Doctoral Thesis

Molecular insights into nanoconfined electrical double layers

Author(s): Zachariah, Zita

Publication Date: 2017

Permanent Link:
https://doi.org/10.3929/ethz-b-000179834

Rights / License:
In Copyright - Non-Commercial Use Permitted

This page was generated automatically upon download from the ETH Zurich Research Collection. For more information please consult the Terms of use.
MOLECULAR INSIGHTS INTO NANOCONFINED ELECTRICAL DOUBLE LAYERS

A thesis submitted to attain the degree of
DOCTOR OF SCIENCES of ETH ZURICH
(Dr.sc. ETH Zurich)

presented by
ZITA ZACHARIAH
Master of Engineering, Indian Institute of Science Bangalore

born on 07.10.1987
citizen of India

accepted on the recommendation of
Prof. Dr. Manfred P. Heuberger, examiner
Prof. Dr. Rosa M. Espinosa-Marzal, examiner
Prof. Dr. Hugo Christenson, co-examiner
Prof. Dr. Nicholas. D. Spencer, co-examiner
Prof. Dr. Manfred Fiebig, co-examiner

2017
Dedicated to Dead Cows
We cannot define anything precisely. If we attempt to, we get into that paralysis of thought that comes to philosophers, who sit opposite each other, one saying to the other, "You don't know what you are talking about!". The second one says, "What do you mean by know? What do you mean by talking? What do you mean by you?" and so on. In order to be able to talk constructively, we just have to agree that we are talking about roughly the same things.

*The Feynman Lectures on Physics, Feynman, R. P.; Leighton, R. B.; Sands, M.*

*Volume 1: Mainly Mechanics, Radiation and Heat, Lecture 8, "Motion"; section 8-1, "Description of motion"; p. 8-2*
Abstract

Electrical double layers, comprising of a surface charge and counterbalancing excess ions in solution, are of critical importance in applications such as colloid science, energy storage devices and water desalination. When two charged surfaces and their accompanying double layers approach each other, the double layers first begin to overlap and finally collapse under confinement. In nanofluidic devices or nanopores where double layers are in such a confined state, transport phenomena and physicochemical reactions depend on the composition and properties of the collapsed electrical double layer. The classical DLVO theory fails to predict the interaction forces accurately at nanometer separations or high ionic concentrations since it disregards, among other things, confinement induced effects such as ion dehydration. This work aims to address these open questions, namely the interaction between surfaces at nanometer separations and the changes in the interfacial adhesion due to the presence of counterions. The collective transitions between structural elements in nanometer-thick monovalent aqueous electrolytic films as well as interfacial adhesion were studied via direct force measurements between atomically smooth mica surfaces using the enhanced sensitivity of film thickness measurement. Changing concentration or pH provides the means to shift chemical potentials and interfacial populations, and therefore also to shift the relative stability of structural elements and gain valuable insights into the structural diversity at the interface.
We provide new evidence that the oscillatory surface force appearing at the final stages of collapse of the electrical double layer is initially due to layering transitions between hydrated ions, which finally develop into transitions between highly confined adsorbed ion states. Changing the pH further reveals that the excess of hydronium ions at the surface at low pH can significantly alter the stepwise collapse of two overlapping electrical double layers. The counterion specificity of this phenomenon was investigated by comparing three counter ion species, Na\(^+\), K\(^+\), and Cs\(^+\), which are known for their distinct hydration structure. Different pathways of double layer collapse as a function of the counter-ion species were demonstrated. Based on these studies we propose a generalized model for the collapsed electrical double layer, which undoubtedly reflects the film stability discretization introduced by hydrated ion layering.
Abstrakt


Diese Arbeit versucht die offene Fragen zu klären, nämlich, die Wechselwirkung zwischen Oberflächen bei Nanometertrennungen und die Veränderungen der Grenzflächenhaftung durch Gegenionen zu behandeln. Die kollektiven Übergänge zwischen strukturellen Elementen in nanometerdicken monovalenten wässrigen Elektrolytfilmen sowie die Grenzflächenadhäsion wurden durch direkte Kraftmessungen zwischen atomar glättenden Glimmeroberflächen mittels der erhöhten Empfindlichkeit
der Schichtdickenmessung untersucht. Eine Änderung der Konzentration oder des pH-Wertes bietet die Möglichkeit, chemische Potentiale und Grenzflächenpopulationen zu verschieben und damit auch die relative Stabilität der Strukturelemente zu verschieben und wertvolle Einblicke in die Strukturvielfalt an der Grenzfläche zu gewinnen.

TABLE OF CONTENTS

1. **Chapter 1: Introduction** 1
   1.1. The Electrical Double Layer 3
   1.2. DLVO theory 5
      1.2.1. Deviations from DLVO theory: Hydration forces 7
      1.2.2. Deviations from DLVO theory: Oscillatory solvation forces 10
   1.3. Model surface: muscovite mica 13
   1.4. Hydrated ions 15
   1.5. Hydrated ion layering and the π-transition in aqueous KNO₃ 17
   1.6. Ion specificity 20
      1.6.1. Origin of ion specificity 21
      1.6.2. Cation specificity in aqueous electrolyte solutions 24
   1.7. Scope of the thesis 25

2. **Chapter 2: Experimental methods** 26
   2.1. The extended Surface Force Apparatus
      2.1.1. Surface Force Apparatus 26
      2.1.2. eSFA 30
      2.1.3. Instrumental details 30
      2.1.4. Sensitivity to the spring constant and instrumental limitations 33
   2.2. Mica deformation issue 34
   2.3. Sample preparation 38
   2.4. Experimental procedure 40
2.5. Time of Flight Secondary Ion Mass Spectroscopy

2.5.1. The Technique

2.5.2. Motivation

2.5.3. Experiments

2.5.4. Results

2.5.5. Conclusions

3. Chapter 3: Stepwise collapse of overlapping Electrical Double layers

3.1. The π-transition

3.2. Film-thickness transitions

3.3. Fitting force curves to the DLVO theory

3.4. Experimental Results

3.4.1. Pull-off forces

3.4.2. Film-thickness transitions

3.5. Contributions to the pull-off force

3.6. Competition between K⁺ and H₃O⁺

3.6.1. Surface concentration of K⁺ assuming H⁺ is the potential determining ion

3.6.2. Surface concentration of K⁺: Mass action model

3.7. Hydrated K⁺ and H₃O⁺ ions

3.8. Previous models explaining hydration forces

3.9. Hydrated ion layering model

3.10. Oscillatory forces

3.11. Conclusions
# Chapter 4: Ion specific pathways to Electrical Double Layer collapse

4.1. Compression isotherms in NaNO$_3$, KNO$_3$, CsNO$_3$ 88

4.2. Pull-off forces in NaNO$_3$, KNO$_3$, CsNO$_3$ and the $\pi_L$-transition 90

4.3. Film thickness transitions in NaNO$_3$, KNO$_3$, CsNO$_3$ 92

4.4. The effect of pH 95

4.5. Discussion 96

4.5.1. Ion specific effects 98

4.5.2. Influence of counterion population on pull-off forces 101

4.5.3. Hypothesis for the $\pi_L$-transition and $\pi_{ML}$-transition 102

4.6. Summary 107

# Chapter 5: Summary and Outlook

5.1. Summary 108

5.1.1. What did we set out to study? 108

5.1.2. What have we learnt? 109

5.2. Open questions 111

5.2.1. History effects 111

5.2.2. Role of the anion 114

5.2.3. Role of hydronium in decreasing the pull-off force 116

5.2.4. Mica hard wall and the absolute zero 118

5.2.5. Transition to the
solidification regime 118

5.2.6. The π-transition in the presence of multivalent ions 120

5.3. Afterword 121

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bibliography</td>
<td>123</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>135</td>
</tr>
<tr>
<td>Curriculum Vitae</td>
<td>137</td>
</tr>
</tbody>
</table>
Chapter 1
Introduction

When a charged surface is in contact with an aqueous electrolyte solution, electrostatic interactions lead to the accumulation of oppositely charged counter-ions near it, thus leading to the formation of an Electrical Double Layer (EDL) comprising of the surface charge and adsorbed counter-ions. This double layer regulates the surface structure, reactivity as well as capacitance. When two such surfaces are present close to each other, their interaction is determined by the overlap of the double layers associated to each surface.

Systems of thin fluid films confined between charged surfaces are widely present in nature as well as technology. Hence, understanding the behavior of confined fluids and their interactions with and between the confining surfaces is of fundamental importance in order to control and manage them. For instance, colloids such as milk, paints, ink and blood rely on the repulsive interactions between individual particles to maintain stability. On the other hand, during salt crystallization in a porous material, the repulsive forces across the confined electrolyte solution between a growing crystal and pore wall are detrimental and lead to damage of the wall [1]. The removal of this thin supersaturated film between the surfaces would relieve the crystallization pressure and protect material from damage [2]. In addition, the adsorption of counterions to the charged interface in the form of the double layer governs the trapping of toxic metal
ions near electrodes during waste water treatment [3, 4], solute interactions with the channel walls in nanofluidic systems [5, 6], the efficacy of electrochemical capacitors [7, 8] as well as the behavior of charged biological membranes [9, 10]. The interfacial structure in thin films give rise to different dynamic and shear properties which are of crucial importance in lubrication [11]. Incidentally, the manufacture of cheese begins with manipulating the double layer forces between protein micelles in milk. The coagulation of the casein protein micelles which were in a colloidal suspension stabilized by double layers in milk is the first step in the production of most cheeses[12].

Models of the electrical double layer, describing the interaction of ions in solution with a charged surface, have been formulated more than a century ago [13, 14] and the interaction between overlapping double layers was quantified by the well-known DLVO theory of colloidal stability, proposed in the 1940’s independently by Derjaguin and Landau in the USSR and Verwey and Overbeek in the Netherlands [15, 16]. However, such continuum theories fail to correctly predict forces at nanometer separations or in concentrated electrolytes. Additional open questions include: (a) the role of the water in the hydration shells always associated to ions in aqueous solutions (b) the structure induced in the thin fluid film due to the presence of the surface (that may be different from the bulk fluid [17]), which is required to accurately predict the interaction forces between surfaces [18]. The scope of this thesis is the investigation of forces between charged mineral surfaces...
interacting across a thin (<5 nm) film of aqueous electrolyte and to shed light on the ion specific hydration and structural forces that become increasingly prominent at such narrow surface separations. The shifting of energy balances with electrolyte concentration lead to instabilities in the interfacial phenomena which will be the focus of this thesis.

1.1 The Electrical Double Layer
A charged surface in an aqueous electrolyte solution causes the rearrangement of oppositely charged counter-ions in the solution adjacent to it in order to screen its charge. The surface charge and the counter-ions thus form an Electrical Double Layer (EDL). The term double layer comes from the earliest models of the EDL when it was believed that it consists of two oppositely charged layers (the surface charge and the counter ions) at the interface. Though the name persists to this day, the EDL is now considered to consist of (a) the surface charge, (b) a layer of adsorbed counterions and (c) a diffuse ionic atmosphere where the counterions are present in excess of their concentration in the bulk reservoir and the co-ions (which have the same sign as the surface charge) are deficient. A history of the phenomenological models of the EDL can be found in [19].

Figure 1.1 shows a schematic illustration of the distribution of ions in the EDL according to the commonly accepted Gouy-Chapman-Stern model. The ions are surrounded by a hydration shell of water molecules due to interactions of the polar water molecules with the charged ion- as will be described later in Section 1.4. The surface charge is screened
due to the EDL, which consists of a fixed Stern layer of adsorbed counterions and a diffuse cloud of counter ions whose charge distribution as a function of distance from the surface follows the Boltzmann distribution. The Stern layer [20] was introduced as correction to the Gouy-Chapman model[13, 14], which assumed that there was no physical limit to the approach of the ions to the surface. According to Stern, the ions cannot approach the surface closer than a specific distance (which is usually taken as the radius of the ion) and hence the ions of the diffuse cloud of the double layer are not at the surface. The potential drops linearly in the Stern layer from the surface potential at the surface to the zeta potential at the start of the diffuse layer. In the diffuse layer, the electric potential decays approximately exponentially with distance with a characteristic decay length known as the Debye-Hückel screening length.

![Figure 1.1. Gouy-Chapman-Stern model of the EDL associated to a charged mica surface for a 1:1 electrolyte. The innermost part of the double layer consists of the surface charge and a Stern Layer of immobile counterions.](image-url)
The Inner Helmholtz Plane (IHP) is the distance of closest approach of the adsorbed ions. The Outer Helmholtz Plane (OHP) is the plane beyond which the counter and co-ion concentrations follow the Boltzmann distribution and the potential is obtained from the solution of the Poisson-Boltzmann equation. The potential drops in a linear manner from the Surface potential at the surface to the Zeta potential at the OHP. Figure adapted from [21, 22].

1.2. DLVO theory
The interaction forces between two such charged surfaces and their associated EDLs in electrolyte solution has been described by the DLVO theory [15, 16] as a balance between the repulsive double layer forces and the attractive surface-surface van der Waals forces (Hamaker forces). This balance leads to a minimum in the interaction potential at small surface separations when the attractive Hamaker forces exceed the repulsive electrolytic repulsion. Adhesion in this primary minimum is irreversible. The double layer repulsion stems from the electrostatic repulsion between the counterions and their entropy of mixing [22, 23].

As seen in Figure 1.2 and in greater detail in Figure 14.13 in Reference[22], depending on the electrolyte concentration and surface charge, the DLVO theory predicts either an energy barrier below with the surfaces adhere together in a primary minimum(which is shown in Figure 1.2) or a secondary minimum in with the surfaces adhere in a kinetically stable potential or an unstable system in which the surfaces adhere together at all concentrations.
Figure 1.2. Calculated DLVO force profiles between mica surfaces with surface potential -25mV in 1mM KNO₃ at 22°C. The primary minimum is the minimum in potential energy at contact. The Hamaker Constant was taken to be $2 \times 10^{-20}$ J.

The theoretical primary minimum arises from the continuum description of the solvent that ignores the structuring of the liquid induced by presence of the surface. The DLVO theory fails to describe the interaction forces at high electrolyte concentrations, most notably the repulsive forces that prevent surface-surface contact in the primary minimum. Such deviations from the DLVO theory have been reported in concentrations as low as 0.3mM K⁺ and at surface separations < 5 nm [24, 25]. Under such conditions, the role of ion-ion correlations, ion-specific effects, ion hydration
and molecular structure, which are unaccounted for in the DLVO theory, are not negligible [22, 26].

1.2.1. Deviations from DLVO theory: The Hydration force
At low surface separations (<5-10nm), the confined medium attains a different structure between the surfaces due to the presence of the surface, (for instance a different local density or orientational distribution of water molecules) which in turn depend on the properties of the solute and solvent molecules as well as the surface. The layer(s) of fluid adjoining the surface with properties different from the bulk liquid is called the solvation layer [27]. Solvation forces can be monotonically attractive, repulsive or oscillatory. The monotonically repulsive solvation forces between surfaces in water and aqueous solutions are called hydration forces and they are strongest at short distances (decay length ≈1nm) and hence play a role in surface adhesion. Hydration forces prevent surface-surface contact in the primary minimum, which would have been the case had only DLVO or oscillatory solvation forces (described later in Section 1.2.2) been present.

Hydration forces are proposed to occur due to the “perturbation of hydration layers” via compression and dehydration of hydrated groups at the surface upon surface-surface proximity [28]. A detailed study of the interaction forces between mica surfaces in electrolyte solutions over a wide range of concentrations by Pashley [24, 25, 29] concluded that the hydration forces arise above a critical
electrolyte concentration when the hydrated counterions are prevented from leaving the surface at high salt concentrations and in all other cases only the DLVO forces are present (Schematically illustrated in Figure 1.3). The abrupt appearance of hydration forces on increasing the bulk electrolyte concentration has been proposed to be due to the unfavourable free energy required to replace the metal counterions which is a specific value for each ion depending on their degree of ion hydration [24].

**Figure 1.3.** Schematic illustration of (a) the replacement of hydrated metal ions by hydrogen ions (b) contact in the primary minimum in the case where the metal ions are removed. No hydration forces were present in this case (c) hydrated metal ions left in the contact leading to the
presence of hydration forces and low adhesion. Figure from Pashley [24]

As seen in Figure 1.4, based on the decay lengths of the hydration forces observed in a variety of systems, the hydration forces have been distinguished into the short-range “primary” hydration forces (decay length ≈2-4 Å) and the longer-range “secondary” hydration forces (decay length ≈1 nm). The primary hydration forces likely stem from the dehydration of surface groups or reduction in entropy of water layers associated to the surface while the counterion and (possibly) coion specific secondary hydration forces are possibly due to the hydration shell of the ions, surface-ion dispersion and dehydration of ions during compression [30].

**Figure 1.4.** Schematic force curve resolved into the primary hydration with decay length <1 nm and secondary hydration with decay length >1 nm. The proposed causes of the hydration forces are also shown. Figure adapted from[30, 31].
The experiments in this thesis primarily deal with the secondary hydration forces arising from the hydrated ions since the surface hydration layer on the hydrophilic mica surfaces used here are most likely never expelled. The exact structure and ordering of hydrated ions at the interface is still an active subject of investigation. Open questions include whether the exponential hydration force causes depletion of ionic solutes in the water layer near the surface [30] and whether there are signs of the forced adsorption (or surface condensation) of ions or expulsion of the bound water upon application of external forces [32-35].

1.2.2. Deviations from DLVO theory: Oscillatory solvation forces

At a solid-liquid interface, molecules order into “quasi-discrete layers” next to the surface due to attraction to the surface as well as its geometric constraining effect, resulting in an oscillatory density profile. The possible configurations of close packed layers of spherical molecules that lead to an oscillatory force profile are shown in Figure 1.5. Oscillatory forces are generally observed in simple liquids that are composed of hard-sphere atoms whose interaction potential can be described by the 6-12 Lennard-Jones pair potential [36]. They have been experimentally detected with rigid molecules such as Octamethycyclotetrasiloxane (OMCTS)[37, 38], benzene [39] and polypropylene carbonate [40]. The density profiles of water molecules has been predicted by molecular dynamics simulations [41] as well as measured using X Ray Reflectivity on single mica surfaces [42] and confined mica surfaces [43].
Figure 1.5. Proposed origin of oscillatory forces between fluids confined between two smooth surfaces. Assuming the molecules in the film exchange freely with the bulk, the density of the fluid also varies in a similar oscillatory manner. The molecular ordering at each maxima and minima are shown. In case additional forces are present, the force curve need not be symmetrical about the X-axis. The dotted arrows are Film Thickness Transitions (FTTs) measured during approach of the surfaces. Figure adapted from [22].

