Ionic liquids: The solid-liquid interface and surface forces

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"We are at the very beginning of time for the human race. It is not unreasonable that we grapple with problems. But there are tens of thousands of years in the future. Our responsibility is to do what we can, learn what we can, improve the solutions, and pass them on."

Richard P. Feynman, 1988
Abstract

Ionic liquids (ILs) present new approaches for controlling interactions at the solid-liquid interface. ILs are defined as liquids consisting of bulky and asymmetric ions, with a melting point below 373 K. Owing to their amphiphilic character they are powerful solvents but also possess other interesting properties. For example, ILs can self-assemble and are attracted to surfaces due to their charged nature. As a result, they are capable of forming nanostructures both in bulk and at interfaces. This thesis describes how the solid-IL interface responds to external influences such as elevated temperatures, the addition of salt and polarisation. An improved understanding of how these factors govern the surface composition can provide tools for tuning systems to specific applications such as friction.

Normal and friction forces are measured for ethylammonium nitrate (EAN) immersed between a mica surface and a silica probe, at different temperatures or salt concentrations. The results demonstrate that an increase in temperature or low concentrations of added salt only induce small changes in the interfacial structure and that the boundary layer properties remain intact. In contrast, at sufficiently large salt concentrations the smaller lithium ion prevails and the surface composition changes. The interfacial layer of a similar IL is also investigated upon the addition of salt and the results reveal that lithium ions affect the surface composition differently depending on the ion structure of the IL. This demonstrates that the surface selectivity strongly depends on the ion chemistry.
Remarkably, a repulsive double layer force manifests itself for EAN at 393 K, which is not observed for lower temperatures. This indicates a temperature dependent change in EAN’s microscopic association behaviour and has general implications for how ILs are perceived.

A new method is developed based on a quartz crystal microbalance to investigate how the surface compositions of ILs respond to polarisation. The approach demonstrates that interfacial layers of both a neat IL and an IL dissolved in oil can be controlled using potentials of different magnitudes and signs. Furthermore, the method enables two independent approaches for monitoring the charges during polarisation which can be used to quantify the surface composition. The technique also provides information on ion kinetics and surface selectivity.

This work contributes to the fundamental understanding of the solid-IL interface and demonstrates that the surface composition of ILs can be controlled and monitored using different approaches.

**Keywords:** Ionic liquids, solid-liquid interface, surface forces, nanotribology, atomic force microscopy, quartz crystal microbalance
Sammanfattning

Jonvätskor möjliggör nya tillvägagångssätt för att kontrollera interaktioner vid gränsskiktet mellan fasta ytor och vätskor. Jonvätskor definieras som vätskor som består av stora och asymmetriska joner med en smältpunkt under 373 K. På grund av sin amfifila karaktär är de starka lösningsmedel men har också andra intressanta egenskaper. Jonvätskor kan till exempel självorganisera sig och attraheras till ytor på grund av sin laddning. En följd av detta är att de bildar nanostrukturer både i bulk och på ytor. Denna avhandling beskriver hur gränsskiktet mellan fasta ytor och jonvätskor svarar på yttre påverkan såsom en ökning i temperatur, tillsättning av ett salt samt polarisering. En ökad förståelse för hur dessa faktorer styr ytkompositionen av jonvätskor kan bidra med verktyg för att kontrollera system till specifika applikationer såsom friktion.

En repulsiv dubbellagerkraft yttrar sig anmärkningsvärt för EAN vid 393 K vilket inte observeras vid lägre temperaturer. Detta indikerar en ändring i EANs mikroskopiska sammansättningsbeteende och har generella återverkningar för hur jonvätskor uppfattas.

En ny metod har utvecklats baserad på en kvartskristall mikrovåg för att undersöka hur ytsammansättningen av jonvätskor reagerar på polarisering. Denna metod visar att det adsorberade lagret av både en ren jonvätska och en jonvätska löst i olja kan kontrolleras genom att applicera spänningar med olika tecken och storlekar. Dessutom möjliggör metoden två oberoende tillvägagångssätt för att övervaka laddningarna under polarisering vilket kan användas för att kvantifiera ytsammansättningen. Tekniken ger också information om jonkinetik och ytselectivitet.

Detta arbete bidrar till den grundläggande förståelsen av gränsskiktet mellan fasta ytor och jonvätskor och visar att ytsammansättningen av jonvätskor kan kontrolleras och övervakas med olika tillvägagångssätt.

