Adsorption At Solid-liquid Interfaces Studied With Surface Sensitive Techniques

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ADSORPTION AT SOLID-LIQUID INTERFACES STUDIED WITH SURFACE SENSITIVE TECHNIQUES
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DISSERTATION

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In this thesis, we study (in)organic molecular adsorption phenomena at solid-liquid interfaces, in the context of the low salinity water flooding process in Enhanced Oil Recovery (EOR). Studies are conducted with various surface sensitive techniques and microfluidics.

In Chapter 3, we investigate cation adsorption at silica-water interfaces with internal reflection ellipsometry. In the data analysis, the measured polarization-dependent reflectivity is compared to calculations from an optical model of stacked layers, where the electric double layer is modeled as a separate layer. With this technique, we are able to quantify the adsorption of Na\(^+\) and Ca\(^{2+}\) ions from aqueous solutions of their chloride salts as a function of their bulk concentrations at pH 3 and 10. Our measurements demonstrate a stronger adsorption of the Ca\(^{2+}\) counterions. The experimental results are well described by calculations using a triple layer surface complexation model for the electric double layer, using equilibrium constants from literature.

In Chapter 4, we discuss the development of a concentration gradient generator, which creates a dilution series, in contact with a substrate, on a microfluidic platform. The device is based on steady-state diffusion of the analyte, between two control channels where liquid is pumped through. The device generates a near-linear distribution of concentrations. We demonstrate this via experiments with dye solutions, and comparison to numerical finite-element simulations. In a subsequent step, the device is combined with total internal reflection ellipsometry to study the adsorption of (cat)ions on silica surfaces from CsCl solutions at various pH. The measured optical thickness is compared to calculations from a triple layer model for the ion distribution, where surface complexation reactions of the silica are taken into account. Our results show a clear enhancement of the ion adsorption with increasing pH, which can be well
described with reasonable values for the equilibrium constants of the surface reactions.

In Chapter 5, we explore the adsorption of hexanoate from aqueous solutions on silica, alumina and gibbsite (each of these substrates bears chemical similarity to clays as found on rock surface). The solutions contain as cations H⁺, Na⁺ and in most cases also Ca²⁺ and as anions hexanoate, OH⁻ and Cl⁻. (Mass) adsorption curves for these small molecules, measured with a Quartz Crystal Microbalance (QCM-D, using several overtones for enhanced accuracy), suggest different adsorption mechanisms on these oxide surfaces. On silica, Ca²⁺ ions can enhance the adsorption, mainly via the formation of ion bridges between the negatively charged silica surface and hexanoate molecules. On alumina, the adsorption behavior is consistent with a ligand exchange process (replacing –OH by hexanoate), where pH is the dominant factor. On gibbsite, the adsorption shows a non-monotonic behavior as a function of CaCl₂ concentration. This points at a competition between Cl⁻ and hexanoate ions for the adsorption sites.

In EOR-waterflooding, the stability of adsorbed organic films on the inorganic rock surface is of key importance in enabling the aqueous phase to change the wettability. In Chapter 6, we investigate the stability (upon exposure to water) of stearic acid monolayers deposited on silica via a Langmuir-Blodgett (LB) transfer. Both contact angle measurements and image analysis with AFM and ellipsometry reveal that the LB films prepared with divalent cations (Ca²⁺) demonstrate a higher stability (a less complete breakdown) than those prepared in presence of Na⁺ ions. This can be explained by the formation of cation bridges by divalent ions.

In summary, we have developed techniques which can be used to study small molecule adsorption at solid-liquid interfaces fast and efficiently. Moreover, the important role of divalent cations such as Ca²⁺ has been demonstrated.
Samenvatting

In dit proefschrift wordt het adsorptie gedrag van ionen en kleine moleculen aan vast-vloeistof grensvlakken beschreven. Dit wordt gedaan vanuit de invalshoek van (verbeterde) olie winning, waarbij water met weinig opgelost zout in gesteente wordt gepompt om de olie los te weken. Onze experimenten werden uitgevoerd met diverse oppervlakte-gevoelige technieken, en microfluidics.

In Hoofdstuk 3 bestuderen we de adsorptie van kationen aan silica-water grensvlakken met Interne Reflectie Ellipsometrie. In de data analyse wordt de polarisatie afhankelijkheid van de gemeten reflectiviteit vergeleken met model berekeningen voor een stapeling van optische laagjes, waarbij de elektrische dubbellaag wordt gemodelleerd als een aparte laag. Met deze methode was het mogelijk om de adsorptie van Na⁺ en Ca²⁺ ionen te kwantificeren als functie van de bulk concentraties van hun chloride zouten, bij pH 3 en pH 10. Onze metingen laten zien dat Ca²⁺ sterker adsorbeert dan Na⁺. De meetresultaten kunnen goed beschreven worden met een model waarbij de elektrische dubbellaag in drie afzonderlijke laagjes wordt opgedeeld, en chemische reacties aan het grensvlak worden beschreven met evenwichtsconstanten uit de literatuur.

In Hoofdstuk 4 bespreken we het ontwerp, de validatie en het gebruik van een microfluidische chip waarmee een verdunningsreeks wordt gemaakt, in contact met een substraat. Het ontwerp is gebaseerd op diffusie in de stationaire toestand, tussen twee kanalen waar vloeistoffen met gekozen concentraties worden door-gepompt. Hiermee is het mogelijk om een lineaire concentratie verdeling van de te onderzoeken chemische component te maken. De werking van deze chip wordt gedemonstreerd met inkt oplossingen, en gevalideerd met numerieke ‘eindige elementen’ simulaties. In een volgende stap wordt de chip gebruikt voor Interne Reflectie Ellipsometrie, om de adsorptie van (kat)ionen op silica substraten te bestuderen bij verschillende CsCl concentraties en pH
waarden. De gemeten optische laagdikte wordt vergeleken met berekeningen volgens het genoemde drie lagen model met oppervlakte reacties. Onze resultaten tonen een duidelijke toename van de ionen adsorptie met toenemende pH; deze trend kan goed beschreven worden met realistische waarden voor de evenwichtsconstanten van de oppervlakte reacties.

In *Hoofdstuk 5* onderzoeken we de adsorptie van hexanoaat vanuit waterige oplossingen op silica, alumina en gibbsiet oppervlakken. Elk van deze substraten heeft een chemische verwantschap aan klei deeltjes, zoals die op olie houdende rots worden aangetroffen. De oplossingen bevatten H⁺, Na⁺ en meestal ook Ca²⁺ als kationen, en OH⁻ en Cl⁻ als anionen. Met een Quartz Crystal Microbalance (QCM-D) kan de verschuiving in resonantie frequentie (alsmede de energie dissipatie) worden gemeten voor verschillende ‘boventonen’, wat de techniek extra gevoelig maakt. Uit het verband tussen ionen concentraties in de bulk, en de geadsorbeerde massa kan worden opgemaakt dat verschillende adsorptie mechanismen werkzaam zijn op de verschillende substraten. Op silica treedt een verhoogde adsorptie van hexanoaat op via de vorming van Ca²⁺ bruggen. Het adsorptie gedrag op alumina stemt overeen met een proces waarbij –OH liganden op het substraat worden vervangen door hexanoaat; hierbij is de pH een dominante factor. Op gibbsiet vertoont de adsorptie een niet-monotoon gedrag als functie van CaCl₂ concentratie. Dit wijst op een competitie tussen hexanoaat en Cl⁻ ionen voor de adsorptie plaatsen.

In verbeterde oliewinning via het inpompen van water met geoptimaliseerde ionen samenstelling, is de stabiliteit van de eerder op de rots geadsorbeerde organische film van groot belang voor de al dan niet succesvolle verandering van de bevochtigingseigenschappen van de rots. In *Hoofdstuk 6* bestuderen we de stabiliteit van monolagen van stearinezuur (complexen) op silica substraten, door deze in contact te brengen met water. De monolagen waren aangebracht via de Langmuir Blodgett techniek. Metingen van de contacthoek en beeldanalyse met AFM en ellipsometrie laten zien dat de samenstelling van de sub fase tijdens de
bereiding van de LB film, belangrijk is: de aanwezigheid van Ca\textsuperscript{2+} leidt tot significant minder afbraak van de film (door water), in vergelijking tot Na\textsuperscript{+}. Dit kan worden verklaard met de vorming van stearaat-substraat bruggen door het divalente kation.

Kort samengevat hebben wij technieken ontwikkeld, waarmee de adsorptie van kleine moleculen aan vast-vloeistof grensvlakken snel en efficiënt kan worden bestudeerd. Bovendien is de belangrijke rol van divalente kationen zoals Ca\textsuperscript{2+} aangetoond.
CHAPTER 1
INTRODUCTION

This thesis is motivated by the scientific questions underlying the low salinity water flooding process in enhanced oil recovery. As an emerging technique in oil recovery, low salinity water flooding has gained a lot of attention in the last decades. Laboratory experiments as well as field tests have demonstrated possibilities for an increased oil recovery with this method. A wettability alteration is generally considered to be responsible for releasing oil from clay-rock surfaces in oil reservoir. However, the microscopic origin of this phenomenon still remains unclear. Several plausible mechanisms have been suggested, however, none of them has been identified as the main mechanism. This leaves specific research questions to be answered. In this chapter, we present a concise review about the oil recovery, especially the low salinity water flooding process in enhanced oil recovery, address the scientific questions studied in this thesis, and present the thesis outline.
1.1 Motivation

1.1.1 Oil reservoir

Oil reservoirs are pools of hydrocarbons, located beneath the earth’s surface in porous rock structures. Crude oil found in the oil reservoir originates from the remains of living organisms, which can date back to thousands or even millions of years ago. At that time the sea was rich in simple living organisms. When these living organisms die, a stack of mud and organic remains may pile up on the sea floor. Given enough time, the overlying sediments that are constantly being deposited will bury these organic remains and mud so deeply that they will eventually be turned into solid rock. When the ambient conditions are proper, usually involving high temperature and intense pressure, various chemical reactions take place, transforming the soft parts of ancient organisms in the deep-sea sludge into oil and natural gas. Oil created by the source rock is not stored in the form of a pool. Instead, most of the oil is trapped inside porous and permeable rocks. The latter is known as reservoir rock, and sandstone is one of the most common types. Besides the above mentioned water environment, the formation of oil or gas reservoirs also requires another condition: the trapping by impermeable rock, as presented in Fig.1.1.

Sandstone is a clastic sedimentary rock composed of minerals and rock grains, with a typical size between 62 μm to 2 mm. It allows percolation of water and other fluids and is porous enough to store large volumes of fluid, making it very suitable as aquifers and petroleum reservoirs. Most sandstone is composed of quartz and feldspar. Additionally, there are some common cementing materials attached as a coating to the grains, such as silica, calcium carbonate, Montmorillonite, Kaolinite, etc. These cementing materials constitute most of the surface area that is in contact with fluids such as oil and connate water.

The presence of crude oil, saline water and sandstone together contribute to the complexity of oil reservoirs. The principal component of oil is hydrocarbons, mostly in the form of alkanes, cycloalkanes and various aromatic hydrocarbons.
But also polar organic compounds containing nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium are present. In particular, these polar components can interact with clay minerals, and control the wettability of rock reservoir. The saline water usually contains a variety of salts. The brines in the connate water, together with the chemical composition of the solutions injected during oil recovery, have a strong influence on the wetting properties of the rock. Changing these in favor of oil release (making the rock more water-wet), forms the basic idea of enhanced oil recovery.

![Diagram of oil reservoir](image)

**Fig.1.1** Schematic illustration of oil reservoir.

### 1.1.2 Oil recovery

Oil has been the world’s main energy source since the first commercial well was drilled in Northwestern Pennsylvania in 1859[1], and the demand for this energy source is still increasing today. In order to meet the increasing demand and keep a sustainable oil supply, the ultimate recoverable oil reserve should increase. While this could be achieved via discovery of new reservoirs, also the application of improved recovery techniques to mature oil fields can be used to increase the
oil reserve. Exploration and development of new oil reserves is costly and requires new installation and infrastructure. Moreover, the last decades have witnessed a decline of oil discoveries. So it is believed that the Enhanced Oil Recovery (EOR) technology, which utilizes existing fractures in developed oil reservoirs, is more efficient and will play a key role in meeting the energy demand in the years to come.

Oil is normally produced from the reservoir via three different stages: primary recovery, secondary recovery and tertiary recovery, which is also known as Enhanced Oil Recovery (EOR). Primary recovery production takes place as a first step after the discovery of an oilfield, and uses naturally stored mechanical energy to move oil to the well: the expansion of volatile components drives this process. In later stages, pumping of individual wells can be applied to assist the natural drive. When the stored mechanical energy is depleted, oil production declines and the secondary recovery starts. The secondary recovery is referred to as pressure maintenance. In this stage, gas/water is injected to increase the reservoir pressure and therefore assist in driving out oil. After the primary and secondary recovery, usually two thirds of the oil, or even more, still remains in the reservoir[2]. The (further) recovery of the oil is hampered by various mechanisms. In particular, the reservoir heterogeneities may cause a large volume of oil to be bypassed and remain within a field. This happens because the injected displacement water moves preferentially through higher permeability zones on its way towards the production well. Another mechanism is that residual oil is held in the pores by capillary forces.

Many techniques have been applied to increase the recovery of oil: either to increase the efficiency of the displacement medium by increasing the viscosity of the flooding water or decreasing the viscosity of the oil; or to extract the oil with a proper solvent; as well as reducing the interfacial tension between oil and water[3]. These techniques have been exploited individually or together in the EOR processes. Generally, EOR can be classified into four categories based on
the dominant source energy in each process: thermal based, gas based, water based and hybrid (combined) EOR.

Water based EOR processes are those methods in which water is the fundamental element in the displacing fluid. In these methods, the physical chemical properties of the flooding water are changed via the addition of chemicals or by manipulating the salinity. Low salinity water flooding which is an emerging and promising water based EOR process is the main interest of this work, and therefore it will be described in the next section.

1.1.3 Low salinity water flooding

Low salinity water flooding is an enhanced oil recovery method that uses water with a low concentration of dissolved salts as a flooding medium. A number of laboratory tests by Morrow and coworkers[4, 5], as well as by researchers in BP[6] have confirmed that oil recovery can be enhanced by using flooding water with salinity in the range of 1000-2000 ppm. Lager[7] has reported an average increase in recovery of about 14% by low salinity water flooding. This is based on tests from 14 different sandstone reservoirs. Laboratory observations were also confirmed by field tests, for instance, a single well test performed in an Alaskan reservoir[8].

With more and more results from laboratory experiments published, various mechanisms lying behind the low salinity water flooding have been suggested. However, none of these mechanisms could be identified as the dominant mechanism, because of the complex composition of the oil reservoir, in which the properties of crude oil, rock or clay surfaces, and brine solutions (salinity, composition, and presence of multivalent ions) should all be taken into consideration. Laboratory evidences supporting or opposing the proposed mechanisms are growing.

One proposed mechanism is that low salinity flooding water causes a pH change[9, 10], which can be explained by two chemical reactions: carbonate
dissolution and cation exchange. Carbonate dissolution is very slow and strongly depends on the clay fraction. In contrast, cation exchange (protons from the aqueous phase substitute the cations at the mineral surface), resulting in a pH increase of the effluent, is much faster. The increased pH close to the clay surface can lead to desorption of the organic materials from the solid surface, turning the clay surface to more water-wet. However, some studies have shown an absence of correlation between pH variation and increased oil recovery with low salinity water[6]. Another mechanism is related to the fines migration, this has been reported by Tang and Morrow[4]. When exposed to low salinity solutions, fine clay particles would detach from the rock surface, and remove the retained oil drop. However, this is not a general observation, either in the laboratory or in field tests[11].

It is commonly believed that the wettability alteration towards a more water-wet state is the reason for the oil mobilization and production[12, 13]. In the oil reservoir, the rock surface is hydrophobic due to the precipitation over time of large molecular crude oil components like asphaltene, or the adsorption of polar components. Adsorption of basic or acidic organic components would take place via the electrostatic interaction, or the binding of divalent ions like Ca$^{2+}$. Recent investigations have revealed that stability of adsorbed films would be enhanced by Ca$^{2+}$[14], suggesting that lowering of the local divalent cation concentrations would make the rock surface more hydrophilic[15]. By injecting a low salinity solution, some of these adsorbed cations can be removed or displaced, facilitating desorption and release of organic molecules from the pore surfaces. This is another suggested mechanism of the low salinity water flooding. Yet another mechanism, associated with cation exchange, has been invoked to explain the low salinity effect. In the so-called double layer expansion mechanism, the injection of low salinity solution increases the electrostatic repulsion between brine/oil and brine/rock interfaces bordering a brine film between rock and oil; this leads to the expansion of two electric double layers formed at each interfaces. Consequently,
the film becomes thicker and more stable, resulting in the more water wet rock surfaces[16].

1.2 Thesis outline

In this thesis, we investigate several aspects related to the adsorption of organic or inorganic molecules in the context of the low salinity water flooding. Simple oil reservoir model systems are exploited to interpret sub-aspects like the cation adsorption, effects of divalent cations on the adsorption of organic molecules, etc. In Chapter 2, we review the theory of ion adsorption phenomena at solid-liquid interfaces, and we describe the methods and techniques used in this thesis.

Chapter 3 describes the detection of ion adsorption at a silica-water interface with internal reflection ellipsometry. The measured polarization-dependent reflectivity is compared to calculations from an optical layer stack model, where the electric double layer is modeled as a separate layer. The adsorption of Na\(^+\) and Ca\(^{2+}\) ions from aqueous solutions of their chloride salts as a function of their bulk concentrations at pH 3 and 10, are quantitatively presented. These experimental results are well described by calculations using a triple layer surface complexation model for the electric double layer, making use of equilibrium constants from literature.

Chapter 4 is an extension of Chapter 3, where ellipsometry was combined with a microfluidic platform that can generate a concentration gradient. The combined setup enables efficient screening studies at solid-liquid interfaces. The device was calibrated and further verified with numerical modeling. As a demonstration of the device, the Cs\(^+\) ion adsorption from CsCl solutions at various pH conditions was studied. The experimental results are subjected to a comparison to theoretical calculations with the surface complexation modeling.

Chapter 5 describes the adsorption of hexanoate ions from various aqueous solutions containing sodium hexanoate, NaCl or/and CaCl\(_2\) to various oxide
surfaces: silica, alumina and gibbsite. Based on the quantitative results obtained with a mass sensitive technique Quartz Crystal Microbalance technique (QCM-D), effects of various ions (Na\(^+\), Ca\(^{2+}\) as well as Cl\(^-\)) are demonstrated on different surfaces, and possible adsorption mechanisms on these oxide surfaces are proposed. On silica, Ca\(^{2+}\) ions strongly enhance the adsorption of hexanoate, suggesting that the divalent cations act as ion bridges between the carboxylate group and deprotonated silanol groups on the surface. On alumina, hexanoate adsorption is found to depend weakly on the salt composition, suggesting that the adsorption is caused by a direct interaction of the carboxylate group with the surface, consistent with a ligand-exchange mechanism. The adsorption behavior on partially gibbsite-covered silica surfaces is particularly rich and displays a strong but non-monotonic dependence on the Ca\(^{2+}\) concentration. Comparison to earlier work and control experiments suggest an important role of Cl\(^-\) anions, which compete with the carboxylate group for adsorption sites.

**Chapter 6** is focused on stearic acid Langmuir-Blodgett (LB) films which were deposited on silica surfaces. Stability of the LB films was dependent on the ions present in the sub-phases, which were used for the film deposition. Effects of divalent and monovalent ions are compared with the representative Ca\(^{2+}\) and Na\(^+\) ions. It is found that LB films prepared with Ca\(^{2+}\) ions demonstrated better stability compared to LB films prepared with Na\(^+\), suggesting the higher binding efficiency of divalent ions.

The overall summary and outlook are presented in **Chapter 7**.