It has been suggested that the monotonically varying hydration forces in aqueous electrolytes described in the previous section are actually “spatially averaged (oscillatory)
solvation forces” [44]. Two years after Pashley’s comprehensive study of DLVO and hydration forces [24], Israelachvili and Pashley published their landmark paper demonstrating the oscillatory nature of these forces and the molecular ordering of water between confined mica surfaces in a monovalent electrolyte solution [45]. Using the Surface Force Apparatus, they measured oscillatory forces with a periodicity of 2.5±3Å at surface separations ≤ 1.5 nm. Since this is similar to the size of the water molecule and building on the knowledge that the mica surface is covered with hydrated potassium ions, it was proposed that these oscillations were due to the ordered layering of the water molecules that were in the hydration shells of the adsorbed ions [46].

Recent force measurements using the extended Surface Force Apparatus have revealed that the layering entities are actually the hydrated counterions themselves [34]. Unlike with hard-sphere molecules like OMCTS, the layering of hydrated ions may involve additional effects other than geometry and entropy such as ion-ion and ion-surface correlations. The excluded volume and strength of the hydration shells associated to the ion should be taken into account as well. Since hydration energy gradually decreases with each additional hydration shell, there is no sharp boundary between the bulk water and hydration water. Consequently the hydrated ions behave as soft spheres whose size depends on the energy of the probing interaction. The layering of hydrated ions has not been experimentally explored in comparable detail as the layering of hard-sphere
molecules. Although molecular-dynamics simulations have shown that the overlap of hydration shells can lead to a strong repulsive hydration force [47], the structural or energetic contribution of other counter-ions and excess co-ions present at the interface has received far less attention.

1.3. Model surface: Muscovite Mica
The model surface of choice to study surface forces over micrometer length scales is the (001) plane of muscovite mica. The crystal structure of muscovite mica consists of a layered aluminosilicate structure with octahedral sheets of Al$^{3+}$ sandwiched between tetrahedral sheets of Al$^{3+}$ and Si$^{4+}$ (Figure 1.5). Muscovite mica has long been used to measure surfaces forces in the SFA [48] due to its atomic flatness, transparency that enables the use of Multiple Beam Interferometry, easy cleavage along the (001) plane [49], flexibility that allows it to be mounted in the cross cylinder geometry, high surface energy that ensures strong adsorption of molecules to the surface etc. A recent detailed review by Christenson and Thompson [50] on mica surfaces cleaved in air concluded that the mica surface is covered by upto 1 formula unit of K$_2$CO$_3$/nm$^2$, which dissolves once immersed in water or aqueous solutions. Other substrates such as silica [51] and sapphire [52] have been used, though with sub-optimal results.

The permanent negative lattice charge of the mica results from the 1:4 random substitution of Si$^{4+}$ by Al$^{3+}$ in the tetrahedral layer, which is balanced in the crystal by interlayer K$^+$ positioned at 1.7 Å above the outermost basal
**Figure 1.6.** Idealized structure of mica. The description of the crystal structure can be found in the text. Figure adapted from [53, 54].

Oxygen atoms. The weakest bonds in the structure are between the potassium and the oxygen and hence cleavage takes place along this plane. Cleavage of the mica along this plane ((001) direction) results in half of the interlayer $K^+$ atoms remaining on one of the created surfaces in order to balance the surface charge and hence creating strong surface electric dipoles [54, 55]. It has been observed that the cleavage does not disturb the atomic structure below the cleavage plane [54]. When in contact with an aqueous electrolyte solution, the interlayer cation is solvated and hence goes into the solution leaving the negative mica lattice charge of $1e^-$ per $47\text{Å}^2$ to be balanced by an excess of mobile and adsorbed counter ions in the EDL [56]. Some inhomogeneities in the mica charge distribution can certainly not be ruled out, and provide locally inhomogeneous electrostatic environments for the surface vicinal ions [57]. Zeta potential measurement have shown the absence of an isoelectric point on mica surfaces [58] and the hydrophilic
mica surfaces are readily hydrated by water thus reducing the mica-mica adhesion [31, 59].

1.4. Hydrated ions

The International Union for Pure and Applied Chemistry (IUPAC) definition of solvation (or hydration in case of aqueous solutions) is any “stabilizing interaction of the solute with the solvent molecules that generally involves electrostatic, van der Waal’s or hydrogen bond formation”[60]. The charged cation or anions bind water molecules (Figure 1.7) to the ion such that they no longer behave like bulk water [61]. Water molecules are bound in hydration shells with each shell containing a certain number of water molecules that is called its coordination number. For instance, the coordination number of K$^+$ in the first, second and third hydration shells are 5, 16, 36 respectively [62]. The greater the coordination number of the ion, the lesser is its mobility, since the ion has to drag more water molecules with it and is hence less mobile[63].

![Figure 1.7.](image)

**Figure 1.7. Orientation of water molecule around (a) cation (b) anion. Figure from [64].**

Ion hydration modulates the adsorption energy of ions at charged interfaces [57]. Namely, it has been suggested that
counter-ions adsorbing on a charged mica surface can take the following adsorption sites: $\text{OS}_{\text{ext}}$ (external Outer Sphere), when the hydrated cation is located above the surface hydration layer retaining its hydration shell, $\text{OS}_{\text{ads}}$ (adsorbed Outer Sphere), when the hydrated cation disturbs or displaces the surface hydration layer and somehow “adsorbs” to the mica, and IS (Inner Sphere), when the cation is partially dehydrated of its primary hydration shell and forms close bonds with the oxygen atoms within the mica surface [65, 66]. This has been schematically illustrated in Figure 1.8.

**Figure 1.8. Interfacial cation speciation at the mica-solution interface.** The ions adsorbed in the OS external state are above the surface hydration layer or retain their higher order hydration shells. The OS adsorbed ion displaces the surface hydration layer but retains its primary hydration shell. Additional dehydration of the primary hydration shell and bond formation with the oxygen atoms of the mica surface results in the IS complex. It is expected that the surface charge is least compensated by the OS ions that are held farther away from the surface. Figure adapted from [65, 67].
The population of the OS and IS ions at the interface is ion specific and depends on the strength of the ion-water interaction (hydration enthalpy). The layering of the hydrated ions when confined between smooth surfaces and particularly their proposed dehydration and condensation into the surface has not been discussed in light of recent insights into the mica-electrolyte interfacial structure and improved force measurements between mica surfaces. This discussion will be the focus of this thesis.

1.5. **Hydrated ion layering and the π-transition in aqueous KNO₃**

Espinosa-Marzal et al. [34] measured compression isotherms (surface force vs. distance) in aqueous KNO₃ electrolyte confined between mica surfaces with an extended Surface Force Apparatus as a function of electrolyte concentration (0.08mM-2.6M). They identified three different phenomenological regimes of KNO₃ concentration, characterized by distinct features seen in force-distance curves, film-thickness transitions and pull-off forces. These are the “DLVO” regime below 0.3 mM, the “ordering” regime above 0.3 mM where hydrated ion layering took place and the “solidification” regime above 20 mM KNO₃ (Figure 1.9).

(a) DLVO regime: Below concentrations of \(\approx 0.3\) mM KNO₃, the interaction between the surfaces followed the DLVO theory and the surfaces “jumped into contact” with each other when the gradient of the interaction force was equal to the spring constant of the instrument due to the dominant Van der Waals
attraction. The adhesion is relatively high and mica-mica surface separation is zero though the adhesion steadily decreases with increasing concentration.

(b) Ordering regime: Above 0.3 mM, layering of hydrated K\(^+\) ions led to multiple film-thickness transitions of 4±1 Å size. The final hydrated ion layer—reminiscent of the Inner Helmholtz Plane (OHP)—was either pushed out of the gap in a 5.8±0.3 Å collective transition, or was semi-dehydrated and pushed into the surfaces in a 2.9±0.3 Å transition as schematically illustrated in Figure 1.9. These two pathways resulted in different pull-off forces; and was reduced in the latter. The exact concentration of the crossover from the DLVO to the ordering regime could be affected by the individual properties of the surface as well as the electrolyte. The sudden drop in pull-off force always coincided with the disappearance of the 5.8 Å transition and the appearance of the 2.9 Å FTT over a narrow concentration range suggesting a discontinuous change of the interfacial structure.

(c) Solidification regime: Finally, at concentrations above ≈20 mM, attractive non-DLVO forces were observed followed by an attractive minimum at concentrations above 100mM. When this attractive force was fitted to a van der Waals interaction, the Hamaker constant obtained was 0.78±0.13×10\(^{-20}\) J. Such a low Hamaker constant can be achieved when the dielectric constant of the medium is ≈10-15, which is similar to that of several ionic liquids.
Hence, this solid was depicted to be an ionic condensate of cations and anions held together by attractive ion interactions.

The transition from the “DLVO” to the “ordering” regimes, marked by the sharp decrease in pull-off force (dotted line in Figure 1.9), which we shall henceforth call the $\pi$-transition ($\pi$ being the pull-off force), is accompanied by the appearance of film-thickness transitions and occurs over a narrow bulk electrolyte concentration. The sudden

![Figure 1.9. Pull-off force measured as a function of KNO$_3$ concentration. The superimposed grey line highlights the decrease in pull off force and the dotted part is the concentration range where no measurements were taken and where an abrupt decrease in the pull-off force is expected. In the ordering regime, hydrated ion layering of size $4 \pm 1$ Å followed by forced surface association of the ions after the final $2.9 \pm 0.3$ Å. Data and figure adapted from Espinosa-Marzal et al [34].](image-url)
occurrence of repulsive hydration forces accompanied by low interfacial adhesion energies have been previously observed by Pashley at similar concentrations in aqueous chloride solutions \([24]\). This work investigates the \(\pi\)-transition in detail, which, as seen in Figure 1.9, occurs in a narrow concentration (0.3-1mM) in aqueous KNO\(_3\) (pH \(\approx\)5.7) and where it is expected that different structural elements are present at similar strength.

1.6. Ion specificity- Hofmeister effects

As mentioned earlier, the DLVO theory and the Poisson Boltzmann equation it is based on considers ions as point charges and hence neglects, among other effects, the hydration shells associated to the ions and ion-ion correlations, which are ion specific. Hence, unsurprisingly, the deviations from the DLVO theory described above, namely the hydration forces and oscillatory solvation forces also turn out to be dependent on the nature of the ion.

Specific ion effects were first recorded in 1888 when Hofmeister arranged ions in sequences according to the concentration of salt required to precipitate suspensions of egg white \([68]\). Hofmeister effects refer to the “relative effectiveness of cations or anions on several phenomena” and are not predicted by classical electrostatic theories. They have been reviewed several times \([69-71]\), although a general theory to explain them has not been developed yet. Hofmeister effects are generally seen at salt concentrations >100 mM where charge screening lowers the electrostatic energy to levels comparable to the ionic dispersion energies.
[72, 73]. However, they are increasingly being observed at lower concentrations as well [74] [24, 72, 75]. The minimum/maximum concentrations required to generate specific ion effects in electrolyte solutions remains an open question [76].

1.6.1. Origin of ion specificity

Ion specificity is the consequence of the properties of individual atoms that are determined by their electronic configurations, which in turn determine ion size as well as polarizibility (dispersion interactions) and hydration. For instance, a computational study of the hydration of Na\(^+\) and K\(^+\) concluded that Na\(^+\) (hydration number: 5-6) has a stronger interaction with its first hydration shell than K\(^+\) (hydration number 5-10), resulting in K\(^+\) having a more flexible structure [77, 78].

Ion specificity is a consequence of ion polarizability, hydration, and size. Dispersion forces reflect the subtle balance between ion polarizibility and ion size; they increase with polarizibility that scales with ion size but the increased size in turn reduces the dispersion interaction between ion and surface [76]. There have been several attempts to include ion specificity in the classical Poisson Boltzmann (PB) theory, which was originally based on a mean field approximation and assumed the ions as point charges. The Stern layer was the first concept that took into account ion-charged surface interactions other than the Boltzmann distribution of ions in a mean field potential by considering the volume exclusion due to the finite size of the ions at the
interface [79]. Grahame [80] extended this theory to account for specifically adsorbed ions that have lost their hydration shell and hence can approach the surface closer. Recent approaches to ion specificity include addition of ionic-surface dispersion interactions [31, 81], or addition of the free energy change due to the volume exclusion generated by hydration to the EDL free energy [82, 83] and most recently adding a hydration potential in addition to the electrostatic potential to derive a hydration modified PB model [84]. There have also been attempts to calculate the (ion specific) hydration forces by subtracting the experimentally measured forces from those predicted by theory (DLVO/HNC calculations/Lifshitz/extensions to PB theory) and attributing the difference to surface hydration forces which is an unsatisfactory approach due to the error in the theories themselves[76].

![Division of monovalent cations and anions into kosmotropes (water structure makers) and chaotropes](image)

**Figure 1.10.** Division of monovalent cations and anions into kosmotropes (water structure makers) and chaotropes
(water structure breakers) based on the positive and negative values of $\Delta S = \text{Entropy of water near the ion-entropy of pure water}$. The ions are drawn approximately to scale and the figure is adapted from [61].

The Law of Matching Water Affinities (LMWA) qualitatively orders ions by taking into account their chaotropic or kosmotropic nature, which is characteristic of the strength of their hydration shells [61, 69, 85]. As seen in Figure 1.10, chaotropic ions are monovalent ions of low surface charge density where the strength of the ion-water interactions is less than the water-water interactions in bulk solution i.e. the entropy of water near the ions is greater than in the bulk. Hence, the chaotropic ion induces disorder in the surrounding water structure. The reverse is true of the kosmotropic ions. Ion hydration results in an ordering of the water molecules around the ion due to the effect of the electric field of the ion as well as a disordering effect in the local solvent structure due to the presence of the ion. The ordering effect (less mobile water in the hydration shell than in bulk water) dominates in kosmotropes such as Li$^+$, Mg$^{2+}$, Al$^{3+}$, SO$_4^{2-}$, resulting in them having a strong hydration shell while the disordering effect (more mobile water than in bulk water) prevails in chaotropic ions like Cs$^+$, ClO$_4^{-}$. The key result of the LMWA is that ion pairs are only formed between chaotropic ion pairs or cosmotropic ion pairs and that a chaotropic ion may not penetrate the hydration shell of a cosmotropic ion.
1.6.2. Cation specificity in aqueous electrolyte solutions

The role of the cation specificity in EDLs at the mineral-electrolyte interface have been probed via force measurements [24, 75], XRR studies [57, 67] as well as XPS on liquid microjets [21]. It was observed that in 1:1 electrolytes, the absolute surface potential of silica nanoparticles in aqueous electrolytes increases (becomes more negative) in the order Cs$^+<$K$^+<$Na$^+$, since with increasing hydrated cation size, the ions are held further away from the surface, causing a larger potential drop across the Stern layer[21]. The salt concentration above which hydration forces appear during force measurements between mica surfaces in aqueous electrolytes also increases in the order Cs$^+<$Na$^+<$Li$^+$ for the same anion, which was attributed to the strongly hydrated ions not being readily dehydrated and adsorbed to the surface [24].

In this work, we investigate ion specificity in highly confined Electrical Double Layers (EDLs), particularly focusing on the $\pi$-transition, that occurs when charged surfaces immersed in electrolyte solution are approached towards each other, entailing strong overlap and finally collapse of the double layer structure below $\approx 2$ nm. At vanishing surface separations, the hydrated ion structure at the electrolyte-solid interface determines the surface hydration structure [32] and is hence expected to be ion-specific.
1.7. Scope of the thesis
This thesis is inspired by the work of Pashley [24] and Espinosa-Marzal et al [34] who investigated the interaction forces between mica surfaces in aqueous electrolytes across a wide range of concentration. We begin by probing the sharp drop in the pull-off force (π-transition) occurring in the narrow concentration regime of 0.3-1mM for aqueous KNO₃. It is to be recalled that the abrupt decrease in adhesion coincided with the onset of hydration forces (observed by Pashley) and hydrated ion layering (observed by Espinosa-Marzal). On confirming that the π-transition is actually an instability in the pull-off forces and not a gradual decrease with increasing concentration, we proceed to take a closer look at the final film-thickness transitions (FTT), which are observed during the approach of the surfaces. The idea was that it would be the final FTT recorded that would determine the interfacial structure and consequently the pull-off force. Based on the knowledge of the different hydrated states that the K⁺ ion adopts on the mica-electrolyte interface [67], we proceed to assign our final FTTs to different transitions between hydrated ions states. Again proceeding from Pashley’s argument that hydration forces (which we see as FTTs) occurs due to the metal ion not being exchanged by hydronium and thus being left in the gap between the surfaces (Figure 1.3), we proceed to tune the K⁺/H₃O⁺ balance by changing the pH. We make several interesting observations about the π-transition, hydrated ion layering as well as the hydrated ion states at the interface. These have been described in Chapter 3. Since we know that hydrated ion states are ion specific, we proceed to extend our
model of the stepwise collapse of EDLs by choosing the Na\(^+\) and Cs\(^+\) ions, which are more and less weakly hydrated than K\(^+\) respectively. We gain additional insights into the interfacial structure and the pull-off forces that will be elucidated in Chapter 4. Chapter 5 summarizes the results of this investigation as well as proposes additional effects that could affect this phenomenon and future pathways to explore.
Chapter 2
Experimental Methods

The extended Surface Force Apparatus was the major instrument used to probe the mica-electrolyte interface in this thesis. The Surface Force Apparatus and Atomic Force Microscopy have been extensively used prior to this work for direct force measurements of DLVO and structural forces in aqueous solutions [86, 87].

