute this to the formation of double or multilayers. Substrates with bare areas, monolayers and multilayers were already shown in Figure 6.4b for one of these samples. The chemical nature and in particular the termination of the multilayers are not clear. Yet, we suspect that the multilayers contain calcium stearate and that they expose the hydrophilic head groups to the aqueous phase (see discussion below). This compound is known to be a particularly stable, which was – amongst others – found to precipitate easily at oil-water interfaces if dissolved in oil [8]. (Few images also display very high round features that look very different from the decomposed areas of the film. We identify these features as salt crystallites that appear as we blow off the residual drop and dry the sample).

To examine the consistency between our macroscopic contact angle measurements and the microscopic characterizations using AFM, we calculate theoretical contact angles, by combining the area fraction obtained from the AFM images with Cassie's equation for the contact angle of heterogeneous surfaces $\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2$ (f_i , θ_i : area fraction and contact angle of phase i ; i =LB film, substrate.) Using a Young angle of $\theta_1 = 100^\circ$ for the LB film and $\theta_2 = 5^\circ$ for the bare substrate and taking $f_1 = 1 - A_{des}$ and $f_2 = A_{des}$ from Figure 6.6, we find the contact angles indicated by the round symbols shown in Figure 6.5b. (Here, the values of θ_1 and θ_2 are typical values for the contact angle of compact layers of self-assembled monolayers and cleaned silica surfaces, respectively [35, 36]. Note

that the absolute values are not very critical and may be varied by 5° without substantial impact on the agreement with the experimental data.) Despite the rather wide range of A_{des} covered for the various conditions, the values for θ calculated from the AFM images agree within 10% with the macroscopic measurements. Note that the success of the Cassie equation is not trivial. It implies in the first place that the variations observed in the center of the solid-liquid interfacial area are representative of the local (de)composition at the contact line, *i.e.* at the location where the contact angle is determined. (This aspect has been discussed intensively in recent years following up a critical note by Gao and McCarthy) [37-39]. Second, the agreement suggests that the advancing contact angle that we measure under the conditions of our slowly spreading drops is indeed close to the equilibrium angle, as determined by Cassie's equation. This is again not trivial since the closeness of the Cassie angle to the advancing and receding angle depends on the nature of the defects with respect to the majority species on the surface as pointed out by Priest et al. [40].

The SA-Ca+Na and SA-Na films exposed to CaCl_2 solutions (symbols in parenthesis) deviate from this general trend. These, however, are the samples shown in the bottom right quadrant of Figure 6.6, which display the formation of multilayers after exposure to the electrolyte solution. Their experimental contact angle is much smaller than the one predicted by Cassie's law under the assumption $\theta_1=100^\circ$. This apparent discrepancy disappears however, if we assume that the multilayers are not terminated by the hydrophobic tail but rather expose the hydrophilic carboxylic acid group towards the solution, leading to a much smaller value of θ_1 (see phase contrast corresponding to multilayer formation in Figure 6.4b). This behavior is consistent with observations in other experiments with decomposing surfactant layers [13].

The behavior of the SA-Ca+Na films in pure water cannot be explained in this manner. The thickness of the residual film is close to 2 nm, as concluded from the depth of the holes in film. The desorption ratio suggests that approximately one third of the layer should still be present in its original form with a hydrophobic termination exposed to the water. It leads to a contact angle of approximately 50° by calculating with Cassie's equation, exceeding the experimental value by $\sim 20^\circ$. We do not have any explanation for this deviation, which has been found to persist over several independent measurements spread over a period of several months.

Figure 6.6 AFM viewgraphs of LB films prepared with all combinations of subphases after exposure to water and liquid compositions. Image size: $5 \times 5 \mu\text{m}^2$. Desorption area A_{des} indicates area fraction of exposed bare substrate. Insets show representative cross sections. Vertical scale: in nm. Horizontal scale: $5 \mu\text{m}$.