**References**


1. Introduction


CHAPTER 2
SCIENTIFIC BACKGROUND
AND METHODOLOGY

In this chapter, we present a brief introduction of ion adsorption and the Electric Double Layer (EDL) in the first part. Furthermore, we describe the surface complexation model which is exploited as a theoretical approach to verify the experimental results in Chapter 3 and Chapter 4. In the second methodology part, we describe the theoretical aspects of characterization techniques: Quartz Crystal Microbalance (QCM), and Ellipsometry such as the working principle, and data analysis process. Moreover, we give a short introduction about the photolithography technique exploited in Chapter 3 and 4 to prepare the microfluidic devices. Finally, the Langmuir-Blodgett technique is described from a theoretical viewpoints as it is the sample preparation technique in Chapter 6.
Chapter 2

2.1 Scientific background

In this section, we review ion adsorption at solid-liquid interfaces in the context of Electric Double Layer (EDL) theory. As it is a well-developed theory, we present brief description here. Moreover, a surface complexation model is also described, because we exploit this model for theoretical calculation of ion adsorption for comparison with experimental results in Chapter 3 and Chapter 4.

2.1.1 Adsorption of ions

When mobile ions are present in a (aqueous) system that contains a charged surface, a spatial distribution of ions (perpendicular to the surface) is observed, as a consequence of the tendency of ions to minimize their electrochemical potential. Here, ions with different charges (sign and valence) follow different concentration profiles in the vicinity of the charged interface. The result of the ion distribution is an Electric Double Layer (EDL)[1]. The concept of a double layer at the surface in contact with an electrolyte solution was introduced in 1879 by Helmholtz [2], who assumed the presence of a compact layer of ions in contact with the charged surface. An improved model was developed by Gouy and Chapman[3, 4], who introduced the diffuse layer, in which the accumulated ions extend to some distance from the solid surface due to the Boltzmann distribution. Stern (in 1924)[5] suggested the presence of both the rigid Helmholtz layer and the diffuse layer which had been proposed by Gouy and Chapman at charged solid-liquid interfaces.

When the EDL was introduced, it was described primarily from the perspective of electrostatic potential. The surface charge density and surface potential \( \psi \), are related via the Poisson equation:

\[
\nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{\rho_e}{\varepsilon \varepsilon_0}
\]  

(2.1)
scientific background & methodology

where $\rho_e$ is the local charge density, $\varepsilon$ is the dielectric constant of solution, and $\varepsilon_0$ is the dielectric permittivity in vacuum. In the case of a flat plane, Eq. (2.1) can be reduced to a one dimensional form (in x-direction):

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{\rho_e}{\varepsilon \varepsilon_0}$$

(2.2)

where $x$ is the distance from the interface. The local charge density $\rho_e$ is associated with the charge distribution $n(x)$, which follows the Boltzmann equation:

$$n_i(x) = n_i^\infty \exp \left[-\frac{Z_i e_0 \psi(x)}{k_B T}\right]$$

(2.3)

where $n_i(x)$ is the concentration of ion $i$ at the interface region; $n_i^\infty$ is the concentration of that ion far from the interface; $Z_i$ is the valence of ion $i$, containing both magnitude and sign; $e_0$ is the elementary charge; $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. $Z_i e_0 \psi(x)$ is the work required to bring an ion from infinity to the position $x$ where the potential is $\psi(x)$. The local charge density is found by summing overall ions:

$$\rho_e = \sum_i Z_i e_0 n_i(z) = \sum_i Z_i e_0 n_i^\infty \exp \left[-\frac{Z_i e_0 \psi(x)}{k_B T}\right]$$

(2.4)

Thus the Poisson equation can be written as:

$$\nabla^2 \psi = -\frac{e_0}{\varepsilon \varepsilon_0} \sum_i Z_i n_i^\infty \exp \left[-\frac{Z_i e_0 \psi(x)}{k_B T}\right]$$

(2.5)

which is the well-known Poisson-Boltzmann equation. This equation defines the electric potential distribution in the diffuse ionic layer adjacent to a charged surface, subject to appropriate boundary conditions.
Chapter 2

Equation (2.5) does not have explicit general solution, and it can only be solved in certain limited cases. If we further consider a planar surface in symmetric electrolyte (both the cations and anions have the same valence, i.e. NaCl, CuSO₄): $Z_+ = -Z_- = Z$, Eq. (2.5) can be rewritten as:

$$\nabla^2 \psi = -\frac{Z\varepsilon_0 n\infty}{\varepsilon_\infty} \left[ \exp \left( -\frac{Ze_0 \psi(x)}{k_B T} \right) - \exp \left( \frac{Ze_0 \psi(x)}{k_B T} \right) \right]$$

(2.6)

where $n_+\infty = n_-\infty = n\infty$, the ionic number concentration in the bulk solution where $\psi = 0$. With the boundary conditions: $x = 0, \psi = \psi_0$, $\psi_0$ is the surface potential, and $x \to \infty, \psi = 0$. If the surface potential is low, i.e. $Ze_0 \psi(x) \ll k_B T \approx 25 \text{ mV}$, the solution of equation (2.6) can be obtained:

$$\psi = \psi_0 e^{-\kappa x}$$

(2.7)

In Eq. (2.7), $\kappa^{-1}$ is the Debye length (i.e. typical length scale) of the electric double layer, which is defined as:

$$\kappa^{-1} = \left( \frac{\varepsilon\varepsilon_0 k_B T}{2e_0^2 Z^2 n\infty} \right)^{\frac{1}{2}}$$

(2.8)

where $\varepsilon\varepsilon_0$ denotes the dielectric permittivity of the solvent; $n\infty$ is the bulk concentration and $Z$ is the valence of ions. Eq. (2.7) is the linearized Poisson-Boltzmann equation and the low potential model assumption is called the Debye-Hückel approximation[1].

As the planar surface is placed in the electrolyte, the acquired surface charge must be balanced within the EDL, to maintain overall electro-neutrality. Therefore the surface charge density $\sigma$ can be related to the electric charge density $\rho_e$ using the following equation:
The Graham equation describes the relation between charge and potential:

$$\sigma = -\int_0^\infty \rho_e \, dx = \varepsilon \varepsilon_0 \int_0^\infty \frac{d^2 \psi}{dx^2} \, dx = -\varepsilon \varepsilon_0 \frac{d\psi}{dx} (x = 0) \quad (2.9)$$

This is the so-called Gouy-Chapman model. It dictates that the ion distribution follows the Boltzmann equation, only considering the electrostatic potential.

The Gouy-Chapman model dictates that the ion distribution follows the Boltzmann equation considering only electrostatic potential. However at the interface, the chemical energy of ion adsorption can also make a significant contribution. Ions from solution may directly bond to the solid surface forming a distinct layer—Stern layer, at a well-defined distance from the solid surface. The Stern layer can be modeled as a parallel plate capacitor:

$$\frac{\psi_0 - \psi_c}{z_c} = \frac{\sigma_c}{\varepsilon_c} \quad (2.11)$$

where \( \psi_c \), \( \sigma_c \), and \( z_c \) are the potential, charge density, and thickness of Stern layer, and \( \varepsilon_c \) is the permittivity within Stern layer. Stern proposed Langmuir type adsorption to describe the equilibrium between ions adsorbed in the Stern layer and those in the diffuse layer. The surface coverage fraction of the occupied surface sites, \( \theta \), can be described as:

$$\theta = \frac{\sigma_c}{\sigma_0} = \frac{n^\infty}{n^\infty + \frac{N_A}{V_m} \exp \left( \frac{Ze_0 \psi_c + \Phi}{K_B T} \right) \quad (2.12)$$

where \( \sigma_0 \) is the surface charge density corresponding to a monolayer of counterions; \( N_A \) is the Avogadro constant and \( V_m \) is the molar volume of the
solvent and \( n^\infty \) is the bulk concentration. The term \( Z e_0 \psi_c \) is the electrostatic energy associated with the ion in the Stern layer. \( \Phi \) is the specific chemical energy associated with the adsorption process [6].

By combining Eq. (2.11) and (2.12), it follows that

\[
\frac{\psi_0 - \psi_c}{z_c} = \frac{\sigma_c}{\varepsilon_c} = \frac{\theta \sigma_a}{\varepsilon_c}
\]  

(2.13)

we thus find that the potential drop in Stern layer increases with the surface occupation, and approaches a constant once saturated adsorption occurs (\( \theta = 1 \)).

\[Fig.2.1 \] Schematic illustration of the electric double layer. \( 0 \)-plane (where protons and hydroxyls adsorb) and the \( \beta \)-plane (where the electrolyte ions adsorb).

In this thesis, we are mainly interested in the EDL at solid-liquid interfaces, to be more specific, in silica-aqueous solution interfaces. Silica surfaces are charged
in aqueous solutions, due to the protonation/deprotonation of the surface oxygen atoms. Instead of simply considering the silica surface as a hard wall with charges that just depend on pH, the chemical reactions between several adsorbed ions and surface sites should be taken into consideration. Here an example of silica surface in NaCl solution is presented, where a triple-layer model with one type of proton adsorption site is adopted, as shown in Fig. 2.1.

According to the so-called Triple Layer Model [7, 8], protons and hydroxide ions directly adsorb at the surface or 0-plane, resulting in the surface charge density $\sigma_0$. Other cations and anions adsorb at the so-called $\beta$-plane, resulting in charge density $\sigma_\beta$. To neutralize the total charge ($\sigma_0 + \sigma_\beta$), in the diffuse layer, a d-plane is defined which (effectively) contains the countercharge. Electric potentials $\psi_0$, $\psi_\beta$, and $\psi_d$ are associated with each plane of charge. The three layers of charge are modeled as two parallel-plate capacitors, with capacitance $C_1$ and $C_2$. The complexation reactions at silica surfaces (in case of added sodium salt) are:

\[
-SiOH \leftrightarrow -SiO^- + H^+ \quad K_H
\]

\[
-SiO^-Na^+ \leftrightarrow -SiO^- + Na^+ \quad K_{Na}
\]

where $K_H$ and $K_{Na}$ are the equilibrium constants, defined as:

\[
K_H = \frac{\{-SiO^-\} \times [H^+]_0}{\{-SiOH\}} = \frac{\{-SiO^-\} \times [H^+]_0 \exp(-Z_H e_0 \psi_0 / k_B T)}{\{-SiOH\}}
\]

\[
K_{Na} = \frac{\{-SiO^-\} \times [Na^+]_\beta}{\{-SiONa\}} = \frac{\{-SiO^-\} \times [Na^+]_\beta \exp(-Z_{Na} e_0 \psi_\beta / k_B T)}{\{-SiONa\}}
\]

In the above equations, $\{-SiO^-\}$, $\{-SiONa\}$ and $\{-SiOH\}$ are the corresponding site concentrations at the surface. $[H^+]_0$ and $[Na^+]_\beta$ are the ion concentrations in the bulk solution; $Z_H$ and $Z_{Na}$ are the valences of $H^+$ and $Na^+$. With these
equations, the relationship between surface potential and equilibrium constant is established.

The total number density of surface silanols is a constant (for which 8 nm\(^2\) is used in this thesis):

\[
\Gamma = \Gamma_{SiOH} + \Gamma_{SiO^-} + \Gamma_{SiONa}
\]  

(2.18)

which can be expressed as:

\[
\Gamma = \{-SiOH\} + \{-SiO^-\} + \{-SiONa\}
\]  

(2.19)

where the number density for the various species can be written as:

\[
\{-SiO^-\} = \frac{\Gamma}{[H^+]_0 + 1 + [Na^+]_\beta K_{Na}}
\]  

(2.20)

\[
\{-SiOH\} = \frac{\Gamma}{[H^+]_0 + 1 + [Na^+]_\beta K_{Na}} \times \frac{[H^+]_0}{K_H}
\]  

(2.21)

\[
\{-SiONa\} = \frac{\Gamma}{[H^+]_0 + 1 + [Na^+]_\beta K_{Na}} \times \frac{[Na^+]_\beta}{K_Na}
\]  

(2.22)

The surface charge density can be expressed as: \(\sigma_i = Z_i e \Gamma_i\), while \(\sum \sigma_i = 0\) due to the electro-neutrality. The above equations can be solved numerically. The solutions gives a detailed description of the charging behavior of silica-electrolyte solutions in terms of the model.

2.2 Methodology
In this section, we present an introduction to the theoretical aspects for the techniques exploited in this thesis. First, we review the characterization techniques: Quartz Crystal Microbalance (QCM) and Ellipsometry. Then we give a short description to the microfluidic technique. And finally, we discuss the Langmuir-Blodgett technique.

2.2.1 Quartz Crystal Microbalance

The Quartz Crystal Microbalance (QCM) is a cost-effective and mass sensitive technique based on the piezoelectric effect. The piezoelectric effect was first discovered by the brothers Curie via the effects of pressure on quartz crystals in 1880[9]. The Quartz crystal was discovered as an analytical device in 1959 when Sauerbrey demonstrated the linear relation between the mass change and frequency response of the crystal[10]. Applications of QCM in the 1960s and 70s were to measure the mass accumulated on the crystal surface from gas phase or vacuum. And it is still used to determine thicknesses of deposited layers in the laboratory today. In the 1980s, a solution based QCM was developed as an oscillator technology to measure changes in frequency that are related to the viscosity and density in highly damping liquid media[11, 12]. This recently developed QCM, denoted as QCM-D, is capable of measuring mass changes at solid-liquid interfaces, as well as the energy dissipation and viscoelastic properties of the deposited mass. Because of this, QCM has gained progressive attention in many applications, in particular in the field of biotechnology.

The heart of the QCM sensor is a quartz plate which is sandwiched between two electrodes. So called α-quartz crystals are mostly employed for QCM applications, because of their superior mechanical and piezoelectric properties. The cut-angle with respect to the crystal orientation determines the mode of oscillation. The AT cut crystal, which is the most commonly used for QCM applications, is fabricated by slicing through a quartz rod with a cut angle of 35°10' with respect to the optical axis, as shown in Fig.2.2. This cut-angle produces a shear displacement
perpendicular to the resonator surface. The advantage of the AT cut quartz crystal is that it displays a tremendous frequency stability and a temperature coefficient which is close to zero between 0 and 50°C.

**Fig.2.2** A) AT-cut angle of the crystal, taken from ref. [13]; B) an image of QCM sensor; C) Two oscillating standing waves corresponding to the fundamental and first overtone resonance frequency are drawn on top of the crystal section.

When an alternating potential difference is applied to the electrodes of the QCM crystal sensor, shear waves of opposite polarity are generated at the electrodes on either side of the crystal, such that the shear displacement is in plane with the crystal surface (Fig.2.2). Both waves traverse across the quartz thickness, are reflected at the opposing crystal face and then return to their origin. Constructive interference of incident and return waves occurs when the acoustic wavelength ($\lambda$)
meets the following condition Eq. (2.23), leading to resonance in the crystal with an eigen-frequency $f_n$ expressed as

$$\lambda = \frac{2d_q}{n}$$

$$f_n = \frac{n v_q}{2d_q}$$  \hspace{1cm} (2.23)

where $v_q$ is the propagation velocity of acoustic waves in quartz, $d_q$ is the crystal thickness, and $n=1, 3...$ is the overtone number. Resonance frequencies of typical QCM crystals are of the order of MHz, normally in the range of 5-20 MHz, with higher resonant frequencies corresponding to thinner crystals.

Deposition of mass on the QCM sensor surface leads to a decrease of the resonance frequency. This relation can be expressed via the Sauerbrey equation\[10]\:

$$\Delta f = -\frac{f_0}{d_q \rho_q} \times \Delta m = -\frac{n \times \Delta m}{C}$$  \hspace{1cm} (2.24)

where $\rho_q$ is the mass density of the quartz, $f_0$ is the fundamental frequency, and $d_q$ is the thickness of the quartz crystal. $C$ is the mass sensitivity constant ($C = 17.7 \text{ ng} \cdot \text{cm}^{-2} \cdot \text{Hz}^{-1}$ at 5 MHz), and $n$ indicates the overtone ($n = 1, 3,...$). The conditions for the Sauerbrey equation to hold are that: i) the adsorbed mass is evenly distributed on the crystal surfaces; ii) the adsorbed mass is much smaller than that of the crystal; iii) the adsorbed film should couple perfectly with the shear oscillation of the sensor.

However, the latter is not always the case, especially when the adsorbed film is viscous and does not follow the mechanical oscillation of the sensor. In this case, the frequency shift will not only depend on the mass change but also on the viscous and elastic nature of the adsorbed film. To take away these limitations, Rodahl and coworkers\[14\] modified the setup, to allow for simultaneous measurement of the resonant frequency and the absolute dissipation factor, $D$. 
The dissipation factor is the inverse of the $Q$-factor. It describes the damping in the system and is defined as:

$$D = \frac{1}{Q} = \frac{E_d}{2\pi \times E_s}$$

(2.25)

where $E_d$ is the energy dissipated in one period of oscillation, and $E_s$ is the energy stored in the oscillation system. If the film is viscous, energy is dissipated due to the oscillatory motion induced in the film (i.e., by internal friction in the film). With $D$ measured simultaneously with $f$ one has in principle access to a quantity that can indicate whether the Sauerbrey equation is applicable or not[15].

Fig.2.3 Schematic illustration of quartz crystal microbalance principle and the parameters used to simulate the quartz crystal covered with a viscoelastic film in contact between the sensor surface and a semi-infinite Newtonian liquid.

Voinova [16] found that the viscous loss of energy in the overlayers causes a deviation from Sauerbrey behavior and results in a non-trivial reduction in measured surface mass of the film. In this case, a more sophisticated model than
the Sauerbrey equation should be exploited to extract quantitative results. Rodahl [15] proposed a model, in which the crystal is treated as a harmonic oscillator and the Navier-Stokes equations for flow in the viscous over layers are used to calculate the changes in both resonance frequency and dissipation factor of the QCM. This model was adapted by Voinova [17], who derived an analytical expression for the resonance frequency shift and dissipation factor response of a thin viscoelastic film in contact with liquid. In this model, which is called the Voigt-based representation [17] of a viscoelastic solid, the adsorbed film is represented by a (frequency-dependent) complex shear modulus according to:

\[
G = G' + iG'' = \mu_f + i2\pi f \eta_f = \mu_f \left(1 + i2\pi f \tau_f\right)
\]  

(2.26)

where \(\mu_f\) is the elastic shear (storage) modulus, \(\eta_f\) the shear viscosity (related to the loss modulus), \(f\) the oscillation frequency, and \(\tau_f\) the characteristic relaxation time of the film. The adsorbed film is further represented by a uniform thickness, \(d_f\) and a uniform density, \(\rho_f\). The adsorbed film is situated between the QCM electrode and a semi-infinite Newtonian liquid under no-slip boundary conditions, as depicted in Fig. 2.3. In this case, the changes in the resonant frequency, \(\Delta f\), and the dissipation factor, \(\Delta D\) become [18]:

\[
\Delta f = Im(\beta)/2\pi d_q \rho_q
\]

(2.27)

\[
\Delta D = -Re(\beta)/\pi f d_q \rho_q
\]

(2.28)

where

\[
\beta = \xi_1 \xi_2 \frac{2\pi f \eta_f - i\mu_f}{2\pi f} \frac{1 - \alpha \exp(2\xi_1 d_f)}{1 + \alpha \exp(2\xi_1 d_f)}
\]

\[
\alpha = \frac{\xi_1 2\pi f \eta_f - i\mu_f}{2\pi f \eta_f} + 1
\]

\[
= \frac{\xi_1 2\pi f \eta_f - i\mu_f}{2\pi f \eta_f} - 1
\]

\[
\xi_1 = \frac{2\pi f \eta_f - i\mu_f}{2\pi f \eta_f} + 1
\]

\[
\xi_2 = \frac{2\pi f \eta_f - i\mu_f}{2\pi f \eta_f} - 1
\]
\[ \xi_1 = \sqrt{-\frac{(2\pi f)^2 \rho_f}{\mu_f + i2\pi\eta_f}} \]

\[ \xi_2 = \sqrt{\frac{2\pi f \rho_l}{\eta_l}} \]

Parameters of the adsorbed film can be extracted by fitting those values, once
the parameters of the quartz crystal and the bulk liquid are known. This
mathematical fitting can be done within the Q-tool, an analysis software made
available by Q-sense.

In general, the detection limit (2 ng/cm²) of quartz crystal microbalance is
poorer than that of optical techniques, such as surface plasma resonance,
reflectometry [19], etc. In most cases, the lower sensitivity does not hinder the
investigations of polymer or biomolecules. However, when it comes to small
molecules like ions, some more sensitive techniques may have to be exploited. In
the next sections, I will further discuss the more sensitive optical techniques.