2.1. The extended Surface Force Apparatus (eSFA)
2.1.1. Surface Force Apparatus
In 1969, Tabor and Winterton [88] measured the normal and retarded van der Waals forces in air between cross cylindered mica sheets, whose contact geometry is equivalent to that of a sphere on a flat surface. The optical interference technique was used to measure the separation between the surfaces from 5-30 nm with an accuracy of ±3 Å. The force was measured in the following manner: When the surfaces were slowly approached towards each other, they jump-in to contact with each other from a distance (surface separation) when the attractive force overcomes the stiffness of the spring to which one of the surfaces was attached. The stiffness of the spring was varied to achieve different jump-in distances, which are a measure of the surface force. Each time, a new spring was fitted to the apparatus, necessitating realignment and recalibration. This jump method could be used for accurate force measurement only upto surface separations of 20nm due to the increasing effect of external vibrations. In 1972, the range of the
apparatus was increased to 1.5-130nm by Israelachvili and Tabor [89]. The forces from 1.5 to 20nm were measured using the jump method described above. From 10-130nm, the forces were determined using the resonant frequency. One of the surfaces was supported on a piezo crystal, which could be vibrated at the required frequencies, while the other surface was supported on a spring whose natural frequency depended both on the spring stiffness as well as the van der Waals forces exerted on it by the first surface. The resonant frequency was determined as a function of surface separation and hence the force was deduced [89]. The stiffness of the spring was adjusted by varying the clamping position along the cantilever length.

The details of the first SFA (SFA Mark I) were published by Israelachvili and Adams in 1976 [90] and was used to measure forces between mica surfaces in aqueous electrolytes in the distance range 0-100nm. The Fringes of Equal Chromatic Order (FECO) resulting from Multiple Beam Interferometry (MBI) between the silver mirrors coated on one side of the mica surfaces were used to measure the distance, refractive index of the medium between the surfaces as well as monitor the shape and deformation of the surfaces. The force was calculated from the spring deflection in the following manner:

As seen in Figure 2.1, x=0 is defined as the position of the lower surface where there is zero interaction between the two surfaces. When the upper surface is moved from x=∞ to x=D₀, the interaction force between the two surfaces causes the lower surface to be deflected to x=-(D-D₀). Hence the interaction force between the surfaces F(D) has been
balanced by the restoring force in the spring which is given by the product of the spring deflection \((D-D_0)\) and the spring stiffness \(K\). Hence, the interaction force is \(F(D) = K(D - D_0)\), where \(F(D) > 0\) for repulsion and \(F(D) < 0\) for attraction.

**Figure 2.1.** When mica surfaces are separated by a distance \(D\), the force between them \(F(D)\) causes the spring to deflect by \(D - D_0\). Further details of the force measurement are given in the text. Figure from [90].

The spring stiffness \(K\) is calibrated before each experiment by placing weights on the sample holders that will hold the mica surfaces during the experiment and noting the deflection using a telescope and glass scale. The spring deflection \((D-D_0)\) is measured optically during the experiment.
Successively improved versions of the instrument include the Mark II [48], Mark III [91], Mark IV [92] and the glass cell SFA[93].

2.1.2. extended Surface Force Apparatus (eSFA)
The two eSFAs used in this thesis were built at ETH Zürich and have been described in detail in the PhD theses of M. Zäch (eSFA I) [94] and T. Balmer (eSFA II) [95]. eSFA I was built by modification of a Mark III SFA. eSFA II (Figure 2.2) is a new design made from a minimum number of mechanical parts and can be mounted in different configurations. The eSFAs were automatized by utilizing Fast Spectral Correlation [96] which reduces the processing time, resulting in real time calculation of surface separation and refractive index. They also feature significant improvements in drift, temperature control and instrumental stability [97-99]. The statistical precision of the surface-separation measurement is ±20 pm, due to an automated simultaneous evaluation of multiple fringe wavelengths.

2.1.3. Instrumental details
The white light source is a Xe arc lamp (Müller Elektronik-Optik, Germany SVX-1450) or an FOT 150 lamp. The optical path is marked by the dotted arrows. The surfaces are moved using the motor (eSFA I)/ piezocontroller (eSFA II) during the experiments. The range of the motor in eSFA I is ≈6 μm and in eSFA II is 25 μm. The force is measured from the deflection of a double cantilever spring. The different spring constants were measured to be 235±4, 1262±62, 1600±54 N/m. The Point of Closest Approach (PCA) of the
surfaces is adjusted using a motorized XY scanning stage while another motorized stage is used to adjust the focus. There are openings to insert and remove fluids as well as inject a steady stream of nitrogen or air into the sample chamber. The whole setup is enclosed in an insulating Styrofoam box and placed on an active anti-vibration table (Halcyonics GmbH, Germany) in order to damp external oscillations. The eSFAs are controlled by Labview.

The spectrometer and white light calibration were carried out weekly, that is, prior to
Figure 2.2. Schematic of eSFA II (a) side view (b) top view showing the optical path.

the start of any series of experiments. Figure 2.3 shows that the wavelength assigned to the first pixel of the spectrometer, measured over a 6-month period, deviated by only 5 Å. The spring calibration was done each time a new spring was inserted into the SFA.
2.1.4. Sensitivity to the spring constant and instrumental limitations

While running test experiments, we observed that in the low-force region (F/R<0.2 mN/m or F<4 μN or 3.18 mJ/m²), there occurred oscillations in the measured force (Figure 2.4a). The spring constant in these measurements was 1262 N/m. In order to ascertain whether these oscillations were the result of a physical reality of the double layer system or an artifact of the instrument (optics or motor linearity), we repeated the above experiments using a softer spring (k= 235 N/m). It was observed that the amplitude of the waviness was reduced by approximately 6 times when the softer spring was used (Figure 2.4b). Therefore we can conclude that the waviness is an artifact of the optics of the instrument and not a characteristic of the EDL system.

**Figure 2.3.** Histogram showing the variation of the wavelength assigned to the first pixel of the spectrometer from the calibrations over a period of 6 months.
Figure 2.4. (a) Representative waviness in the measured force-distance curves during approach in the low-force region. (b) Comparison of the waviness of force-distance curves measured with a spring constant equal to 1262 N/m (black) and 235 N/m (red), respectively.

In addition, we observed that the force at which the final film thickness transition takes place was much higher when using the soft spring (not shown). With the soft spring it takes more time to achieve a particular load as compared to a stiffer spring at the same approach speed. This may indicate that the film thickness transitions that we measure are not strictly equilibrium transitions: when the system has more time to relax and reorder itself, a different order i.e. structure, is achieved. Another possibility may be that a stiffer spring couples inevitable mechanical vibrations differently into the EDL structure.

2.2. Mica deformation issue
The accurate measurement of surface separation is a key element of the SFA experiment if one wants to study
interfacial structures in saline solution. The distance between the mica surfaces in the SFA is calculated by analysis of interference patterns from a Fabry-Perot Interferometer formed by the surfaces. However, under external load or even in presence of adhesive forces, the compression of mica can affect the optical path, thereby inducing a systematic underestimation of the distance measurement. The photoelastic effect of the mica refractive index has to be taken into account because it also affects the optical path measured here. As a result of these effects, the surface separation, and to lesser extent, also the force at high compressions (>10mN/m) are subject to systematic errors; visible for example, as a

![Compression isotherm at 1 mM NaNO₃](image)

**Figure 2.5.** Measured forces during approach of mica surfaces in 1mM NaNO₃ solutions. The arrow points to the Film thickness transition measured during the approach. The deformation of the mica was responsible for the negative slope of the force curves at high loads. Both the surface separation and the surface interaction above
≈10mN/m is a rough estimation. It is to be noted that the Film thickness transitions, which are analysed in detail in this thesis are not affected by mica compression since they take place at the same load.

tilted slope artifact in the compression isotherms of salt solutions (Figure 2.5), that lead to difficulties while interpreting nanometer thick molecular films. These systematic errors have to be corrected in order to obtain more reliable structural information from the eSFA.

It is generally assumed from the shape of the FECO fringes that the contact area is flat. On taking a closer look at our high resolution experimental data and measuring the contact profiles we observe a distinct curvature at the edges, which is the result of a pressure distribution in the contact and the compression of the mica. There has been proposed a model independent solution to measure the pressure in the buried contact as well as correct the optical zero by obtaining the uncompressed mica thickness using data from the interferometric profile (Heuberger, in preparation). Using a lateral scan of the contact area, the pressure distribution inside the contact area could be calculated. A typical 2D scan profile is shown in Figure 2.6. Calculation of the uncompressed mica thickness and the pressure distribution in the contact required a reliable determination of the contact radii from this optically measured profile. The radii were determined by two methods: (a) by fitting a circle to the measured 2D profile and (b) calculating the second derivative of the spline interpolated data points which
showed a clear peak at the edge of the contact. The surface profiles were measured during loading and unloading (at the rate of 1nm/s) at different loads. Although we measured the contact profiles of 30 pairs of mica surfaces, we were not yet able to get reliable measurements of the pressure integral from our data. The main problems are linked to effects of surface-surface friction and exact determination of contact area. Hence, we were unable to correct the force-distance curves for the mica compression and thus refrain from defining a mica hard wall from our force-distance data or inferring anything from the absolute distance values. It is to be noted that we restrict our high resolution analysis to the film-thickness transitions, that take place at constant load and are hence unaffected by mica compression.

Figure 2.6. Contact profiles measured at different external loads. After correction of the photo-elastic effect, these
profiles reflect the amount of compression of the mica surface inside the contact area. The curvature throughout the entire contact can be clearly seen. The evaluation of the contact profiles was done by M. Heuberger.

2.3. Sample preparation
The preparation of the mica samples has been schematically illustrated in Figure 2.7. Mica sheets (Grade I Muscovite mica, S&J Trading, New York) of 2-5 μm thickness were cleaved and cut using ceramic surgical scissors into samples of ≈1×1 cm size. It is to be noted that this procedure was followed to ensure clean surfaces since the conventional melt cut technique using a hot Platinum wire to cut the mica has been found to contaminate the mica surface with Pt particles [100, 101]. The freshly cleaved mica samples were immediately placed onto a (freshly cleaved) mica backing sheet. The backing sheet was placed in a Silver evaporater and 40 nm of Silver (99.99% purity, Abcr Chemicals) was deposited on it under a pressure of <10⁻⁶ mbar at a deposition rate of approx. 1 Å/s. Silica discs (radius of curvature 20mm) were cleaned with chloroform and acetone and polished with optical cleaning paper (Neolab 17218). They were spin coated with a layer of epoxy resin diluted with chloroform (10g 1004F (EPON R, Shell) and 40g CHCl₃). The glue was then melted by placing the glued discs on a hot plate heated to 140 °C. The backsilvered mica samples were carefully placed on the melted glue and smoothly come into contact with it under gravity, capillary forces and air flow. The discs that were glued with mica sheets of same thickness were mounted in the eSFA such that their cylinder axes were
perpendicular to each other and covered with a cuvette. The eSFA was immediately placed on its stand and purged with nitrogen to ensure cleanliness of the system. All sample preparation and mounting was done in a laminar flow hood and all the tweezers, cuvettes etc were ultrasonicated in acetone prior to use.

**Figure 2.7.** Preparation of the mica samples: After cutting with ceramic scissors, the individual mica sheets are placed on the backing sheets with the top (clean) side downwards and partially overlapping with the strip of Scotch tape to facilitate lift off. The backsilvered mica sheets are carefully placed on the melted glue such that the one edge of the sample makes contact and then released as shown above. The mica sheet is then dragged down due to the laminar air flow and capillary forces into conformal contact with the glass disc. The entire sample preparation (except for the silvering) and mounting to the SFA takes place in the laminar flow hood.
2.4. Experimental procedure

Alignment of the optical path: Coarse adjustment of the surface separation was done by manually approaching the mica surfaces with a micrometer screw to a distance of ≈1 μm.

Setting the Point of Closest Approach (PCA): Since the transmitted light through the surfaces passes through a bandpass filter prior to entering the camera, the primary interference effects (Newton Rings) occurring in the PCA region can be seen in the camera. The Newton rings (concentric bright and dark rings due to constructive and destructive interference) become increasingly brighter and clearer as the surface separation decreases. In case of contamination or misalignment of the surfaces, the Newton rings appear deformed or elliptical respectively and hence the image in the camera serves as a first check of surface quality and alignment. The setup has been arranged such that the focus of the spectrometer and the CCD camera are at the same distance and hence the PCA can be adjusted to the center of the spectrometer with the help of the CCD camera.

Estimate mica thickness: The surfaces are separated again and the secondary fringes, resulting from MBI between the gap-mica and mica-silver interfaces (Interferometer shown in Figure 2.8), are used to input a rough estimate of the mica thickness. This would enable the software to calculate a rough estimate of the surface separation. The surfaces are separated to ≈ 1 μm and the instrument was allowed to equilibrate while the instrumental drift was continuously monitored without actuator action at a safe surface separation of around D~1-2 μm.
Figure 2.8. The white light transmission spectrum from the interferometer in the SFA yields characteristic Fringes of Equal Chromatic Order (not shown). The peak positions of the spectrum from the central axis (PCA) shown here is used to calculated the gap distance $D$.

**Determination of optical zero/ mica thickness from primary fringes:** Equilibrium was deemed to be achieved when the instrumental drift rate of surface separation was measured to be less than 1Å/min. The PCA has to be realigned to the center of the spectrometer since it could have shifted during the equilibration process. This is done in the following manner: 1. The PCA area is linearly scanned along the X axis. 2. This cross section scan is fitted to a circle of radius $R_x$. 3. The stage on which the spectrometer is fixed is moved to the center of this circle. 4. The above procedure is repeated along the Y axis. 5. The whole process is repeated iteratively till the fitted circles from successive scans (in the X and Y axis) have the same center within a range of ±1 μm. The radius of curvature used to normalize the force curves 

$$R = \sqrt{R_x R_y}$$

is noted before each experiment.
The surfaces were approached at a constant actuator velocity of 5 Å/s. Since the distance was calculated in real time by the FSC software, it was used to verify that the actuator motion was linear at distances outside the range of expected surface forces, i.e. >0.5 μm, i.e. the optically measured speed of approach of the surfaces was checked to be equal to the set actuator speed. The linear approach of the surfaces at large surface separations will be later used to calibrate the zero force (Figure 2.9).

**Figure 2.9.** The Distance vs time graph that is continuously monitored during the experiment.

At close separations, (<20 nm in air) the surfaces “jumped in” to primary (mica-mica) contact at which point the actuator was immediately stopped. This occurs when the gradient of the Van der Waals force exceeds the spring constant. The linear approach of the surfaces and the occurrence of the Van der Waals jump-in were taken as checks of the cleanliness of the surfaces. The peak detector settings such as peak width and threshold level, which were
used to filter the spectrum from the interferometer (Transmission interference spectrum at the PCA shown in Figure 2.8) and detect the peak positions for determination of the gap distance, were adjusted and the mica thickness was determined using the primary fringes. The optical zero, which defines D=0, was set at the adhesive yet externally unloaded mica-mica contact in air, relative to which all the surface separations, D, are reported here. While this method standardizes mica compression effects due to loading and mica-mica adhesion, it may still include a small shift due to a tightly bound hydration layer remaining on the mica surfaces in contact. Such errors affecting the absolute measurement of film thickness at the (sub)nanometer level were thus maintained constant as well as possible throughout the experimental series. All the force curves shown in this thesis are raw data, i.e. without cosmetic shifting of the D-axis, and may therefore also include negative values in cases of significant mica compression at higher loads. The surfaces were separated at 5 Å /s. (During coarse adjustment of the distance the position of the linear actuator was set such that there was sufficient range (>5μm) in order to separate the surfaces without manual intervention.) The jump-out distance at which the surfaces snapped out of contact was also a check of the surface cleanliness. Typical so determined pull-off force values of mica surfaces in air are ≈1000mN/m in air and 80 mN/m in pure water. The temperature of all measurements was controlled to be 22.0(2) °C.
**Insertion of liquids:** We performed our experiments with the surfaces fully immersed in liquid unless otherwise stated. The prepared solutions were stored and equilibrated in a stainless steel container prior to transfer into eSFA I. In eSFA II, the cuvette was filled by slowly injecting the liquid using a clean syringe. While exchanging solutions, the new solution was carefully filled and emptied thrice in order to ensure complete solution exchange. We observe that the volume of solution left in the eSFA after emptying is <1 ml. The error in the concentration due to dilution with the previous solution, which has been calculated and shown in Figure 2.10, is therefore expected to be less than 5%.

![Graph showing calculated error in salt concentration due to solution exchange.](image) **Figure 2.10.** The calculated error in the salt concentration due to solution exchange.

We also experimentally confirmed this by randomly testing control samples before and after the experiment using Ion
Chromatography where the error in salt concentration was again found to be less than 5%.

After inserting the liquid, equilibrium was achieved in approximately 1 hour. The PCA was adjusted again using a lateral scanning along the X and Y axis.

*Surface force measurement:* Multiple consecutive force-distance approach and retraction curves were recorded by programming the piezo to reverse direction at the set limits. As is commonly practiced, we have chosen to plot the normalized force, F/R(D), generally termed the “force curve”. The geometric normalization F/R relates to the equivalent interaction energy E between flat surfaces, according to the Derjaguin approximation \( F/R = 2\pi E \) [102].

The maximum F/R-value applied in our measurements was 700 mN/m. As the contact geometry appreciably flattens above some 10mN/m, the F/R-values are overestimated because, in the normalization process, we choose to ignore the increase of R upon deformation. The absolute optical error of D is typically smaller than 2 nm at the applied maximum load. Possible systematic errors due to mica-layer compression do not affect the size of the measured film-thickness transitions considered here, since each of them is occurring over a particular but fixed load.

### 2.5. Time of Flight Secondary Ion Mass Spectroscopy (ToFSIMS)

In order to obtain information about chemical changes on the mica surface that were subjected to ion exchange in
electrolyte solutions followed by consecutive approaches and retractions in the eSFA, we performed ToFSIMS on the mica samples after surface force measurement in the eSFA. Unfortunately, though the ToFSIMS technique is very sensitive to light metal ions such as $K^+$, our experiments were not successful for reasons that will be explained below. The ToFSIMS experiments were conducted at EMPA, Dübendorf by Dr. L. Bernard.