**Nyckelord:** Jonvätskor, gränsskiktet mellan fasta ytor och vätskor, ytkrafter, nanotribologi, atomkraftsmikroskopi, kvartskristall mikrovåg
List of appended papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals:

I. **Is the boundary layer of an ionic liquid equally lubricated at elevated temperatures?**
   N. Hjalmarsson, R. Atkin, M. W. Rutland
   *Phys. Chem. Chem. Phys.*, 2016, 18, 9232-9239

II. **Effect of lithium ions on rheology and interfacial forces in ethylammonium nitrate and ethanolammonium nitrate**
    N. Hjalmarsson, R. Atkin, M. W. Rutland
    *Submitted*

III. **Long-range double layer force measured for a protic ionic liquid**
     N. Hjalmarsson, R. Atkin, M. W. Rutland
     *Manuscript*

IV. **Weighing the surface charge of an ionic liquid**
    N. Hjalmarsson, D. Wallinder, S. Glavatskih, R. Atkin, T. Aastrup, M. W. Rutland
    *Nanoscale*, 2015, 7, 16039-16045

V. **Electro-responsive surface composition and kinetics of an ionic liquid in a polar oil**
   N. Hjalmarsson, E. Bergendal, Y. Wang, D. Wallinder, S. Glavatskih, T. Aastrup, R. Atkin, M. W. Rutland
   *Manuscript*
The author’s contribution to the papers:

I. All the experiments and major part of planning, evaluation and writing

II. All the experiments and major part of planning, evaluation and writing

III. All the experiments and major part of planning, evaluation and writing

IV. All the experiments and major part of planning, evaluation and writing

V. Supervision of experiments and major part of planning, evaluation and writing
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1 Introduction
As society searches for ways to reduce global energy consumption it has become increasingly important to understand and improve the underlying processes that could secure such a development. Some of these processes are found in areas such as lubrication, corrosion, catalysis and battery applications, which all strive for increasing the energy efficiency and/or reducing material deterioration. Furthermore, the implementation of novel materials in such systems requires new theories and approaches to be established. A common denominator for many of these applications is the interface between a solid material and liquid molecules and a more profound understanding of this interface will aid their development.

Liquid molecules in bulk are surrounded by other (un)like molecules and interact with each other over short distances (typically the nearest neighbours only), whereas long-range interactions are largely absent. However, the introduction of a solid surface changes the structure and dynamics of the liquid molecules. The same forces within the bulk might be involved at the interface but manifest themselves differently. The properties of the solid-liquid interface are consequently determined by both the surface and the liquid. For example, the surface roughness, homogeneity and hydrophilicity as well as the liquid molecule geometry and chemical structure (charge, polarity etc.) will influence the spatial distribution of molecules at the interface. Much effort has been spent on understanding the fundamental properties that govern these interactions, aided by the invention of sensitive techniques capable of accurately probing the solid-liquid interface.\textsuperscript{1-3} In spite of this, the interfacial structure and dynamics are not fully understood for many systems.\textsuperscript{4,5}
The chemistry at the solid-liquid interface can also be altered by introducing external influences to the system. Changes in pH, ionic strength, temperature and the application of electric potentials are a few things that can modify the surface composition. For example, in the latter case it is possible to actively apply electric fields across a sample with charged molecules and thus modify their surface composition. This has already been demonstrated to alter the friction for several one-component systems but the changes in surface composition are still not fully understood. The active tailoring of systems at the solid-liquid interface thus raises questions. What is the actual surface composition at the solid-liquid interface for different potentials? How do the dynamics/geometries of the involved molecules affect these changes? What happens with the surface composition if a second component is introduced? How stable is the structure against temperature increases?

This thesis aims to provide insight into these questions for selected ionic liquid (IL) systems and contribute to the fundamental understanding of the solid-IL interface. ILs are particularly interesting at the solid-liquid interface given their amphiphilic surfactant-like charged nature, which enables favourable interactions with surfaces compared to other molecular liquids. Furthermore, they can be tuned to specific applications by altering their ion structure. In this thesis, ILs are first defined and some of their more common classifications and features briefly summarised. Short descriptions of a few typical surface forces and a brief introduction to tribology is then provided followed by an outline of the IL nanostructure at solid-liquid interfaces. This overview is followed by a summary of the main experimental techniques and methods used and the ILs studied in this work. Finally, the main results are presented and discussed.
2 Background

2.1 Ionic liquids

ILs are pure salts with a melting point below 373 K. The cations and anions are often bulky and have a delocalised charge, leading to poor coordination and weaker Coulombic forces (Figure 1 shows a few examples of molecular structures for different groups of cations and anions). Ultimately, this prevents stable crystal lattices and greatly reduces the melting point. In contrast, NaCl melts at 1074 K due to its localised charge and symmetrical (spherical) and small ions, which facilitate the formation of a crystal lattice.\textsuperscript{12}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{Some common groups of cations and anions used to synthesise ILs. Note that resonance structures are not included where appropriate and that only examples of $R$ are mentioned.}
\end{figure}