### 2.2.2 Ellipsometry

Ellipsometry is a non-destructive optical technique. It allows for very accurate
and precise analysis of optical properties of various thin film systems including
the thickness and dielectric constants. Ellipsometry was first developed by Paul
Drude around 1900 [20-22]. At that time, ellipsometers were operated manually
which consumed a lot of time, as compared to modern devices. Rapid growth and
wide applicability of ellipsometry have been observed in the past 20 to 30 years,
due to the important progress in automation of measurement and data analysis.

Ellipsometry is based on the measurement of the state of polarization of light
upon reflection from the sample surface. Changes in the polarization state of
reflected light are due to the differences in electric fields which are induced by
the p- and s-components (which refer to parallel and perpendicular with respect
to the plane of incidence) of the incident light. The polarization changes can be
described by two ellipsometric angles: $\Psi$ and $\Delta$. $\Psi$ describes the changes in the ratio of the amplitudes of $p$- and $s$-components of the electric field, according to:

$$\tan \Psi = \frac{|E_p^r|/|E_p^i|}{|E_s^r|/|E_s^i|}$$  \hspace{1cm} (2.29)

where indices $i$ and $r$ correspond to the incident light and reflected light respectively. The angle $\Delta$ describes the shifts differences in phase between $p$- and $s$-components as:

$$\Delta = (\delta_p^r - \delta_p^i) - (\delta_s^r - \delta_s^i)$$  \hspace{1cm} (2.30)

where $\delta$ denotes a phase. The reflective properties of the sample are described by the reflectivity coefficients $r_p$ and $r_s$, which depend on the change in phase and amplitude of the reflected electric field $E^r$ according to:

$$r_p = \frac{E_p^r}{E_p^i} e^{i(\delta_p^r - \delta_p^i)}$$  \hspace{1cm} (2.31)

$$r_s = \frac{E_s^r}{E_s^i} e^{i(\delta_s^r - \delta_s^i)}$$  \hspace{1cm} (2.32)

from the above equations, we can derive the basic ellipsometry equation:

$$\tan \Psi \cdot e^{i\Delta} = \frac{r_p}{r_s} = \rho$$  \hspace{1cm} (2.33)

where $\rho$ is the complex reflectance ratio. The ellipsometry equation relates the measured ellipsometric angles to the reflectivity coefficients of the optical system (i.e. specimen). Optical characteristics of the system including thickness and refractive index of the layer on the sample are set as adjustable parameters to
find the best fit between experimental measurement and theoretically calculated reflectance, as predicted by the Fresnel equations, which describe the reflection and transmission of light at the interface between two media with different refractive indices. These Fresnel equations provide the reflection and transmission coefficients for the p- and s-components of the reflected and transmitted light, respectively [23].

Fig.2.4 Polarizer-Compensator-Sample-Analyzer (PCS A) configuration of an Ellipsometer.

Fig.2.4 presents a typical nulling-ellipsometry setup. It consists of a light source (laser), polarizer, compensator, analyzer and detector. The arm equipped with the laser, polarizer and compensator produces a light beam with known polarization state incident onto the sample surface. The arm with the analyzer is used to detect the polarization state after the light has been reflected off the sample surface.

In monochromatic ellipsometry, the measured parameters include a single pair of $\Psi$ and $\Delta$ at a fixed angle of incidence. Therefore at most two parameters can be
simultaneously determined from the measurement, such as the film thickness and the refractive index. In order to increase the sensitivity and precision, measurement is often performed at various incident angles. The output of the measurement is then not one pair of $\Psi$ and $\Delta$, but a set of angular dependent $\Psi$ and $\Delta$ values. Hence, each pair of $\Psi$ and $\Delta$ contains the information about the sample properties. This opens possibilities for studying more complex samples, where the density gradient, roughness, and other features of the probed film can be determined in addition to its thickness and refractive index.

As can be seen from the previous discussion, ellipsometry is an indirect technique, what we get from the measurement is just the ellipsometric angle, which do not have any physical meaning without the proper data fitting. In order to extract the physical properties of the sample, an optical layered stack model in combination with Fresnel equations has to be utilized, as schematically depicted.

**Fig. 2.5** A. an example of sample and its corresponding optical model: $d$ (thickness) and $n$ (refractive index); B. route of ellipsometry data analysis.
in Fig. 2.5. Ideally, an optical model should include all the information that is known about the sample before the measurement is done. Once the optical model is constructed, the corresponding $\Psi$ and $\Delta$ can be calculated. The model parameters, such as film thickness, refractive index or other properties of the sample, are fitted numerically to match the experimentally measured $\Psi$ and $\Delta$ data.

2.2.3 Microfluidics

Microfluidic techniques provide a powerful platform for biological or chemical assays. They offer many advantages, including small amount of solvents or sample, low-cost, potential for parallel operation, integration with other devices, etc. [24-26]. In this thesis, we combine microfluidics with other techniques as a screening tool for our studies.

![Fig. 2.6](image)

**Fig. 2.6** A) Example of a typical sequence of lithographic processing steps; B) an image of the prepared microfluidic device, illustration of dye.
Poly(dimethylsiloxane) (PDMS) is a widely used material for producing microfluidic devices. The reasons for its popularity are that this chemical is inexpensive, flexible, has a good bio-compatibility, is impermeable to water, and non-toxic to cells. And, most importantly, microfluidic devices can be easily fabricated with this material and bonded to many surfaces. Briefly, the procedure for fabricating a geometry in PDMS involves two steps: preparing the master mold and producing the PDMS device. The master mold is fabricated using the standard SU-8 negative resist photolithography technique. First, an SU-8 layer is spun onto a silicon wafer to create a layer. Then it is exposed to UV light via a high resolution photomask with the design of the microfluidic geometry. After the UV exposure and a post-bake (i.e. heating at 95°C for 30 min), the structure in the SU-8 layer becomes visible, and is subsequently developed as a mold for the microfluidic channels[27]. The mold is then treated with 1H,1H,2H,2H-Perfluoroctyl-trichlorosilane (FOTS), to prevent irreversible bonding of PDMS. A liquid PDMS precursor with a 1:10 ratio of curing agent to base component is poured onto the mold. In the following step the PDMS is degassed and put in an oven at 70°C for at least 1 hour to make sure it is totally cured. Finally, PDMS bearing the microstructure is peeled off from the mold, and small holes, for connecting channels with tubings, are punched with sharp tips. Next a cover slip (i.e. glass slide) is cleaned with organic solvents and prepared for the bonding steps. In order to prevent potential leakage and trapping of air bubbles, the PDMS slab and cover slip are exposed to air-plasma for 30 seconds prior to bonding. This oxidizes the -OSi(CH₃)₂- groups of PDMS to Si-OH, making the surface more hydrophilic, and also removes any organic contaminants which might interfere with the bonding. The fabricating processes and one device are presented in Fig. 2.6.

2.2.4 Langmuir-Blodgett technique
In Chapter 6, we studied the stability of Stearic acid Langmuir-Blodgett (LB) film. In the present section, we review the Langmuir-Blodgett technique and present a short description of LB film preparation.

A Langmuir monolayer or insoluble monolayer is a one-molecule thick layer of an insoluble (organic) material spread onto an aqueous sub-phase. Traditional compounds used to prepare Langmuir monolayers are amphiphilic molecules which possess a hydrophilic head group and a hydrophobic tail. In 1920, Langmuir introduced a technique which could transfer the floating monolayer to a solid surface by raising a hydrophilic substrate slowly through a liquid surface covered with monolayer[28]. In 1935, Blodgett succeeded in transferring successive monolayers onto the same solid surface[29] by vertically dipping the plate in and out of the monolayer covered liquid surface. Therefore, the transfer of floating monolayers onto solid surfaces is called Langmuir-Blodgett, or LB deposition.

**Fig.2.7** Langmuir trough (cartoon). Surface pressure-area isotherm of a Langmuir film and molecules at different phases.
A compressed monolayer can be considered as a two-dimensional solid. Before the monolayer is maximally compressed, a number of distinct phases can be seen on the so-called isotherm, which describes the dependence of the surface pressure on the area per molecule. The phase behavior of the monolayer is mainly determined by the physical and chemical properties of the amphiphilic molecules, the sub-phase temperature and the sub-phase composition[30, 31].

A simple terminology used to classify different monolayer phases of fatty acids was proposed by W.D. Harkins in 1952[32]. At very low coverage densities, the monolayers mostly present a gaseous state (G). On compression, a phase transition to the liquid-expanded state (L1) is observed. Upon further compression, the L1 phase undergoes a transition to the liquid-condensed state (L2), and at even higher densities the monolayer finally reaches the solid state (S). If the monolayer is further compressed after reaching the S state, the monolayer will collapse into three-dimensional structures. The collapse causes a rapid decrease in the surface pressure as shown in Fig.2.7. However, some studies[33, 34] have shown that phase behaviors of long chain compounds are much more complex than this assignment implies.

LB deposition is traditionally carried out in the ‘solid’ state where surface pressure is high enough to ensure sufficient cohesion in the monolayer. This means that attraction between the molecules in the monolayer is sufficient to prevent the monolayer from falling apart during transfer to the solid substrate and ensures the buildup of homogeneous multilayers (if needed). The surface pressure that gives the best results depends on the nature of the monolayer and is usually established empirically. Generally, amphiphilic molecules can seldom be successfully deposited at surface pressures lower than 10 mN/m, and at surface pressures above 40 mN/m, collapse and film rigidity often pose problems. When the solid substrate is hydrophilic, the first layer is deposited by raising the solid substrate from the sub-phase through the monolayer, whereas if the solid
substrate is hydrophobic, the first layer is deposited by lowering the substrate into the sub-phase through the monolayer.

Just like for the monolayer, several parameters such as the nature of the spread film, the sub-phase composition and temperature will affect the type of LB film produced. Additionally, the surface pressure during the deposition and the deposition speed, the type and nature of the solid substrate and the time the solid substrate is stored in air or in the sub-phase between the deposition cycles also play an important role in the deposition. The quantity and the quality of the deposited monolayer on a solid support are measured by the transfer ratio (TR), Eq. (2.34). An ideal transfer has a TR that is equal to 1.

\[ TR = \frac{\text{decrease in area of Langmuir monolayer}}{\text{area of the transferred film on solid substrate}} \tag{2.34} \]

References


In this chapter, we use imaging Internal Reflection Ellipsometry (IRE) in combination with a microfluidic device to study the adsorption of inorganic salt ions to silica-water interfaces. In our data analysis, the measured polarization-dependent reflectivity is compared to calculations from a layer stack model, where the electric double layer is modeled as a separate layer. Due to the high resolution of our technique, we are able to quantify the adsorption of Na\(^+\) and Ca\(^{2+}\) ions from aqueous solutions of their chloride salts as a function of their bulk concentrations at pH 3 and 10. Our measurements demonstrate a preferential adsorption of Ca\(^{2+}\) counterions. The experimental results are well described by calculations using a triple layer surface complexation model for the electric double layer with published equilibrium constants.

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3.1 Introduction

Changes of surface structure and function upon adsorption have important consequences in many fields such as lubrication [1], catalysis [2,3], oil recovery [4], drug delivery [5], nuclear waste disposal [6], etc. Among these applications, the silicate mineral-water system is particularly important because many chemical processes in the aquatic ecosystem occur on mineral surfaces in the presence of organic or inorganic molecules. Experimental studies have shown that ions, in particular divalent ions, can serve as a bridge to stabilize organic molecules both at solid/liquid [7-11] and liquid/liquid interfaces [12]. Some of these findings have important implications for industry, like the low salinity water flooding process in enhanced oil recovery [13-16]. Despite numerous studies, the interactions between ions and solid surfaces are still incompletely understood. They are the result of a complex interplay, involving chemical and structural changes, as well as a dynamics that includes not only the adsorption reaction but also the competition and exchange of ions and correlations amongst them. Ambient conditions such as pH, ionic strength, the presence of competing or promoting ions as well as the nature and the amount of substrate, also have significant effects on the distribution of cations and anions over the solid-solution interface [17].

Many approaches, both experimental and computational, have been developed to understand adsorption phenomena. Classical potentiometric titration [18] and streaming potential measurements [19] are widely used for characterizing ion adsorption to solid substrates. And the results have been compared with predictions from competing theoretical approaches such as Surface Complexation Models (SCM) [20], Density Functional Theory (DFT) [25], Monte Carlo (MC) [21,22] and Molecular dynamics (MD) simulations, and others [23]. Each of these theoretical approaches has its advantages and limitations. For example, SCM is unable to explain surface overcharging. Its application is limited to certain electrolytes or oxides at restricted ionic strengths and surface coverages. And the
magnitudes of the equilibrium constants are not always transferable to experiments without corrections for differences in site density, capacitances and surface area. DFT is restricted by its use of very large surface unit cells, while MC and MD require a huge computational effort and are subjected to limitations in both the number of molecules they can deal with, and the time range over which the molecular system can be studied. More details can be found in detailed review of Rimola et al. [23]. Ellipsometry [24] and reflectometry [25] give insights into the distribution and adsorption of ions. Recent progress in Atomic Force Microscopy (AFM) has provided the capability to study ion adsorption at the molecular scale, revealing complex and striking behaviors [26,27].

Compared to AFM, optical techniques have the advantage of being fast and non-intrusive, and they allow – under favorable conditions – chemically specific sensing and real-time signal processing. Specific methods such as Surface Plasmon Resonance, reflectometry, and ellipsometry all possess a very high sensitivity that allows for the detection of fractions of monolayers of adsorbed organic or inorganic material – provided that adsorbate and ambient solution have sufficiently distinct optical properties. In the present work, we use ellipsometry to study the adsorption of ions from an aqueous solution to solid-liquid interfaces based on the changes in polarization state of the light upon reflection at the interface. In particular, we use ellipsometry in an imaging mode in combination with microfluidic channels that allow us to investigate several fluid compositions in parallel.

Common ellipsometry operates in “external” mode, the incident light comes from a low refractive index medium (air or liquid) to a higher one (a solid or liquid) implying that the light passes through the liquid phase. The latter aspect makes it difficult to combine with microfluidic channels. Therefore, we operate ellipsometry in internal reflection mode (so-called Internal Reflection Ellipsometry (IRE)) which is hardly affected by microfluidic structures on the fluid side.
In this work, we make use of an IRE setup to explore the effects of concentration, salinity, and pH on the adsorption behavior of mono- and divalent ions at silica-water interfaces. The amounts of adsorbed ions at different pH conditions are determined by fitting the ellipsometric angles using a suitable optical layer stack model. Finally, optical thickness of the ion adsorption layer extracted from the experiments is compared to predictions from a triple layer Surface Complexation Model (SCM).

3.2 Experimental Details

3.2.1 Materials

CaCl$_2$·2H$_2$O and NaCl (ACS reagent grade, Sigma Aldrich) and deionized water with a resistivity of 18.2 MΩ·cm (Synergy-UV, Millipore) were used to prepare the solutions. The pH was adjusted with HCl and NaOH standard solutions. BK-7 glass substrates with a deposited Nb$_2$O$_5$ layer (to enhance internal reflection) and an additional silica layer on top were purchased from ST Instruments. Before experiments, substrates were cleaned by rinsing with Millipore water, ethanol and isopropanol and gently dried with N$_2$. Then, samples were exposed to an air plasma treatment (Harrick Plasma) for 15 min. Roughness and morphology of the silica surface were assessed by AFM in tapping mode (Icon, Veeco). The surface is very smooth and reveals no spatial structure, with root-mean square roughness smaller than 0.4 nm.

3.2.2 Methods

The measurements were carried out on a commercial imaging nulling-ellipsometer (EP3 Nanoscope, Accurion). The instrument is additionally equipped with an equilateral prism and a home-made microfluidic cell which enables parallel measurements under flow injection conditions. For liquid handling, a peristaltic pump (REGLO Digital MS-2/12) was used. Using the vacuum induced by the pump, solutions are carefully sucked into the cell, to avoid the formation of
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Air-bubbles. A laser beam ($\lambda=658$ nm) first passes through a polarizer and is then refracted into the prism, which provides coupling of the light beam into the layer of Nb$_2$O$_5$. The silica layer is exposed to an aqueous solution that is flushed through the microfluidic channel, as shown in Fig. 3.1a. Close to the Brewster angle, the reflectivity is very sensitive to the presence of thin adsorbed layers at the solid-liquid interface and the angle $\Psi$ displays a minimum, as shown in Fig. 3.1b. IRE measures the polarization changes of the reflected light, expressed in terms of $\Psi$ and $\Delta$. Optical properties of samples can be obtained by inserting these two parameters in Fresnel’s equation [28].

Fig. 3.1 (a). Central part of the IRE setup, equipped with a microfluidic cell. The silica-coated BK7/Nb$_2$O$_5$ substrate is directly attached to the prism with index matching oil. Fluids with adsorbing species are flushed through microfluidic channels, having the silica sensor surface as their ceiling; (b). A typical IRE measurement showing the ellipsometric angles $\Psi$ (top) and $\Delta$ (bottom) vs. the Angle Of Incidence (AOI): with water (olive diamonds) and 1 M CaCl$_2$ solution (magenta triangles) in the flow cell, solid lines guide the eye; (c). 6 parallel channels in the field of view. Light gray areas correspond to the channels filled with solution; the dark areas show the PDMS walls.
To achieve the highest sensitivity, one first has to find the critical angle from
the dependence of the ellipsometric angles on the Angle of Incidence (AOI). This
is done under static conditions (i.e. no flow) with deionized water in the flow cell.
The $\Psi$ and $\Delta$ angles are recorded in the AOI range from $48^\circ$ to $56^\circ$, the AOI is
varied in steps of $0.2^\circ$ (Fig.3.1b). At the minimum of $\Psi_0$, $\Delta_0$ displays a maximum
slope (Fig.3.1b). This is the condition of optimum sensitivity. Fig.3.1b also shows
the upward shift of the $\Psi$ and $\Delta$ vs. AOI curves by approximately $1^\circ$ for a 1 M
CaCl$_2$ solution (magenta) as compared to pure water (olive). Experimentally, we
can detect shifts of $\Psi$ and $\Delta$ down to approximately $0.01^\circ$ and $0.05^\circ$, respectively.
To extract the optical properties, the sample (including adsorbed layer) is
represented by a one-dimensional layer stack (see Fig.3.2c). Each layer $i$ is
characterized by its thickness $d_i$ and its refractive index $n_i$ (see Table 3.1). For
the glass substrate, the Nb$_2$O$_5$ layer and the SiO$_2$ layer, these properties are
calibrated in initial measurements with pure water. Subsequently, the properties
of these layers are kept fixed in the analysis of the $\Psi$ and $\Delta$ curves obtained
during the ion adsorption measurements at variable fluid compositions. The
electric double layer forming at the solid-liquid interface has a complex internal
structure consisting of a Stern layer and a diffuse layer with a resulting complex
refractive index profile which is related to the density profile (Fig.3.2b). The
ellipsometric measurement captures only the net integrated effect of this profile.
Hence, we represent the entire electric double layer by a single adsorbed layer
with an effective refractive index $n_a$ and an effective thickness $d_a$ (Fig.3.2c),
following the standard approach (see e.g. [29]). Below, we will discuss some
limitations of this approach regarding the interpretation of the data in terms of
simultaneously adsorbed counter-ions and depleted co-ions.

The measured AOI dependent $\Psi$ and $\Delta$ curves are fitted by adjusting the values
of $n_a$ and $d_a$, as well as the bulk refractive index $n_{\text{bulk}}$. Fitting of the $\Psi$, $\Delta$ curves
is carried out using the commercial software EP4 (Accurion).
Table 3.1 Layer stack model for IRE data analysis.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Parameters</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>4. BK-7 glass</td>
<td>n= 1.515, k=0</td>
<td>Fixed during fitting</td>
</tr>
<tr>
<td>3. Nb₂O₅</td>
<td>n=2.310, k=0</td>
<td>The values of d are obtained by fitting IRE data for every new sample, then both of them are kept fixed for further fittings.</td>
</tr>
<tr>
<td></td>
<td>d: 70-80 nm</td>
<td></td>
</tr>
<tr>
<td>2. SiO₂</td>
<td>n=1.456, k=0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>d: 15-25 nm</td>
<td></td>
</tr>
<tr>
<td>1. Adsorbed layer*</td>
<td>nₐ and dₐ to be determined</td>
<td></td>
</tr>
<tr>
<td>0. Water**</td>
<td>n=1.332, k=0</td>
<td>Fixed during fitting</td>
</tr>
</tbody>
</table>

(Note: all optical parameters are at wavelength 658 nm;
* For the measurement with water in the flow cell, this layer is not included in the model; In the analysis of adsorbed layer, region of nₐ is fixed between 1~2, dₐ can be fixed anywhere between 0.5 nm to 5 nm, see the discussion for details.
** When other salt solutions are used, n_bulk is obtained by fitting IRE data.)