**2.5.1. The Technique:**
Secondary Ion Mass Spectroscopy (SIMS) is used to analyze the chemical composition of a surface. In this work, the surface was scanned with a focused primary ion Bi$^+$ beam (TOFSIMS 5, ION-TOF, Münster). The ions that are extracted from the surface (secondary ions) are accelerated to the detector and analyzed using the principle that the Time of Flight (TOF) of ions of different masses are different. The total ion dose counts is kept low to ensure that only the surface (monolayer) is being analyzed. An electron flood gun is used simultaneously with the primary ion beam for charge compensation.

It is to be noted that the ToFSIMS technique provides only semi-quantitative information about the surface composition, i.e. we can only compare the ratios between samples analyzed at the same time. In addition to this inherent limitation, the curvature of our mica samples would result in an approximately 90% decrease in intensity and the intensity will become a function of position as well instead of only the mass concentration of the ions. Moreover, since vacuum has to be maintained in the chamber during measurement, the
mica samples will have to be rinsed and dried. This step could change the conditions on the surface. Hence, it is also uncertain whether the technique will be able to detect the contact area (PCA from the surface force measurements) of the mica samples, assuming that there is a higher $K^+$ concentration at the contact that remains even when the surfaces are separated, rinsed and flushed with $N_2$ prior to the ToFSIMS measurements.

### 2.5.2. Motivation

The observation of the sharp decrease in pull-off force ($\pi$-transition) over a narrow electrolyte concentration range (Figure 1.9) lead to the hypothesis that this was due to a forced condensation of $K^+$ ions into the mica surface leading to a change in the surface properties. The purpose of analyzing the mica surface was to obtain information about the $\pi$-transition by correlating the decrease in adhesion with a change in the surface properties/composition of the mica. In addition, we also observed that the energy required for the FTTs as well as the size of the FTTs changes on consecutive approaches, suggesting changes on the mica surface (Figure 5.2 in Chapter 5). Our aim was to see whether we could see a change in the surface properties of the mica in different approaches and different concentrations and thus gain information about the kinetics of ion exchange.

### 2.5.3. Experiments

An area of $500 \times 500 \mu m^2$ of the surface (at 10 different points) was scanned. At each pixel, we acquired a complete mass spectrum, thus providing information about the
chemical composition at each area analyzed. Thus each composition value calculated was an average of these 10 measurements. We acquire the spectra for the positively charged ions as we are primarily interested in the role of the cation in the double layer, specifically the K⁺, which is present both in the mica as well as in the electrolyte solution (KNO₃). The following samples were analyzed: freshly cleaved mica, freshly cleaved mica that was rinsed with deionized water (reference samples), mica treated with HNO₃ (to ensure complete ion exchange) and mica that was treated with 0.6mM KNO₃ (for comparison with the eSFA experiments).

2.5.4. Results
The following is a description of our attempts to characterize the mica using the ToFSIMS technique.

**Trial 1**

**Aim:** To check whether K⁺ ion on the mica sample could be detected and to locate the point/area of contact on the curved mica sample from the eSFA experiment.

**Samples prepared:**
1. flat freshly cleaved mica (reference sample)
2. curved samples (C1 and C2) from eSFA experiment- The samples were from a regular eSFA experiment in 0.6mM KNO₃ and in which the load was applied till 200mN/m, 2 film thickness transitions were detected and the π-transition had taken place. The samples were
taken put of the eSFA and immediately rinsed in cold water, blow dried with N₂ and placed in the sample box.

**Results:**
The K⁺ was detected from all the samples analyzed. The intensities of the different ions detected (area under the peak) was normalized by the total intensity for comparison in Figure 2.11.

![Figure 2.11. Mica surface composition from all the samples. The values are the average of 10 measurements.](image)

It was observed that the largest intensity was from the K⁺ signal. We also see that Na⁺ present in the freshly cleaved mica is washed off after exposure to solution. However, the reduction in intensity of K⁺ in the samples C1 and C2 is not explainable. It is expected that C1 and C2 would show the same K⁺ intensity since they were equivalent surfaces pressed into contact. Though C1 and C2 show a lesser K⁺ intensity than freshly cleaved mica as expected, the samples C1 and C2 themselves do not show the same K⁺ intensity. This could be an effect of the rinsing step which we will attempt to determine later. It was also interesting to note that
the $^{41}\text{K}^+$ isotope which is abundantly present in the freshly cleaved mica seems to have reduced in the samples subjected to ion exchange. We can speculate that there is a different distribution of the $^{39}\text{K}$ and $^{41}\text{K}$ isotopes in the mica lattice and the KNO$_3$ solution.

**Trial 2**

**Aim:** (a) To quantify the effect of rinsing with water (b) to see if differences in the K$^+$ composition of mica samples subjected to ion exchange with different solutions can be detected on a flat sample. One solution chosen was HNO$_3$, which is the extreme case where all the K$^+$ on the mica should be replaced by H$^+$.

**Samples prepared:**
1. flat freshly cleaved mica (reference sample)
2. flat freshly cleaved mica rinsed with milliQ water
3. flat freshly cleaved mica immersed in 0.6mM KNO$_3$ for 1 hour at 50°C
4. flat freshly cleaved mica immersed in 30% HNO$_3$ at 50°C

**Results**
Strangely, the K$^+$ composition after rinsing with water is higher than the freshly cleaved mica (Figure 2.12). Moreover, though the K$^+$ composition in the mica subjected to ion exchange in 0.6mM KNO$_3$ is higher when compared to the acid washed mica as expected, it seems that the difference is small even on comparing such extreme cases (dotted circle). Thus, it is unlikely that the narrow
concentration ranges of electrolyte that we aim to examine (0.3-1mM KNO₃) will yield reliable results.

Figure 2.12. Mica surface composition of the flat samples under different conditions.

Trial 3

Aim: (a) To investigate the effect of the rinsing (b) Detect contact area in flat samples which have been kept in contact in solution.

Samples prepared:
1. flat freshly cleaved mica (reference sample)
2. flat freshly cleaved mica immersed in 10mM KNO₃ at 50°C for 1 hour and rinsed with water followed by flushing with N₂.
3. flat freshly cleaved mica immersed in 10mM KNO₃ at 50°C for 1 hour and immediately flushed with N₂.
4,5,6. Flat mica immersed in 10mM KNO₃ for 12 hours, rinsed with water and flushed with N₂.
7,8,9. Flat mica immersed in 100mM KNO₃ for 12 hours, rinsed with water and flushed with N₂
Results:
From Figure 2.13, it is also clear that rinsing the mica with water removes $K^+$ from the surface when compared with only air drying. However, it would be difficult to quantify the effect of the rinsing: whether it is uniform each time and whether $K^+$ is being removed from the former contact area or from the whole sample.

**Figure 2.13.** Mica surface composition showing the effect of rinsing with water.

Detection of contact area in flat samples that have been in contact in solution:
Two sets of flat mica samples were placed in contact in KNO$_3$ solutions of concentration 10mM and 100mM. Analysis of the different parts of the sample showed that while the concentration of $K^+$ inside the contact area is higher than outside the contact area, the concentration of $K^+$ inside the contact areas of the two surfaces has no correlation to each other (Figure 2.14). This could arise from the rinsing procedure, which is non-uniform in both the samples.
Figure 2.14. Mica surface composition of samples immersed in (a) 10mM (b) 100mM KNO$_3$.

2.5.5. Conclusions

In conclusion, we did not proceed with these experiments for the following reasons:

1. Uncertainty in localization of the contact area on the curved mica samples.

2. Even on a flat surface, the difference in the K$^+$ concentration detected between mica surfaces subjected to ion exchange between the extreme case of HNO$_3$ and 0.6mM KNO$_3$ is minimal, questioning our efforts to can detect differences
over narrow electrolyte concentration ranges (0.3-1mM KNO$_3$).

3. Uncertainty of the effect of the water rinsing on the K$^+$ concentration.
Chapter 3
Stepwise Collapse of Overlapping Electrical Double Layers

The EDLs accompanying charged mica surfaces in aqueous electrolyte solution and structure of the confined fluid were probed using force measurements in the eSFA. The eSFA measures the mechanical response of the nanoconfined film to the applied load. With reference to a previous surface force study on overlapping double layers by Espinosa-Marzal et al[34], which defined three phenomenological regimes of salt concentration, this work begins by focusing on the narrow concentration range (0.3-1mM KNO₃) at the crossover from the “DLVO” to the “ordering” regime. This chapter has been adapted and extended from the publication Z. Zachariah et al[103].

3.1. The π-transition
The discontinuous decrease of the pull-off force π, defined as the “π–transition” which takes place over a narrow concentration range at the crossover from the DLVO to the ordering regimes has been described in detail in Section 1.5. The sudden nature of the π–transition suggests the presence of an underlying molecular mechanism, linked to a structural instability. We have studied the evolution of this π-transition in great detail by analyzing the associated film-thickness transitions (FTTs) (measured during approach of the surfaces) and the pull-off forces (measured during the retraction of the surfaces), in order to propose a detailed structural hypothesis for the underlying molecular
mechanisms and probe the molecular structure of the confined interface. It is to be noted that these experiments were done by driving the surfaces to the final load and then retracting them until the pull-off force was attained.

In agreement with earlier results [34], the measured pull-off force initially decreases gradually with [K+] concentration, followed by a prominent discontinuous reduction of the pull-off force near 1 mM KNO₃ at pH ≈5.7 (Figure 3.1). The magnitude of this π-transition (see arrow) is in the order of 20 mN/m (equivalent to 3.18 mJ/m² according to the Derjaguin approximation[102]).

![Figure 3.1. The π-transition, measured as abrupt decrease of pull-off force upon surface separation in KNO₃ solution at the concentration C_π ≈ 1 mM (shifting with pH as we shall see). The presented measurements were made without](image)

**Figure 3.1.** The π-transition, measured as abrupt decrease of pull-off force upon surface separation in KNO₃ solution at the concentration C_π ≈ 1 mM (shifting with pH as we shall see). The presented measurements were made without
rigorous pH control at pH≈5.7, i.e. under a solution that was at equilibrium with air. Two independent data sets are included here that were measured with two completely different eSFA apparatus designs. There is excellent quantitative overlap of the two data sets. The initial pull-off forces measured in deionized water are included along the left axis (0.001 mM KNO$_3$) as a reference.

3.2. Film-thickness transitions
The abrupt nature of the π-transition suggests a sudden change of molecular structure at the buried interface, which reduces the adhesion energy. The hypothesis of an instability mechanism involving hydrated-ion layering was previously suggested based on the observation of concurrent small film-thickness transitions (FTT) during the mechanical loading of the contact [34]. Indeed, if a large number of molecules throughout a load-bearing confined film collectively undergo a concerted structural transition, this is detected by the instrument as a discontinuous, often rapid, FTT. The observed size of such a film-thickness transition cannot be directly assigned to the size of a structural element like a particular molecule or complex at the interface, because it rather represents the difference between two molecular arrangements. In terms of mechanics, a FTT occurs if the second derivative of the effective surface interaction potential exceeds the spring constant of the force measuring spring, i.e. stiffness of the apparatus. It is important to note that not all FTTs are necessarily due to structural forces, because the surface interaction potential can be equal to the spring constant for
various different reasons. For example, at a surface separation of some 1-4 nm, which is typically before any hydrated-ion layering is detected, the gradient of the attractive Van der Waals interaction between the surfaces counteracts the EDL repulsion until the total gradient exceeds the spring constant of the apparatus; a first mechanical instability occurs, which causes the surfaces to accelerate and jump closer, often to a small yet positive distance. We refer to this well-known initial mechanical instability as the VdW-jump (VdW=van der Waals). Its magnitude should not to be analyzed and interpreted together with structural FTTs, since a VdW-jump also occurs in vacuum and contains no information about structural elements.

In practice, it is straightforward to identify the initial VdW jump from any subsequent FTTs due to its distance of occurrence and size, which is often >1nm, as seen in Figures 3.2b. In this context, we note that the size of the Van der Waals jump decreases with increasing pH while maintaining the ionic strength constant, as seen in Figure 3.2b. Since the Debye length is not changing with pH if ionic strength is kept constant, this is thus an effect of surface potential. The surface potential is more negative at higher pH, which strengthens repulsive EDL contributions at small distances and therefore brings the point of critical gradient (i.e. equal to the spring constant) to smaller distances.

We measured the size of FTTs at high resolution and carefully analyzed the data with statistical tools. The goal was to find and discern prominent characteristic sizes, which
can provide additional information about structural elements present.

Figure 3.2. (a) Typical Force-distance curve measured during loading, illustrating the VdW-jump followed by one FTT at a concentration of 0.7 mM KNO$_3$; The dotted line at
D>4nm is a fit using the DLVO theory and assumes constant surface charge, with resulting surface potential -130 mV. (b) Magnitude of different film-thickness transitions and their dependence on pH at a total K⁺ concentration kept constant at 0.1mM; the magnitude of the VdW-jump decreases with pH; (c) Filtering out the VdW jump-in from the FTTs.

3.3. Fitting forces curves to the DLVO theory

For the determination of EDL physical quantities, the surface forces measured at distances before the VdW-jump can be fitted to the DLVO equation using the expression developed by Chan et al. for the electrostatic repulsion at low electrolyte concentration boundary under conditions of constant surface charge[104]. This is a numerical solution of the non-linear Poisson-Boltzmann equation. The fitting parameters include surface potential and salt concentration. The calculated Hamaker constant (for the mica-water-mica system) used is $1.9 \times 10^{-20}$ J. We note however that this fitting procedure is inadequate to determine very small concentration differences ($\pm 0.1$ mM), the reason being the accuracy in force measurements ($\pm 10 \mu$N/m). Thus, for a true concentration on the order of 0.1 mM, the fitting procedure would lead to $\pm 0.3$ mM typical errors (i.e. 200% rel. error) as estimated from attempts to fit many measured force curves. (Figure 3.3). Nevertheless, we have ensured that the bulk electrolyte concentration was accurate by testing a random 10% of the samples using ion chromatography and found the mean absolute error in concentration was 0.016 mM.
Figure 3.3. The nominal concentration plotted against the concentration obtained by fitted the force curves at pH 5.7 to the DLVO equation using the expression developed by Chan et al. for the electrostatic repulsion at low electrolyte concentration boundary under conditions of constant surface charge[104].

3.4. Experimental Results
It was previously reported that multiple FTTs start to occur coincidently at the concentration where the \( \pi \)-transition is observed [34]. Using the finer resolution of salt concentrations used in the present data we shall attempt to establish the causalities and structural elements involved in this \( \pi \)-transition. In order to test the hypothesis that different structural elements at similar strengths coexist in this unique concentration range, we change salt concentration or pH, which shifts chemical potentials and interfacial populations,
and therefore the relative stability of these elements and thus gain valuable insights into the structural diversity in this unique concentration range.

3.4.1. Pull-off forces

Figure 3.4 shows how the $\pi$-transition as well as the relevant concentration thresholds shift with pH. These thresholds shall be referred to as $C_\pi$, the concentration at which the $\pi$-transition occurs, $C_L$, the concentration above which FTT’s are first observed, and, $C_{ML}$, the concentration above which multiple (more than one) FTTs are observed. The main characteristics of the $\pi$-transition are a sudden decrease in pull-off force, which is seen at all pH values, albeit less clearly at pH=3.3. The insets show histograms of the pull-off forces measured over the displayed range of concentrations and they reveal a notable value gap, indicated by arrows. It is also evident from Figure 3.4 that the values $C_\pi$, $C_L$ and $C_{ML}$ are altogether shifted to higher concentrations for lower pH. Remarkably, $C_\pi$ and $C_{ML}$ remain grouped together over this rather wide range of pH, which suggests a profounder link between the $\pi$-transition and (multiple) hydrated ion layering (see also Table 1). We also observe how, at low pH, hydronium plays the role of an antagonist that delays and weakens both the $\pi$-transition as well as multiple layering; see also Figure 3.8b for a schematic illustration of hydronium at the interface. We also note that the values of $C_L$ have intrinsic uncertainty, subject to the limited selection of solution concentrations probed. One can recognize a general trend to higher threshold concentrations, $C_L$, with decreasing pH and a similar or even stronger trend can be
Figure 3.4. The π-transition measured over a wide range of pH. The pull-off forces are measured after loaded contact of mica surfaces in KNO$_3$ solutions; an increasing hydronium concentration (lower pH) tends to shift the concentration thresholds, $C_\pi$ and $C_{ML}$ to higher salt concentrations. At pH=3.3, the π-transition has virtually ceased to exist. The bar near the bottom illustrates the effective uncertainty of $C_\pi$. Gray bands are added to guide the eye. Inset: Histogram of pull-off forces at a given pH value illustrating the data gap (arrow) resulting from the discontinuous character of the π-transition.
observed for the multiple-layering threshold, $C_{ML}$ (Table 1).

<table>
<thead>
<tr>
<th>KNO$_3$</th>
<th>pH 9.7</th>
<th>pH 5.7</th>
<th>pH 4</th>
<th>pH 3.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_L$</td>
<td>0.05</td>
<td>0.3</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>$C_{ML}$</td>
<td>0.05</td>
<td>0.6</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>$C_\pi$</td>
<td>0.22</td>
<td>0.8</td>
<td>10</td>
<td>20?</td>
</tr>
</tbody>
</table>

**Table 1.** Concentrations above which a single FTT ($C_L$) and multiple FTTs ($C_{ML}$) occur and at which the $\pi$ transition ($C_\pi$) occurs.

3.4.2. Film thickness transitions

Figure 3.5 shows an analysis of a large number of FTTs that were detected under various conditions. The evolution of the FTT size with concentration is displayed as histograms presenting their frequency of occurrence over the concentration range. Figure 3.5 emphasizes the final FTTs, since this final FTT establishes the final interfacial structure—defining the pull-off force and hence is accountable for the $\pi$-transition. The size of the final FTTs is displayed in Figures 3.5a, 3.5c, 3.5e, 3.5g for different pH values, across the concentration range of the $\pi$-transition. There is a general trend showing an initially broader or bimodal distribution, which eventually converges towards the previously reported [34] final FTT size around 3 Å at higher concentrations (indicated by gray bands).