6.4. DISCUSSION

Overall, our experiments clearly show that the presence of Ca^{2+} ions (whether from the subphase or from the exposure solution) strongly stabilizes LB films of stearic acid deposited on silica surfaces [24, 41-46]. To discuss the stabilization mechanism, we consider the preparation of the LB film and its subsequent decomposition upon exposure to aqueous liquid separately. Figure 6.7 sketches the relevant processes during adsorption-desorption of the monolayer. The Langmuir film initially residing on the subphase consists of a close-packed layer of stearate molecules (Figure 6.7a). The structure and stability of this Langmuir monolayer are known to change in different ways, depending on the presence of mono- and divalent ions, as well as the pH in the subphase. At sufficiently high pH, monovalent cations in the subphase cause the monolayer to become less ordered. Divalent cations (at sufficiently high pH) have the opposite effect: they effectively compress the monolayer into a tightly packed untilted structure, leading to enhanced crystalline order[47], changes in viscoelastic response[48], and make it more easily transferable to solid substrates [29].

In this work, the subphase pH is chosen high enough to ensure that the carboxylic acid groups are largely deprotonated. The ionization fraction of the molecules at the interface (χ) has been related to the pH of the subphase by the Gouy-Chapman equation[24, 49]

$$\text{pH}_{\text{subphase}} = \text{pK}_a + \log\left(\frac{\chi}{1-\chi}\right) + \frac{0.87}{z} \sinh^{-1}\left(\frac{136\chi}{A\sqrt{c}}\right),$$

where z is the valency of the ions, A is the molecular area ($\text{\AA}^2$) and c is the concentration of the counterions (moles/L). Inserting $\text{pK}_a = 5.6$ [50] and using the aqueous compositions in our experiments, we obtain a deprotonation ratio of 86.4% for 0.01 M CaCl_2 and 82.3% for 0.5 M NaCl solutions at pH 9.5. According to literature, divalent cations (D^{2+}) can form different complexes with ionized stearic acid ($\text{R}^- = \text{CH}_3(\text{CH}_2)_{16} \text{COO}^-$): positive RD^+ , neutral R_2D or both of these complexes simultaneously [51-54]. The presence of both R^- and RD^+ can make the Langmuir layer electrically neutral at high pH, as has been found for Ca^{2+} both theoretically [51, 53] and experimentally [55, 56]. In contrast, monovalent cations only form neutral RM complexes and therefore the monolayer remains mainly negatively charged because of dissociated R^- [51].

When we transfer these neutral or negatively charged layers to our silica substrates, they come in contact with a negatively charged surface (Figure 6.7b) [43, 44, 57].

Under these conditions, positively charged SACa^+ (RD^+) moieties can associate with negatively charged sites on the silica surface to form strongly bound neutral complexes. Neutral SA_2Ca (R_2D) can be stabilized by lateral interactions (van der Waals and hydrophobic forces) between alkyl chains which can also lead to a strongly bound LB film [58]. In the contrasting case of sublayers containing only Na^+ cations, a partially dissociated Langmuir layer, carrying some negative charges, is deposited onto a strongly negatively charged solid surface. This precludes the collective self-assembly of cation-stabilized complexes between stearate molecules and deprotonated silanol (SiO^-) groups. Moreover, charge neutrality will require the incorporation of even more cations between the film and the substrates to compensate for the excess negative charges. The combination of both aspects leads to an LB film which can only be weakly bound to the substrate and stabilized by only lateral interactions within the film presumably.

Figure 6.7 Schematic illustration of monolayer adsorption-desorption process (a) formation of salt complexes with dissociated fatty acid at air–water interface (b) negatively charged substrate dipped under subphase (c) desorption of monolayer after water exposure.

The behavior of the SA-Ca+Na films with the mixed subphases is more complex. The partial stability of the layers upon exposure to pure water suggests that some adsorbed Ca^{2+} is present and able to stabilize the LB films. However, this stabilization is clearly not as strong as in the case of a pure 0.01 M CaCl_2 subphase. The competition between the stronger binding Ca^{2+} ions and the 50 times more concentrated Na^+ ions in the subphase leads to a mixed association of R^- and SiO^- with the two cationic species. Upon exposure to pure NaCl solutions, the gradients in chemical potential for Ca^{2+} and Na^+ apparently lead to a complete destabilization of the films, suggesting that Ca^{2+} and/or SACa^+ ions initially stabilizing the LB film can be exchanged with Na^+ ions from the bulk exposure solution resulting in the complete decomposition of layer. The behavior upon exposure to pure Ca^{2+} solutions again suggests an exchange of ions between the bulk solution and loosely bound parts of the LB monolayer.