In dynamic (i.e. time dependent) adsorption measurements, the AOI is fixed at the value where Ψ is found to be minimal, i.e. 51° in our experiments with the silica exposed to pure water. A measurement then consists of a continuous recording of Ψ and Δ as a function of time, while solutions are flushed through the microfluidic channels at typical flow rates of order of 1 μL/min. Each recording of a (Ψ, Δ data point takes approximately 9 s. All measurements were carried out in a temperature controlled room (22±1°C). The thickness of the bare silica layer is measured at the beginning and at the end of the experiment for each sample. It is typically found to vary by less than ±0.1 nm. This indicates that neither dissolution of the silica layer nor permanent adsorption play an important role in these measurements.
Fig. 3.2 (a) Schematic illustration of laser path inside the prism (BK-7 glass) and the Electric Double Layer (EDL); (b) distribution of cations and anions in EDL; (c) refractive index profile used in the analysis of IRE measurement: the dashed line representing the EDL is modeled as an effectively homogeneous layer.

3.3 Results and Discussion

To demonstrate the strength and sensitivity of the technique, we studied the adsorption of ions to solid-liquid interfaces. As a well-characterized system, we select aqueous solutions of NaCl, CaCl₂ and silica surfaces. The adsorption behavior of both salts was studied while tuning the surface charge of the silica via the pH. At pH 3, silica surfaces are essentially uncharged because this is close to the point of zero charge [30]. At pH 10, the silanol groups are largely deprotonated and the silica surface carries a negative charge [31]. To compensate this charge, cations need to adsorb to the interfaces.

Experimental data of Ψ and Δ vs. AOI for a variety of CaCl₂ solutions at the two pH values studied under quasi-static conditions are displayed in Fig. 3.3. In Fig. 3.4 dynamic (i.e. time dependent) adsorption measurements for water and 0.5 M CaCl₂ at two pH conditions are shown. In the latter measurements, Ψ and Δ are
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continuously recorded as a function of time, keeping the AOI fixed, while solutions are flushed through the microfluidic channels. In the present work, where ions are the adsorbing species, the typical timescale of the adsorption process is (much) shorter than the time resolution of our setup. So we only show the measurement at equilibrium conditions as displayed by the plateaus in Fig.3.4. Similar results are obtained for NaCl and CaCl$_2$ solutions with concentrations ranging from 0.01 M to 1 M (data not shown).

**Fig.3.3** Ellipsometric angles $\Psi$ and $\Delta$ as a function of Angle Of Incidence (AOI) for various concentrations of CaCl$_2$ at pH 3 (a) and pH 10 (b). Symbols are the experimental data, and solid lines are calculations from a layer stack model. For (a) and the inset in (b), we used a four-layer model including the 1$^{st}$, 2$^{nd}$, 3$^{rd}$ and 5$^{th}$ layer in Table 3.1, leaving $n_{bulk}$ as a fitting parameter. For the main panel of (b), we used a model which includes all five layers in Table 3.1, assuming $d_\alpha$ as 0.5 nm and leaving $n_{\alpha}$, $n_{bulk}$ as fitting parameters.
Variations of ellipsometric angle shifts vs. AOI or time when flushing with ‘pure’ (without additional salt) water at pH 3 and 10 are indistinguishable, i.e. the addition of 0.1 M HCl or NaOH to vary the pH has a negligible effect on the refractive index of the solutions below the detection limit of our instrument. This is especially clear in Fig.3.4, where solutions at both pH conditions are flushed and results are displayed in the same graph. Because the pH induced variations of the surface charge alone remain undetected, the observed variations of the signals in Fig.3.3 and Fig.3.4 must be caused by the added salt. The Δ angle shifts are larger than those of Ψ. For pH 3, the shifts in Ψ and Δ can be fitted quantitatively by assuming variations of the bulk refractive index $n_{\text{bulk}}$, with the 4-layer model: BK-7 glass $\rightarrow$ Nb$_2$O$_5$ $\rightarrow$SiO$_2$ $\rightarrow$bulk solution (Fig.3.3a). The extracted $n_{\text{bulk}}$ values are the same as measured independently by a refractometer (Fig.3.5). Fig.3.4 also shows that the adsorption and desorption processes are perfectly reversible within the resolution of our experiment.

![Fig.3.4 Time dependent IRE measurement: Ψ and Δ angle shifts upon consecutive flushing water and 0.5 M CaCl$_2$ (aq) at pH 3 and pH 10. Only the data obtained after reaching equilibrium are shown.](image)
This result is consistent with the general picture that silica-water interfaces at pH 3 are uncharged and the adsorption of ions thus negligible. At pH 10, however, following the same approach to fit the shifts of $\Psi$ and $\Delta$ observed is no longer possible (see insets of Fig.3.3b). To fit the pH 10 data, we need to add one additional layer representing the electric double layer to the optical model. We leave $n_a$ and $n_{\text{bulk}}$ as fitting parameters, $d_a$ is fixed at 0.5 nm. As expected, the extracted values of $n_{\text{bulk}}$ turn out to be consistent with the values measured with the refractometer and also correspond well to the data for pH 3, see Fig.3.5. This justifies use of the five-layer stack model at pH 10. Fitted curves of other salt solutions look similar to those in Fig.3.3.

![Figure 3.5: Comparison between refractive index values of CaCl$_2$ solutions: extracted from modeling (cross, with the layer stack model used in Fig.3.3 for pH 3 and 10 respectively) and measured with refractometer (open square and circle). Black is at pH 10, and red is at pH 3.](image-url)
As noted above, the resulting optical parameters \( n_a \) and \( d_a \) of the adsorption layer are effective values that represent the actual refractive index profile. Following de Feijter et al.[29] we can express them as:

\[
\begin{align*}
    n_a &= \frac{\int n(z)(n(z) - n_{\text{bulk}})dz}{\int (n(z) - n_{\text{bulk}})dz} \quad (3.1) \\
    d_a &= \frac{\int (n(z) - n_{\text{bulk}})dz}{n_a - n_{\text{bulk}}} \quad (3.2)
\end{align*}
\]

where the integrals extend from zero to infinity, \textit{i.e.} from the surface into the bulk liquid. Upon fitting the 5 layer stack model to the experimental data, it turns out that the values obtained for \( n_a \) and \( d_a \) are highly correlated. Fits of similar quality can be obtained for \( 0.5 \text{ nm} < d_a < 5 \text{ nm} \) and \( n_a \) varying in such a manner that the excess optical thickness \( \Delta n_a d_a = (n_a - n_{\text{bulk}})d_a \) due to the ion adsorption remains essentially constant, \textit{i.e.} independent of the choice of \( d_a \). We find values \( \Delta n_a d_a \ll 1 \text{ nm} \) for all experimental conditions. For such small values, it is well-known that ellipsometry does not provide a reliable distinction between refractive index and thickness [28,32,33]. Fig.6 shows that \( \Delta n_a d_a \) increases with increasing (cation) concentration for both NaCl and CaCl\(_2\) at pH 10. The excess optical thickness for the CaCl\(_2\) salt exceeds the one for NaCl by approximately a factor four, indicating a much stronger adsorption for the divalent salts. For pH 3 the excess optical thickness is found to be zero within experimental error for both salts at all concentrations (data not shown).
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**Fig.3.6** Optical thickness of NaCl(square) and CaCl\(_2\)(circle) vs. the salt concentration at pH 10. The solid symbols are the experimental results and the lines are the calculations from surface complexation model. For NaCl, three pK\(_{Na}\) values are used: 2.65 (Blue dash dot line), 1.65 (red solid line) and 0.65 (black dash line).

To relate the measured excess optical thickness to the physical surface excess of adsorbed ions, we express the local refractive index \(n(z)\) of the salt solution in terms of the local excess concentration \(\Delta c_i(z) = c_i(z) - c_{i,bulk}\) for each ionic species \(i\), as caused by adsorption and depletion (see Fig.3.2b).

\[
n(z) = n_{bulk} + \sum_i \alpha_i \Delta c_i(z)
\]  

(3.3)

Here, the sum runs over all species in the solution, \(i.e.\) the anions and cations in our case. The coefficients \(\alpha_i = dn/dc_i\) indicate the increment of the refractive
index with increasing concentration of species \( i \). Combining these equations with the standard definition for the surface excess for each species

\[
\Gamma_i = \int \Delta c_i(z) \, dz
\]  

(3.4)

we can write

\[
\Delta n_a \, d_a = \sum_i \alpha_i \Gamma_i
\]  

(3.5)

where \( \Delta n_a = L^{-1} \int_0^L (n(z) - n_{\text{bulk}}) \, dz \), with an arbitrary normalization thickness \( L \gg d_a \). The excess optical thickness of the adsorption layer thus has a direct physical meaning and expresses the combined surface excess of all ions in the solution, each weighted by its refractive index increment \( \alpha_i \). For the specific case of our salt solutions, Eq. 3.5 simplifies to

\[
\Delta n_a \, d_a = \alpha_+ \Gamma_+ + \alpha_- \Gamma_- = \alpha_+ \left( \Gamma_+ - \frac{1}{Z} \Gamma \right) + \frac{dn \, 1}{dc \, \Gamma} \]  

(3.6)

where \( \Gamma_+/\Gamma_- \) and \( \alpha_+/\alpha_- \) denote the excess and the refractive index increment of the cations and anions, \( Z \) is the valence of cations and \( dn/dc \) is the bulk increment of the refractive index upon adding salt, which is known experimentally. For NaCl and CaCl\(_2\), we use \( (dn/dc)_{\text{NaCl}} = 10.17 \, mL/mol \) and \( (dn/dc)_{\text{CaCl}_2} = 23.59 \, mL/mol \). Moreover, we use \( \alpha_{\text{Na}^+} = 7.1 \, mL/mol \), \( \alpha_{\text{Ca}^{2+}} = 17.59 \, mL/mol \), as reported by Porus et al.[21].

To compare our experimental results to a model, we calculate the expected surface excess using the standard triple layer model of the electric double layer [20,34]. Coupling the Poisson-Boltzmann theory for the diffuse layer to surface complexation reactions [35,36] including the equilibrium constants as specified in Table 3.2, we can calculate the expected surface excess \( \Gamma_i \) for each ionic species, as shown in Fig.3.7. The solid lines in Fig.3.6 show that the resulting model predictions are in good agreement with the experimental data. To illustrate the level of sensitivity, we also plot two competing lines for NaCl adsorption
assuming $pK_{Na}$ values one unit higher and lower than reported in refs. [37,38].
The resulting dashed and dotted lines in Fig.3.6 are still compatible with the
experimental data, indicating the range of uncertainty in the analysis.

**Table 3.2** Surface complexation reactions and parameters used in triple layer
model.

<table>
<thead>
<tr>
<th>Surface complexation reactions</th>
<th>Equilibrium constant, $K_i$ (mol/L)</th>
<th>Capacitance ($F/m^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H $\text{SiOH} \leftrightarrow \text{SiO}^- + H^+$</td>
<td>$10^{-6.9}$ [20,39,40]</td>
<td>$C_1$</td>
</tr>
<tr>
<td>NaCl $\text{SiO}^- \text{Na}^+ \leftrightarrow \text{SiO}^- + \text{Na}^+$</td>
<td>$10^{-4.65}$ [36,37,40]</td>
<td>1.0 $C_2$</td>
</tr>
<tr>
<td>CaCl$_2$ $\text{SiO}^- \text{Ca}^{2+} \leftrightarrow \text{SiO}^- + \text{Ca}^{2+}$</td>
<td>$10^{-0.7}$</td>
<td>1.4 $C_2$</td>
</tr>
<tr>
<td>$\text{SiO}^- (\text{CaOH})^+ + H^+ \leftrightarrow \text{SiO}^- + \text{Ca}^{2+} + H_2O$ [38,41,42]</td>
<td>$10^{8.2}$</td>
<td></td>
</tr>
</tbody>
</table>

(Note: The site density is the surface concentration of silanol surface groups,
indicating the maximum number of sites that can get deprotonated.)

Given the reasonable agreement between model and experimental data, we
explore the consequences of the surface complexation model in more detail. In
Fig.3.7, we plot the excess of cations and anions for the Stern layer and the
diffuse layer separately. Again, we only show the data for pH 10 because
adsorption at pH 3 is negligible. As expected, a strong positive excess is found for
the counter ions (*i.e.* the cations) in the Stern layer. Simultaneously, there is,
however, a positive excess of counter ions and depletion (negative excess) of co-
ions from the diffuse layer, too. All excesses display a finite dependence on the
salt concentration for concentrations below approximately 0.2 M and saturate for
higher concentrations. Multiplying each excess with the corresponding refractive
index increment, we find that the optical thickness shown in Fig.3.6 is dominated by the contribution from the Stern layer, as concluded earlier by Porus et al. [25]. Yet, the contribution of the diffuse layer is not negligible and amounts to approximately 15% of the total excess of ions.

**Fig.3.7** Calculation of Surface excess of cations in stern layer (black line), cations in diffuse layer (blue dash line), and anions in diffuse layer (red dash dot line) from surface complexation model as a function of NaCl (a) and CaCl$_2$ (b) concentrations at pH 10.

From Fig.3.7, we also conclude that the total adsorption of Ca$^{2+}$ (*i.e.* –SiO–Ca$^{2+}$ and –SiO–(CaOH)$^+$ species together) to the surface is much more pronounced than the adsorption of Na$^+$. According to the model this contribution is largely caused by the strong adsorption of CaOH$^+$ with its rather high pK value. This strong adsorption implies an enhanced Ca-induced deprotonation of silanol groups, which is required to preserve overall charge neutrality.

The use of the Poisson Boltzmann theory in combination with surface complexation models has been criticized (see [44] for an extensive discussion). In particular for divalent cations such as Ca$^{2+}$ at elevated concentrations, extensions of the Poisson Boltzmann theory that take into account lateral interactions with the adsorbed layer, e.g. due to the finite volume of the ions, electrostatic and
hydrogen bonding interactions (see e.g.[45]) are generally relevant. Porus et al. [21] argue that any mean field theory is inadequate to study such systems. Recent work on Ca$^{2+}$ adsorption on gibbsite using a combination of high resolution atomic force microscopy and density functional theory [25] also suggests a high degree of complexity exceeding the present surface complexation analysis. Nevertheless, the latter provides a reasonable description of the adsorption data presented here that is consistent with various other earlier potentiometric titration [46-48]. The data presented in this work are insufficient to provide strong arguments in favor of any of the competing models. Possibly our results could be equally explained in terms of ion correlations, as in ref.[21].

To disprove either of the theories, it would be important to design experiments that can be described by one approach but not by others. Next to a broader set of experimental data this will probably require the combination of several complementary probes, including perhaps optical spectroscopies to detect beyond doubt the presence of certain species at the interface. Another interesting option is the combination of optical measurements (like the present one) and force measurements. While the latter ones probe the total charge in the diffuse layer, the former ones – as the present experiments suggest – only probe cations from the salt but not protons and hydroxyl ions. Exploring this complementarity in a single experiment is expected to provide additional insights. Optical experiments in combination with microfluidics that allow for a high degree of parallelization as demonstrated here are expected to offer a pathway to the required rapid screening of large parameter spaces of fluid compositions.

3.4 Conclusions

We presented a sensitive optical technique – Internal Reflection Ellipsometry – for probing adsorption at liquid-solid interfaces in combination with microfluidic channels. The sensitivity of this technique is demonstrated by its ability to detect adsorption and depletion of monovalent and divalent salt ions at silica-water
interfaces under various pH conditions. The adsorption and desorption reactions are found to be perfectly reversible. The measured excess optical thickness of adsorbed ions is linked to the Gibbs surface excess of each ion species. The presented adsorption isotherms are successfully modeled using a mean field Poisson Boltzmann theory in combination with a triple layer surface complexation model. We anticipate that the combination with more sophisticated microfluidics device will enable efficient high speed screening of adsorption/desorption processes for a wide range of applications.

References

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CHAPTER 4
MICROFLUIDICS AND TOTAL INTERNAL REFLECTION ELLIPSOMETRY FOR ADSORPTION STUDY

Establishing and maintaining a concentration gradient which is stable in space and time is critical for a variety of screening applications on solid substrates, through (bio)chemical reactions or physical adsorption. In this work, we develop a simple and compact microfluidic device based on steady-state diffusion of the analyte, between two control channels where liquid is pumped through. The device generates a near-linear distribution of concentrations. We demonstrate this via experiments with dye solutions and comparison to finite-element numerical simulations. In a subsequent step, the device is combined with total internal reflection ellipsometry to study the adsorption of (cat)ions on silica surfaces from CsCl solutions at various pH. Such combined setup permits a fast determination of adsorption isotherm. The measured optical thickness is compared to calculations from a triple layer model for the ion distribution, where surface complexation reactions of the silica are taken into account. Our results show a clear enhancement of the ion adsorption with increasing pH, which can be well described with reasonable values for the equilibrium constants of the surface reactions.

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4.1 Introduction

Chemical gradients are an important factor for guiding the growth or migration of biomolecules [1, 2, 3], the differentiation of cells [4] in living tissues, and for controlling adsorption behaviors at solid-liquid or liquid-liquid interfaces in various technical applications [5, 6, 7, 8]. Interest in elucidating these phenomena has led to the development of numerous microfluidic gradient generators. Generally, these devices can be categorized into two types depending on the methods used: convective-based, and diffusion-based microfluidics.

Convection-based gradient generation methods have for example been used to study chemotaxis of cells [9, 10]. A unique advantage of convection-based methods over diffusion-based ones is that they allow an immediate in situ control over concentration profiles via the flow rates [11, 12]. A successful example of this kind is the “Christmas tree” microfluidic device first presented by Whitesides and coworkers [13, 14, 15]. In this scheme, two laminar streams carrying different chemical agents are repeatedly split, mixed, and recombined. However adverse effects of the involved flow on the process under study (e.g. the secretion of molecules by biological cells [16]) might occur. The viscous shear stress introduced by the flow can also interfere with the migration of biomolecules [17]. Therefore, for some studies, diffusion-based microfluidics is preferred.

Great efforts have been spent on developing the diffusion-based gradient microfluidics in the past years. In these methods, membranes [18, 19] or hydrogels [17, 20] are widely utilized, as these materials can minimize the convection, while they still allow the diffusion of small molecules. Additionally, hydrogels are biocompatible which is important for their use in biological studies. To integrate the membrane or hydrogel into the microfluidic device, usually these devices contain two additional layers, to “sandwich” the membrane or hydrogel. This complex fabrication process requires expertise, limiting a wide exploitation by biologists and chemists.
Considering aforementioned drawbacks of the existing convection-based and diffusion-based microfluidic devices, we developed a diffusion-based concentration gradient generator, which is easier to fabricate and operate. This device can generate a large number of (well spread) discrete concentrations. Besides a mold and a PDMS precursor, no additional parts (i.e. hydrogels or membranes) are required once the design is made. The principle of the device is simple: a concentration gradient is generated across flow-free channels which connect the “source” and “sink” -channels. A similar design has been used by Saadi and coworkers [21]. Their device, termed as Ladder Chamber, creates a continuous linear concentration profile (or a constant concentration gradient) along a uniform flow-free channel. In comparison, our flow-free channel design consists of large wells linked by small connectors; this ensures well-defined concentrations in discrete areas that are easy to sample. Besides that, with our method various concentration profiles can be generated via a simple and proper design of the mass transfer resistances of the small connectors.