Research into ILs has witnessed a considerable growth over the last few decades but were discovered much earlier.\textsuperscript{4} In 1914 a German Chemist called Paul Walden synthesised a pure salt that was liquid at room temperature (ethylammonium nitrate, EAN), which was a surprising finding at that time.\textsuperscript{13} It was previously thought that ions had to be diluted in a molecular solvent to exist as a liquid at ambient
temperatures. In many ways, EAN shares similar properties to those of water (e.g. clear, colour- and odourless) except for one key attribute: the conductivity. Walden had already studied ions in solution and empirically derived relationships between molar conductivity, viscosity and density (known as the Walden rule). He could therefore demonstrate from EAN’s conductivity data that it behaved as a pure liquid salt with (mostly) un-associated ions. Although liquid salts with melting points below 373 K had been synthesised earlier, the discovery of a pure salt at room temperature with intrinsic conductivity was unique at the time. The Walden rule demonstrates that the product of the viscosity of an electrolyte, $\eta$, and its molar conductivity, $\Lambda_m$, is constant for infinitely diluted electrolyte solutions according to:

$$\Lambda_m \eta = k$$  \hspace{0.5cm} (1)

where $k$ is a temperature-dependent constant. Equation 1 can be rewritten as:

$$\log \Lambda_m = \log \eta^{-1} + \log k$$  \hspace{0.5cm} (2)

It is thus possible to plot the logarithmic molar conductivity as a function of the logarithmic inverse viscosity if those properties are measured as a function of temperature. This allows the construction of a Walden plot where an ideal electrolyte solution of 0.01 M KCl is commonly used as a reference. A comparison to the studied electrolyte’s ion association is therefore provided. Typically, ILs have a weak ion association if they are within one order of magnitude below the reference line and $k$ is linear with temperature. Otherwise, they are believed to form ion-pairs or else associate. A Walden plot for EAN is shown in Chapter 5.1 (Figure 10), however, a larger range of ILs have previously been studied, with mixed results concerning their association behaviour.
ILs are generally divided into two main groups: protic and aprotic. Protic ILs are made by reacting equimolar amounts of a Brønsted base with a Brønsted acid. They usually have no by-products and are inexpensive and simple to make. The nature of proton transfer allows for extensive hydrogen-bonding and EAN is a well-studied example of hydrogen-bonding in a protic IL, with three donor and accepting sites. Aprotic ILs, on the other hand, are more difficult to synthesise as they require breaking and forming covalent bonds, often in multiple steps and the purification thus becomes more challenging. However, the principles behind the more arduous synthesis leads to increased stability against thermal and electrochemical decomposition provided all by-products are removed. For example, typical electrochemical windows for aprotic ILs can reach 5-6 V whereas protic ILs are usually stable in a more limited range (2-3 V), which explains why most of the research focus concerning electrochemical applications has been on aprotic ILs.

High thermal and electrochemical stabilities and low vapour pressures are just a few of the desirable properties normally associated with ILs. There are (in theory) an infinite amount of possible cation-anion combinations, resulting in a large variety of physico-chemical properties. This has earned ILs the reputation of “tuneable solvents”. It has also led to an interest in predictably controlling the desired properties. For example, the viscosity of ILs ranges over many orders of magnitude but even low viscosity ILs are more viscous than water. The viscosity is also very sensitive to contaminants such as water and decreases greatly with increasing temperature. Most rheological studies have focused on aprotic ILs and have systematically changed the structure of either the anion or cation, whilst keeping the other constant. Such studies have found that a more localised charge results in an increasingly viscous IL. The ion size and charge delocalisation are
thus important parameters. A similar dependency is found for the
density of ILs, which are often more dense than water.

Another important property of ILs (and required together with
density and viscosity to construct a Walden plot) is their
cconductivity. Despite the fact that ILs consist solely of ions they have
a relatively moderate conductivity, with typical values ranging
between 0.1-50 mS cm$^{-1}$ at room temperature (compared with 200-
800 mS cm$^{-1}$ for conventional aqueous electrolytes used in
electrochemistry, such as sulfuric acid)$^{25, 40, 41}$ This can be explained
by the large and often bulky ions causing a reduced mobility.
Furthermore, the number of charge carriers depend on their
association behaviour so ILs with weak ion associations will have a
larger conductivity, whereas stronger ion association will reduce the
conductivity of an IL. External parameters such as temperature
and/or adding unlike molecules also affect the conductivity. Water
and organic solvents, such as acetonitrile and propylene carbonate,
are known to increase conductivity and reduce viscosity but in return,
water reduces the electrochemical stability and the organic solvents
are thermally unstable and volatile.$^{35, 42, 43}$ Another proposed
possibility to tune the transport properties of ILs has been to
introduce Li$^+$ ions for use in battery applications. ILs favourably
dissolve lithium ions but the changes in transport properties are not
fully understood, with some studies demonstrating an increase in
conductivity whilst others measure a decrease.$^{44-61}$ However, several
studies agree that the addition of Li$^+$ increases the viscosity of the
solution, which is generally regarded as a disadvantage in many
applications because of already large mass transport limitations from
the IL viscosities.$^{48, 50, 51, 53, 62}$
There are, however, exceptions to these general properties that can have a profound implication for some of their uses. Recent studies have identified ILs that can be distilled, are toxic, hazardous or are in other ways environmentally unfriendly.\textsuperscript{63-68} Moreover, there are thousands of different ILs reported in literature and the combinations for synthesising novel ILs are endless. This makes it next to impossible to categorise them all into one group with cohesive properties. Rather, it is their cation-anion interaction, shape and charge density that determines many properties.\textsuperscript{5} Despite this, ILs are being considered for or are already used in CO\textsubscript{2}-capture, lubrication, as solvents in synthesis or as electrolytes in electrochemical applications.\textsuperscript{69-75} Table 1 (Chapter 4) describes some physico-chemical properties for the ILs used in this thesis.