Such rearrangements are not uncommon. For multilayer LB films, they have been studied in great detail [10, 12, 29]. In particular, X-ray reflectivity and X-ray photoemission spectroscopy demonstrated a very strong mobility and exchange of cations bound in LB multilayers [9]. These studies also suggest that ion exchange is facilitated by swelling of the LB films. To explore this possibility, we performed some additional ‘*in-situ*’ AFM experiments, in which the LB films were imaged under aqueous liquid (instead of air). These experiments showed film decomposition patterns that are consistent with the *ex-situ* experiments (see Appendix Figure 6.A4). However, the depth of the holes in the LB films is more than twice as large as in the *ex-situ* images recorded on the same surface after drying. Explanations for this swelling behavior and other possible rearrangements (e.g. tilting as a result of partial desorption) are the subject of an ongoing follow-up study.

The Ca^{2+} -induced stabilization of LB films might also provide a strategy to develop more stable hydrophobic layers for surface forces measurements. Investigations of fundamental interaction forces between hydrophobic surfaces immersed into water have long been compromised by problems with the stability

of hydrophobic layers [13, 16]. LB films stabilized by Ca^{2+} or even higher valence cations might provide a route to overcome these problems.

Overall, the observations described in this work are consistent with the multiple ion exchange mechanism of the low salinity water flooding process as proposed by Lager et al. [5]. Ionically bound layers of SA on silica surfaces indeed partially come off the solid surface and render it more hydrophilic if exposed to pure water rather than highly saline electrolytes. As in core flooding oil recovery experiments divalent ions also play a crucial role in the present generic model system. It is interesting to note, though, that ions present in the subphase during the preparation of the LB films have a stronger influence than those added subsequently to the exposure solution. This might suggest that the salinity of the formation water, which was present when the oil invaded a certain initially water saturated reservoir rock, plays an important role for the stability of the hydrophobizing layers and thus for the subsequent success of low salinity water flooding. While it is encouraging that the same qualitative behavior is also found on mica substrates (serving as a model for clays that are typically present in many rock formations), more extensive experiments involving different classes of polar organic components from crude oil obviously need to be performed to confirm the general applicability of the multivalent ion exchange concept.

6.5. CONCLUSIONS

The stability of Langmuir Blodgett films of stearic acid upon exposure to water is strongly enhanced by the presence of Ca^{2+} ions. Strongly bound LB films transferred in the presence of an excess of Ca^{2+} are very stable independent of the composition of the aqueous phase it is exposed to, suggesting that Ca^{2+} can efficiently bind negatively charged SA to negatively charged surfaces. In contrast, Na^+ ions are unable to provide such stabilization. For weakly bound LB films transferred in the presence of mixtures of Na^+ and Ca^{2+} , high concentrations of Na^+ in the ambient exposure fluid can even destabilize ionically bound organic layers. This destabilization can be rationalized by the replacement of initially present stabilizing Ca^{2+} ions implying a rapid exchange of ions between the ionic layer binding the LB film to the substrate and the ambient electrolyte. Clearly, the competition of several simultaneously present ionic species, which is characteristic for most geological, biological, and technological environments, adds substantial complexity and deserves additional attention in future research.

From an applied perspective, the Ca^{2+} -induced stabilization reported here implies a destabilization and easy removal of ionically bound organic layers in the absence of divalent ions. This is desired in the context of enhanced oil recovery. We anticipate that the fatty acid layers investigated can indeed be exploited as a model system for further studies of various complex geophysical and technological processes in well-defined laboratory experiments.

6.6. REFERENCES

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6.7. APPENDIX

A- Effect of preparation conditions on SA monolayer morphology:

We have observed that the topography, thickness and roughness of the monolayers highly depend on details of sample cleaning, preparation, drying protocols and deposition pressure. For the non- optimized conditions, the monolayer could also have some holes in it just after the preparation.

Figure 6.A1. Variation of the morphology of steric acid monolayers with deposition conditions: height and phase images of SA-Na monolayer just after deposition (a) on silicon wafer with thick oxide layer ($\sim 35\text{nm}$) (b) without any thick oxide layer (c) deposition pressure is not controlled.

B- Water contact angle variation with different substrate and deposition condition:

Figure 6.A2: Macroscopic wettability of the SA monolayers deposited on optimized (surface pressure= 30, 45 mN/m) and non-optimized conditions.