For the following discussion it is important to realize how the final FTTs are different from non-final FTTs above $C_{ML}$. From the histograms in Figures 3.5b, d, f, h, one can readily see that the final FTTs are of small size (3 Å) at low pH, while at neutral and basic pH, these final FFTs reveal much
more structural diversity. At pH 5.7 and pH 9.7, the distribution is clearly multi-modal and thus exhibits at least two characteristic transition sizes. In contrast, the histograms of the non-final FTTs (above C_{ML}) in Figures 3.5b, d, f, h (blue bars) show a distinctively different statistical distribution than the final FTTs (grey bars). The overall trend is that the characteristic size of the non-final FTTs is 0.5-1.5 Å higher than that of the final FTT. We are aware, of course, that the classification “final” FTT remains somewhat arbitrary because it refers to the last experimentally observed FTT, before reversing the actuator direction at a chosen maximal spring load of 700 mN/m; one could never exclude occurrence of additional FTTs possibly occurring at even higher loads. To justify the term “final”, the maximum spring load was chosen to be at least five times higher than the maximum load usually applied in such loading experiments [105].

3.5. Contributions to the pull-off force

The adhesive energy of a dry mica-mica contact is known to be stronger than expected from Van der Waals interactions alone, and thus the polar component is substantial [50]. Indeed, mica is cleaved along its basal plane during sample preparation; this is the crystal plane that consists of a charge layer of potassium cations compensating for the crystal lattice charge. Solvation dissociation of these ions is responsible for the negative charging of mica in aqueous solutions. In deionized water, the pull-off force between two basal cleaved mica surfaces is reduced by roughly an order of magnitude compared to that of a comparable dry
Figure 3.5. (a)(c)(e)(g) Sizes of measured final FTTs as a function of electrolyte concentration obtained each on at
least five different pairs of mica surfaces; note that the VdW jump-in was dismissed for this analysis. The gray bands are added to guide the eye. Graphs (b)(d)(f)(h) display FTT size distributions in the form of normalized histograms showing the size distribution of non-final (light blue) and final (black) FTTs at (b) pH=9.7;(d) pH≈5.7;(f) pH=4.0;(h) pH=3.3; the superposed light blue and black colors appear as dark blue. For normalization, the frequency of occurrence in the histograms was divided by the number of experiments done at each concentration to represent a measure for probability of occurrence. Between the thresholds $C_L$ and $C_{ML}$ the single FTT is counted as the final FTT. At pH≈5.7, the pH of the solution was not actively controlled. The positions of the peaks (uni- and bimodal Gauss fitted) are given numerically in the upper right corner. At lower pH we observe a single dominant peak around 3 Å whereas the data at higher pH contains two or more different structural elements. Two noticeably distinct FTT sizes are present at the high pH=9.7 where the interface is largely depleted of hydronium and predominately populated by $K^+$ ions. The displayed concentration range was extended for the data sets at lower pH as required by the shift of the π-transition to higher concentrations.

contact[106]. While an important part of the reduction has been attributed to the high dielectric constant of water and/or the exchange of the interlayer $K^+$ by $H_3O^+$[107]; adhesion has also been hypothesized to be reduced by counter-ion hydration forces [25] and experimentally shown to depend on the relative crystallographic mismatch between the mica
surfaces in a narrow angular range $\Delta \theta \pm 1^\circ$ near perfect crystallographic alignment [108]. While this angular dependence was reported to be relevant in similar salt solutions to those used here (i.e. 1.2mM KCl), all experiments presented here were obtained with two surfaces aligned at around $90\pm 5^\circ$ relative to each other, in order to minimize optical birefringence effects, i.e. we are not expecting to see such mica alignment effects. For reference, we always measured the pull-off force in deionized water with each set of mica surfaces and found a consistent average value of $\pi = 90\pm 20$ mN/m, which is well in agreement with above literature values.

Finally, what determines the pull-off force of our loaded interface after collapse of the EDL is predominantly a mixture of contributions from i) remaining surface separation, ii) local polar interactions and iii) entropic modulations due to molecular ordering; the latter involves ions and water molecules alike. Essentially, the pull-off force is an integral yet sensitive indicator for changes of the molecular arrangement at the interface[22].

3.6. Competition between $[K^+]$ and $[H_3O^+]$

The competition between $[K^+]$ and $[H_3O^+]$ at the interface is particularly relevant to our discussion about the origin of the $\pi$-transition [24]. The mere fact that the $\pi$-transition occurs with increasing $[K^+]$ concentration, yet is retarded and weakened at lower pH (i.e. higher $[H_3O^+]$), suggests that $K^+$ is indeed the ion species that enables the $\pi$-transition. These observations suggest that the number of $K^+$ ions at the
collapsed interface must abruptly increase at \( C_\pi \). In order to ascertain this, we calculate the surface concentration of \( K^+ \) from different models of equilibria at the mica-electrolyte interface.

### 3.6.1. Surface concentration of \( K^+ \) calculated by assuming \( H^+ \) is the potential determining ion [22]

In our experiments, the \( K^+ / H_3O^+ \) surface excess balance is tuned by varying the pH of the solution in the range 3.3 – 9.69, while the co-ionic strength is maintained constant by adding either HNO\(_3\) or KOH under concurrent reduction of KNO\(_3\). Since it has been observed that the proton has a 1000 fold higher probability to occupy the mica surface site as compared to alkali metal ions due to its ability to penetrate the space between the three oxygen atoms of the Si-O tetrahedron [25, 109], H\(_3O^+\) can be considered as essentially the surface potential determining ion. The mass action equation of the surface is then given by:

\[
SH \rightleftharpoons S^- + H^+ \tag{1}
\]

where \( SH \) is the concentration of the neutralized sites on the mica surface, \( S^- \) is the concentration of the negative surface sites available for ion exchange and \( H^+ \) is the concentration of the protons, where \( K_d \) is surface dissociation constant. The surface charge, \( \sigma \), can be determined from the dissociation constant, the surface potential \( \psi_0 \) and the pH according to [22]

\[
\sigma = \alpha \sigma_0 = \frac{K_d}{K_d + [HNO_3_{\infty} e^{-\psi_0/25.7}] \sigma_0} \tag{2}
\]
The surface charge of mica $\sigma_0$ is independent of bulk pH and it remains constant [67, 110]. The Grahame equation relates surface charge and surface potential at a single surface as a function of the electrolyte concentration:

$$\sigma = 0.117 \sinh \left( \frac{\psi_0}{51.4} \right) \sqrt{[KNO_3]_\infty + [HNO_3]_\infty}$$

(3)

Thus, knowing that the maximum surface charge density of mica $\sigma_0$ is 1 charge per 47 A$^2$ (i.e. 0.33 C/m$^2$ [56]) and the surface dissociation constant, which remains constant with pH, is $10^{-2}$ M (since the pK of mica is approximately 2 and the $K_d$ can be directly related to the pK), we obtain the surface potential $\psi_0$ and the surface coverage $\alpha$. The contact values of $K^+$ at the surface can finally be estimated from the Boltzmann distribution of ions near a charged surface in electrolyte solutions as

$$[K^+]_0 = [K^+]_\infty e^{-e\psi_0/kT}$$

(4)

We can use this contact value to display the $\pi$-transition in terms of interfacial $K^+$ ion concentration in Figure 3.6, with the limitation, of course, that the calculated contact values of $K^+$ are for a single surface.

The striped region highlights the area of inexistent data points, which marks the location of the $\pi$-instability. The critical interfacial $K^+$ concentration at the $\pi$-instability is strongly dependent on pH. At the lowest investigated pH-
Figure 3.6. Measured pull-off forces as a function of the contact values of $K^+$ calculated from Graham’s equation for a single surface for different pH values. For the reader’s convenience, the striped area highlights absence of measured points, which is characteristic for the $\pi$-transition.

values (pH 3.3), the contact value of $K^+$ remains so low that there are no clear traces of a $\pi$-instability. The gray area in Figure 3.6 indicates that the $\pi$-instability first occurs at a critical $K^+$ contact value somewhere around $3\pm1\text{M}$; this is when layering forces start to play a role. Thus, although better models are needed, this points out that surface population equilibria alone cannot explain the abrupt nature of the observed $\pi$-instability.(5)
3.6.2. Surface concentration of $K^+$ from Mass action model[24]

Surface dissociation of mica can be described by the following equilibrium equations:

$$S^- + M^+ \rightleftharpoons SM$$  \hspace{1cm} (5)

$$S^- + H^+ \rightleftharpoons SH$$  \hspace{1cm} (6)

where $S^-$ is the available unoccupied lattice sites and $M^+$ is the metal ion. Assuming that all the lattice sites are available for binding, the mass action equations are:

$$ \frac{[S^-][M^+]}{[SM]} = K'_M $$  \hspace{1cm} (7)

$$ \frac{[S^-][H^+]}{[SH]} = K'_H $$  \hspace{1cm} (8)

By assuming a Boltzmann distribution of ions in the EDL and reasonable values of the dissociation constant, the number of metal and hydrogen ions exchanged on unit area of the surface can be calculated. Figure 3.7 shows that the thus calculated ion densities of $K^+$ and $H^+$ at pH 5.7 are equal at 0.3mM, which coincides with our $C_L$ value. This is in line with Pashley’s hypothesis that the hydration forces occur when the $K^+$ ions dominates at the surface and is no longer exchanged by $H^+$. However, this model does not show any such correlation at high or low pHs, possibly due to the dissociation constants used that were assumed at pH 5.7. Thus, we cannot prove with this model that a critical surface coverage
Figure 3.7. Theoretically calculated surface adsorbed $H^+$ and $K^+$ on single mica surfaces from the mass action model at different pHs.

of the $K^+$ ions leads to the hydration forces or $\pi$-transition.

Hence, we conclude that the attempt to relate $C_\pi$ to the contact value of $K^+$ is not meaningful because the underlying models do not account for confinement-induced structural or molecular ordering effects that start to dominate the thin film behavior at such small surface separations, i.e. < 3-5 nm. Furthermore, the predicted $K^+$ surface-population equilibria are predicted to change in a continuous manner with bulk
concentration and therefore cannot provide an explanation for the abrupt nature of the observed $\pi$-transition. The conclusion is that any comparison with existing EDL theory is inherently insufficient since the collapsed EDL no longer is an EDL.

3.7. Hydrated $\mathbf{K}^+$ and $\mathbf{H}_3\mathbf{O}^+$ ions

It is interesting to note that $\mathbf{K}^+$ and $\mathbf{H}_3\mathbf{O}^+$ ions are known to have distinctive properties, not only regarding the affinity to the mica surface, but perhaps more importantly, regarding the associated water structure [67]. Already for single mica surfaces, recent XRR studies have shown that $\mathbf{K}^+$ adsorbs discernably as 63% inner-sphere (IS) complexes and the rest as outer-sphere (OS) complexes. The hydronium ion is rather different; at pH 2.5, where hydronium largely predominates at the mica surface, the electron density appears fairly diffuse, indicating the absence of well-defined hydration layers [57, 67]. In bulk water, the hydronium ion does not have a hydration shell structure as such but rather a water complexing or delocalized clustering effect [111-113], corresponding to a picture of a diffuse water cushion covering the surface. Furthermore, Monte Carlo simulations [114, 115] also support this view and show that $\mathbf{K}^+$ adsorbs discernably in IS and OS states at 2.15 Å and ~5 Å, respectively, above the (001) mica surface, while $\mathbf{H}_3\mathbf{O}^+$ smears out over a distance range of 1-3 Å away from the surface in the form of polygonal water islands. Thus, the different hydration structures adopted by $\mathbf{K}^+$ and $\mathbf{H}_3\mathbf{O}^+$ ion species lead to considerably pH-dependent hydration structures at the interface (Figure 3.8). It is to be
remembered that these are all studies on single surfaces, and hence, they are expected to be modified or amplified under conditions of strong nanoconfinement between two surfaces. Both types of ions may be mutually affected by the presence of the other. Though the effect of bulk pH on the hydration structure of metal ions has not been studied in detail, XRR studies on single mica surfaces have shown that the pH can definitely influence how Sr\(^{2+}\) binds to the mica interface, namely as an IS or OS variant [116].

In addition, it has been conjectured that the rigid hydration shells of metal ions, such as K\(^+\), could be responsible for the “load-bearing capacity” of the

**Figure 3.8.** Schematic illustration of different ion-hydration structures discussed here; black dots represent K\(^+\) ions and the graded blue halo is the hydration water associated to the ion; a) different adsorbed ion states of K\(^+\) on a single mica surface according to Fenter et al. [67]. Translation into transition magnitudes between the outer-sphere states (OS) and inner-sphere state (IS) are \(\Delta=2.15\,\text{Å}\) and \(\Delta=3.49\,\text{Å}\), respectively, pretending similar adsorbed states under confinement. The inner adsorbed state (IS) would correspond to the least polar configuration. d) at low pH the interface structure is ruled by hydronium, which predominantly neutralizes surface charge; hydrated potassium layering is weak and the \(\pi\)-transitions vanish.
electrolyte [117] between mica surfaces. Meanwhile, it has been calculated that a stress on the order of 1000 MPa would be required to expel the final hydration water between mica surfaces [118]. In comparison, the maximum force we apply is 700 mN/m (i.e. a maximum Hertzian contact pressure of 16.7 MPa), which would probably be insufficient to push out this very last bound hydration water layer.

3.8. Previous models explaining hydration forces
The abrupt nature of the \( \pi \)-transition is particularly clear from the gap of \( \pi \)-values found in the histograms of Figure 3.4 (insets). It suggests that an instability mechanism, which presumably depends on the number of \( \text{K}^+ \) ions during collapse of the interface, is causing the phenomenon. The final FTT and the associated mechanical instability must be key to understanding the sudden change in pull-off force.

A picture, which is historically used to describe the interaction between two hydrated mica surface in salt solution, invokes multiple water layers at the interface[45]. Two years before the oscillatory nature of these forces was resolved by Israelachvili, Pashley recognized that exponentially repulsive hydration forces, seen at surface separations below some 2-3 nm, are related to hydrated counter-ions adsorbed onto the mica surface [24, 25]. The situation is schematically illustrated in Figure 3.9a. It was also noted by Pashley that these repulsive hydration forces suddenly appear around a concentration of 0.3mM of KCl at pH≈5.7. We note that his finding coincides perfectly with the \( C_L \) value found for KNO\(_3\) in this work. Both historic
interpretations seem to be guided by the available data with the limited instrumental resolution at that time.

An interpretation of our results within these traditional models is however not satisfactory: According to the traditional model by Pashley, hydronium ions substitute K\(^+\) counter-ions at the interface during the van der Waals jump-in (i.e. collapse), at initially low salt concentration (Figure 1.3). At the concentration \(C_L\), this substitution would come to an end and extra repulsive hydration forces due to trapped hydrated potassium ions would appear that could explain the reduction of pull-off force; if measured at high resolution, a maximum of only one FTT per surface is expected to be observed—the model is thus in fundamental contradiction with the observation of multiple (>2) FTTs. In contrast to Israelachvili’s data, our statistical analysis of step sizes clearly shows that FTTs are structurally diversified, and, for example, the non-final transitions are of significantly too large in size, which is in disagreement with the proposed interpretation of a periodic oscillatory potential due to \(\approx 2.5 \text{ Å} \) water layering. The interpretation suggested by Israelachvili does not really clarify the role of ions and the physical mechanisms leading to the many apparently periodic oscillations. We conclude that, while traditional interpretations provided by Pashley or Israelachvili were able to provide a hypothesis for the historical data, these models cannot account for the existence of a \(\pi\)-transition nor the structural richness presented here.
Figure 3.9. Schematic illustration (a) traditional model of adsorbed ions that bind water at the surface, which are hypothesized to cause (oscillatory) hydration forces; this hydration force increases with concentration until full surface coverage by adsorbed hydrated ions is achieved (b) hydrated-ion layering with “soft-sphere” characteristics and a FTT magnitude $\geq 4\,\text{Å}$.

3.9. Hydrated ion layering model

We now consider the hydrated-ion-layering model proposed by Espinosa-Marzal et al.[34] (Figure 3.9b). At the concentrations used in the present study, hydrated K$^+$ ions can be seen as quasi spherical particles with associated mobility in water. It is known both experimentally and theoretically that spherical molecules, vesicles or colloids in solution near a flat surface tend to produce layering effects [119] due to the geometrical constraint imposed by the surface. Oscillatory layering forces superposed on a repulsive force arise because the (multi-)layered system as a whole resists reordering with an energetic (mainly entropic) barrier, which can be overcome by external loading. It is interesting to note that layering displays a quantized yet overall exponentially increasing repulsive force during stepwise drainage—a feature also assigned to the “hydration” forces measured early on, using the conventional SFA [25]. Every time when the layering energy
is overcome by external work, i.e. when the second derivative of potential equals the apparatus compliance, a typical FTT is observed with step size resembling some 0.8-1\(\sigma\), being \(\sigma\) the layering particle diameter. The number of layers at the interface changes abruptly from \(N\) to \(N-1\). Layering transitions thus represent a mechanical instability mechanism that can be observed in the form of FTTs. While the layering phenomenon is maximally prominent in a neat liquid of spherical molecules, the magnitude of the force modulation is now a function of concentration for dissolved spherical particles [120, 121]. In agreement with theory, Richetti et al. observed in a system with dissolved monodisperse spherical micelles in the SFA that an increasing micellar volume fraction in the solution resulted in more and stronger oscillations in the force profile due to the layering [122]. A similar trend was observed for mixtures of water and a protic ionic liquid by Horn and Israelachvili [123]. To maintain overall charge neutrality layering of hydrated ions must involve hydrated co-ions of similar particle size.