### 2.2 Surface interactions

This work focuses on the solid-IL interface at the nanoscale and the forces governing these interactions must therefore be understood in order to interpret their behaviour. Some of these forces are ubiquitous in liquids and exert themselves between molecules or bodies regardless of their surroundings such as the van der Waals force. The strength of these forces, however, can change dramatically with the introduction of a surface.\textsuperscript{3} Other forces, such as solvation, entropic and (usually) electrostatic double layer forces arise due to the surface. Many important applications such as lubrication, protein folding, colloidal stability, catalysis and batteries, directly depend on the structural arrangement and chemistry at the interface.\textsuperscript{76-80} This section briefly discusses some surface forces and tribology before describing a few important observations of ILs at the solid-liquid interface.
2.2.1 Surface forces

Depending on the composition of a system, different forces are involved when a medium interacts with a surface. The van der Waals interaction is an important example and the force can either be attractive or repulsive (uncommon). Typically, there are three types of interactions that form the overall van der Waals force: the Keesom force between permanent dipoles, the Debye force between a permanent and an induced dipole and the London force between an induced and instantaneous dipole. Instantaneous dipoles can form in any molecule (nonpolar included) making the London force the most important of the three. The van der Waals force, although omnipresent, is a weak force at larger distances and decays as $1/r^6$ but expresses itself more at short distances. For example, van der Waals interactions have been measured at short-ranges between ILs and non-charged surfaces. They also participate in forming the bulk and nanostructures of ILs.

Accurate equations for calculating the van der Waals force between a molecular pair are straightforward but become increasingly complicated when considering an ensemble of molecules interacting with each other. A major breakthrough came in 1937 when Hamaker introduced a theory for evaluating the van der Waals force, $F_{vdW}$, between two macroscopic bodies by summing all the interactions to obtain a total energy. The theory estimated the interaction energy according to the following equation for a sphere against a flat surface:

$$\frac{F_{vdW}}{R} = \frac{-A}{6D^2}$$

where $R$ is the radius of the sphere, $D$ is the distance between the surfaces and $A$ is the Hamaker constant, which depends on the properties of the interacting molecules. Typical values are of the order of $10^{-19}$-$10^{-21}$ J.
A limitation in Hamaker’s theory was that it neglected neighbouring bodies and could not accurately describe the interaction when a liquid medium was present between the two bodies. This restriction was addressed by the Lifshitz theory, where the entire system was treated as a continuum. The approach proposed a revised Hamaker constant in which only the dielectric responses (real and imaginary) of the interacting bodies and media were required. However, the dielectric constants (or the closely related refractive indices) are often enough to estimate a van der Waals force.

Another important force is the electrical double layer (EDL), which arises between charged surfaces across liquids. In aqueous solutions for example, water (which has a high dielectric constant) dissociates chemical groups at the surface and the resulting surface charges are screened by counterions accumulating close to the surface (Stern layer) and in a diffuse layer. Together these layers form the EDL and the force itself arises from an overlap between the diffuse layers of the two surfaces, resulting in an ion concentration gradient. This is countered by an osmotic pressure building up across the system. The force is repulsive when the surface charge of the two surfaces have the same sign and increases exponentially with decreasing separation. The thickness of the diffuse layer can be estimated from the decay length, $\kappa^{-1}$:

$$
\kappa^{-1} = \sqrt{\frac{k_B T \varepsilon_0 \varepsilon_r}{e^2 \sum \rho_i z_i^2}}
$$

where $k_B$ is the Boltzmann’s constant, $T$ is the temperature, $\varepsilon_0$ and $\varepsilon_r$ are the permittivities of vacuum and the relative dielectric constant of the medium, respectively, $e$ is the electronic charge, $\rho_i$ is the number density of ion species $i$ and $z_i$ is the valence. Equation 4 therefore provides a measure of the strength of the EDL where, for example, a high ionic strength greatly reduces the strength of the force.
The theories behind the EDL (Gouy-Chapman-Stern model) for aqueous solutions assume that the ion-ion interaction is weak compared to the ion-solvent interaction and that the ions are spherical and small.\textsuperscript{90-92} This is not the case for ILs, which typically consist of ions that are large and bulky (Figure 1). The ionic strength for ILs is also generally considered to be large, which would suggest that the double layer force for ILs is completely screened (Equation 4). However, this is a subject of ongoing debate as EDL forces have been measured for ILs.\textsuperscript{93-100} The main discussion point refers back to whether the ions in ILs should be conceptualised as mostly free or if they associate into structures such as ionic networks. In Paper III, this is further discussed and an example is shown of a measured EDL force for an IL.