C- *In-situ* AFM imaging:

Figure 6.A4: AFM imaging on SA-Ca monolayer exposed to water: a and a'; 0.01 M NaCl solution: b and b'. (a and b: in-situ imaging, a' and b': imaged after drying). Height profiles corresponding to (c) water (d) 0.01M NaCl exposure are shown for in-situ and ex-situ imaging.

CONCLUSIONS AND OUTLOOK

7.1. CONCLUSIONS

In this thesis, we investigated the charging behaviour of rock/clay materials and adsorption/desorption of model oil components on these surfaces under different aqueous conditions using high resolution AFM. *First*, we established the method to extract the surface charge from dynamic force spectroscopy measurements, by analysing the interaction forces with DLVO theory. Later, we studied the effect of the electrolyte composition (i.e. pH, concentration, valency, ion size) on the surface charge. In this section, we present the highlights of our findings.

One of the main finding of our results is that the surface charge is heterogeneously distributed on the basal plane of the kaolinite particles. The surface charge values vary from $+0.015$ to 0 e/nm² for gibbsite facet and 0 to -0.045 e/nm² for silica facet. Such high resolution information of the charge distribution is not possible to capture by using standard macroscopic techniques such as titration and electrokinetic measurements. Using sharp AFM tips (tip radius ~ 3 nm) in non-contact AM-AFM, we resolved the atomic structure of the two facets of kaolinite and extract their lattice parameters. The combination of AFM spectroscopy and high resolution imaging offers a unique experimental capability to investigate charge characteristics of complex clay systems.

Using these methods, we further investigated the effect of salt concentration and pH on the surface charge of kaolinite particles. We found out that the surface charge of the kaolinite basal planes is pH dependent which contradicts the assumption that both basal planes carry a permanent negative charge due to isomorphous substitution. The surface charge of the silica facet is always negative and increases in magnitude with increasing pH. While for the gibbsite facet, the surface charge is positive for $4 < \text{pH} < 6$, and becomes negative for higher pH ~ 7 . Further, we found that the surface charge of the gibbsite facet at pH 6, increases up to a concentration of 10 mM CaCl₂ and starts to decrease upon further increasing the salt concentration to 50 mM. With the help of atomic scale imaging and the DFT calculations, we demonstrated that the surface charge is

increased due to Ca^{2+} ion adsorption, while it is reduced due to Cl^- ion adsorption at higher CaCl_2 concentrations.

After investigating kaolinite particles, which represent 1:1 type clay minerals, we further investigated the charging behavior of mica, which represents 2:1 layer type clay minerals. Specifically, we studied the effect of pH, salt type and salt concentration on the surface charge of mica. It is observed that the surface charge of mica decreases with increasing monovalent salt concentration. As we go to a bigger monovalent cation radius ($\text{Li}^+ < \text{Na}^+ < \text{Cs}^+$), the decrease in surface charge is more pronounced. This is explained with the idea that larger cations are more polarizable and hence have a stronger affinity due to somewhat stronger dispersion attraction towards the surface. Also, the larger ions have loosely bound hydration shell, which leads to weaker repulsion between hydrated ions and hydrated mica. In case of divalent ions, the surface charge of mica is reversed and becomes positive above ~ 20 mM concentration. In atomic scale images, we observed that the divalent ions adsorb strongly to the mica surface and alter the hexagonal surface pattern to a rectangular pattern. They have greater capacity to adsorb in both the tetrahedral and octahedral interstitial site of the mica crystal, which leads to the charge reversal. This is not possible in case of monovalent ions, as they are loosely bounded. In presence of Na^+ ions, we observe a hexagonal surface pattern, which is due to the mica crystal lattice. While in case of Cs^+ ions, some domain formation is observed, partially covering the mica lattice. Hence, the negative surface charge of mica is compensated more effectively compared to other monovalent ions but it is still not sufficient for charge reversal. We also observed that the effect of pH on surface charge of mica is significant in the range of 4 to 6, while charge changes slightly with further increasing the pH from 6 to 9.