The experimental results can be described with this model as follows: The stability of a first occurring layer of hydrated ions at the interface gradually increases with hydrated-ion concentration. A layer may be present undetected before any FTT is measured as long as the Van der Waals attraction wins over the layering force. The force associated with layering transition grows further with hydrated-ion concentration. As the concentration of \(K^+\) ions reaches \(C_L\) in the bulk, layering forces start to dominate over the Van der
Waals attraction and additional external load is required to destabilize this first layer—one single FTT at the size of the hydrated ion layer (>3.5Å) is observed. The appearance of this first FTT in the data is rather sudden because it is based on a mechanical instability condition (the repulsive part of the layering-force gradient being stronger than the attractive VdW force gradient). Nevertheless, the interfacial structure and pull-off force do not change as of yet at $C_L$ because the layered ions are still collectively expelled from the contact during the final collapse (i.e. collective squeeze out) as schematically illustrated in Figure 3.10a. It seems sensible that hydronium ions (i.e. protons) still compensate for surface charge during and after collective expulsion of hydrated ions at this stage. Some adsorbed $K^+$ ions neutralize the contact to the

![Diagram of EDL collapse](image)

**Figure 3.10.** Schematic illustration of our model of the stepwise collapse of the confined EDLs (a) Collective squeeze out of the metal ions similar to Pashely’s model[24]. (b) Collective collapse of a layer of hydrated ions into a highly condensed state. (c) At higher concentrations,
hydrated ion layering is followed by the forced condensation of the final layer.

extent of the gradual and slow decrease in the pull-off force before the instability, similarly to the model originally proposed by Pashley. The situation changes suddenly at a slightly higher concentration $C_{\pi}$, namely when the layering force grows to the next threshold strength, that is the force to collectively collapse the entire layer of hydrated ions into a highly confined or surface-condensed state (Figure 3.10b). It is important to note that the resulting single FTT (later to become the final FTT) is consequently not a layering transition per se, but a transition between confined adsorbed states of the ions, which involves a change of water structure such as a suggested partial dehydration. Existence of an additional adsorbed “condensed-ion state” was previously also proposed by Raviv et al.\[35\] to explain an experimentally revealed change of EDL forces after mica-mica contact. An estimation of the “condensed” state release barrier of 33 kT and associated lifetime of 11 minutes was given by these authors. More recently, Fenter et al. have obtained more detailed evidence for the existence of different equilibrium adsorbed states of $K^+$ on single mica surfaces using an independent X-Ray scattering method \[67\]. For $K^+$ ions at a single mica surface (in the absence of mechanical loading) at pH≈5.7 three different states with characteristic surface offset were described, as shown in Figure 5 c. Above a concentration $C_{ML}$ one can observe and distinguish up to three different types of film-thickness transitions: i)
Van der Waals jump, ii) hydrated-ion layering and iii) transitions into or between different confined adsorbed states (Figure 3.10c). The existence of different adsorbed ion states in combination with a forced transition between them is key to the correct interpretation of the $\pi$-transition, because it provides the structural factor needed to explain the observed sudden reduction in pull-off force by a change of polarity at the interface.

Although we have no extra information concerning the detailed structure of the collapsed interface in contact we can expect that both effective charge and the dipole moments generated by counter-ions adsorbed at the negatively charged surface will be reduced, the closer the counter-ion is adsorbed to the center of charge. An adsorbed state similar to the IS-state is expected to best fulfill this criterion and therefore effectively reduce the polar component of the mica-mica adhesion, which will reduce the measured pull-off force.

It is also worth noting that both the hydrated-ion layering as well as the existence of different adsorbed states extends the classical DLVO theory with physically new features. The previously suggested upper validity bound of the “DLVO” regime at $C_{\pi}$ is thus physically justified [34].

Comparing the sizes of the observed FTTs we can surmise that the film-thickness transitions recorded preceding the final FTT are layering FTTs due to successive squeezing out/reordering of hydrated ion layers; until a highly confined layer of hydrated ions (predominantly K$^+$) is left.
Although, we note a coincidence between the surface separation differences of adsorbed states as reported at pH≈5.7 [67] (Δ_{\text{OSads→IS}}=1.34 Å, Δ_{\text{OSext→OSads}}=2.15 Å, Δ_{\text{OSext→IS}}=3.49 Å) and the histogram peaks of Figure 4 (d) at pH≈5.7, we cannot make a more detailed statement about the role of such adsorbed states under high confinement from direct force measurements alone.

Since the interplay of hydrated-ion layering and transitions between different adsorbed potassium states should account for the existence of the π-transition, it should disappear with the weakening of layering at lower pH. This seems to be the case, as can be seen in Figure 3 (d), where at pH=3.3 the π-transition has mostly disappeared.

3.10. Oscillatory forces

Until now, we have presented and analyzed recent FTT data measured with the eSFA. Typically, these are measured in an automated fashion under constant external loading rate and the actuator is reversed only at the final load. This is not the most commonly used procedure in traditional SFA measurements. The bulk of data measured with overlapping double layers was obtained in the conventional surface forces apparatus by manually controlling the actuator speed and direction. In practice, such oscillatory forces in the SFA are measured by superimposing several approach and retraction curves since the SFA cannot measure attractive forces in an oscillatory without instrumental instability [124]. The maxima are detected as FTTs on approach and the minima are detected as the pull-off forces upon retraction of the surfaces.
In order to relate the different procedures and data sets, we reproduced the repeated progressive loading-unloading patterns used traditionally. For example, Israelachvili and Pashley [45] manually reversed the actuator direction after detection of each individual FTT in KCl solutions. Different loading-unloading curves are thus sequentially recorded at progressively increasing loads before the final load is reached and all results are superimposed into a single force curve. We have used our automated eSFA in manual actuation mode to reproduce this scenario while the surface separation was continuously measured with FSC at a fixed rate around 1 Hz. These experiments were again done without pH control to be comparable to the historic data. While existence of an overall connected oscillatory potential is suggested in the former literature, the raw data from different loading-unloading curves, hence measured with the eSFA at higher resolution, cannot be readily overlapped and connected to form a consistent oscillatory potential (Figure 3.11a). We think this mismatch is a systematic error imposed by the compression / decompression of mica at different loads. The compression effect of mica scales with mica thickness, and, at higher loads can even lead to apparently negative distances measured relative to the uncompressed mica thickness (i.e. optical zero). For the sake of simplicity, we will not correct for this systematic error here and cease to connect the individual curves to a master curve. Now, we can determine an individual pull-off force for each of the hence measured and numerated minima and compare these for different salt concentrations as shown in Figure
3.11b. Note how the graph of the innermost “minima 1” (after the final FTT) reveals the \( \pi \)-transition while the two other minima follow their own trends without such discontinuous transition. This finding clearly justifies our hypothesis that i) the final FTT is responsible for the \( \pi \)-transition and ii) the final FTT is physically different from the preceding FTTs (hydrated ion layering).

**Figure 3.11.** (a) Oscillatory forces measured with two mica surfaces in 1mM KNO\(_3\) at uncontrolled pH \( \approx 5.7 \). The forces measured during isothermal compression (filled black dots) and separation (open grey dots) from several cycles are plotted together. Inset: The forces plotted on a linear scale zoomed in to the maximum force at which FTTs were observed. (b) Pull-off forces for individual minima of the (oscillatory) surface potential as a function of concentration showing that the final FTT (minima 1) is the only one that shows the discontinuous \( \pi \)-transition. We note that the \( \pi \)-transition of minima 1 occurs at roughly twice the concentration compared to Figure 1; we think this is due to
small variations in the uncontrolled pH, which we showed in Figure 3 to strongly affect $C_\pi$.

3.11. Conclusions

The narrow concentration regime near the $\pi$-transition is particularly well suited to reveal and study different structural elements during the collapse of EDLs. In this Chapter, we have confirmed that the $\pi$-transition, marked by a sharp drop in pull-off force, coincides with the onset of hydrated ion layering. We propose a model that invokes the collaborative interplay of hydrated-ion layering forces and different confined adsorbed-ion states, to explain the sudden change of interfacial adhesion after EDL collapse at the $\pi$-transition. We also show how the $\pi$-transition shifts to higher bulk $[K^+]$ concentration with decreasing pH, due to progressive substitution of hydrated K$^+$ ions by differently structured hydronium ions. These results demonstrate how the interface structure following collapse of overlapping EDLs can be critically determined by a subtle balance between different structural forces, and how these can combine, leading to inherent instabilities.

Compared to the historical understanding of surface hydration, we can thus draw a more precise and complete picture. Namely, the (oscillatory) hydration force is not due to some periodic layering of water at surfaces but to multiple layering of hydrated ions, which become transitions between different confined adsorbed ion states during the final step of the EDL collapse (Figure 3.12).
Figure 3.12. Schematic representation of the surface interaction potential as found at a concentration above the \( \pi \)-transition. Two or three hydrated ion layering maxima are followed by at least one maximum of highly confined adsorbed states; the last minimum determines the measured pull-off force.
Chapter 4
Ion specific pathways to Electrical Double Layer Collapse

In the previous chapter, the $\pi$–transition was observed to coincide with the onset of hydrated ion layering, ie, after the occurrence of multiple FTTs and it was concluded that the $\pi$–transition was due to the a forced condensation of counterions during the stepwise collapse of the EDLs. Since the strength of the hydration shell affects the ease of dehydrating an ion as well as the population of different adsorbed states of the ion at the surface, we can expect different pathways of EDL collapse depending on the counter-ion species. Hence, in this chapter, we set out to investigate the counterion-specificity of the $\pi$–transition by comparing three counter ion species, namely Na$^+$, K$^+$ and Cs$^+$, which are known for their different hydration structures. The Na$^+$ is the most strongly hydrated ion, followed by K$^+$, while the Cs$^+$ ion is so weakly hydrated that it readily condenses into the mica lattice. We will propose a more generalized mechanism for the $\pi$–transition, which undoubtedly reflects the film stability discretization introduced by hydrated ion layering. This chapter has been adapted and extended from the publications Z. Zachariah et al[125] and M. Heuberger et. al[126]

4.1. Compression isotherms in NaNO$_3$, KNO$_3$, CsNO$_3$
In order to investigate the role of the counter ion type on the $\pi$-transition that was previously observed in KNO$_3$ solutions, we selected NaNO$_3$ and CsNO$_3$ solutions at concentrations
between 0.1 mM up to saturation (10.58 M for NaNO₃, 3.35 M for KNO₃ and 1.1 M for CsNO₃ at 22 °C). The measured force-distance curves (Figure 4.1) were fitted to the DLVO equation using the algorithm developed by Chan et al.[104] for the EDL force under conditions of constant surface charge at surface separations above 5 nm and electrolyte concentrations below 10 mM. We note that a shift of the Outer Helmholtz plane (OHP) has been proposed to account for the different size of the surface-adsorbed hydrated ions [22]. However, we have not attempted to shift the OHP in order to fit our force-distance curves, since our results (as discussed later) indicate that different adsorbed ion states populate the interface to compensate the surface charge, and hence, the position of the OHP is not a well-defined quantity.

![Figure 4.1](image)

**Figure 4.1.** The force-distance approach curves in 1mM NaNO₃, KNO₃ and CsNO₃ solution. It is to be noted that
these are from three separate pairs of mica surfaces. The fitted surface potential according to the DLVO theory is \(\sim -90, -80, -60\) mV for NaNO\(_3\), KNO\(_3\) and CsNO\(_3\), respectively.

An increase in screening length with concentration was previously observed above ionic diameter/Debye length ratios of \(\sim 1.5\) by Smith et al. [127]. Although the maximum value of this ratio in our experiments is reaching a similar magnitude, namely \(\sim 3\) for NaNO\(_3\), \(\sim 2\) for KNO\(_3\) and \(\sim 1\) for CsNO\(_3\) (at saturation), we did not observe an increase in the electrostatic screening length with concentration up to saturation. The absence of hydration and EDL forces in CsCl and CsNO\(_3\) solutions has been previously reported and attributed to surface-condensation of Cs\(^+\) on mica [128]. However, our results agree better with Pashley’s work that shows a repulsive force in the presence of Cs\(^+\)[24], but absence of hydration related short range structural forces.

4.2. Pull-off forces in NaNO\(_3\), KNO\(_3\), CsNO\(_3\) and the \(\pi_L\)-transition
Figures 4.2a-c show the pull-off forces measured during separation of the surfaces after loading to a fixed external load of 700 mN/m at uncontrolled pH \(\approx 5.7\). If oscillatory forces are present, this pull-off force is equivalent to the adhesive minimum at the smallest surface separation. The pull-off forces have been color coded to show the number of FTTs that occurred during their respective approach curves. The black symbols are cases where no FTTs were recorded, the red symbols are cases while a single FTT was recorded and the blue symbols are cases where multiple FTTs were
measured. As previously found for KNO$_3$ solutions [34], we can also readily distinguish the three concentration regimes for NaNO$_3$ albeit at shifted concentrations: (1) the DLVO regime up to 1 mM NaNO$_3$, where the pull-off forces were high and no FTTs were detected, (2) the ordering regime from 10 mM to 1 M NaNO$_3$ with low pull-off forces and multiple FTTs, and (3) the solidification regime at concentrations >1 M NaNO$_3$, where the repulsive force decreases and the force-distance curves, when fitted to the DLVO equation, yield a Hamaker constant of $0.4 \times 10^{-20}$ J. As we suggested in our earlier publication [34], this value for the Hamaker constant is characteristic of ionic liquids, where stronger ion-ion correlations, mainly of electrostatic origin [129], are expected.

There is a concentration regime between 1 and 10 mM of NaNO$_3$, which is characterized by a step-wise but incomplete reduction of the pull-off force, called the $\pi_L$-transition (due to its coincidence with one FTT (layer)) and marked by a dotted arrow in 4.2a. This pre-transition concurs with the appearance of a single FTT. It is followed by a more shallow gradual decrease in pull-off force and eventually the actual $\pi$-transition, characterized by a low pull-off force and occurrence of multiple FTTs, as was previously seen in KNO$_3$ in Chapter 3. We shall henceforth call this the $\pi_{ML}$-transition due to its coincidence with the occurrence of multiple FTTs (multiple layering). On taking a closer look at the pull-off forces in KNO$_3$ (Figure 4.2b) in light of these observations in NaNO$_3$, we note that the coincidence of single and multiple layering makes it almost impossible to distinguish whether a $\pi_L$-transition occurs in
For CsNO$_3$ (Figure 4.2c), on the other hand, there seems to be no $\pi$–transition ($\pi_L$ or $\pi_{ML}$) at all, but rather a continuous gradual decrease in the pull-off force up to a concentration of 5 mM; followed by a concentration range of low pull-off forces extending up to a concentration of 100 mM, where an unusual increase of pull-off force was observed in a very narrow range. So, the $\pi_{ML}$-transition either does not exist or is too small to be detected or has a totally different form in CsNO$_3$. Absence of a $\pi_{ML}$-transition would actually be in line with the absence of multiple film-thickness transition; these usually appear together.

**4.3. Film thickness transitions in NaNO$_3$, KNO$_3$, CsNO$_3$**

Figures 4.2d-f show the size of the FTTs measured during approach of the surfaces. We previously proposed a model based on K$^+$ counter ions that invoked the collaborative interplay of hydrated-ion layering and different adsorbed-ion states to explain the sudden change of interfacial adhesion after EDL collapse at the $\pi$-transition. $A_L$ and $A_{ML}$ are the ion activities above which a single FTT and multiple FTTs, respectively, were observed. Note that we use ion activities in this chapter instead of ion concentrations as used in the previous chapter since, from a thermodynamics point of view, the chemical potential of a non-ideal solution depends on the ion activity at constant temperature and hence more appropriate to use when comparing different ions. In accordance to the nomenclature adopted in [130], $A_{\pi ML}$ designates the ion activity where the $\pi_{ML}$-transition occurs. The activities for $A_L$, $A_{\pi L}$, $A_{ML}$ and $A_{\pi ML}$ are summarized in Table 4.1.
Table 4.1. Ion activities at which the $\pi$ transition ($A_{\pi}$) and the $\pi_{ML}$ transition ($A_{\pi ML}$) occur and above which a single FTT ($A_L$) and multiple FTTs ($A_{ML}$) occur. The pH was 5.7.

<table>
<thead>
<tr>
<th>Counterion activity (mM)</th>
<th>$A_L$</th>
<th>$A_{\pi L}$</th>
<th>$A_{ML}$</th>
<th>$A_{\pi ML}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO$_3$</td>
<td>1</td>
<td>2</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>KNO$_3$</td>
<td>0.3</td>
<td>N/A</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>CsNO$_3$</td>
<td>1</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 4.1 shows that for the K$^+$ counter ions, the ion activity of the $\pi_{ML}$-transition ($A_{\pi ML}$) follows closely the onset of multiple hydrated-ion layering $A_{ML}$. The first film thickness transition is present above a concentration of $A_L \approx 0.3$ mM, where we still observe a gradual decrease in pull-off force.

For the more strongly hydrated Na$^+$ (NaNO$_3$) shown in Figures 4.2a and 2d, the pull-off force is reduced in two steps. A first partial step occurs at $A_{\pi L} \approx 2$ mM, with an initial drop from $\approx 80$ to 50 mN/m. Finally, at $A_{\pi ML} \approx 10$ mM, the pull-off force drops from 40 to 5 mN/m. We note that $A_{\pi L}$ follows $A_L$, while $A_{\pi ML}$ follows $A_{ML}$ (Table 1). Compared to KNO$_3$, the $\pi$–transition ($A_{\pi ML}$) in NaNO$_3$ has shifted to higher salt activities. Furthermore, $A_L$ and $A_{ML}$ differ from each other by one order of magnitude.

Figures 4.2c and 4.2f show pull-off force and size of the FTTs for CsNO$_3$. Here, only single FTTs were detected in
the concentration range 1-10 mM. They are at a typical transition size of 3.8±1.1 Å and were accompanied by simply a gradual decrease in pull-off force.

**Figure 4.2.** Pull-off forces measured in (a) NaNO₃, (b) KNO₃ and (c) CsNO₃ solutions at pH ≈5.7. The pull-off forces data in KNO₃ are taken from previous work by Espinosa-Marzal et al. [34] and Zachariah et al. [103]. The pull-off forces have been color coded to show the number of FTTs that occurred to reach maximum loading, i.e. before each pull-off force was measured. Bold and dotted arrow point at πₜₐₐ and πₗ-transition, respectively. The insets show the histograms; the gaps show the πₜₐₐ and πₗ-transition. FTTs measured in (d) NaNO₃, (e) KNO₃ and (f) CsNO₃ solutions; the final FTT (red) is distinguished from layering FTTs (black). For CsNO₃ only a single transition is measured.
4.4. The effect of pH

As shown in Chapter 3, the solution pH can tune the interfacial structure of the strongly collapsed EDL [103]. Figure 4.3a shows that the $\pi_{\text{ML}}$-transition for NaNO$_3$ shifts to higher salt concentrations by decreasing the pH to 4 and it vanishes at the lowest pH, in agreement with the results observed for KNO$_3$. Further, the $\pi_{\text{L}}$-transition vanishes at the pH-values of 9.7, 4 and 3.3. At the highest pH, the critical concentrations $A_\pi$ and $A_{\text{ML}}$ coincide with each other, similar to the results for KNO$_3$ solutions at pH 5.7 in Figure 4.2b.