Regardless, much effort has been spent to accurately describe the EDL of an IL, as highlighted in a recent review.\textsuperscript{5} In a 2007 paper, a continuum theory was developed to predict the EDL-structure of ILs on charged surfaces.\textsuperscript{101} The work concluded that as long as the surface charge was lower than the charge of one monolayer of counterions, the surface would be overscreened by the first monolayer (Figure 2a). This would in turn be compensated for by an excess of coions in the next layer and so on until the charges had been screened. However, if the surface charge was large enough to completely screen the charge of the monolayer of counterions, the system would compensate by crowding the second monolayer with counterions too, pushing the coions further away (Figure 2b).

Although several assumptions were made in this study, including treating the ions as point charges, both theoretical and experimental studies have confirmed and further developed the theory to account for different shapes and sizes of ions.\textsuperscript{85,102-118}
Figure 2. Illustrative pictures of the EDL-structures for spherical ions at a) low and b) high negative surface charge.

In a system with two charged surfaces immersed in a liquid medium, the total interaction can often be described by the combination of van der Waals and EDL forces. This interaction is commonly known as the DLVO theory (Derjaguin, Landau, Verwey and Overbeek).\textsuperscript{119, 120} However, it often fails to describe observations at short separations and may also be screened by increasing the salt concentration of the liquid medium. Therefore, at separations of a few nanometers or less other forces can render both DLVO forces irrelevant. One such interaction is the solvation force, where liquid molecules are forced to form discrete layers due to confinement (\textit{i.e.} achieve higher ordering). The interaction strength depends largely on the geometrical shape of the molecules, although, other factors can affect this interaction too. For example, the physical and chemical properties of the surface(s) can influence the packing of the molecules and the interaction between the surface(s) and molecule(s). Furthermore, liquid-liquid interactions do, to some extent, determine the strength of the interaction.
Figure 3. Schematic of a typical oscillatory solvation force profile that increases in magnitude with decreasing separation.

The invention of sensitive techniques capable of measuring surface forces made it possible to measure solvation forces with great accuracy. In a landmark paper from 1981 oscillatory forces were detected for a nonpolar and spherical silicone liquid (octamethylcyclotetrasiloxane) confined between two mica surfaces using a surface force apparatus (SFA). It was demonstrated that the periodicity of the oscillation corresponded to the mean diameter of the molecule. The resulting confinement thus squeezed out discrete layers of liquid with decreasing surface separation (Figure 3). Many more neat polar and nonpolar liquids as well as mixtures of liquids have since been investigated. Those studies have found that oscillatory solvation forces are only marginally temperature dependent and that the rigidity of the molecules affect the range.
They have also shown that small amounts of water in a nonpolar liquid preferentially adsorb to the surface and thus completely change the interaction. A more complete and extensive list can be found elsewhere.\textsuperscript{3}

\subsection*{2.2.2 Tribology}

Two interacting surfaces in relative motion exhibit a force resisting this movement (friction). Friction forces can remove or deform materials from the surfaces (wear) but this can be reduced by using substances that protect these surfaces (lubrication). Tribology is the study which investigates these principles and the modern field was founded in the 1960’s when “The Jost Report” was published.\textsuperscript{130} The report revealed that some 1-2 \% of the gross domestic product for an industrialised country could be saved each year by applying tribological solutions to industrial applications.

Friction is an energy dissipative mechanism that arises between fluid layers and/or solid surfaces. The earliest registered friction studies date back to the 15\textsuperscript{th} century and Leonardo da Vinci. However, Guillaume Amontons is usually credited as the pioneer of the field as he postulated a set of empirical rules in 1699.\textsuperscript{131} Amontons’ rules state that i) the relationship between friction force and load is linear, ii) the friction force is independent of contact area and iii) the friction force is independent of the sliding velocity. The first rule is written as:

\begin{equation}
F_F = \mu F_N
\end{equation}

where $F_F$ is the friction force, $\mu$ is the friction coefficient and $F_N$ is the applied load. At the nanoscale an additional parameter must sometimes be added to compensate for the adhesion acting on the system.\textsuperscript{132} Remarkably, Amontons’ rules accurately describe the friction behaviour for many systems despite being based on empirical
observations. Today, the rules are still the most common approach of quantitatively describing friction between surfaces.\textsuperscript{133, 134}

In this work, friction is measured as a function of load for ILs and the results are described in \textbf{Paper I and II}. The focus was on the friction at the nanoscale, which has created its own field within tribology, namely nanotribology.\textsuperscript{79, 135, 136} Both atomic and molecular scale friction are encompassed in this field, where the main goal is to understand the underlying fundamental phenomena that govern friction.\textsuperscript{135-138} At these length scales the surface-area-to-volume ratio is large so surface forces dominate these interactions. An important breakthrough in nanotribology came when it was demonstrated that surface roughness reduces the real contact area significantly from the apparent contact area.\textsuperscript{139} All surfaces have some roughness associated with them, whether on the nano- or micrometer scale, and friction is therefore often determined by asperities in contact. The development of the atomic force microscope in 1986 allowed such interactions to be measured with great accuracy and this technique is currently one of the cornerstones in modern nanotribology.\textsuperscript{1, 2, 140-142}