In the last phase of the thesis, we investigated the adsorption desorption of model oil to the model rock surface. We studied the stability of Langmuir-Blodgett (LB) films of stearic acid (representative of polar organic components of oil) deposited on silica in presence of Ca^{2+} and/or Na^+ ions. Both contact angle and AFM imaging experiments revealed that the LB films prepared in presence of divalent ions (Ca^{2+}) are more stable compared to monovalent ions (Na^+). This is explained by the cation bridging mechanism between negatively charged silica surface and negatively charge head group of stearic acid in presence of divalent ions.

7.2. OUTLOOK

We have demonstrated AFM as a useful tool for surface charge characterization of rock clay materials with very high lateral resolution. Now using these techniques, we can explore much more complex oil reservoirs conditions such as high pressure, high temperature, different rock/clay materials, and different water flooding conditions.

7.2.1. Rock reservoirs

We have studied the surface charge of silica only as the model rock surface for the sandstone reservoirs. It would be useful to study the surface charge of more complex sandstones like Bandera brown, Fontainebleau rock which have more roughness and different ratios of quartz and clay minerals. Beside sandstone, carbonate reservoirs are also very commonly found in many oil fields. These rocks are positively charged. Hence, the anion present in the sea water such as sulphates, chlorates would play a significant role in influencing their surface charge. Also, it would be of great importance to study the adsorption/ desorption of positively charged oil components in presence of these anions [1].

7.2.2. Polymer/surfactant flooding

In this thesis, we mainly focused on the basic mechanisms of low salinity water flooding. Another popular flooding technique for tertiary oil recovery is surfactant/polymer flooding. Surfactants mainly reduce interfacial tension, increase oil mobility thus allowing better displacement of oil by injected water. Surfactant flooding also alters the wettability of porous rocks allowing water to flow through them faster thereby displacing more oil. One of the main challenges in this process is the loss of surfactant due to adsorption on reservoir rocks. In fact, high adsorption of surfactant can make the flooding processes economically-unfeasible [2, 3]. It would be of great interest to study the adsorption desorption mechanism of surfactant molecules in presence of monovalent and divalent ions. The surface charge characterization of rocks in presence of surfactant molecules, would give more insights into the adsorption of the oil molecules on these rock surfaces.

7.2.3. High pressure and high temperature

In this work, we have performed all our experiments at room temperature and atmospheric pressure. However, the temperature and pressure is quite high in an oil reservoir. The temperature ranges from 100-150 °C while pressure can be as high as 120 bar. Using zeta potential measurements, Rodriguez et al. have studied the effect of temperature and pressure on the zeta potential values of reservoir minerals

[4]. They have reported that the zeta potential becomes more negative with increasing temperature at a rate characteristic of each mineral; values are ~ -2.3 mV/°C for quartz, -0.96 mV/°C for kaolinite, and -2.1 mV/°C for calcite for pressure values less than 45 psi. Similar results for quartz and kaolinite were also obtained by Ramachandran and Somasundaran [5]. These results were explained in terms of possible dissolution of the minerals and the surface reactions at different temperatures. The effect of pressure is found to depend on the mineral nature and pH of the electrolytic solution [4]. In the case of quartz, the zeta potential decreases (becomes less negative) with increasing pressure, whereas it increases (becomes more negative) for the kaolinite.

Schembre et al. studied the wettability alteration of reservoir cores as a function of temperature by water imbibition [6]. They found that an increase in temperature (from 45 to 230 °C) results in a significant shift in the wettability, from weakly water-wet to strongly water-wet. Fine migration was proposed as a mechanism for wettability shift towards increased water-wetness at elevated temperature.

It is evident from these macroscopic measurements that both temperature and pressure have significant effect on the electrochemical properties of the reservoir minerals. As shown from our results, there exist a significant heterogeneity in the charge values on a single clay particle. Therefore, it would be of great importance to study the charging behaviour of these minerals with high resolution AFM technique under such elevated temperature and pressure conditions.

7.3. REFERENCES

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In this thesis, we investigate the charging behavior and ion adsorption at solid-liquid interfaces. These phenomena play a crucial role in a wide range of fields, such as colloid science, self-assembly, wetting, electrochemistry, and molecular biology. The aim of this work is to understand the scientific challenges in enhanced oil recovery (EOR) processes. Surface charge properties of rock/clay surface plays an important role in understanding various fluid-rock/clay interactions in an oil reservoir. In this regard, we characterize the surface charge properties of rock/clay-water interface in various electrolyte solutions.