The empty symbols in Figure 4.3b indicate that multiple FTTs are resolved. Thus, the dotted lines in Figure 4.3a and 4.3b demonstrate that the $\pi_{\text{ML}}$-transition coincides with the appearance of multiple FTTs at the pH of 9.7 and 4. The size of the FTTs also depends on the pH; at pH 9.7 the size of the resolved FTTs is larger than at lower pH-values.

![Figure 4.3](image.png)

**Figure 4.3. Pull-off forces and size of FTTs of different pHs in NaNO$_3$ solution showing a) the shift of the $\pi_{\text{ML}}$-transition**
wit pH and b) the occurrence of larger sized FTTs at high pH. The dotted lines help to illustrate that the π_{ML} -transition coincides with the appearance of multiple FTTs at the pH of 9.7 and 4.

### 4.5. Discussion

Before we develop viable hypotheses for the origin of the ion-specific π-transition let us set the stage by reviewing some important facts.

First of all, we acknowledge that the observed sudden reductions in pull-off forces (π_{L} - and π_{ML} - transitions) are occurring over a surprisingly small range of metal counter ion Me^{+} bulk solution concentrations. This means that a critical number of Me^{+} ions at the interface is necessary for the transitions to occur. Furthermore, the sharpness of the transition as well as its prominent occurrence at high pH suggests existence of an underlying instability caused by this critical number presence of Me^{+} ions.

We recall that, in the case of K^{+} ions, an interplay of hydrated ion layering forces and transitions between different adsorbed states was invoked to explain the origin of mechanical instabilities [34, 103]. Indeed, there is persistent coincidence between the occurrence of film-thickness transitions, which are indeed mechanical instabilities, and the discussed π-transitions. These considerations correspondingly hold for the case of Na^{+} ions as we shall see below.
Previous investigations into the interfacial structure of the unconfined (001) mica-electrolyte interface by synchrotron XRR studies have shown that the population of the mica-solution interface is ion specific (Figure 4.4 a-c). While Na\(^+\) counter ions adsorb predominantly as Outer Sphere (OS) complexes (99\%) at 5-6 Å above the mica surface; Cs\(^+\) counter ions adsorb predominantly in the Inner Sphere (IS) state (97\%) at a distance of \(~2.26\) Å, and a very small population of OS-Cs\(^+\) may adsorb at a distance of \(~4\) Å. In contrast, K\(^+\) counter ions are present as a more balanced mixture of both IS- (63\%) and OS-species (37\%) [57, 67]. These differences are attributed to the different hydration strength of the ions. The molar Gibbs energy of hydration (\(\Delta G\)) of the ions indicates strongest hydration for Na\(^+\) and the weakest for Cs\(^+\); namely, ref. [131] gives \(\Delta G\) for Na\(^+\): -385 kJ/mol, K\(^+\): -305 kJ/mol, and Cs\(^+\): -245 kJ/mol.

Ions adsorbed in the OS state retain their hydration shell while those in the IS state are partially dehydrated and forms bonds with the oxygen atoms on the mica surface.

**Figure 4.4.** Schematic illustration of different equilibrium adsorbed ion states and their population from XRR studies for Na\(^+\) (a), K\(^+\) (b) and Cs\(^+\)(c) on unconfined mica. The blue spheres represent the hydration water associated to the ion.
4.5.1. Ion specific effects
Comparing Figures 4.2a through 4.2c, we clearly identify ion-specific effects for this series of monovalent Na\(^+\), K\(^+\) and Cs\(^+\) ions in our experiment. With respect to the \(\pi\)-transition, Na\(^+\) shows more features than K\(^+\), yet fewer features are seen for Cs\(^+\). We note that this is the same sequence in which the hydration structure of the ions is known to be weaker. To round up this reflection, we also know that Me\(^+\) counter ions are competing with H\(_3\)O\(^+\) hydronium ions to compensate the surface charge, which leads, for example, to the documented pH dependent shifts of C\(_{\pi ML}\), the critical concentration of [Me\(^+\)] at which the \(\pi_{ML}\)-transition occurs [103]. Hydronium ions however are different in terms of hydration structure, since they induce a water clustering effect rather than hydration shells around the extra proton.

Though the adhesion energy between two surfaces in a liquid can be given by their interaction in vacuum since surfaces separate before any liquid molecules enter the interface, this definition can be applied only for flat, rigid surfaces which separate while remaining parallel to each other. This is rarely the case and during separation, liquid molecules immediately enter the gap between the surfaces at the bifurcation line, resulting in the measured adhesion energy being both geometry as well as rate dependent [132]. The pull-off force \(\pi\) that we observe is a measure for the adhesive energy between the surfaces after collapse under maximal external loading. It depends on the molecular organization at the highly confined interface as it emerges from the final film thickness transition, with counterions and
(possibly) coions being trapped in the film. Without the presence of any counter ions at the collapsed charged interface, repulsive electrostatic forces between charged surfaces would largely dominate, even over attractive Van der Waals forces and one would not measure any pull-off force. The pull-off force is thus determined by other interactions that depend on the remaining charge separation (i.e. dipole or multipole moments), and, the structure of hydration water that sum up with van der Waals attraction to result in a macroscopically measured pull-off force. The global trend in our data is that increasing amounts of counter ions (any type) at the interface are decreasing the pull-off force (Figure 4.5) until a minimum, $\pi_{\text{min}}$, is reached around concentrations of $[\text{Na}^+] \approx 100\text{mM}$, $[\text{K}^+] \approx 10\text{mM}$ and $[\text{Cs}^+] \approx 10\text{mM}$. As a remark, the collapsed interface remains attractive even at $\pi_{\text{min}}$, i.e, a pull-off force is always measured, signifying that the repulsive force contribution must be of shorter range than the Van der Waals attraction.

The influence of $\text{H}_3\text{O}^+$ is readily seen in Figure 4.5. The sequence of the curves of different pH at small bulk concentration (marked with colored areas) shows how an increase of hydronium concentration decreases pull-off force (arrows). The pull-off force is also reduced by an increase of $\text{Na}^+$ at the collapsed interface. The low-salt slope $d\pi/dC_{\text{Na}}$ seems larger at pH 9.7, where we expect the species balance at the collapsed interface is considerably in favor of $\text{Na}^+$ counter ions.
Figure 4.5. Pull-off forces in NaNO₃ as a function of pH. Figure 2a and 3a are plotted together with lines to guide the eye.

It is interesting to note that there is a particularly clear quantitative and qualitative difference between the curves of pH 4 and pH 3.3, although the difference ΔpH≈0.7 is fairly small. Upon close inspection, a few points of the pH 4 data seem to fall in place with the pH 3.3 data. This could be a simple measurement scatter, or, an indication that perhaps a πₘₐₗ⁻transition may also be triggered by a rather small change of pH around 3.5 in NaNO₃, if the salt activity was fixed somewhere between 0.1 and 100 mM. A pH-titration of the πₘₐₗ⁻transition could therefore bring additional insights into the role of hydronium at the interface in a future piece of work; namely the existence of such hydronium-triggered
\[ \pi_{\text{ML}} \]-transition could provide valuable new information about the hydronium hydration structure or its interaction with Me\(^+\) hydration structures in presence of multiple kinds of counter ions.

The pull-off force as a function of [Cs\(^+\)] counter ions (Figure 4.3c) does not reveal a \(\pi_{(L,\text{or} \text{ML})}\)-transition at uncontrolled pH (\(\approx 5.7\)). It would be interesting to experimentally measure the pull-off forces at high pH to check if a \(\pi\)-transition appears when the interface is depleted from hydronium. On the other hand, Cs\(^+\) is the counter ion with the weakest hydration structure in our series and therefore has some similarities with H\(_3\)O\(^+\). Similar to a proton that is thought to reside inside the negative mica lattice pocket and effectively neutralize charge as well as local dipole moment, similar behavior is expected with Cs\(^+\) on mica. Indeed, XRD studies on single mica surfaces have revealed that Cs\(^+\) evidently prefers to reside (population 97\%) in the so called inner sphere (IS) state (Figure 4c).

4.5.2. Influence of counterion population on pull-off forces

So, how is it that an increasing number of counter ions can decrease the pull-off force at an interface and how can the molecular arrangement look like? A first corollary of global neutrality is that the number of anions must always increase in parallel to the number of counter-ions. Another effect is an increase of population of adsorbed states at the interface with change of bulk activity. The population of inner sphere states at the single surface is thought to be preserved or enriched in the collapsed state and therefore is relevant for
the lowering of the pull-off force, with the restriction, of course, that the energetic details of adsorbed states may change due to the presence of a second surface and confinement.

The closer a counter ion adsorbs to the surface lattice charge (e.g. IS state), the smaller is the remnant dipole moment. Partially fixed (i.e. frustrated rotation) dipole moments exert a strong and long-range attractive surface force, which can be critically lowered by variation of the adsorbed ion-surface dipole moments. Additionally, an increase of counter-ions and anions at the interface will trap increasing amounts of hydration water and therefore lower adhesion by an increase of the distance between the surfaces, presumably via short-range entropic repulsive structural forces. At slightly larger surface separations, there can be layering forces once a sufficient number of hydrated ions populate the interface. Layering forces represent a molecular scale modulation of entropy, which appears in-plane; it leads to a trapping of the layering units inside the layer and a collective force is opposing drainage of such layer. When this layering effect grows strong enough one can observe multiple layering transitions upon surface approach, which gives rise to an oscillatory surface force. Thanks to a precise surface separation measurement, we can directly observe layering transitions and transitions between different adsorbed states as film thickness transitions (FTT).

**4.5.3. Hypothesis for the $\pi_L$ and $\pi_{ML}$-transitions**

The $\pi$-transition was defined in Chapter 3 as the abrupt reduction of pull-off force, induced by a sudden change in
the mechanical collapse pathways of an electrical double layer structure. The current model invoked a push in of Me\(^+\) counter-ions into intimately adsorbed states once hydrated ion layering forces grow strong enough [103]. According to this terminology, it is the second step at higher concentration in the two-step \(\pi\)-transition of NaNO\(_3\) (Figure 4.2a), which corresponds to the definition of the \(\pi\)-transition (which we have renamed the \(\pi_{\text{ML}}\) in this Chapter) since it occurs after the onset of multiple hydrated ion layering. The low-salt partial transition is called the \(\pi_{\text{L}}\)-transition; it is closely linked to the critical concentration \(A_{\text{L}}\), above which one single film thickness transition appears. As mentioned earlier, since \(A_{\text{L}}(0.3 \text{ mM})\) and \(A_{\text{ML}}(0.5 \text{ mM})\) are very close in KNO\(_3\), we cannot clearly identify a \(\pi_{\text{L}}\) –transition in KNO\(_3\).

We shall propose a hypothesis for the mechanism causing the newly observed \(\pi_{\text{L}}\)-transition (schematically illustrated in Figure 4.6), based our current understanding that the ion hydration structure plays a decisive role.

We hypothesize that at \(\pi_{\text{L}}\), a single layer of hydrated ions is left at the interface and this layer of ions is partially dehydrated and pushed into the surface resulting in a lowered pull-off force. At these low concentrations, a mixture of adsorbed Na\(^+\) and H\(_3\)O\(^+\) populates the interface. At higher salt concentrations (\(<A_{\text{ML}}\)\), the layering forces become stronger and stabilize a second layer between the surfaces i.e. there is a hydrated ion layer associated to each surface. These two layers, under the applied load, in a first
FTT, can be pressed into each other to form a single (higher) concentration layer between the surfaces, which finally is pushed into the surface and partially dehydrated during the $\pi_{\text{ML}}$-transition, resulting in a much lower pull-off force due to the interface now consisting of almost exclusively the dehydrated Na$^+$ ions.

At high pHs, the $\pi_L$-transition is absent due to the higher concentration of ions at the interface, thereby directly leading to multiple layering and the $\pi_{\text{ML}}$-transition. At low pHs, the population of Me$^+$ ions at the interface is too low for the $\pi_L$-transition to occur on the push-in of a single layer. The push-in of the higher concentration layer formed by the interpenetration of two surface layers (i.e. multiple layering) is required to cause a significant drop in the pull-off force, which leads directly to the $\pi_{\text{ML}}$-transition. As shown in Figure 4.5 and Figure 4.3a, the $\pi_L$-transition did not exist in both the high and low pH cases and only the $\pi_{\text{ML}}$-transition (sudden drop in pull-off force coinciding with multiple layering) was observed.

In addition, a detailed analysis of the FTT sizes (Figure 4.2(d)) in the concentration range of the $\pi_L$-transition of NaNO$_3$ reveals a FTT size of $\approx 5 \pm 1$ Å along with a minority of cases of smaller FTT of size around $\approx 3.2$ Å. The $5 \pm 1$ Å FTT is a larger average step size then that observed for FTTs at higher concentrations while the smaller step matches the size of an OS-to-IS transition in Na$^+$. Therefore, the analysis of FTT step sizes favors this explanation of the $\pi_L$-transition.
**Figure 4.6.** Schematic illustration of the hypothesis to explain the ion-specific pathways of the final FTTs at the $\pi_L$-transition based on the stronger hydration structure of Na$^+$ counter ions.

In light of our discovery of the $\pi_L$-transition in NaNO$_3$, we took a closer look at the previously studied $\pi$-transition in KNO$_3$ (Figure 4.7). We can make a case that both the $\pi_L$ as well as the $\pi_{ML}$-transition occurs in KNO$_3$ as well, albeit nearly at the same salt activities.

**Figure 4.7.** Zooming into the $\pi$-transition in KNO$_3$: Pull-off forces as a function of salt activity at pH 5.7 in the region of the the $\pi$-transition.
According to our hypothesis, the $\pi_L$-transition in KNO$_3$ can already lead to a low pull-off force due to the higher equilibrium population of adsorbed K$^+$ IS ions at the surface directly leading to the scenario (e) in Figure 4.6. In summary, we conclude that the $\pi_L$-transition is due to a push-in of a single layer of hydrated Na$^+$ ions into the mica interface occurring in a window of moderate pH values. For a more complete and detailed discussion of such a pH window, additional data at smaller intervals of pH value would be required.

To round up this discussion, we have also measured the pull-off force in solutions of CsNO$_3$. Figure 4.2c illustrates a rather featureless continuous reduction of pull-off force with [Cs$^+$] concentration. The reduced absolute values of the pull-off force as well as the similar slope $d\pi/dC$ suggest that Cs$^+$ counter ions exhibit similar behavior as hydronium at lower pH. This is in agreement with the known fact that Cs$^+$ has the weakest hydration structure and appears predominantly in inner adsorbed states. In our understanding, the remaining surface dipoles are small and therefore also the pull-off forces. It is interesting to note that hydrated ion layering still occurs with CsNO$_3$ above $C_L \approx 1$ mM; yet only one single FTT is observed of a characteristic size around 3.8±1.1 Å. This is an interesting observation because it suggests that the mainly inner adsorbed Cs$^+$ counter ions counteract the tendency of multiple layering. A similar antagonistic effect is observed from the influence of hydronium; namely shifts of $C_{ML}$ and $C_\pi$ to higher concentrations at lower pH (Figure 4.3 and [103]). So it seems as if surface charge and electrostatic
interaction can promote the layering of hydrated counterions just as one might expect. We emphasize that multiple hydrated ion layering is expected (and observed) only in cases where ions are present in the OS hydrated state, such as with Na\textsuperscript{+} and K\textsuperscript{+}.

4.6. Summary
The detailed analysis of pull-off forces measured after mechanical collapse of EDLs is a valuable tool to sensitively detect changes in interface structure. We show that specific ion effects can be scrutinized at great detail in pull-off force measurements and FTT analysis, and argue that such effects are related to the population of different adsorbed states and hydrated ion layering effects under strong confinement. In combination with precise film thickness measurements during collapse we could discriminate important mechanisms of dynamic ion-exchange, which can explain existence of a $\pi_L$–transition that precedes the previously discovered $\pi_{ML}$–transition. It is found that the $\pi_L$–transition exists only in a small pH window and that its occurrence is highly ion specific. The new understanding gained from these studies adds to a new picture of the mechanisms and instabilities at work in such highly confined electrical double layers.
Chapter 5
Summary and Outlook

5.1. Summary
We have investigated the interaction between mica surfaces in aqueous electrolyte solutions at nanometer separations focusing on the role of hydrated cation on interfacial phenomena. The correlation between the layering phenomena and the pull-off forces was used to propose an improved and more detailed model of the collapse of the electrical double layers at the mica-electrolyte interface. Since Chapter 3 and 4 already lay out the partial conclusions in detail, only the major conclusions will be summarized here.

5.1.1. What did we set out to study?
We set out to address the open questions of (a) What happens at charged solid-electrolyte interfaces at nanometer separations when the classical DLVO theory fails to predict the interaction forces accurately? (b) What is the role of the hydration water associated to the metal ions, which is reflected in their different adsorption states at the interface, during the collapse of the EDL? Chapter 3 is devoted answering the first question while Chapter 4 concentrates on the latter.
This was done in the muscovite mica-aqueous inorganic electrolyte model system by probing the changes that occur at the interface with increasing electrolyte concentration and external pressure. We began by investigating the \( \pi \)-transition, which was the first indication of an abrupt
alteration of the interface, observed in the narrow concentration regime of 0.3-1 mM in aqueous KNO$_3$ [34]. Over the course of this thesis, multiple (>110) experiments were performed in the narrow concentration ranges that the $\pi$-transition occurred in, thereby enabling us to carry out a statistical analysis of the phenomena taking place during the collapse of the EDLs. The role of the bound hydration water was examined by comparing different counterions as well as varying the pH.