In this work, we demonstrate a microfluidic device which generates a near linear discretized concentration profile. Measured concentrations are compared with a full finite-element numerical simulation as well as a simple circuit model. The good agreement between the experiments and the two theories validates our concept of device design. As an application demonstration, we combined this microfluidic device with total internal reflection ellipsometry to achieve a high throughput measurement of cesium ion adsorption from CsCl solutions at various pH conditions. The relation between the optical signal and the adsorbed amounts, allows us to get quantitative results. Finally, the experimental results are compared with theoretical calculations for the ion distribution; here we assume a triple layer model, and combine this with surface complexation reactions.
4.2 Materials and methods

4.2.1 Device design and fabrication

Fig. 4.1 Microfluidic platform and design. A) Image of the microfluidic chip studied with imaging ellipsometry. The channel structure in PDMS is sandwiched between a gold coated glass slide (top side, under the prism) and normal glass slide (bottom side). A layer of silica, coated onto the gold is in contact with the solutions; B) Microfluidic chip loaded with dye; C) Steady state concentration distribution, where the top channel is loaded with 0.1 M KMnO₄, and the bottom channel with DI water; D) Top and side view of the channel design. Each cylindrical well has a diameter of 300 μm and a depth of 118 μm. The length of the connecting channels is ~20 μm, the width varies from 10 to 100 μm, while the depth is fixed at 12 μm. E) Serial arrangement of (coded) elements as used in the circuit model for concentration distribution (see text for details).
A real microfluidic device is shown in Fig. 4.1B, and the details of its design are given in Fig. 4.1D. The key feature of the device is an array of wells flanked by two parallel inlet feeding channels. There are 4 rows of wells in the device, and every row has 3 wells which are connected by small channels. When the two feeding channels are supplied with two different concentrations of one analyte of the same flow rate (this keeps pressure balance between two feeding channels, thus eliminating flow in wells), the diffusion takes place across the device. At the steady state, a set of well spread discrete concentrations could be established in 12 wells by proper design of dimensions of the small connections between the wells and the feeding channels. To ensure homogenous concentrations in wells and minimize convection in the wells, the height of small connections (12µm) is designed to be much smaller than that of wells and feeding channels (118 µm).

The fabrication of microfluidic device is shown in Fig. 4.2. It was prepared using the standard SU-8 negative resist photo-lithography technique. A two-layer fabrication method was used to create the two parallel flow channels and the 12 circular sample wells (depth: 118 µm), and the perpendicular running connecting channels (depth: 12 µm). First, the SU-8 (MicroChem, SU-8 2010) is spun onto a silicon wafer to create the 12 µm layer (Fig. 4.2 A1). Then it is exposed to UV light via a high resolution quartz photo-mask with the complete design of the microfluidic network (Fig. 4.2 A2). After UV exposure and post-baking (95°C, 3 min), the second layer of SU-8 (MicroChem, SU-8 50) is spun (Fig. 4.2 A3). This layer of 106 µm is exposed with a second mask, which only contains the pattern of the flow channels and wells (Fig. 4.2 A4). Both patterns are superimposed with the large gap alignment option on the mask aligner (EVG620). After the same treatment (UV exposure and post-baking) as done on the first layer, the two-layer SU-8 is developed into a master template[22], as shown in Fig. 4.2 A5. Then the mold is treated with 1H,1H,2H,2H-Perfluoro-octyltrichlorosilane (FOTS), to prevent irreversible bonding of PDMS. Liquid PDMS with a 1:10 ratio of curing agent to base polymer is poured onto the mold (Fig. 4.2 B1). Next the PDMS is degassed and put in oven at 70°C for 1 hour for curing. At last, the PDMS bearing
the microstructure is peeled off from the mold (Fig. 4.2 B2), and small holes for connecting the channels with tubings, are punched with sharp tips.

The silica coated substrate for ellipsometry experiments is prepared with e-beam evaporation. SF10 glass is coated with the following layers: titanium, gold, titanium and silica. The thickness of the titanium adhesion layers is controlled at ~1 nm; those of gold and silica are 30 nm and 20 nm respectively. After the preparation, the slide is rinsed with a mixture of ethanol and isopropanol, and dried with nitrogen. Thereafter, all layer thicknesses are (more precisely) measured with ellipsometry.

**Fig. 4.2** Sketch of the fabrication of the microfluidic master mold (A1 to A5) and the preparation of the microfluidic device (B1 to B3).
4. Microfluidics and total internal reflection ellipsometry for adsorption study

The PDMS slab and substrate slide are then ready, but their surfaces still need to be made adhesive, to enable assembly of a chip without any leakage or trapping of air bubbles. Exposure to air-plasma for 30 seconds leads to oxidation of the -Si(CH₃)₂- groups of PDMS to Si-OH, making the surface more hydrophilic, and also removes any organic contaminants—which might otherwise interfere with the binding. Then the PDMS slab and the silica coated glass slide are bonded as shown in Fig.4.2 B3.

4.2.2 Concentration gradient characterization and validation

To validate the microfluidic device, a solution of 0.1 M KMnO₄ in DI water was used. Before each experiment, the microfluidic device was filled with DI water by fully submerging it in degassed water inside a vacuum chamber. This prevents the formation of bubbles in the microfluidic device. Then the device was connected with tubings of equal length and dimension (to keep identical conditions on both inlet sides and hence maintain a balanced pressure). Next the two liquids were loaded in the separate inlet channels. A syringe (60 mL, BD) together with a syringe pump (PHD 2000, Harvard) was connected at the outlet. The syringe pump was kept running (i.e. sucking fluid) during the entire measurement at a flow rate of 0.1 mL/min. Observations of the time and location dependent image-brightness were made using a Nikon TE2000 inverted microscope. Images were grabbed every 5 minutes and post-processed with ImageJ (shareware from National Institute of Health), using the Lambert-Beer law to relate distinction to concentration, and hence extract the concentration distribution, after subtracting the background.

The design of the device was done with numerical calculations using COMSOL Multiphysics 5.0 software (COMSOL Inc.). The flow and concentration fields in the device were modeled by the Navier-Stokes (NS) equation and convection-diffusion equation, respectively:
\[
\rho \frac{\partial \mathbf{u}}{\partial t} = -\nabla p + \mu \nabla^2 \mathbf{u}
\]  

(4.1)

\[
\frac{\partial \mathbf{c}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{c} = D \nabla^2 \mathbf{c}
\]  

(4.2)

where \( \rho \) is the liquid mass density, \( p \) is the pressure, \( \mu \) is the dynamic viscosity, \( \mathbf{c} \) is the analyte concentration, and \( D \) is diffusion coefficient. The vector \( \mathbf{u} \) represents the velocity of the fluid. The flow in the microfluidic device is dominated by viscous effects, \textit{i.e.}, very small Reynolds number, so the convective term has been neglected in the NS equation (4.1). Eq. (4.1) and (4.2) were solved within COMSOL. It was noted that the momentum transport reaches steady state much faster than the mass transport, since the momentum diffusivity \( \frac{\mu}{\rho}, O(10^{-6} \text{m}^2/\text{s}) \) was 3 orders of magnitude higher than the mass diffusivity, \( O(10^{-9} \text{m}^2/\text{s}) \). In the simulation, we could safely treat the flow problem to be pseudo-steady, by neglecting the left hand side of Eq.(4.1). Further, for Eq.(4.1), a no-slip boundary condition was used on all channel walls, while the outlet was given the flow rate as generated by the syringe pump, and the pressure of the two inlets was set to zero as a reference. For Eq.(4.2), a no-flux boundary condition was specified on all channel walls, two inlets were prescribed with the respective concentrations, and a convection-only boundary was used at the channel outlet.

According to the simulation results, it typically takes \( \sim 40 \) min to establish the steady-state concentration gradient. This agrees with the rough estimation based on diffusion time scale \( O(L^2/D) \), wherein \( L \) is the separation between the “source” and “sink” channels. This implies that with the flow rate (0.1 mL/min) and the syringe volume (60 mL) exploited in this work, the stability of the established concentration should last for around five hours.
4. Microfluidics and total internal reflection ellipsometry for adsorption study

4.2.3 Ion adsorption

The ion adsorption experiment was conducted using a commercial imaging ellipsometer (Accurion, Germany). In our previous study [23], we found that at pH 3, no ion adsorption occurs at a silica surface either from CaCl₂ or NaCl solutions. Changes in the ellipsometric angles can then be totally ascribed to the change in bulk refractive index, which shows a linear dependence on salt concentration. A measurement was performed with a 0.5 M CsCl solution at pH 3 to verify whether Cs⁺ ion adsorption occurs at this condition. The dependences of the ellipsometric angles $\Psi$ and $\Delta$ on the incident angle agreed well with the results of a layer-stack model as shown in Fig.4.3. Here, the optical properties of layers I, IV and the composite layer II were taken from previous characterizations, while an optimization was made for the properties of (the adsorbed) layer III. (Comparison between the experimental and modeling results is provided in Appendix Fig.A1). From it, we conclude that no adsorption takes place from CsCl solution onto silica surface at pH 3. Hence this pH condition can be used as a reference to determine the salt concentration inside each well.

These calibration measurements were performed as follows: initially, an aqueous solution of 1 M CsCl (pH 3) and water (DI, with pH adjusted to 3 with HCl) were loaded into the separate inlet channels (as displayed in Fig.4.1 C). Then the incident angle was fixed and $\Psi$ and $\Delta$ angles were recorded for each well simultaneously as a function of time. Once both recorded angles had reached their respective plateaus in each wells (concentration gradient established), they were measured as a function of the incident angle (this improves the accuracy of the measurement). Refractive indices of the salt solutions inside the wells were extracted by fitting the ellipsometry data with the stack of layers I, II and IV as discussed in Fig.4.3. Concentrations of CsCl were then calculated from their linear relation with refractive index.
i) To determine the salt concentration inside each well, a zero-adsorption condition is created (pH set to 3) and layers I, II and IV are included in the modeling. Refractive indices in II are loaded from the database in Accurion’s EP 4 software, while the thicknesses in II are characterized in absence of salt. ii) In the ion adsorption studies, all layers are included in the model. $n$ and $d$ are the refractive index and thickness.

In the ion adsorption studies, experimental procedures were the same as the reference measurement with pH 3 solutions. However, we now explored pH values of 4.5, 6, 7 and 8. In case of ion adsorption, an additional layer must be taken into account in the stack model. The model then includes the following layers: silica coated chip — adsorbed layer ($n_a, d_a$) — bulk solution ($n_{\text{bulk}}$), all four parts shown in Fig.4.3. Optical parameters for the silica-coated chip, as well as the refractive indices of the bulk solutions were taken from the previous characterizations. Since the adsorbed layer is thin, only a combined quantity, called the optical thickness could be obtained. It is defined as $l = (n_a - n_{\text{bulk}}) \times d_a$. Fixing the thickness of the adsorbed layer $d_a$ to 0.4 nm, the refractive index of the adsorbed layer was extracted. More details regarding this analysis approach were described in our previous work [23].

![Fig.4.3 Layer stack model for ellipsometry data analysis.](image-url)
4.3 Results and Discussion

4.3.1 Experimental setup, device characterization

To validate the microfluidic design, we first performed an experiment with dye solution; in this case also the top slide was taken from glass, see Fig. 4.1B. Dye solution and DI water were supplied through the two inlet feeding channels, as demonstrated in Fig. 4.1C.

Fig. 4.4 A) Evolution of the concentration in three wells (numbered in Fig. 4.1 C) during the first 50 min. after loading: well 1 (black squares), well 5 (red circles), and well 9 (blue triangles); Solid symbols are experiments, while open symbols correspond to COMSOL simulations. B) Comparison of experiments and simulations in the steady state.

To measure the concentrations in the wells, 0.1 M KMnO₄ and DI water were sucked into the separate inlet channels, and a sequence of images was captured at different instants to track the transient buildup of concentration in the wells. Fig. 4.1C shows the concentration distribution in the microfluidic device after 60 min of pumping. The concentration field in the device at this instant does not change with time anymore, signifying a steady state. To make a quantitative comparison, we plotted the evolutions of the concentrations in wells 1, 5 and 9 for both the experiment and the numerical simulation in Fig. 4.4A. It is seen that
numerical model presented in section 2.2 predicts the transient development of the concentrations in the device rather well. Here the diffusion coefficient of the MnO₄⁻ ion was taken to be $1.632 \times 10^{-9} \text{ m}^2/\text{s}$ [24]). Generally, it takes about 50 minutes to reach the steady state. Fig.4.4B demonstrates the concentrations in the 12 wells at the steady state (after flowing solutions for more than 60 min). These data are the average values obtained from five different devices and are mostly consistent with the numerical calculations. The simulation results (Simulation 0) correspond to the dimensions of the device as designed. The notable discrepancy with the experiments for wells 11 and 12 is likely attributable to deviations (i.e. fabrication errors) in the dimensions of the small connections. In a new simulation (simulation 1) where we slightly modified the dimensions of small connections to wells 11 and 12 (reduce the width by 5µm as compared to original design), a very good agreement was obtained with the experiments in all wells.

Albeit less accurate than that obtained with the detailed numerical model, the steady state concentrations in the 12 wells can also be predicted fairly well with a simple circuit model. Fig.4.1 E sketches the circuit model for one row of wells, where $C_i$ is the concentration inside the indicated well, and $L_i$, $w_i$ and $h_i$ are the length, width and height of the individual small connecting channels. Using the mass conservation law, we have the following relations,

$$D \frac{C_{i+1} - C_i}{L_i} (w_i h_i) = D \frac{C_{i+2} - C_{i+1}}{L_{i+1}} (w_{i+1} h_{i+1}), \quad i = 1, 2, 3, 4 \quad (4.3)$$

where $D$ is the diffusion coefficient. In analogy with an electric circuit, Eq.(4.3) can be transformed to

$$\frac{C_{i+1} - C_i}{R_i} = \frac{C_{i+2} - C_{i+1}}{R_{i+1}} \quad (4.4)$$
where $R_i$ is the resistance for mass transfer, which can be related to the dimensions of the connection $i$ by $R_i = L_i/(w_i h_i)$. Eq.(4.4) defines three equations from which we can solve the concentrations in the three wells ($C_2$, $C_3$ and $C_4$) as

$$C_j = C_1 + \frac{C_5-C_1}{\sum_{i=1}^4 R_i} \sum_{i=1}^{j-1} R_i, j = 2, 3 \text{ and } 4$$

(4.5)

Since the concentrations of the solutions in two feed channels ($C_1$ and $C_5$) as well as the resistances of all connections ($R_i$), are known, we can readily calculate the concentrations in each well in our device. It should be mentioned that the validity of the circuit model requires that concentration field has reached the steady state, and also that the concentrations in the wells are uniform, or equivalently the mass transfer resistance of the wells is vanishingly small. These assumptions are justified by Fig.4.5 which shows the transient evolvement of the concentration along the centerline of the leftmost row of wells from the full numerical simulation. The concentration profiles within each of the three wells (wells 1, 5 and 9) show good homogeneity in the steady state, and the major mass-transfer resistance is contributed by the small connections in which the concentrations change drastically.

The results from the circuit model are also included in Fig.4.4 B. One notes that the circuit model agrees well with both the experiments and the full numerical simulation. In comparison to the COMSOL model, the circuit model has a distinctive advantage: for a given set of predefined concentrations, the circuit model allows us to determine the dimensions of small connections very efficiently and conveniently during the course of device design. The circuit model slightly disagrees with the full numerical model, probably because of the finite resistance of the wells which is omitted in the circuit model.
Chapter 4

Fig. 4.5  Numerical prediction of the time evolution of concentration along the centerline of the leftmost row of wells (1, 5 and 9 as numbered in Fig. 1 C) after loading DI water and KMnO₄ solution into two feeding channels. The 6 instant concentration profiles are at 5, 10, 20, 30, 40 and 50 min, as is chosen in Fig. 4.4 A.

With the previous analytical expression Eq.(4.5), we can calculate the concentration profile. However, the microfluidic device allows the establishment of a 3D concentration gradient which also involves the flow and diffusion, thus simulation with COMSOL provides both transient and steady state results more accurately.

We emphasize that the stability of the concentration gradient depends on the flow. As long as the flow is properly balanced between the two inlets, and maintained, the gradient remains stable. The flow rates and the volume of the syringe determine the lifetime of the stable gradient. With the flow rate 0.1 mL/min used in our work, the gradient can be maintained for more than 5 h if the syringe is selected large enough (i.e. 60 mL).
4. Microfluidics and total internal reflection ellipsometry for adsorption study

4.3.2 Ion adsorption studies

In the adsorption studies, we combined the microfluidic device with ellipsometry working in total internal reflection mode. This mode offers several advantages compared to standard ellipsometry, such as higher sensitivity [25, 26] and applicability to opaque media [26]. Here we exploited the combined setup to study ion adsorption at silica-water interfaces.

Clearly, the “bulk” concentration of salt inside each well (as shown in Fig.4.1 C) now needs to be known precisely. Considering that the point of zero charge of silica is close to 2 [27], we tuned the salt solution at pH 3. Adsorption of common ions (e.g. Na+, Ca2+, Cl) can then safely be neglected, which allows to ascribe the recorded ellipsometric signals fully to the changes in the “bulk” refractive index of the solution. Measurements (with all concentrations in the steady state) of $\Psi$ and $\Delta$ as a function of angle of incidence were fitted with the optical model: glass→ gold, silica and titanium layer→ bulk solution, as I, II, and IV shown in Fig.4.3. Only the refractive index of the bulk solution was taken as an unknown parameter, and from its fitted local values, the salt concentration was extracted per well. Generally, these concentrations are consistent with the simulation results and the circuit model, as shown in Fig.4.6 B. Discrepancy with experiments is observed at well number 12 for the first simulation (Simulation 0) with the dimensions of devices taken from the original design. Again, this could be the result of slightly deviating channel dimensions in the fabrication process. The second simulation (Simulation 1) with slightly modified dimensions (reduce the width of the small connection between well 12 and the feeding channel by 5µm) predicts the measurements very accurately in all wells. The simple circuit model apparently also works quite well. We emphasize that the discrepancy between experiment and predictions does not create any uncertainty in the concentrations: in the adsorption study, the salt concentration inside each well is extracted from the layer stack model without comparison to any other measurement.
Silica surface groups get significantly deprotonated when the pH is increased to (well) above 2. The ensuing negative surface charge needs to be compensated by the charge distribution in the electric double layer, see Fig. 4.7. The optical layer stack as used for modeling the data at pH 3 now has to be extended to include the electric double layer. Clearly, in reality the refractive index of this adsorbed layer cannot be constant, since the concentrations of both cations and anions change gradually from the silica surface to the bulk solution. In the optical layer stack model, the ion adsorption is therefore taken into account via a single layer with an effective thickness and refractive index. For thin layers, only the product of the two can be extracted from the measurement[7]. We therefore assume a thickness $d_a$ of 0.4 nm, corresponding to the radius of the hydrated Cs$^+$ ions, and fit for the refractive index change. The refractive index of the bulk solution is set equal to the one measured at pH 3. We then obtain the optical thickness $l$:

$$l = \Delta n \times d_a = (n_a - n_{bulk}) \times d_a \quad (4.6)$$
4. Microfluidics and total internal reflection ellipsometry for adsorption study

where $n_a$ and $n_{bulk}$ are the refractive index of the adsorbed layer and bulk solution respectively. Following de Feijter [28], the optical thickness can also be written as:

$$\Delta n \times d_a = \alpha_+ \Gamma_+ + \alpha_- \Gamma_-$$  \hspace{1cm} (4.7)

where $\alpha_{+/−}$ and $\Gamma_{+/−}$ denote the refractive index increment and excess of the cations and anions, respectively. For CsCl, $\left(\frac{dn}{dc}\right)_{CsCl} = 12.66 \text{ mL/mol}$, and $\alpha_- = 3 \text{ mL/mol}$ [23, 29], so $\alpha_+ = 9.66 \text{ mL/mol}$ was used in this work. The right hand side of Eq.(4.7) shows that we measure an optically weighted average, where the individual adsorbed amounts per ion can be positive or negative. In the present case (a negative substrate and absence of specific adsorption by the anions), not only $\alpha$ but also $\Gamma$ should be larger for the cation; this means that the adsorption signal will be dominated by the Cs$^+$ ions.

As shown in Fig.4.8, the optical thickness increases with pH, and the maximum adsorption at pH 8 is almost twice the one measured at pH 6. One can also find that the adsorption increases with salt concentration at a fixed pH. From pH 6 to...
pH 8, the optical thickness increases steeply at low salt concentration and approaches a plateau at high salt concentration. At pH 4.5, the optical thickness increases gradually with increasing salt concentration. Such effects are due to the progressive dissociation of the silanol groups, which require an increasing amount of cations to neutralize the charge.