In *chapter 2*, we provide an overview of the rock/clay materials, experimental techniques and theoretical models used in the research. Firstly, clays in terms of their morphology and charge characteristics are discussed. We introduce kaolinite and mica as representative of 1:1 and 2:1 layer type clay mineral, respectively. Secondly, the techniques used to characterize the rock/clay-water interface i.e. AFM, contact angle goniometry and Langmuir trough are explained. We use dynamic force spectroscopy to record the tip-sample interaction forces in different aqueous conditions. We briefly discuss the force inversion formulae for amplitude modulation (AM) and frequency modulation (FM) modes. Further, a detailed description is presented of the theoretical model used to calculate the surface charge by analyzing the tip-sample interaction forces using DLVO theory with charge regulation boundary conditions. Lastly, we discuss the numerical approach to solve the Poisson-Boltzmann equation using a point and shoot method.

As kaolinite is the most abundant clay material, we start our research by exploring its charging behavior. In *Chapter 3*, we determine the surface charge distribution on the two facets of kaolinite by selectively orient them on mica or sapphire substrates. The surface charge density is extracted from the measured force distance curves using DLVO theory. It is found that the surface charge is heterogeneously distributed on the basal plane of the kaolinite particles. The surface charge values vary from + 0.015 to 0 e/nm² for gibbsite facet and 0 to - 0.045 e/nm² for silica facet. Using sharp AFM tips (tip radius ~ 3 nm) in non-contact AM-AFM, we resolved the atomic structure of the two facets of kaolinite and extract their lattice parameters. The combination of AFM spectroscopy and

high resolution imaging offers a unique experimental capability to investigate charge characteristics of complex clay systems.

In Chapter 3 we discuss only a single case: one concentration and a fixed pH, although oil reservoirs are much more complicated. Therefore, in *Chapter 4*, using the same methods and techniques, we investigate the effect of salt concentration and pH on the surface charge of kaolinite particles. The surface charge of the silica facet is always negative and increases in magnitude with increasing pH. While for the gibbsite facet, the surface charge is positive for $4 < \text{pH} < 6$, and becomes negative for higher pH ~ 7 . Further, it is found that the surface charge of the gibbsite facet at pH 6, increases up to a concentration of 10 mM CaCl_2 and starts to decrease upon further increasing the salt concentration to 50 mM. With the help of atomic scale imaging and the DFT calculations, we demonstrate that the surface charge is increased due to Ca^{2+} ion adsorption, while it is reduced due to Cl^- ion adsorption at higher CaCl_2 concentrations.

After surface charge characterization of kaolinite particles, we focus in *Chapter 5* our attention on the charging behavior of mica, which is a 2:1 type clay material. Specifically, we study the effect of pH, salt type and salt concentration on the surface charge of mica. It is observed that the surface charge of mica decreases with increasing monovalent salt concentration. As we go to a bigger monovalent cation radius ($\text{Li}^+ < \text{Na}^+ < \text{Cs}^+$), the decrease in surface charge is more pronounced. The surface charge of mica in presence of divalent ions is reversed and becomes positive above a concentration of ~ 20 mM. In atomic scale images, we observe that the divalent ions (Ca^{2+}) adsorb strongly to the mica surface and alter the hexagonal surface pattern to a rectangular pattern. In presence of Na^+ ions, we observe a hexagonal surface pattern, which is due to the mica crystal lattice. While in case of Cs^+ ions, some domain formation is observed, partially covering the mica lattice. The surface charge of mica is also pH dependent. It is observed that the effect of pH on surface charge of mica is significant in the range of 4 to 6, while charge changes slightly with further increasing the pH from 6 to 9.

In *Chapter 6*, we investigate the adsorption/desorption of model oil to the model rock surface. Langmuir-Blodgett (LB) films of stearic acid (representative of polar organic components of oil) are deposited on silica in the presence of Ca^{2+} and/or Na^+ ions. Large differences in macroscopic wettability (contact angles) are observed between the monolayer prepared in Ca^{2+} and Na^+ ions sub-phases. Both contact angle and AFM imaging experiments reveal that the LB films prepared in

presence of divalent ions (Ca^{2+}) are more stable compared to monovalent ions (Na^+). The observations on varying the composition of the droplets corroborated the stabilizing effect of Ca^{2+} . We attribute these findings to the cation-bridging ability of Ca^{2+} ions, which can bind the negatively charged stearate groups to the negatively charged substrates.