5.1.2. What have we learnt?
In Chapter 3, we have experimentally proven that hydrated metal cation is responsible for the $\pi$-transition by showing that the $\pi$-transition can be shifted to higher electrolyte concentrations and even suppressed by tuning the counter-ion/H$_3$O$^+$ balance at the interface. The sudden drop in interfacial adhesion occurs after the onset of hydrated ion layering and when the layer of hydrated ions is no longer pushed out of the gap but is partially dehydrated into different adsorbed ion states. While this picture is in line with the historical understanding that hydration forces are due to the trapping of the metal cations at the mica surface [24], we clarify that the oscillatory nature of these forces do not stem from the molecular ordering of water molecules imported by the hydrated cations [45] but instead from the multiple layering of hydrated ions. While the details of our model are in Figure 3.10, Figure 5.1 summarizes our findings succinctly.
Figure 5.1. Our model of the stepwise collapse of EDLs superimposed on the oscillatory force curve observed during approach of the surfaces. The oscillatory part is ascribed to hydrated ion layering and the final FTT is due to transitions between adsorbed ion states. (a) Before the \( \pi \)-transition, the final layer of ions are pushed out of the gap and replaced by hydronium similar to Pashley’s model. (b) After the \( \pi \)-transition, the ions are pushed into different adsorbed ion states leading to lower adhesion the interface.

In Chapter 4, we see that the strength of the hydration shell of the ions plays a role in the pathway to the \( \pi \)-transition, which was renamed the \( \pi_{\text{ML}} \)-transition due to its coincidence with multiple FTTs. We discover that, in the case of the relatively strongly hydrated Na\(^+\) ion (population of IS ions <1%), there is an additional \( \pi_{\text{L}} \)-transition, a drop in the pull-off force coinciding with the detection of a single FTT.

On the other hand, in the presence of a weakly hydrated counter-ion such as Cs\(^+\), neither the \( \pi_{\text{L}} \)-transition nor the \( \pi_{\text{ML}} \)-transition was observed. An interesting observation is that hydrated ion layering is suppressed at low pHs as well as at the weakly hydrated Cs\(^+\)-mica interface.

We propose that the \( \pi_{\text{L}} \)-transition occurs due to the forced dehydration and condensation of a single layer of hydrated
ions at the mica surface while the $\pi_{\text{ML}}$-transition occurs when
the two hydrated ion layers forms between the two surfaces
either merge into one layer of higher counter-ion population
or both partially dehydrate and adsorb onto their nearest
surface. The $\pi_{\text{IL}}$-transition and $\pi_{\text{ML}}$-transition are most
clearly seen in the Na$^+$ due to the fact that Na$^+$ exists in the
fully hydrated OS state near the mica surface. In the case of
K$^+$, a relatively higher population of adsorbed IS ions (63%) is
present at the surface. Hence, the collective dehydration of
a single layer of hydrated ions can already lead to the low
pull-off force typical for the $\pi$-transition. In the case of Cs$^+$,
which exists predominantly in the IS state (99%), neither the
$\pi_{\text{IL}}$-transition nor the $\pi_{\text{ML}}$-transition exist due to the absence
of a forced dehydration of hydrated ions step during the
collapse of the EDLs.
We thus extend our model of the stepwise collapse of EDLs
to include ion-specific effects, more specifically the
influence of the strength of the hydration shell. Our
conclusions are summarized in Figure 5.2.

5.2. Open questions
The following are some of the observations made during the
course of this thesis that could serve as future pathways to
explore.

5.2.1. History effects
The general assumption in all studies is that the measured
forces are in equilibrium and are reversible. It has been
shown that the exchange of surface ions in mica takes place
Figure 5.2. Pathways of EDL collapse; The $\pi_L$-transition illustrated by the red pathways are enabled with single hydrated-ion layering; The $\pi_{ML}$-transition, which is illustrated by the green pathways are enabled by multiple layering.

in a few minutes [133, 134]. Raviv et al. demonstrated that that the surface charge density of mica, as obtained from fitting the DLVO theory to the measured force curves in the SFA, remains constant after an equilibration time of 25 minutes, which is the time required for the adsorbed counter ions to be released back into the solution [35]. Though we provide sufficient equilibration time before each force measurement (>1h), we have noticed some changes with time even after this. For instance, when the surfaces were approached and separated multiple times, the energy
required for the FTTs as well as the size of the FTTs change on consecutive approaches, an illustrative example being given in Figure 5.2, suggesting changes on the mica surface with time. Though the number of observed FTTs remains the same during consecutive approaches, we see that the FTTs are increasing in size while the layering forces get weaker, seen as layering transitions taking place at decreasing external loads.

![Figure 5.3](image)

**Figure 5.3.** The size of the final and pre-final FTTs and force at which they occur plotted as function of the approach number. The electrolyte concentration was 0.7mM KNO₃, pH 5.7. The shaded lines are to guide the eye.

In addition, we observed that the force at which the final transition takes place was much higher when using the soft spring (Figure 5.3). With the soft spring (spring constant=235N/m) it takes more time to achieve a particular load (red dots) as compared to a stiffer spring (spring constant=1262N/m) at the same approach speed. We learn that the film thickness transitions that we measure are not strictly equilibrium transitions: when the system has more
time to relax and reorder itself, a different order i.e. structure, is achieved.

**Figure 5.4.** Comparison of the force at which the final transition takes place at the concentrations of 0.4 mM (a) and 0.8 mM (b) as obtained with the soft (red) and with the stiff spring (black), respectively.

### 5.2.2. Role of the anion

The effect of the anion near negatively charged surfaces such as mica is usually assumed to be insignificant due to the basic electrostatic argument that the anions are depleted in the region of the double layer that regulates the surface properties. Hence it is assumed that the anion resides beyond the OHP and does not influence the properties of the interface. Figure 1.1 shows the counterion and coion population as a function of distance from the surface. It is to be noted that the co-ions (anions in our case) are present in the interfacial region albeit in lesser concentrations than in the bulk solution.

In the few experimental studies that focused on the anions, there were discrepancies regarding the significance of the
anion when different measurement techniques were used. The role of the anion on the surface potential near a negatively charged silica nanoparticle has been found to be negligible in ATR-FTIR and XPS studies [135]. However, it has been found at low pH values (pH < 2), the electrokinetic behavior of silica was anion dependent [136]. It was also expected that at pH > 2.5, such anion effects would be insignificant due to depletion of the anion from the interfacial region due to electrostatic repulsion. In contrast, studies of different sodium electrolytes have shown specific anion effects at pH 10 and none at pH 5.7 [135, 137, 138]. Finally, AFM studies have noted no difference in the force-distance curves between NaCl and NaBr up to 200 mM [139]. Incidentally, the self-assembly of collagen molecules, the structural component of connective tissues in mammals, on flat surfaces such as mica has been found to be dependent on the anion, with different anions resulting in different structures at the interface [140]. In our studies, we have observed that the oscillatory force curves and the FTTs measured are similar in 1 mM KNO$_3$ and KCl, although ongoing work by Espinosa-Marzal et al. has observed possible anion specific effects in NaNO$_3$ and NaCl at high salt concentrations.

In addition to a role in the surface properties, it is reasonable to expect that the anion will stabilize the hydrated ion layers formed in the confinement if the hydrated anions and cations are of similar size. This effect would be prominent in cases of low pH and weakly hydrated cations where the anions would face less electrostatic repulsion from the surfaces. Since the size of the hydrated NO$_3^-$ ion is ≈3 Å while that of
the Na\(^+\) ions is \(\approx\)4-4.5 Å, K\(^+\) is \(\approx\)3 Å and Cs\(^+\) is \(\approx\)2.5 Å [141], we expect that under such conditions, the hydrated ion layers consist of both cations as well as anions.

In conclusion, there isn’t a consensus in literature regarding the role of the anion (co-ion), though generally it is neglected in favour of the cation (counterion).

5.2.3. Role of hydronium in decreasing pull-off force
The H\(_3\)O\(^+\) ion has generally been assumed to be a special ion that not to decrease the pull-off force significantly when compared to any other positively charged ion. (Though of course, the pull-off force is lower in pure water when compared to air). The understanding is that that the protons (or hydronium) condense readily into the mica lattice sites thereby neutralizing the surfaces. This results in the strong adhesive molecular contact due to the Van der Waals attraction between the surfaces [35]. In fact, when it is no longer energetically favorable for the H\(_3\)O\(^+\) to replace the metal ions in the contact, this leads to the repulsive hydration forces accompanied by a drop in adhesion [24].

We have observed that lowering the pH (increasing the H\(_3\)O) decreases the pull-off force at the same salt concentration as indicated by the arrows in Figure 4.5. This is of course before the π-transition and the same trend is followed in KNO\(_3\) too.

In addition, even when we keep the total anion (NO\(_3^-\)) concentration constant at 0.1 mM and 1 mM and vary the concentration of the cations (K\(^+\) and H\(_3\)O\(^+\)) while keeping the total cationic ionic strength ([K\(^+\)] + [H\(_3\)O\(^+\)]) constant, we
observe that decreasing the pH (i.e. decreasing the K$^+$ concentration at the surface) leads to a decrease in the pull-off force, i.e. the H$_3$O$^+$ also decreases the pull-off force (Figure 5.5a,b). The pull-off force increased initially when the acid (H$_3$O$^+$) was added, as would be expected if the K$^+$ only were responsible for the decrease in the pull-off force. However, on increasing the H$_3$O$^+$ concentration further, the pull-off force persistently decreased. This effect was reproducible even when this series of experiments were conducted in reverse, i.e. starting from pure acid, incidentally also indicating that the mica was not ageing under these conditions.

![Graph showing pull-off forces at a total counterion (K$^+$+H$^+$) concentration of (a) 1mM (b) 0.1mM. (c) VdW jump-in and FTTs measured.](image)

**Figure 5.5.** Pull-off forces at a total counterion (K$^+$+H$^+$) concentration of (a) 1mM (b) 0.1mM. (c) VdW jump-in and FTTs measured.

The role of H$_3$O$^+$ with its unique hydration structure consisting of the proton hopping around six water molecules
in reducing adhesion will provide for an interesting research topic.

**5.2.4. Mica hard wall and the absolute zero**

As described in Section 2.2, the compression of the mica creates uncertainties in determining the mica hard wall and the absolute distances due to the systematic error in the distance measurement. An increase in the hard wall thickness would be proof of a changed interface due to accumulation of ions. Though other authors have shown a shift in the hard wall (Figure 2 in [32]), it is usually defined at the maximum load applied, which is a random quantity and disregards the compression of the mica. Though we too have used the argument of the absolute zero as a supplementary evidence of our hypotheses, we recognize the fact that there are inherent errors in this value and much more improvement is required. The shift in the optical zero due to mica compression has been estimated to be of the order of ±1.2nm (Heuberger, in Preparation). A reliable determination of the absolute zero and correction for the mica compression is necessary to interpret the nanometer sized fluid films. A more reliable force-distance measurement could even lead to a better fitting of the DLVO theory to enable us to distinguish the small concentration differences we use here (±0.1mM).

**5.2.5. Transition to the solidification regime**

An increase in the pull-off force was observed in the high concentration solidification regime along with the presence of a 1-3nm hard wall. The remarkable increase of pull-off
force in 100mM CsNO$_3$ is a clear example of this (Figure 4.2c). This was accompanied by an attractive force which, when assumed to be a Van der Waals attraction, yields a Hamaker constant characteristic of some ionic liquids (Figure 5.6). This is indicative that the confined fluid has properties similar to an ionic condensate with strong attractive interactions.

In contrast, Perkins et al. observed an increase in the electrostatic screening length at high concentration electrolyte solutions[142]. Careful studies need to be conducted in this regime of salt concentration, where the solution is close to saturation. In addition, the role of ion-ion correlations when the ions are confined in thin films under load needs to be investigated even under lower electrolyte concentrations.

Figure 5.6. Measured force-distance curves in 1M NaNO$_3$. An attractive force at surface separations smaller than 5 nm
leads to an energetic minimum characteristic of the solidification regime. Upon further approach, a strong hard-wall repulsion is measured though no mica-mica contact has yet been achieved. The solid lines is the DLVO theory fitted to the experimental results with a Hamaker constant $2.2 \times 10^{-20} \text{J}$ for the mica-water-mica system and a lower value of $0.4 \times 10^{-20} \text{J}$.

5.2.6. The $\pi$-transition in the presence of multivalent ions
In the presence of multivalent counterions above a critical concentration, the $\pi$-transition is expected to disappear or be preceded by an increase in the pull-off force with increasing electrolyte concentration due to overscreening. An indication of this was already seen by Tan et. al[33], although the mechanisms for the reduction in the pull-off force in the system of multivalent ions is no longer the forced condensation of ions, but is related to ion-ion correlations and charge inversion. Interestingly, charge reversal in confinement has been observed to occur at higher concentrations than on a single surface, because part of the ions that lead to charge reversal are squeezed out.

Finally, it would be useful to devise method other than force measurements in order to chemically characterize the structure of the mica surface and thus provide more information about the changes occurring at the interface. The ToFSIMS measurements we conducted were a step in this direction.
5.3. Afterword
The ion exchange and surface properties of layered aluminosilicates such as mica is of importance not only in basic research but also in industrial applications such as in electrical insulation and paints. Although we focus on a model system of muscovite mica, these results are also of relevance for many other confined mineral interfaces that are capable of ion exchange. Interactions that happen at the nanoconfined mineral-solution interface are central to many natural processes occurring at or near the Earth’s surface, e.g. to inorganically or organically mediated precipitation and dissolution of minerals, CO$_2$ geologic sequestration, and adsorption of inorganic contaminants by minerals.

Accounting for the behavior of the hydrated ion in confined EDLs has implications for improving the capacitive energy storage mechanisms in EDL capacitors[143], which utilize ion adsorption for charge storage. EDL capacitors or supercapacitors, with their high power densities and long cycle lives than conventional batteries, have been heralded to be part of the next generation of energy storage devices [144]. A recent review of the future of hybrid energy devices has pointed out that one of the glaring gaps in current knowledge is the “influence of surface chemistry on the electrochemistry of materials” [145]. The importance of the questions that we have attempted to address in this thesis, namely the role of hydration water in EDL behavior at nanometer separations, is highlighted by the fact that the discovery of ion desolvation in pores smaller than the hydrated ion size increasing capacitance, lead to the
revitalization of the field of supercapacitors [7]. Hence, insights into the collective dehydration of ions have implications for devices utilizing energy storage in the EDL. Hydrated ion transport in nanoconfined spaces also has implications in water desalination using electrodialysis [146]. Furthermore, advances in the physical chemistry of electrolytes provides insights into biological systems which consist of similar, though more complex, charged interfaces through which ion transport takes place, such as in ion channels in a cell membrane[147].
Biblography


47. Leng, Y.S., Y.J. Lei, and P.T. Cummings, Comparative studies on the structure and diffusion dynamics of aqueous and nonpolar liquid films under nanometers confinement. Modelling and Simulation in Materials Science and Engineering, 2010. 18(3).


89. Israeliac.Jn and D. Tabor, *Measurement of Vanderwaals Dispersion Forces in Range 1.5 to 130 Nm*. Proceedings of the


139. Dishon, M., O. Zohar, and U. Sivan, *Effect of Cation Size and Charge on the Interaction between Silica Surfaces in 1:1, 2:1,


Acknowledgements

I would like to thank Prof. Manfred P. Heuberger and Prof. Rosa M. Espinosa-Marzal for giving me an opportunity to pursue a PhD under their supervision and Prof. Nicholas D. Spencer for welcoming me to the LSST group. I am grateful to Prof. Heuberger for teaching me about “real” bread and putting up with my undecipherable ‘OKs’ amidst our scientific discussions. As I gain my license to do research, I hope to inculcate your motto of questioning everything. Prof. Espinosa-Marzal will always serve as a role model to me as one of the scarce women in research. I thank her for her unstinting support and guidance from across the ocean though good and bad times. Your dedication and work ethic fill me equally with awe and intimidation.

I would also like to thank Prof. Hugo Christenson for his interest in my work and for agreeing to be my co-examiner as well as Prof. Manfred Fiebig for chairing my defence committee.

Chester and Ruby, with whom I spent almost three years underground, deserve a special mention. Thank you for never letting me down apart from the odd trouble with the lamps.

I must thank Tomas Bartos for solving all the IT troubles, Giovanni Cossu and Martin Elsener for solving all the mechanical troubles and Josephine Baer for solving all the other troubles in my life at ETH. Dr. Laeticia Bernard at
EMPA Dübendorf performed all the TofSIMS experiments in this thesis and introduced me to the evaluation software. The Laboratory of Surface Science and Technology at ETH as well as the Laboratory for Smart Interfaces in Environmental Nanotechnology at UIUC where I worked both served as fertile grounds to develop scientific and personal relationships. I would like to thank all my labmates, especially Manjesh, Shiva, Prathima, Ella, Moh, Fabiana, Andrea, Clément and Rebecca for all their help.

I must acknowledge the support of the Swiss National Science Foundation for financing my PhD project as well as for providing a project extension.

I am grateful to Prof. U. Ramamurty and the Laboratory for Micro and Nanomechanics of Materials at the Indian Institute of Science Bangalore for stoking my interest in research and its endless possibilities. I thank Prof. Ram for all the interesting discussions we had and for teaching me value of pursuing knowledge over wealth.

On the personal front, I must thank my friends Elizabeth and Tom Philip for all their help and my family for giving me freedom as well as support: my late grandparents Lily and John Zachariah, my husband Shanoob Nair and mother-in-law Ushakumari. And of course little Noah, who will always be the love of my life, for patiently waiting at the Kinderkrippe, Hönnggerberg for me to finish writing this thesis.
Curriculum Vitae

ZITA ZACHARIAH

98 Girinagar
Kadavanthra
Kochi-682020, India
zitazachariah@gmail.com

Date of birth: 07.10.1987

EDUCATION

02.2013-03.2017 Swiss Federal Institute of Technology (ETHZ), Zürich, Switzerland
PhD, Laboratory for Surface Science and Technology

09.2015-02.2016 University of Illinois at Urbana-Champaign (UIUC), Illinois, USA
Laboratory of Smart Interfaces in Environmental Nanotechnology
Visiting research scholar

08.2010-07.2012 Indian Institute of Science (IISc), Bangalore, India
Master of Engineering in Materials Engineering, Final grade: 6.8/8
Master thesis: Effect of State of Stress on Deformation Mechanisms in the Mg alloy AM30
06.2005-05.2009 Anna University, Chennai, India
Bachelor of Technology in Chemical Engineering, Final grade: 89%
Bachelor Thesis: Hydrogen generation from Sodium Borohydride for fuel cell applications

PUBLICATIONS