\subsection*{2.2.3 Ionic liquids at interfaces}

Before discussing the structure of ILs at the solid-liquid interface it is worthwhile to briefly discuss their bulk structure which (at least partially) influences their behaviour at solid surfaces.\textsuperscript{143} Groups of ILs can be built from different building blocks with a variety of chemical modifications such as different functional groups and/or alkyl chain lengths. This allows for incredible diversity when designing new systems (Figure 1). A common behaviour is that they segregate into polar and nonpolar domains, which is reminiscent of the micellar phase structures for conventional amphiphiles. ILs are therefore better described as structured solvents rather than a system with no coordination. Many ILs form structures such as hydrogen-
bonding networks, self-assemblies and ion clusters. For example, a recent study investigated the crystal structure of EAN below its melting point and found sheets of cations, where the short alkyl chains segregated separately and the charged groups pointed away from the apolar domain. The nitrate anions interacted strongly through electrostatic forces with the charged group of the cation but only weakly with the alkyl chains through van der Waals forces. Above its melting point, EAN has demonstrated an extensive hydrogen-bonding network and a bulk structure of a bicontinuous sponge phase. The exchange of a terminal hydrogen on the cation alkyl chain with a hydroxide group however, changes the structure since the solvophobic attraction between the alkyl chains weakens. As a result, ethanolammonium nitrate (EtAN) has a much less pronounced bulk structure. Conversely, increasing the chain length of the alkyl chain strengthens the solvophobic interaction and produces a better defined structure. Clearly, there is a complex interplay that determines their intramolecular interactions and the literature reports a wealth of different IL bulk structures but this is beyond the scope of this work.

The confinement of two solid surfaces introduces an organising effect and Figure 3 demonstrates an example of such behaviour with spherical non-charged molecules. As the molecules are confined, layers were squeezed out of contact, which results in oscillatory force profiles. One of the differences between ILs and other molecular liquids is their ability to self-assemble, which provides an additional force for forming structures at interfaces (as well as in bulk) despite the often unfavourable geometries. The interfacial structure of an IL was first revealed in 1988 using a surface force apparatus (SFA). An oscillatory force profile was obtained from two mica surfaces approaching each other immersed in EAN. The distance between the oscillations corresponded well with the ion-pair diameter. Many
more studies have since reported similar force profiles for both protic and aprotic ILs. Generally, the force profile for the IL interfacial structure is explained by ion-pairs being squeezed out of contact but bilayers have also been reported. The layering usually extends a few ion-pair distances away from the surface but depends on the ion structure of the ILs and their ability to self-assemble. EtAN, for example, displayed fewer steps compared to EAN when an atomic force microscopy (AFM) tip was used to investigate the interfacial structure of protic ILs. This is related to the bulk structure being much weaker for EtAN, as discussed earlier. Additionally, applied electrical potentials, addition of other ions, and the length of alkyl chains have demonstrated that the interfacial structure of ILs can be controlled. It was also a breakthrough when the lateral structure of EAN was elucidated using amplitude modulated AFM. The scanned images revealed worm-like structures of cations at the surface that were very firmly adsorbed. Furthermore, a lamellar arrangement was identified in the near surface volume, confirming previous studies demonstrating layered structures. Many ILs are potentially excellent lubricants due to their strong interactions with surfaces and self-assembling capabilities. ILs can therefore form boundary films on surfaces and resist squeeze out. Consequently, it is of importance to understand what nanoscale interactions govern friction and thus tune the design of ILs for lubrication. In an elegant SFA study it was demonstrated that the nanoscale friction for an IL was quantized. Each IL layer had a unique friction coefficient with the layer closest to the surface having the largest friction. This was ascribed to a larger degree of interlocking between layers due to the higher order of structure at the surface. AFM studies have similarly found that the different layers or steps in the interfacial structure correspond to separate friction regions.
3 Experimental techniques and methods

3.1 Atomic force microscopy

3.1.1 General
The AFM was invented 30 years ago as a method of investigating the surface morphology for insulating materials, which were not accessible with the scanning tunnelling microscope. Today AFM is used in a number of different ways, such as imaging surface properties and measuring normal and lateral forces at the nanoscale. In a typical AFM (Figure 4), the sample is glued to a metal disc and then placed directly on top of the scanner stage. A holder is mounted above the sample (not shown in Figure 4) with a cantilever attached to it. The sample is scanned with a probe attached to the free end of a rectangular or v-shaped cantilever. A piezoelectric scanner allows the sample and probe to move relative to each other in x, y, and z coordinates with great accuracy. Any resulting interaction between the probe and sample is monitored by a laser focused on the free end of the backside of the cantilever and then reflected to a quartered photodiode. The photodiode transforms the deflection and twist of the cantilever response to topography images or normal and lateral forces, depending on the mode. A feedback system adjusts the position of the piezoelectric scanner to keep the deflection or tapping amplitude constant during scanning. AFM experiments can be performed in several different controlled environments, such as in vacuum or liquid. In this thesis the cantilever is mounted in a liquid cell to contain the ILs and minimise water contamination from the atmosphere.
3.1.2 Colloidal probe and calibration of cantilevers