**Fig.4.8** Optical thickness of CsCl adsorption at silica water interfaces at different pH conditions: pH 4.5 (square), pH 6 (circle), pH 7 (up triangle) and pH 8 (down triangle); these experimental results are extracted from the ellipsometry data. Solid lines are the theoretical calculation using surface complexation triple layer model.

To corroborate these ellipsometry results, we performed theoretical calculations with the standard triple layer model of the electric double layer [30, 31] (see Fig.4.7A). In this model, the deprotonation of silanol group takes place at 0 plane, β plane is where cations bind with deprotonated surface sites, d plane defines the closest approach of fully hydrated ions to the surface. Clearly, β and d planes divide the entire double layer into three sublayers, two electroneutral inner sublayers which can be described by capacitance $C_1$ and $C_2$, and one charged diffuse layer.
4. Microfluidics and total internal reflection ellipsometry for adsorption study

(Beyond d plane) which is described by the Poisson-Boltzmann (PB) equation. The surface charge (boundary condition for PB equation) is calculated from surface complexation reactions at 0 and \( \beta \) planes, which are expressed by equilibrium constants (see Table 4.1). This allows to obtain the surface excess and from it, to calculate the optical thickness (using Eq.4.7). We emphasize that the total surface excess includes the positive excess of counter-ions in Stern layer and diffuse layer, as well as the depletion of co-ions in the diffuse layer [23].

<table>
<thead>
<tr>
<th>Surface complexation reactions</th>
<th>Equilibrium constant, ( K_i ) (mol/L)</th>
<th>Capacitance (F/m²)[30, 32]</th>
<th>( C_1 )</th>
<th>( C_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H )</td>
<td>( -SiOH \leftrightarrow H^+ + -SiO^- )</td>
<td>10^{-6.9}[31, 33]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( CsCl )</td>
<td>( -SiO^-Cs^+ \leftrightarrow -SiO^- + Cs^+ )</td>
<td>10^{-1.69} *</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Site Density ( (nm^{-2})[33] )</td>
<td>8.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Note: * optimized value by fitting all the data at various pH conditions).

Generally, the theoretical calculations and experimental results show agreement; the dependencies on pH and concentration are well reproduced. This corroborates the validity of the measurements. However, one can still find some discrepancies between the numerical calculation and experiments. In the modeling, there are many parameters such as capacitance \( C_1 \) and \( C_2 \), the equilibrium constant \( K_H \), etc. see Table 4.1. These parameters are not unique and covariant [34]. Better agreement between optical thickness and the theoretical calculations might be obtained with more elaborate parameter estimation.

Besides the electrostatic interaction, the ion specificity also has effects on cation adsorption. Sivan and coworkers have studied cation adsorption on solid surfaces
with AFM, where they pointed out significance of the surface hydration for cation adsorption [35]. To further explore the adsorption mechanism of these ions, the combination of several complementary detection techniques could provide additional insights.

4.4 Conclusions

We developed a microfluidic device which can generate a dilution series of an injected solution by making use of steady state diffusion. The concentration profiles can be generated as desired via appropriate design of the mass transfer resistances. Combined with total internal reflection ellipsometry, the device can be used for studying adsorption phenomena at solid-liquid interfaces. As a demonstration, we studied cesium ion adsorption from their chloride aqueous solutions onto silica surfaces at various pH conditions. Comparison of the ellipsometry measurements to calculations from the surface complexation triple layer model, corroborate the utility of the combined setup for adsorption studies. Application of this device can be easily extended to other chemicals or biomolecules. Therefore, we believe this device will be a very straightforward and useful tool both for chemical and biological scientists to do studies with concentration gradients.

References

4. Microfluidics and total internal reflection ellipsometry for adsorption study


[17]. Kim, M.; Kim, T., Diffusion-based and long-range concentration gradients of multiple chemicals for bacterial chemotaxis assays. *Analytical chemistry* 2010, 82 (22), 9401-9409.


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Appendix

A1. Total Internal Reflection Ellipsometry measurement: 0.5 M CsCl at pH 3

In the modeling, an optical layer stack (A), with fixed values for the (composite) layers I, II, and IV (see Fig. 3) is used: the layer thicknesses of the silica coated glass slide were characterized before this measurement, and the refractive index of the bulk solution was measured with a refractometer. It shows excellent agreement between model and experiment, as shown in Fig. A1, suggesting that no adsorption occurs at pH 3.

![Fig.A1 Ellipsometric angles $\Delta$ and $\Psi$ vs. Angle Of Incidence (AOI), for a 0.5 M CsCl solution at pH 3 in contact with silica (see Fig. 3). Symbols are the experimental data and the solid lines show the best-fit results. This modeling was conducted with EP4 software provided by Accurion.](image)

Furthermore, we introduce layer III into the layer stack model (B), with its thickness fixed at 0.4 nm and parameters of all other layers are the same as in (A), so the refractive index of layer III is the only unknown. We find that $l = (n_a - n_{bulk}) \times d_a \approx 0$, which further supports the conclusion that no adsorption takes place at pH 3. Based on this, it justifies the use of the data at pH 3 as a reference to determine the concentration within each well.
CHAPTER 5
ION EFFECTS IN ADSORPTION OF CARBOXYLATE ON OXIDE SURFACES STUDIED WITH QUARTZ CRYSTAL MICROBALANCE

In this chapter, we chose water-soluble sodium hexanoate as a model organic molecule to study the role of salt ions (Ca$^{2+}$, Na$^+$, Cl$^-$) in the adsorption of carboxylates to mineral surfaces (silica, alumina, gibbsite) of variable surface charge and chemistry. Quartz crystal microbalance (QCM-D) measurements reveal a qualitatively different dependence of the adsorption behavior on the electrolyte composition for the different surfaces at near neutral pH. Overall, hexanoate adsorption is more pronounced on the positively charged alumina surfaces than on negatively charged silica surfaces. On silica, however, Ca$^{2+}$ ions strongly enhance the adsorption of hexanoate, suggesting that the divalent cations act as bridges between carboxylate and deprotonated silanol surface groups. On alumina, hexanoate adsorption is found to depend only weakly on the salt composition, suggesting a direct interaction of the carboxylate group with the surface, consistent with a ligand-exchange mechanism. The adsorption behavior on partially gibbsite-covered silica surfaces is particularly rich and displays a strong non-monotonic dependence on the CaCl$_2$ concentration. Comparison to earlier work and control experiments suggest an important role of Cl$^-$ anions, which compete with the carboxylate group for adsorption sites.

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5.1. Introduction

Adsorption of organic molecules and other species at mineral (clay) water interfaces has been studied for a long time but still attracts great interest of researchers. This is because the adsorption phenomena can have a multitude of effects: they can alter the wettability of macroscopic substrates [1], tune the rheology of particle suspensions [2], modify the sorptive properties [3], etc. As a result, this phenomenon is critical to many industrial applications such as water treatment [4], nanocomposites fabrication [5] and oil recovery [6, 7].

Clay also known as phyllosilicate, mainly consists of aluminosilicate layers, containing silicon dioxide tetrahedral sheets and aluminum oxyhydroxyl octahedral sheets. Therefore in many fundamental studies silica, alumina or gibbsite are used as models of clay minerals. In particular, studies on interactions between organic molecules like carboxylates and the above mineral surfaces have been conducted [8, 9, 10, 11, 12], because carboxylates are commonly found in nature as well as in industrial processes. Effects of pH and ionic strength on the adsorption process have been well covered by several works [8, 12, 13, 14, 15]. However, only few studies were so far aimed at comparing the adsorption behaviors of carboxylates on different substrates and at different aqueous ion compositions (including salt mixtures). An exception is the recent work of Juhl, who reported that the bonding strength between a carboxylate and an alumina surface changes with the solution salinity, and that divalent ions can replace adsorbed monovalent ions on oxide surfaces [16]. Understanding the adsorption mechanism of carboxylates at the different clay surfaces, including the competition between ions during this process, would help to understand many industrial processes.

A good example is given by the water flooding process, which is routinely practiced in oil recovery to release (more) hydrocarbons from the subsurface. Traditionally, (highly saline) sea water is injected into the rock reservoir to repel the mobilized oil from the rock surface. However, it was recently found that the
recovery can be enhanced by flooding with low salinity solutions [17, 18]. This low salinity effect has been attributed to an alteration of the wettability: the rock becomes more water-wet when organic material is desorbed from the clay surface. However, the underlying microscopic mechanisms behind the ad/desorption of organic molecules and other species at clay-mineral surfaces are still not clarified. In previous works, some progress was made along this line. Langmuir-Blodgett films were studied to demonstrate the role of divalent cations as bridging ions between silica substrates and stearic acid molecules [19]. Additionally, atomic resolution AFM was used to examine specific ion adsorption on gibbsite surfaces [20].

In this chapter, we investigate the adsorption of a water soluble, short-chain carboxylate (hexanoate) on various oxide surfaces (silica, alumina, and gibbsite). The aim is to understand the role of cations in particular from mixed electrolytes on the adsorption of carboxylate, as well as the adsorption mechanism of carboxylate on these oxides. The pH value was chosen to be around 7, which is close to the natural conditions. In this regime, the dissociation of the carboxylic acid and the surface charges of the oxides (silica, alumina, and gibbsite) surfaces are all sensitive to the pH. Besides different concentrations of hexanoate, also various compositions of NaCl and CaCl₂ solutions were explored.

The principal technique we have used is the measurement of adsorbed mass using a Quartz Crystal Microbalance capable of quantifying also dissipation (QCM-D). Careful application of this sensitive method allowed us (for the first time) to perform semi-quantitative measurements of the adsorption isotherm for these very small molecules. To support our data analysis, also Atomic Force Microscopy (AFM) experiments were performed; these measurements provided information about the state of charge of the bare substrates. Based on the combined data, adsorption mechanisms on different solid surfaces are proposed.
Chapter 5

5.2. Experimental Section

5.2.1 Materials

Sodium hexanoate (C6), Hexanoic acid, CaCl$_2$·2H$_2$O, and NaCl were obtained from Sigma-Aldrich and used without further purification. Deionized water with a resistivity of 18.2 MΩ·cm (Synergy-UV, Millipore) was used throughout this study.

Silica-coated and alumina-coated quartz crystal sensors were purchased from Q-sense (Gothenburg, Sweden). A suspension of gibbsite nanoparticles was kindly provided by the group of Prof. A.P. Philipse (University of Utrecht, the Netherlands). Synthesis and characterization of the material were described by Wierenga et al. [21]. The gibbsite-coated sensor was prepared by depositing gibbsite particles from a suspension on the silica coated quartz crystal, following the procedures described by Siretanu et al. [20].

5.2.2 AFM imaging and force spectroscopy measurements

Topographical features of the QCM sensor surfaces were studied by using a Multimode8 Atomic Force Microscope with a Nanoscope V controller (Bruker Nano). A Dimension Icon AFM (Bruker) equipped with a Nanoscope V controller was used to study the surface charge of the sensors. All samples were analyzed in amplitude modulation mode. Silicon tips from MikroMasch, NSC36 ($f_0 = 52$ kHz, $c_z = 3.6$ N/m, $Q = 4.8$, tip radius ~ 19 nm) and Bruker FASTSCAN-B cantilevers ($f_0 = 170$ kHz, $c_z = 3$ N/m, $Q = 10$, tip radius ~ 3 nm) were used. Before the measurement, both the tip and cantilever were rinsed with an ethanol/isopropanol (≈ 1:1) mixture and treated further with air plasma (Harrick Plasma) for 15 min. Image analysis was carried out with Nanoscope Analysis version 120 software (Bruker). Roughness data were extracted from three separate images obtained at different regions on each sample. The surface coverage of gibbsite sensor was 55% ± 10%. The surface charge of the substrates in electrolyte solution was determined from analysis of AFM interaction stiffness.
Ion effects in adsorption of carboxylate on oxide surfaces studied with quartz crystal microbalance (force gradient) versus distance curves in the framework of DLVO theory, complemented by a charge regulation boundary condition. The AFM equipment, the operations, and details about force inversion and charge extraction have been described elsewhere [22, 23].

Fig. 5.1 A). Schematic illustration of quartz crystal microbalance principle; B). frequency and dissipation shift recorded with different solutions injected sequentially: water (I), aqueous salt solution (II); (III) to (X) are hexanoate (C6) solutions with the same salt concentration as in (II), while the C6 concentration varies from 0.1 to 10 mM.
5.2.3 Adsorption measurements by QCM

Adsorption experiments were performed as a function of the Na-hexanoate (C6) and salt concentrations. On each sensor, three concentration series were examined. In each of the series, the concentration of C6 was varied from 0 to 10 mM. Since this is far below the solubility (70 mM) [24, 25], no precipitation should occur. The total Na\(^+\) concentration (from C6 and NaCl) was always maintained at 10 mM, while the concentration of CaCl\(_2\) was controlled at 0, 10 and 20 mM. In short, these series are denoted as: 1) C6-Na; 2) C6-Na-10Ca and 3) C6-Na-20Ca. The pH of the samples varies from 6 to 7 with the concentration of C6. Because hexanoic acid is a weak acid (pKa=4.85), the carboxylate groups will occur partly in protonated and partly in deprotonated form. According to Lee [26], at pH 7 the Critical Micelle Concentration (CMC) of Na-carboxylate is approximately 1 M, and that of Ca-dicarboxylate is higher than 0.03 M [27, 28]. Our solutions are always more diluted than this, so that we can safely exclude the presence of micelles.

Adsorption studies are conducted with the QCM-D (E4) instrument from Q-sense (Gothenburg, Sweden). A standard AT-cut quartz crystal sensor with a diameter of 14 mm has a 100 nm thick gold layer as electrode. In our case silica-, alumina- and gibbsite- coated sensors were used. The QCM-D liquid chamber is mounted on a Peltier element, which controls the temperature accurately (at 22±0.1°C) to avoid signal drifts. The fundamental oscillation frequency of the crystal is 5 MHz. Changes in frequency and dissipation are recorded simultaneously at 5, 15, 25, 35... MHz. All measurements are started with DI water, followed by the background salt solution (containing Na\(^+\) and/or Ca\(^{2+}\)), and then the series of C6 solutions from low to high concentrations, as demonstrated in Fig. 5.1. The solution was sucked into the chamber with a peristaltic pump. The pump was stopped after the chamber was filled with fresh solution. Frequency and dissipation signals were recorded continuously. At the moment that a plateau was reached (for both), the next sample solution was sucked into
the chamber. Since the molecules studied in this work are very small, contamination of the small measurement signals had to be avoided as much as possible. Drift was minimized by preparing the experimental setup and the samples overnight before each measurement.

5.2.3.1 Principle of QCM-D and Data analysis

Since QCM plays a prominent role in this study, a brief background is given. The Quartz Crystal Microbalance (QCM) technique is well-known for characterizing adsorbed mass at solid surfaces. It is based on the piezoelectric effect. When an alternating potential is applied to the electrodes, shear stresses is generated in the piezoelectric material, causing the crystal to oscillate at a resonant frequency. Changes in the mass ($\Delta m$) bound to the crystal surfaces cause a shift of the resonance frequency ($\Delta f$). In the absence of significant damping by the ambient environment, the Sauerbrey relation can be used[29]:

$$\Delta f = -\frac{f_o}{t_q \rho_q} \times \Delta m = -\frac{n \times \Delta m}{C} \tag{5.1}$$

where $\rho_q$ is the mass density of the quartz, $f_o$ is the fundamental frequency, and $t_q$ is the thickness of the quartz crystal. $C$ is the mass sensitivity constant ($C = 17.7 \text{ ng}\cdot\text{cm}^{-2}\cdot\text{Hz}^{-1}$ at 5 MHz), and $n$ indicates the overtone number ($n = 1, 3,...$). The conditions for Eq. 5.1 to hold are that: $i)$ the adsorbed mass is evenly distributed over the sensor; $ii)$ the adsorbed mass is much smaller than that of the crystal; $iii)$ the adsorbed film should couple perfectly with the shear oscillation of the sensor. The latter is not always the case, especially if the adsorbed film is viscous and does not follow the mechanical oscillation of the sensor. In this case, the frequency shift also depends on the viscous and elastic nature of the adsorbed film. In QCM-D, the dissipation of a sensor’s energy ($D$), due to the adsorbed viscoelastic layer is also recorded. The dissipation ($D$) is given by:
\[ D = \frac{1}{Q} = \frac{E_d}{2\pi \times E_s} \]  

(5.2)

Where Q is the quality factor, \( E_d \) is the energy dissipated in one period of oscillation, and \( E_s \) is the energy stored in the oscillation system. The measurement of \( D \) allows for a more accurate estimation of the adsorbed mass in a non-rigid film by introducing the viscosity and shear modulus in the modeling.

In the Sauerbrey equation, the adsorbed mass is proportional to the normalized frequency shift, which is independent of the overtone number. However in our case, shown in Fig. 5.1 for a typical dataset, the frequency shift presents an overtone dependent behavior. This suggests that the adsorbed layer might not be perfectly rigid. Therefore, we use, instead, the Voigt-based model [30, 31] for the data analysis, which is implemented in the 'Q-tool' software from Q-sense. In this model, the adsorbate is represented a homogeneous layer (film, as shown in Fig. 1 A) on the sensor surface with density, viscosity and shear modulus: \( (\rho_f, \eta_f, \mu_f) \); the properties of bulk solution (liquid, as displayed in Fig. 5.1 A) are represented by \( (\rho_l, \eta_l) \) for which we used 1002 kg/m\(^3\) and 0.001 kg/m\(\cdot\)s, respectively. The expected mass density of a close packed organic monolayer is 958 kg/m\(^3\), assuming upright hexanoate molecules with a head group of 20 Å\(^2\) [19] and molecular length of 1 nm [32]. Hence in the modeling, only \( \eta_f, \mu_f \) and the adsorbed mass are used as fit parameters. Data from at least three overtones with good signal to noise ratio are therefore needed. The first overtone is not used as it senses mostly the solution and is affected by the clamping [33]. In this work, data from 3rd, 5th, 7th, 9th, 11th overtones are used to find the adsorbed mass because they display stable responses.

Since QCM is an acoustic technique, it cannot discriminate between different chemical species. Hence the number density of individual adsorbed ions and molecules cannot be extracted from the total adsorbed mass. Moreover, water may couple as additional mass due to hydration, or entrapment in the cavities in
the adsorbed layer as observed in other work [30]. Therefore our results do not represent, in a strict sense, adsorption isotherms, although they follow very similar trends, and we will refer to them as 'adsorption curves'. Consequently, we refrain from converting the data into chemical units (mol cm\(^{-2}\)) but present them in weight units (ng cm\(^{-2}\)).

5.3. Results and Discussion

5.3.1 Characterization of Silica, Alumina and Gibbsite-silica sensors

Electrostatic interactions are generally recognized as an important driving force for the adsorption of organic or inorganic ions at solid-liquid interfaces. Since the oxide surfaces used in this work are prone to get charged in contact with aqueous solutions, understanding of ion adsorption should be facilitated by characterization of the electrical state of the substrates.

**Fig.5.2** Topographical features of silica, alumina, gibbsite-silica sensors in water and their corresponding height profile.

Fig.5.2 displays typical height images of the three types of QCM sensors used in this study. Generally, silica and alumina coated sensors present rather smooth surfaces: the height variations have a root-mean square amplitude of 1.2 ± 0.028
nm and 1.6 ± 0.021 nm respectively, and also the gradients in height are very small (note that the line scans in Fig.5.2 are strongly compressed in the horizontal direction). This is also confirmed by the height maps, from which we infer a “true” surface area (i.e. by taking into account the areas of “hills” and “valleys” of the surface contour) that is 9.08 and 9.11 µm² within 9 µm² imaging area, for silica and alumina respectively. The gibbsite-silica sensor demonstrates the typical hexagonal gibbsite particles, with a typical lateral dimension of 100 nm, and heights from 5 to 20 nm, due to the aggregation (stacking) of gibbsite platelets. From the height images, we can estimate the effective surface area of gibbsite-silica surfaces, which is 9.02 µm² corresponding to 9 µm² imaging area.

QCM experiments on gibbsite surfaces were performed with the same sensor, which has a stable coverage of gibbsite (~55%) through all the measurements.