In dit proefschrift onderzoeken we het ladingsmechanisme en ionenadsorptie aan grensoppervlakken tussen water en vaste stoffen. Deze mechanismes hebben een belangrijke rol in veel toepassingen, zoals in colloïdchemie, zelfstructurering, bevochtigbaarheid, elektrochemie en moleculaire biologie. Het doel van dit project is het benaderen van de wetenschappelijke vragen die ontstaan in het verband van verbeterde oliewinning (EOR). Oppervlakte lading eigenschappen van rock / klei oppervlak speelt een belangrijke rol in het begrijpen van diverse vloeistof-rock / klei interacties in een oliereservoir. Daarom karakteriseren we de oppervlaktelading eigenschappen van rots/klei-water grensoppervlakken in verschillende elektrolyt oplossingen.

In hoofdstuk 2 geven we een overzicht van eigenschappen van rots/klei deeltjes, experimentele technieken en theoretische modellen gebruikt in het onderzoek. Ten eerste worden de morfologie en oppervlaktelading eigenschappen van klei behandeld. We introduceren kaolinite en mica als voorbeelden van 1:1 en 2:1 gelaagde kleisoorten. Ten tweede leggen we de technieken uit, zoals atoomkracht microscopie, contacthoek goniometrie en Langmuir trog, die gebruikt worden om de rots/klei-water grensoppervlakken te karakteriseren. We gebruiken dynamische kracht spectroscopie om de tip-substraat krachten te meten in verschillende elektrolyt oplossingen. We behandelen in het kort de krachtinversie vergelijkingen voor amplitude modulatie (AM) en frequentie modulatie (FM) metingen. Verder wordt er een gedetailleerde beschrijving gegeven van het theoretische model, met DLVO theorie met lading regulerende randvoorwaarden, dat gebruikt wordt om de oppervlaktelading te berekenen uit de tip-substraat interactiekrachten. Ten slotte behandelen we de numerieke methode op de Poisson-Boltzmann vergelijking op te lossen met een richt-en-schiet methode.

Aangezien kaolinite de meest aanwezige kleisoort is, starten we ons onderzoek met het bestuderen van het opladingsgedrag van kaolinite. In hoofdstuk 3 bepalen we de verdeling van de oppervlaktelading op de twee verschillende zijden van kaolinite door ze te plaatsen op of een mica of een saffier substraat. De oppervlakteladingsdichtheid wordt berekend vanuit de kracht-afstandsmetingen met behulp van DLVO theorie. We vinden dat de oppervlaktelading heterogeen

verdeeld is op het oppervlak van kaolinite deeltjes. De oppervlakteladingwaardes variëren tussen de 0.015 tot 0 e/nm^2 voor de gibbsite zijde, en 0 tot -0.045 e/nm^2 voor de silica zijde. Met behulp van ultrascherpe naalden (puntradius van ongeveer 3 nm) in geen-contact AM-AFM, verkrijgen we de atomaire structuur en kristalrooster parameters van de twee zijden van kaolinite. Het combineren van dynamische kracht spectroscopie en informatie op een atomair niveau, biedt een unieke experimentele mogelijkheid voor het onderzoeken van ladingsmechanismes van complexe klei systemen.

In hoofdstuk 3 bespreken we de oppervlakteladingverdeling in één enkele soort elektrolyt oplossing, ondanks het feit dat oliereservoirs veel complexer zijn dan dat. Daarom kijken we in hoofdstuk 4 naar het effect van pH en zout concentratie op de oppervlaktelading van kaolinite deeltjes. De oppervlaktelading van de silica zijde is altijd negatief en wordt negatiever naarmate de pH verhoogd wordt. De oppervlaktelading van de gibbsite zijde is echter positief tussen pH 4 en 6, maar wordt negatief bij een pH hoger dan 7. Verder vinden we dat de oppervlaktelading op de gibbsite zijde bij pH 6 verhoogd als de zoutconcentratie verhoogd wordt tot 10 mM calcium chloride, maar kleiner wordt als de zoutconcentratie verder verhoogd wordt tot 50 mM . Met behulp van atomaire resolutie onderzoek en DFT calculaties laten we zien dat de oppervlaktelading verhoogd door de adsorptie van calcium ionen aan het oppervlak, maar bij hogere concentraties daalt door de adsorptie van chloride ionen.