The colloidal probe technique was used to perform all AFM normal and lateral force measurements in this thesis. A colloidal particle was glued to the free end of the cantilever and used as a probe instead of the more common sharp tip. Silica (Bangs Laboratories, Fishers, IN, USA) (Paper I and III) and borosilicate (Duke Scientific, Palo Alto, CA, USA) (Paper II) particles were glued to tipless, rectangular cantilevers made of crystalline silicon (MikroMasch, Tallinn, Estonia), using a micromanipulator connected to an optical microscope. The optical microscope was also used to capture images of the cantilevers and probes and processed using the ImageJ software (NIST, Gaithersburg, MD, USA) to obtain the length and width of the cantilever as well as the radius of the probe.

Colloidal probes have some advantages over standard AFM tips: the probes can be made of almost any material as long as they have a defined geometry and are incompressible. The probes are also less
sensitive to damage compared to sharp tips, which wear down quickly. Comparing measured normal forces with different probe sizes and geometries is not straightforward with this technique but the Derjaguin approximation is commonly used to normalise these forces.\textsuperscript{162} In this approximation the force, $F$, is proportional to an interaction energy per area between two flat surfaces, $W(D)$, and an effective radii, $R_{\text{eff}}$, which depends on the geometry of the interacting surfaces. In a colloidal probe experiment with a spherical particle interacting against a flat surface the effective radii is reduced to the radius of the particle, $R$, and the relationship is therefore:

$$\frac{F}{R} = 2\pi W(D)$$  \hspace{1cm} (6)

The normal and lateral spring constants were determined for each cantilever and the Sader method was used for calculating the normal spring constants due to its simplicity and accuracy.\textsuperscript{163, 164} In this method, the vibration of the cantilever due to thermal motion is measured in a fluid, typically air. A simple harmonic oscillator is then fitted to the thermal power spectra to obtain the normal resonance frequency and quality factor of the cantilever. The length and width of the cantilever are also needed and combined with the normal resonance frequency and quality factor to accurately determine the normal spring constant for the rectangular cantilevers. All cantilevers were calibrated before gluing particles to them which induces a small error in the spring constant due to the negligible mass of the particles. The lateral spring constants were determined using a recently devised model that combines the Sader method with a theoretical approximation based on the plate theory.\textsuperscript{165}
3.1.3 Normal force measurements

An AFM can measure normal forces between a sample and a probe, with or without an interacting fluid in between, by moving the piezoelectric scanner in the z-direction. Two sets of raw data are obtained through this movement: the deflection of the cantilever and the z-position of the piezo. These variables can be plotted against each other to identify three different regions. Firstly, the zero deflection region where the sample is not interacting with the probe and only moving through the intermediate fluid. Secondly, the point of zero separation, which is when the sample first makes contact with the probe and thirdly, the constant compliance region. This latter region describes the response of the probe after contact has been made and is defined as a linear correlation between the z-position of the piezo and the deflection of the cantilever, provided the sample and probe are rigid. By identifying these three regions the raw data can be transformed into normal forces and separation according to the following protocol:\textsuperscript{2}

1. Multiply the measured deflection with the inverse of the slope obtained from the constant compliance region to convert the deflection from volts to metres
2. Use Hooke’s law and the normal spring constant of the cantilever to transform this deflection into a force in newtons
3. Subtract the cantilever movement from the z-movement and take the point of zero separation into account to acquire the apparent separation

In an AFM force measurement, the fluid dynamic force dominates other interactions such as van der Waals and solvation forces when using liquids of large viscosities and high relative approach velocities. Fluid dynamic forces describe the displacement of liquid between two surfaces upon dynamic confinement according to the following equation:\textsuperscript{166}
\[ F = \frac{6\pi R^2 \eta \nu}{D} f^* \]  

(7)

where \( R \) is the radius of curvature, \( \eta \) is the viscosity of the liquid, \( \nu \) is the relative velocity and \( D \) is the separation. If the velocity is non-zero at the interface a slip length has to be included in the correction factor, \( f^* \), and can be calculated according to:

\[ f^* = \frac{D}{3b} \left[ \left(1 + \frac{D}{6b}\right) \ln \left(1 + \frac{6b}{D}\right) - 1 \right] \]  

(8)

where \( b \) is the slip length. The correction factor is equal to 1 in the case of no slip. Additionally, the slip length can be correlated to the boundary layer thickness, \( \delta \), as well as the ratio between bulk viscosity, \( \mu_b \), and interfacial viscosity, \( \mu_s \), according to:\(^{167}\)

\[ b = \delta \left(\frac{\mu_b}{\mu_s} - 1\right) \]  

(9)

The experimental force curve can thus be used to obtain the viscosity of the liquid from the analysis, which can also demonstrate whether the force is fluid dynamic or not. These equations were used in Paper I.