The effective surface charges of the three sensor surfaces were measured at the same electrolyte compositions as used in the adsorption studies. Fig.5.3 presents the force gradient (interaction stiffness) as a function of tip sample distance. On silica surfaces (black symbols in Fig.5.3A and B), the tip experiences a repulsion, which increases monotonically as the tip approaches the surface. This suggests a system of two negatively charged surfaces. On alumina (magenta symbols in Fig.5.3 A) and gibbsite (orange symbols in Fig.5.3 B), the silica tip experiences attraction, indicating an oppositely charged substrate. The observed dependence on the concentration and composition of the salt shows the combined effect of changes in the ion adsorption and in the diffuse double layer.

To obtain more quantitative information, the surface charges were extracted from the interaction stiffness curve using extended DLVO theory, where Charge Regulation (CR) effects, i.e. variations of the surface charge due to confinement-induced ion adsorption, (de)protonation of surface groups, etc., are taken into consideration. For more details, see ref. [23]. The minimum tip-sample distance used for fitting was set to 1 nm, to minimize the influences of short-range forces such as hydration forces, which are not included in the model. The upper
boundary was set to 10 nm, because the interactions are negligible beyond this distance. Fig. 5.3 shows that there is a good agreement between the theoretical curves and the experimental results. The extracted surface charge densities are summarized in Table 5.1.

**Fig. 5.3** Interaction stiffness versus distance measured between a silicon oxide tip and several sensor surfaces: silica (black symbols), alumina (magenta symbols in A) and gibbsite (orange symbols in B). Symbols are experimental data: 10 mM NaCl (triangle), 10 mM NaCl-10 mM CaCl₂ (square), and 10 mM NaCl-20 mM CaCl₂ (circle). Solid lines show the calculated interaction stiffness according to
DLVO theory with charge regulation boundary condition. The surface charge values from this fitting are presented in Table 5.1.

**Table 5.1** Surface charge densities of the three sensors, in contact with different solutions. (Note: Surface charge on silica was extracted from two measurements, see Fig.5.3 A and B)

<table>
<thead>
<tr>
<th>Surface charge (e/nm²)</th>
<th>10 mM NaCl</th>
<th>10 mM NaCl-10 mM CaCl₂</th>
<th>10 mM NaCl-20 mM CaCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>-0.060</td>
<td>-0.019</td>
<td>-0.020</td>
</tr>
<tr>
<td></td>
<td>-0.062</td>
<td>-0.020</td>
<td>-0.018</td>
</tr>
<tr>
<td>Alumina</td>
<td>0.013</td>
<td>0.015</td>
<td>0.023</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>0.023</td>
<td>0.125</td>
<td>0.025</td>
</tr>
</tbody>
</table>

On the silica surface in 10 mM NaCl solution, the charge density is found to be -0.06 e/nm², while it becomes -0.02 e/nm² upon addition of 10 or 20 mM CaCl₂. This behavior is attributed to an adsorption of the Ca²⁺ ions onto the silica, which probably also involves deprotonation, i.e. replacement of Si-OH by Si-OCa⁺.

Both alumina and gibbsite display positively charged surfaces for the electrolytes investigated. On alumina, the surface charge increases upon the addition of CaCl₂. This could be interpreted as a result of the buffering effects of Ca²⁺ ions, which are capable of forming Ca(OH)⁺ [34] and thereby lowering the pH contributing to the increase in surface charge. Moreover, Ca²⁺ might replace the protons at alumina surfaces which also enhances the surface charge.

Remarkably, the surface charge density on gibbsite, shows a maximum at the intermediate (i.e. 10 mM) CaCl₂ concentration. This complies with a previous study [20] where it was interpreted in terms of specific ion adsorption. The
excess positive charge as compared to monovalent cations, can be explained with an adsorption of Ca\textsuperscript{2+} ions on the gibbsite surface. The decrease in net surface charge at higher CaCl\textsubscript{2} concentrations, might be explained by adsorption of Cl\textsuperscript{-} onto the already adsorbed Ca\textsuperscript{2+}.

### 5.3.2 Adsorption of hexanoate

#### 5.3.2.1 Silica surfaces

![Figure 5.4](image)

**Fig. 5.4** Sodium Hexanoate (C6) adsorption on Silica surfaces in presence of salts: i) 10 mM Na ions (black squares); ii) 10 mM Na ions + 10 mM CaCl\textsubscript{2} (red circles); iii) 10 mM Na ions +20 mM CaCl\textsubscript{2} (blue triangles). Lines are drawn for guiding the eye.

Fig.5.4 displays the adsorption curves of hexanoate on silica. Without CaCl\textsubscript{2}, the maximum adsorption density (\(\Gamma\)) (at 10 mM C6) is only \(~20\) ng\cdot cm\(^{-2}\), much less than a densely packed monolayer \(~100\) ng\cdot cm\(^{-2}\) (with the molecular weight of 115 g/mol, and the size of carboxylate head group around 20 Å\(^{2}\) [19]). With 10 mM
CaCl₂, and below 5 mM C6, the [C6] dependent adsorption overlaps with the Ca-free case. Above 5 mM C6, the adsorption increases more steeply. With 20 mM CaCl₂, the adsorption shows a steep initial increase. The difference between the cases of 10 and 20 mM CaCl₂ then remains more or less constant as [C6] is increased. The overall picture that emerges, is that (above certain thresholds for [CaCl₂] and [C6]), adding more CaCl₂ results in a larger adsorbed mass.

To explain this trend, we consider the charge on the silica surface (in absence of C6). At pH ~7 the silica surface is negative, as also corroborated by the AFM measurements (Table 5.1). Most hexanoate molecules are in the form of –COO⁻ at pH~7 because hexanoic acid is a weak organic acid with a pKₐ= 4.85 [35]; this makes adsorption of C6 unfavorable from an electrostatic point of view. Indeed, only small amounts of hexanoate adsorb from solutions of only C6-Na. The fact that a similar behavior was found with hexanoic acid at similar pH on silica surfaces (results not shown), suggests that Na⁺ ions cannot provide strong assistance to the adsorption of C6 on silica. The observation that some adsorption still occurs, and that the amount grows with [C6], might be attributed to weak Van der Waals-London dispersion forces between the alkyl tail and the silica. Weak hydrophobic interactions between neighboring adsorbates might offer additional assistance to the adsorption. However, this effect can only be small, and the in that case expected S-shaped isotherm is not observed.

In the presence of Ca²⁺, significantly larger amounts are adsorbed, and the more so for higher CaCl₂ concentration. Similar effects of divalent cations have also been reported in another study [36]. Another work has found that Langmuir-Blodgett films of stearic acid on silica display higher stability when prepared in presence of Ca²⁺, as compared to Na⁺ [19]. These findings are consistent with an adsorption that is strongly facilitated by the (electrostatic) effects of divalent cations. Apparently, the latter are very effective in establishing cation bridges between a negative surface and the negative hexanoate ion [37].
The observation that the maximum adsorbed amounts are relatively low, and that adding more Ca\(^{2+}\) to a system where [Ca\(^{2+}\)/[C6] was already \(\gg 1\) leads to more adsorption, indicates that the adsorption is weak, and governed by chemical equilibrium. In this picture, the Ca\(^{2+}\) ions in solution form partially dissociated, cationic complexes with carboxylic acid:

\[
\text{Ca}^{2+} + \text{OOC-R} \leftrightarrow \text{R-COOCa}^+ \quad (5.3)
\]

At the silica surface, most likely Ca monohexanoate (with the Ca facing the mineral surface) is the dominant species. The enhancement of the adsorption by both Ca\(^{2+}\) and hexanoate is also consistent with the increase in the initial slope for higher [Ca\(^{2+}\)] as seen in Fig. 5.4.

### 5.3.2.2 Alumina surfaces

![Graph](image)

**Fig.5.5** Sodium Hexanoate (C6) adsorption on Alumina surfaces: i) with 10 mM Na ions (black square); ii) with 10 mM Na ions + 10 mM CaCl\(_2\) (red circle); iii) with 10 mM Na ions + 20 mM CaCl\(_2\) (blue triangle). Lines are drawn for guiding the eye.
On alumina surfaces, the adsorption of C6 is much stronger than on silica. As shown in Fig.5.5, the adsorbed mass per unit area ($\Gamma$) approaches 80 ng•cm$^{-2}$ at the highest [C6], even in the absence of Ca$^{2+}$, where it only reached ~20 ng•cm$^{-2}$ on silica (Fig.5.4). Adding 10 mM CaCl$_2$ to the system has remarkably little effect on the maximum adsorbed amount at 10 mM C6; also this is different from the case of silica, where adding CaCl$_2$ gives rise to a stronger relative increase in $\Gamma$. Another remarkable observation is that at the intermediate CaCl$_2$ concentration of 10 mM, the adsorption isotherm does not appear to be significantly different from that of the pure C6-Na.

Also in this case, charge interactions are expected to play an important role. In contrast to the silica surface, the alumina is slightly positively charged at pH~7. Since most carboxylate molecules are deprotonated and thus negatively charged at that pH, electrostatic attractions should be present. It is plausible that this causes the larger adsorbed amounts. However, the complex dependence on the CaCl$_2$ concentration (no detectable difference on adding 10 mM, but a significant increase in $\Gamma$ at 20 mM) suggests that electrostatics alone is insufficient to explain our observations.

Other indications for this can be found in literature. For electrostatically driven adsorption, the maximum amounts should be found at a pH somewhere between the point of zero charge of alumina and the pKa of the carboxylic acid: the solid surface is then positively charged while most carboxylate groups are deprotonated. However, several researchers [9, 10, 11, 12, 26] have reported maximum adsorption at pH values close to the pKa of carboxylate. Kummert [9] found that the tendency of carboxylic acid to form complexes on alumina surfaces is similar to that of organic ligands to form complexes with Al$^{3+}$ in solution. Vermöhlen [38] found that the carboxylate oxygen can bind to the alumina surface, resulting in a ligand-exchange complex. Lee et al [26] studied carboxylate adsorption on alumina systematically as a function of pH, and also
concluded that ligand-exchange is the dominant mechanism of adsorption. Here, the carboxylate group exchanges with the hydroxyl group:

\[
> \text{Al} - \text{OH} + \text{OOC} - \text{R} \leftrightarrow > \text{Al} - \text{OOC} - \text{R} + \text{OH}^-
\]

At low pH, most carboxylate ions are protonated. Due to the limited number of -OOC-R groups in solution, little adsorption can then occur. At very high pH, hydroxide ions compete for the adsorption sites on alumina, also resulting in little adsorption. At a certain intermediate pH within the above large range (including the pKa value) the maximum adsorption occurs.

It is thus plausible that pH is the dominant factor in the ligand-exchange process. In the solutions studied in this work, both Ca\(^{2+}\) and hexanoate can act as a pH buffer. For Ca\(^{2+}\) this is due to its ability to form CaOH\(^+\) complexes in aqueous solution [34]. Experimental evidence for this was found in a decrease in pH from 5.8 to 5.3, upon addition of 20 mM CaCl\(_2\) to a 10 mM NaCl solution. Hexanoate forms a classical buffer system, in which the pH is governed by the ratio \([\text{–COO}^-]/[\text{–COOH}]\). This ratio varies with the initial concentration of sodium hexanoate. The pH of the solutions thus varies slightly from 6 to 7 on increasing the C6 concentration.

The similar pH values of the C6-Na and C6-Na-10Ca solutions, could thus explain why only few differences are observed between their adsorption curves. In the C6-Na-20Ca system much more free Ca\(^{2+}\) ions are present, especially at low C6 concentration. These can then play a stronger role as a buffer, and shift the pH towards the pKa value. This might explain the steep increase in adsorption at low [C6]. At the higher C6 concentrations, the pH values are more similar for all systems, as they become more dominated by the ratio of \([\text{–COO}^-]/[\text{–COOH}]\). While it is clear that the solution pH plays an important role in the adsorption on alumina, it cannot be ruled out that cation adsorption (in spite of the unfavorable charge interaction) can contribute to the phenomenon as well (e.g. via ion bridging). XPS measurements on alumina that was exposed to a
mixed solution of NaCl and CaCl$_2$ revealed that only Ca$^{2+}$ ions had adsorbed [16]. While this points at an (ion-) specific role for (at least) the calcium, our experiments do not provide an unambiguous connection with the adsorption of C6. The very similar charge densities (Table 5.1) and adsorption curves for the solutions with 10 mM NaCl and with 10 mM NaCl +10 mM CaCl$_2$ does not suggest a strong sensitivity to Ca$^{2+}$ as a specific species.

5.3.2.3 Gibbsite-silica surfaces

![Graph](image)

*Fig.5.6 Sodium Hexanoate (C6) adsorption on 55% Gibbsite covered silica surfaces: i) with 10 mM Na ions (black square); ii) with 10 mM Na ions and 10 mM CaCl$_2$ (red circle); iii) with 10 mM Na ions and 20 mM CaCl$_2$ (blue triangle); iv) is ii) with additional 10 mM NaCl (magenta stars). (The lines are drawn for guiding the eye.)*

The adsorption of hexanoate on the mixed gibbsite-silica sensor displays a remarkable non-monotonic dependence on the CaCl$_2$ concentration, see Fig. 5.6. Maximum adsorption occurs for the system with 10 mM CaCl$_2$. Here the adsorption increases steeply at low C6 concentration, and approaches a plateau for higher [C6], indicating a saturated adsorption. Remarkably few differences
are found between the adsorption curves for the systems without CaCl$_2$ and with 20 mM CaCl$_2$, both of which are very different from the 10 mM CaCl$_2$ case. In these cases the adsorbed amount increases steadily with C6 concentration, and no plateau is observed up to 10 mM C6.

The sensor has a gibbsite surface coverage of ~55%. Using this number together with the adsorption masses per unit area ($\Gamma$) on the pure silica from Fig.5.4, we can calculate the adsorption densities on the gibbsite, which are 109, 235, and 111 ng•cm$^{-2}$ for the C6-Na, C6-Na-10Ca and C6-Na-20Ca systems, respectively. These amounts are much higher than those on silica or alumina, indicating a very different adsorption behavior on gibbsite.

![AFM images of gibbsite particles deposited on silica. A) In-situ image of hexanoate coated gibbsite particles from 10 mM C6+10 mM CaCl$_2$. The line scans compare the local height variations on the platelets, before and after adsorption of C6. B) and C) present zoom-ins of the adsorbed hexanoate layer and the adsorbed calcium ions, suggesting that the organic layer is attached to the solid surface through calcium ions.](image)

Fig.5.7 AFM images of gibbsite particles deposited on silica. A) In-situ image of hexanoate coated gibbsite particles from 10 mM C6+10 mM CaCl$_2$. The line scans compare the local height variations on the platelets, before and after adsorption of C6. B) and C) present zoom-ins of the adsorbed hexanoate layer and the adsorbed calcium ions, suggesting that the organic layer is attached to the solid surface through calcium ions.
Chapter 5

Gibbsite is one of the most common aluminum hydroxide phases. One key aspect of gibbsite is that it displays Lewis acid-base properties [39]: it can interact with both cations and anions, depending on chemical conditions. The adsorption or bonding mechanism of dicarboxylate on gibbsite has been studied before [14]. Similar to the adsorption on alumina, this is also a ligand-exchange process. However, as we can see from Fig.5.5 and Fig.5.6, the adsorption curves look (qualitatively and quantitatively) rather different from those on alumina. We ascribe these differences to the fact that Gibbsite is a crystalline solid, with a clear lattice structure. Unlike the case of alumina, divalent ions (Ca$^{2+}$) can now strongly bind to well-defined adsorption sites forming periodical double row structures, see Fig.5.7, while Na$^+$ or Cl$^-$ ions attach only weakly to the crystal surfaces [20]. In the presence of Ca$^{2+}$ ions, hexanoate molecules can attach to the gibbsite surfaces via these pre-adsorbed divalent ions (Fig.5.7), leading to a significant increase in the adsorbed mass for 10 mM CaCl$_2$. However, increasing the CaCl$_2$ concentration by 10 mM leads to a decrease in $\Gamma$, making it roughly similar to the case without CaCl$_2$. This is probably due to a high concentration of Cl$^-$ ions, which compete for the adsorption sites with hexanoate.

To support the latter hypothesis, another adsorption experiment was conducted with the same gibbsite coated sensor. In this measurement, an additional 10 mM NaCl was added to the C6-Na-10Ca system (see the stars in Fig.5.6). The adsorbed amount indeed decreases, close to the value of C6-Na-20Ca. As Na ions cannot bind to gibbsite surfaces [20], their effects on carboxylate adsorption can be neglected. This furtherly confirms the idea that there is competition between Cl$^-$ and –OOC-R. In Fig.5.6, the plateau is only observed for C6-Na-10Ca system. At this condition, little adsorption of Cl$^-$ occurs as revealed by the AFM image [20]. Thus, only carboxylate adsorbs to the surface, approaching saturated adsorption at high C6 concentration.

If we consider the magnitudes of the adsorbed amount, assuming that they only come from hexanoate (with a molar weight of 115 g/mole), molecular adsorption
densities of 5.5 nm\(^2\), 11.8 nm\(^2\) and 5.6 nm\(^2\) are found for the C6-Na, C6-Na-10Ca and C6-Na-20Ca solutions. The size of a carboxylate head group is around 20 Å\(^2\) [19], which corresponds to 5 nm\(^2\). This indicates that with C6-Na-10Ca solutions, adsorbed masses larger than the amount corresponding to a dense monolayer, are achieved. Moreover, the AFM images in Fig.5.7 show that the height of the adsorbed layer exceeds the molecular length of the hexanoate. These observations suggest that adsorption takes place in the form of a multilayer. In principle, also water uptake by gibbsite [39] or from the hydrated ions might also contribute to the total adsorbed amount measured. The suggestion of trapped water has been made in several studies [40, 41].

**Fig.5.8** Schematic of hexanoate adsorption mechanisms at solid-liquid interfaces:
A) Silica: calcium ions (green) adsorb to silanol groups, and hexanoate molecules bind to the silica via calcium ion bridges. B) Alumina: hexanoate molecules adsorb via ligand exchange, releasing OH\(^-\) to the solution; in the bulk solution, calcium ions bind to hydroxide ions, lowering pH. This promotes hexanoate adsorption. C) Gibbsite: calcium ions (green) adsorb to gibbsite forming a zig-zag structure; hexanoate molecules and chloride ions (purple) compete for the adsorption sites on the pre-adsorbed calcium ion layer.

In Fig.5.8, we summarize the proposed adsorption mechanisms on the three different surfaces. On silica (A), the adsorption of C6 is mainly due to cation
bridging, causing the adsorbed amount to increase with the divalent ion concentration, see Fig. 5.8 A. On alumina (B), the adsorption results mainly from ligand exchange, and pH is the dominant factor in this process. Ca$^{2+}$ has a positive influence on the adsorption process, most of which appears to be via the pH: Ca$^{2+}$ ions have the ability to bind with hydroxyl ions in solution acting as buffer ions adjusting the pH. Additionally, some protons at alumina surfaces can be replaced by Ca$^{2+}$. Since Ca$^{2+}$ also adsorbs onto the alumina surface, we cannot completely rule out (modest) contributions by ion bridging. The adsorption of C6 on gibbsite (C) in presence of (mixed) salts shows a more complex phenomenology. Ca$^{2+}$ ions adsorb to gibbsite, thereby creating adsorption sites for C6. Anions (Cl$^-$ and Hexanoate) compete for these adsorption sites, resulting in a non-monotonous dependence on CaCl$_2$ concentration.

Overall, from our observations in this work, it is clear that divalent cations such as Ca$^{2+}$ are important for carboxylate adsorption, either acting as bridging ions, or as buffering ions adjusting the pH. This corresponds well to the observations in low salinity water flooding process, where low concentrations of divalent ions is a key element [6, 42]. As pointed out in this work, the adsorbed layer contains not only carboxylate, but also some ions like Cl$^-$, or Ca$^{2+}$. To further investigate the composition of the adsorbed layer, other techniques like ellipsometry, SPR, or XPS etc. could be exploited, to confirm the adsorption mechanisms we proposed here.