Na de oppervlakteladingkarakterisering van kaolinite concentreren we ons in hoofdstuk 5 op het ladingsgedrag van mica. Specifieker, we kijken naar het effect van pH, zoutconcentratie en zouttype op de oppervlaktelading van mica. We zien dat de oppervlaktelading van mica vermindert bij het verhogen van de monovalente ionenconcentratie. De oppervlakteladingvermindering wordt sterker naarmate we een oplossing bestuderen met een grotere monovalente ionenradius ($\text{Li}^+ < \text{Na}^+ < \text{Cs}^+$). In het geval van divalente ionen, draait de polariteit van de oppervlaktelading om van negatief naar positief, als de zoutconcentratie verhoogd wordt boven de 20 mM CaCl_2 . In atomaire resolutie plaatjes observeren we dat de divalente ionen (Ca^{2+}) sterk adsorberen op het mica grensoppervlak, waarbij het hexagonale oppervlakpatroon verandert in een vierhoekig patroon. In de aanwezigheid van natrium ionen zien we alleen een hexagonaal patroon, door het hexagonale kristalrooster van mica. Echter, in het geval van Cs^+ ionen zien we de formatie van enkele domeinen, waarbij een gedeelte van het mica kristalrooster

bedekt wordt. De mica oppervlaktelading is ook pH afhankelijk. We observeren dat het effect van de pH op de oppervlaktelading het meest significant is in het bereik van pH 4 tot 6, terwijl we nauwelijks verschil zien tussen pH 6 en 9.

In hoofdstuk 6 onderzoeken we de adsorptie/desorptie van model oliemoleculen aan model rots oppervlakken. Langmuir-Blodgett (LB) laagjes van stearinezuur (representatief voor de polaire componenten aanwezig in de olie) adsorberen op silica oppervlakken in de aanwezigheid van Ca^{2+} en/of Na^+ ionen. Grote verschillen in de macroscopische vochtigheid (contacthoeken) worden geobserveerd tussen de monolaagjes gemaakt met Ca^{2+} en Na^+ ionen. Beide contacthoekmetingen en dynamische kracht spectroscopie metingen onthullen dat de LB laagjes gemaakt in Ca^{2+} oplossingen stabiel zijn dan de laagjes gemaakt in Na^+ oplossingen. Deze bevinding wordt ondersteund door andere metingen met druppels met variërende zouten. We wijden deze bevinding toe aan de kation-brugeigenschap van calcium, waar calcium een brug vormt tussen het negatief geladen stearinemolecuul en het negatief geladen substraatoppervlak.

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LIST OF PUBLICATIONS

From this thesis:

- Naveen Kumar, Igor Siretanu, Cunlu Zhao, Aram Klaasen, Dirk van den Ende and Frieder Mugele, "Characterization of the surface charge distribution on kaolinite particles using high resolution atomic force microscopy", *Geochimica et cosmochimica acta*, vol. 175, pp. 100-112, 2016
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Other Publications

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Naveen Kumar was born on 1st December 1987 in Jhunjhunu, India. After completing his secondary schooling in Jhunjhunu, he went on to do a 5 Year Integrated BS + MS Program in Chemistry from Indian Institute of Technology (IIT) Bombay. During his studies, he developed a particular interest in physical and computational chemistry. As part of this integrated course, he did an internship at University of Oslo under Prof. dr. Trygve Helgaker where he implemented a computational model to calculate VDW and Dispersion Interaction for Helium dimer. He did a second internship at Freie Universität Berlin under Prof. dr. Jörn Manz, where he computed the electronic fluxes accompanying molecular vibrations, specifically for the fluorine gas. In 2011, he obtained his MS degree with his thesis titled “Thermodynamics of Turn Formation in Short Peptides”.

Shortly after Naveen had earned his MS degree, he joined the Physics of Complex Fluids (PCF) Group of Prof. dr. Frieder Mugele at the University of Twente in The Netherlands as a PhD student in Sept 2011. At the PCF group, he worked on surface charge characterization of solid-liquid interfaces using Atomic Force Microscopy. The results of this PhD research are presented in this thesis.

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