5.4. Conclusions

Quartz Crystal Microbalance (QCM) was exploited to study the adsorption of Hexanoate on different substrates: silica, alumina and gibbsite. Specific focus of this paper was on the effects of Ca$^{2+}$ ions (besides omnipresent Na$^+$ ions) on the mechanism of carboxylate adsorption. We found that the adsorption is not simply driven by electrostatic interactions. On the negatively charged silica, bridging by Ca$^{2+}$ ions plays a very important role; while on positively charged alumina,
adsorption of carboxylate takes place via a ligand exchange process, mainly controlled by the solution pH. Ion bridging might also occur, but it does not play a significant role. Compared to a bare silica surface, the presence of gibbsite can significantly enhance the adsorption. In this case, Ca\(^{2+}\) ions first adsorb to the surface forming a double row structure; anions (Cl\(^{-}\) and hexanoate) in the solution then bind to this pre-adsorbed calcium, competing for the adsorption sites. This results in a non-monotonic dependence of hexanoate adsorption on CaCl\(_2\) concentration. The oxides studied in this work, silica, alumina and gibbsite can be seen as clay model surfaces, and the carboxylates are important polar components in oil reservoirs. So the understanding of the adsorption process with these simple model systems in electrolytes will shed some light on real rock reservoir, helping to understand the low salinity effects during water flooding in enhanced oil recovery.

References


[15]. Malgat, A.; Boisvert, J.-P.; Daneault, C., Specific influence of univalent cations on the ionization of alumina-coated TiO2 particles and on the adsorption


Langmuir-Blodgett (LB) films of various amphiphilic molecules have long been used as model systems for the hydrophobization of intrinsically hydrophilic surfaces i.e. silica. Yet, upon exposure to water, LB-films tend to decompose, form bilayers, and/or eventually desorb from the solid surface changing the wettability of solid surfaces. In this chapter, we analyze the stability of LB films of stearic acid transferred onto silica from an aqueous electrolyte at pH≈9.5 containing either NaCl, CaCl₂ or the mixture of NaCl and CaCl₂. Using a combination of macroscopic contact angle goniometry, imaging ellipsometry, and Atomic Force Microscopy, we find that the films transferred in the presence of Ca²⁺ are substantially more stable upon exposure to water than the ones transferred in the presence of Na⁺ only. The observations are attributed to the cation bridging ability of Ca²⁺ ions, which can bind the negatively charged stearate groups to the negatively charged substrates.

6.1 Introduction

The interaction of organic matter with solid surfaces in an ambient aqueous environment plays a crucial role in many processes both in science and technology, *i.e.* water purification, corrosion inhibition, colloidal stability, Langmuir-Blodgett films, enhanced oil recovery [1-5].

Since most solid surfaces, in particular mineral surfaces, assume a finite surface charge in water, usually electrostatic effects contribute strongly to the interactions 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 [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 counterions [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 differences 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 changes: from DLVO-type for the bare surfaces, to long-range attractive in case of some hydrophobized surfaces [12-16]. In the present study we focus on the
question, how the wettability of an adsorbed organic layer can be changed via exposure to pure water.

The purpose of the present study is to explore the effect of cations on the stability of the Langmuir-Blodgett films. 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, which offers unique control of the physico-chemical 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 [17-19] and as LB films deposited onto solid surfaces [11, 20] dating back all the way to the original work of Blodgett [21] and Langmuir [22]. 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 [23, 24]. A summary of early work based to an important extent on surface potential measurements has been summarized by Goddard [25]. At low pH, the carboxylic acid groups remain protonated and the affinity to ions (and interfaces) is weak. In contrast, at high pH carboxylic acid groups are deprotonated and interact strongly with the ions [10, 24, 26, 27], and interfaces. This affects amongst other things the transferability of Langmuir monolayers in the LB process [8, 28] and the stability of the layers [24]. More recently, Graber et al. [29] 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. 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 wafer using LB transfer. Subsequently we expose the surfaces to pure water. We investigate the effect of ions on the film stability by varying the ion contents of the subphases during LB transfer. 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.

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. Solutions of stearic acid (SA) (octadecanoic acid, CH\(_3\)(CH\(_2\))\(_{16}\)COOH, grade 1, approx. 99\%) are dissolved 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 (CaCl\(_2\)·2H\(_2\)O) (both ACS reagent grade) in deionized water (Synergy UV, Millipore, resistance 18.2 M\(\Omega\)-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 [23] and to prevent substantial dissolution of stearate molecules in the bulk water, which occurs for pH >10 [27].

6.2.2 Substrate preparation and LB film deposition

As substrates, we use commercial silicon wafers (100 surface) with a thermally grown oxide layer of ~35 nm thickness. The wafers are cut into pieces of 1×5 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 N₂ 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: θ<5°). AFM is used to verify the smoothness of the substrate. The typical RMS (root means square) roughness is found to be <0.2 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 Fig.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 (40 mN/m).

In the following, we denote the LB layers transferred on 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, 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 ± 0.5°. Droplets of 5–10 μL of pure water 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 to within ± 3°.

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 $\Psi$ and $\Delta$ 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 ($\Psi$, $\Delta$) into a thickness $d_i$ [30]. Fitting $\Psi$ and $\Delta$ for the bare substrate with a two-layer model (Si: $d \to \infty$, $n_{Si} = 3.96–0.02i$ and SiO$_2$: $n_{SiO_2} = 1.5$) 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 $n_{SA}=1.43$ 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, Brucker AXS). All images are collected in tapping mode with ScanAsyst Air and ScanAsyst fluid silicon probes purchased from Bruker with sharp tips. Nominal
Stability of stearic acid Langmuir-Blodgett film upon exposure to water

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 set point values) to protect both tip and sample from damage. 3-4 topography and phase images are recorded at representative neighboring locations on each surface. Image analysis is performed using Bruker’s standard Nanoscope Analysis 1.4 package.

6.3 Results and Discussion

6.3.1 Topography of stearic acid Langmuir-Blodgett film

Fig.6.1 A) Surface pressure vs. molecular area isotherm of stearic acid on a 0.5 M NaCl aqueous subphase; The arrow indicates the point where the LB transfer was performed. B) Ellipsometry imaging of stearic acid Langmuir-Blodgett (LB) film and a corresponding thickness profile.

The stearic acid Langmuir-Blodgett films were imaged with Ellipsometry and AFM after preparation and drying. Those imaging experiments were performed in ambient air under all preparation conditions: i.e. various subphases for the
film transfer. All images demonstrate the flat topography of the LB films with a height roughness of approximately 0.15 nm rms no matter what kind of cation(s) were present in the subphases. Fig.6.1 B displays the typical ellipsometry thickness map and a corresponding height profile. The thickness of the observed film is ~2 nm [31], which is in consistent with the length of stearic acid molecules and the molecular structure as sketched in Fig.6.1 A.

6.3.2 Contact angle measurement

To study the stability of the SA monolayers, we exposed all layers to drops of pure water. Drops with a volume of 10 μL were deposited onto the substrates and left there for 10 min. During this period we continuously monitored the contact angle. The contact angle $\theta$ of the water drop was found to decrease from an initial value $\theta_0$ to a significantly smaller equilibrium value $\theta_e$ within a few seconds. The latter value is stable for several minutes until it begins to decrease slowly due to evaporation. This qualitative behaviour is similar for all samples. The absolute values of $\theta_0$ 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 [32]. For the present study, however, the quantity of interest is the limiting contact angle $\theta_e$ found at a much longer time scale.

As shown in Figure 6.2, $\theta_e$ depends very strongly on the composition of the used subphase and decreases from approximately 80° for the SA-Ca layer, to ~30° for the SA-Ca+Na layer, to < 5° for the SA-Na layer. This very strong dependence of the contact angle on the counterion 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° [33], 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 $\theta_e$ 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 behaviour.

Fig. 6.2 Macroscopic water 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 ($\theta_e$). The axis break in (A) was made to show the equilibrium contact angle.

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 $\theta_e$ were consistently found in all cases. Yet, the absolute values of $\theta_e$ vary substantially depending on details of...
the sample cleaning, preparation, and drying protocol. Occasionally, $\theta_e$ could be as low as 30° even for SA-Ca monolayers.

6.3.3 Ellipsometry and Atomic Force Microscopy measurements

The wettability changes of the LB film 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 layer (after removing the drop and drying the samples) obtained with ellipsometry and AFM are displayed in Fig.6.3.

For the SA-Ca and SA-Ca+Na samples, both ellipsometry and AFM images recorded in the central area of the original drop look similar, as can be seen in Fig.6.3a, b) and 3a’, b’). Ellipsometry indicates a more or less homogeneous coverage with an average thickness of about 1 nm in the former case and approximately 0.5 nm for the latter samples. Both values are substantially lower than the 2 nm corresponding to the all \textit{trans} length of SA molecules before they were exposed to the water drop. Hence we conclude that the LB monolayers must have been partially desorbed. For SA-Na samples (Fig.6.3 c and c’), the situation is clearly different and the residual thickness after water exposure is essentially zero.

When we image the edge of the region exposed to the water drop, a clear contrast is seen between the exposed area with now bare substrate and the intact monolayer around it. While the poor lateral resolution of imaging ellipsometry precludes a more detailed analysis, 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 Fig. 6.3 a’ and b’).
and (dark) holes exposing what seems to be the bare substrate. The phase image (Fig.6.4a) also reveals a clear contrast between the high and the low level, supporting the interpretation that the lower level is indeed the bare substrate. The height of the residual film 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.

**Fig.6.3** Macroscopic and microscopic images of SA-Ca (a and a’), SA-Ca+Na (b and b’) and SA-Na monolayer (c and c’) after exposure to water. a, b and c: imaging ellipsometry; a’, b’ and c’: AFM. Inset images are height profiles corresponding to the white scan line (abscissa in µm; ordinate in nm).

For the SA-Na samples, the 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 image, confirming the idea of different material compositions.

![AFM height and phase images along with section profiles for SA-Ca monolayer exposed to water.](image)

Fig. 6.4. AFM height and phase images along with section profiles for SA-Ca monolayer exposed to water. The (almost discrete) different color levels correspond to bare substrate and stearic acid film.

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 more parallel to the substrate. The present data do not allow drawing a definitive 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.
The presence of Ca\textsuperscript{2+} ions strongly stabilizes LB films of stearic acid deposited on silica surfaces has been reported by other researchers as well [23, 34-38]. To discuss the stabilization mechanism, we consider LB film decomposition upon exposure to aqueous liquid. Fig. 6.5 sketches the relevant processes taking place inside the stearic acid monolayer. The Langmuir film initially residing on the aqueous subphase consists of a close-packed layer of stearate molecules (Fig. 6.5
a). 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 subphase cause the monolayer to become more disordered. 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 [39], changes in viscoelastic response [40], and easier transfer to a solid substrate [28].

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 ($\chi$) has been related to the pH of the subphase by the Gouy-Chapman equation [23, 41]:

$$\text{pH}_{\text{subphase}} = \text{pK}_a + \log\left(\frac{\chi}{1-\chi}\right) + \frac{0.87}{z}\sinh^{-1}\left(\frac{136\chi}{A\sqrt{C}}\right)$$ (6.1)

where $z$ is the valency of the ions, $A$ is the molecular area ($\text{Å}^2$) and $C$ is the concentration of the counterions (mol/L). Inserting $\text{pK}_a = 5.6$ [42] and using the aqueous compositions in our experiments, we obtain a deprotonation ratio of 86.4% for 10 mM CaCl$_2$ and 82.3% for a 0.5 M NaCl solution 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$_2$D or both of these complexes simultaneously [43-46]. 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 [43, 45] and experimentally [47, 48]. In contrast, monovalent cations only form neutral RM complexes and therefore the monolayer remains mainly negatively charged because of dissociated R$^-$ [43].

When we transfer these neutral or negatively charged layers to our silica substrates, they come in contact with a negatively charged surface [37, 49, 50] (Fig.6.5 b). 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 \( \text{SA}_2\text{Ca} \) \((\text{R}_2\text{D})\) 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 [51]. In the contrasting case of sublayers containing only \( \text{Na}^+ \) cations, a partially dissociated Langmuir, 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 (\( \text{SiO}^- \)) 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 lateral interactions within the film presumably.

The behaviour of the \( \text{SA-Ca}^+\text{Na} \) films with mixed subphases is more complex. The partial stability of the layers upon exposure to pure water suggests that some adsorbed \( \text{Ca}^{2+} \) is present and able to stabilize the LB films. However, this stabilization is clearly not as strong as in the case of a pure 10 mM \( \text{CaCl}_2 \) subphase. The competition between the stronger binding \( \text{Ca}^{2+} \) ions and the 50 times more concentrated \( \text{Na}^+ \) ions in the subphase leads to a mixed association of \( \text{R}^- \) and \( \text{SiO}^- \) with the two cationic species. Upon exposure to pure water, some of the cations migrate into the bulk exposure solution, resulting in decomposition of the layer.

Such phenomena have been reported before. Also multilayers of LB films have been studied in great detail [8, 11, 28]. 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 the decomposition of the LB film is facilitated by ion exchange. These aspects are further addressed in [52, 53].
6.4 Conclusions

The stability of Langmuir Blodgett films of stearic acid upon exposure to water is strongly enhanced by the presence of Ca\(^{2+}\) ions, suggesting that Ca\(^{2+}\) can efficiently bind stearate anions to negatively charged surfaces. In contrast, Na\(^+\) ions are unable to provide such stabilization. LB films transferred in the presence of mixtures of Na\(^+\) and Ca\(^{2+}\) are weakly bound to the substrate. The destabilization can be rationalized by the migration of initially present stabilizing Ca\(^{2+}\) ions to the exposed water. 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 many industrial applications, i.e. 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.

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CHAPTER 7
SUMMARY AND OUTLOOK

7.1 Summary

The adsorption or desorption of (in)organic molecules at solid-liquid interfaces has been the basis of many industrial applications. In the low salinity water flooding process in Enhanced Oil Recovery (EOR), it is believed that desorption-induced alteration of the rock surface towards a more water-wet state is the key mechanism for the oil mobilization and production. In this thesis, we investigated the adsorption of both organic and inorganic molecules at (aqueous) liquid-solid interfaces with various surface sensitive techniques and microfluidics. We demonstrated the new functionalities of the developed devices and explored the factors affecting the adsorption.

In Chapter 3, we investigated cation adsorption at silica-water interfaces with internal reflection ellipsometry. The conversion of the (small) optical signal to an adsorption signal is not trivial in the case of continuous ion distributions (electric double layer), and therefore a detailed description was given. Using the De Feijter equation, the measured optical thickness was expressed in the total excess amounts of cations and anions. Theoretical calculations for these adsorbed amounts were obtained from an electrostatic model, taking into account the chemical equilibria for dissociation of the surface groups. Quantitative results show an increased adsorption of metal cations at higher pH, and a preferential adsorption of divalent cations (as compared to monovalent ones) at the same pH condition. This indicates that in mixtures of H\(^+\), Ca\(^{2+}\) and Na\(^+\), the former two are the main competitors for binding to the Si-O\(^-\) groups.
In the real rock reservoir, various sorts of chemical components are present, and different (classes of) chemicals can have different effects on the low salinity water flooding process. To address the challenge of screening many conditions, and speed up our investigations, in Chapter 4, we developed a concentration gradient generator, which creates a dilution series on a microfluidic platform, thus offering parallelization. The principle of the microfluidic device is based on the steady state diffusion of the compounds to be screened (like an adsorbing component, or alternatively a desorption agent). Via a proper design of the hydraulic resistances, various concentration profiles can be generated. Concentration gradients obtained from measurements agreed well with theoretical calculations. As a demonstration of the device, we explored CsCl adsorption at the silica-water interfaces at various pH conditions with total internal reflection ellipsometry. Quantitative results demonstrate the enhanced adsorption with increasing pH.

Both inorganic and organic molecules play a very important role in setting the wettability of rock. Therefore in Chapter 5 and Chapter 6, focus of the study was placed on organic molecules.

In Chapter 5, we explored hexanoate adsorption at silica, alumina and gibbsite-water interfaces, with or without divalent cations. (Mass) adsorption curves for these small molecules, measured with a Quartz Crystal Microbalance (QCM) suggest different adsorption mechanisms on these oxide surfaces (each of them bearing a certain similarity to clays as found on rock surface). On silica, divalent cations can enhance the adsorption, mainly due to the formation of ion bridges between the negatively charged silica surface and hexanoate molecules. On alumina, the adsorption behavior is consistent with a ligand exchange process, where pH is the dominant factor. On gibbsite, the adsorption shows a non-monotonic behavior as a function of CaCl₂ concentration. This is because of a competition between Cl⁻ and hexanoate molecules for the adsorption sites.
The stability of the adsorbed organic film on the solid surface has a large effect on the wettability alternation. In Chapter 6, we investigated the stability of stearic acid monolayers (on exposure to water) after depositing them onto silica surfaces through the Langmuir-Blodgett (LB) technique. Both contact angle measurements and image analysis with AFM and ellipsometry revealed that the LB films prepared with divalent cations (Ca$^{2+}$) demonstrate a higher stability (a less complete breakdown) than those prepared in presence of Na$^+$ ions. This can be explained by the formation of cation bridge with divalent ions.

In summary, we have developed techniques which can be used to study small molecule adsorption at solid-liquid interfaces fast and efficiently. Moreover, the important role of divalent cations such as Ca$^{2+}$ has been demonstrated.

7.2 Outlook

We have exploited various simple model systems (to mimic clay and polar components in the oil-rock reservoir) in this thesis to understand the low salinity water flooding process in EOR. However, the composition in the real oil-rock reservoir is much more complex, considering the rock-clay, many oil components, and the ambient brine solutions. Also physical properties like temperature and pressure are different from ambient conditions in the lab. In order to gain some more understanding, in the future, the following aspects can be studied.

7.2.1 Clay model

Clay also known as phyllosilicate, mainly consists of aluminosilicate layers, containing silicon dioxide tetrahedral sheets and aluminum oxyhydroxyl octahedral sheets. In this thesis we used silica, alumina and gibbsite as model systems. However, this only reflects one aspect of clay, i.e. they only represent either the edge or the basal plane of clay particles considering the electrical state. In future studies, more complex model systems such as Kaolinite, Montmorillonite, Illite, etc. should be investigated.
Chapter 7

7.2.2 Brine solution

In enhanced oil recovery, sea water is frequently used as the flooding solution[1]. In this solution, there exist many different salt ions as shown in Table 7.1[2]. In this thesis, we mainly studied Na⁺ and Ca²⁺ ions. To gain further understanding about the low salinity effects, other salt ions should also be investigated, especially Mg²⁺ as its content is the highest among divalent ions.

Table 7.1 Composition of artificial seawater

<table>
<thead>
<tr>
<th>Type of cation</th>
<th>Salt</th>
<th>Concentration in aqueous solution (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>monovalent</td>
<td>NaCl</td>
<td>426</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₄</td>
<td>29.4</td>
</tr>
<tr>
<td></td>
<td>KCl</td>
<td>9.45</td>
</tr>
<tr>
<td></td>
<td>NaHCO₃</td>
<td>2.43</td>
</tr>
<tr>
<td></td>
<td>KBr</td>
<td>0.857</td>
</tr>
<tr>
<td></td>
<td>H₃BO₃</td>
<td>0.438</td>
</tr>
<tr>
<td></td>
<td>NaF</td>
<td>0.0744</td>
</tr>
<tr>
<td>divalent</td>
<td>MgCl₂·6H₂O</td>
<td>55.5</td>
</tr>
<tr>
<td></td>
<td>CaCl₂·2H₂O</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>SrCl₂·6H₂O</td>
<td>0.0937</td>
</tr>
</tbody>
</table>

7.2.3 Temperature

All the studies presented in this thesis are performed at room temperature. However, in the real oil-rock reservoir, the temperature is substantially higher, which can go up to 100~150°C and is dependent on the depth of the reservoir. Temperature has significant effects on the adsorption behaviors of both inorganic and organic molecules, which lead to the wettability alteration. So future studies on this should be conducted.
7.2.4 Oil phase

In rock reservoir, polar organic molecules initially got adsorbed onto the solid surface from a mixture of water and oil phases, and in the water flooding process they have to desorb again after being exposed to oil and water. The work presented in this thesis was performed with aqueous phase. The adsorption behaviors of organic molecules and ions in oil are expected to be different, considering the different manifestations of electrostatic and hydrophobic interactions, and possibly also the higher complexity of the oil-dissolved molecules. These aspects need to be explored as well.

References

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Acknowledgements
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List of publications


   * indicates equal contribution.