Normal force measurements in this thesis were performed by allowing the piezo scanner to approach the probe on the cantilever at different rates and distances. Typically a 500 nm ramp size was used for measuring long-range forces, such as fluid dynamics whereas solvation forces were probed at ramp sizes of 70-100 nm. The rate of approach varied between 0.02 (solvation forces) and up to 4.4 Hz (long-range forces) and all force curves were converted to \( F/R \) vs. apparent separation according to the protocol described earlier.

### 3.1.4 Lateral force measurements

Friction forces are measured in an AFM by monitoring the twist of the cantilever as it slides at a 90° angle to the cantilever axis. In a representative friction experiment, the load is increased in discrete
steps from zero load to a maximum value and then back until the surfaces are separated from each other (to measure any adhesive contributions). The slow scan axis is often disabled, meaning that the cantilever slides back and forward (commonly denoted trace and retrace) in only one coordinate until a contact mode friction image has been obtained. The corresponding response from this movement produces output signals with opposite signs that reflect the lateral deflection. Images for trace and retrace are therefore subtracted from each other to obtain an averaged output voltage, $\Delta V$, from the resulting data points. The lateral deflection is converted to a friction force, $F_F$, using the following equation:

$$F_F = \frac{\Delta V \cdot k_\phi}{2 \cdot h_{\text{eff}} \cdot \delta}$$

where $k_\phi$ is the torsional spring constant, $h_{\text{eff}}$ is the effective height (diameter of probe plus half the thickness of the cantilever) and $\delta$ is the lateral deflection sensitivity (extracted using the methods in ref\textsuperscript{164, 168}). Typical scan sizes were 1-5 μm in this work with 256-512 points per line and 16-32 lines in total for each contact mode image in a friction experiment. A friction coefficient was extracted from such an experiment as the quotient between lateral and normal forces if they showed a linear dependence (Equation 5). The friction data was processed using the FrictionIT v.2.6.4 software (ForceIT, Sweden).

## 3.2 Quartz crystal microbalance

### 3.2.1 General

A piezoelectric quartz crystal, with metal electrodes deposited on each side, forms the basis of a quartz crystal microbalance (QCM). The crystal is connected to an externally driven oscillator circuit via the metal electrodes so an alternating voltage can be applied over the crystal. The electric field induces the crystal to vibrate at resonance frequency, which is (at least partly) dependent on the crystal
thickness. Loading/unloading a material or fluid at the crystal surface will therefore change the resonance frequency of the crystal, which can be detected by the instrument. A typical AT-cut QCM-crystal resonates at 5-10 MHz and can detect frequency changes below 0.01 Hz, resulting in a highly sensitive technique. The change in resonance frequency, $\Delta f$, is often converted to changes in mass at the surface and the most common approach is the Sauerbrey equation:

$$\Delta f = -\frac{2 f_0^2 \Delta m}{\rho_q v \eta A}$$  \hspace{1cm} (11)

where $f_0$ is the resonance frequency of the crystal, $\Delta m$ the mass change, $\rho_q$ the density of quartz, $v$ the shear wave velocity in quartz, and $A$ the electrode area. It is often rewritten as:

$$\Delta f = -C \Delta m$$  \hspace{1cm} (12)

where $C$ is a constant based on the crystal properties. The equation has some limitations and should only be used if $\Delta f$ is less than 2 % of the crystal’s resonance frequency. It is also assumed that the deposited mass of material or fluid adsorbs evenly and forming a rigid layer. The equation is therefore not suitable for systems with structural flexibility and viscoelastic properties. Other more accurate models have thus been proposed, such as the Johannsmann model, where several overtones are used to derive the sensed mass from a fitted linear line. However, no model correctly accounts for trapped solvent. For example, water can be trapped in an adsorbed layer and is thus included in the overall mass change measured by the QCM. Complimentary techniques, such as ellipsometry, must therefore be used to obtain quantitative data as they are sensitive to the adsorbate alone.
Viscoelasticity is a measure of energy loss and can be measured in a QCM by driving the crystal with an A/C current at resonance frequency. When the current is turned off, the oscillation will be damped, resulting in a sinusoidal curve which can be analysed to extract the dissipation (energy losses). Measured dissipation values for viscoelastic systems will be higher due to greater damping of the crystal oscillations. This technique is called QCM-D and is common for studies of biomolecules, where the dissipation can be high (mainly a viscoelastic adsorbed layer) but is also useful for adsorption studies of other systems.\textsuperscript{174-176}

A QCM is sensitive not only to changes in adsorbed mass but also changes in viscosity and density of fluids. This must be taken into account when performing adsorption studies as it can greatly affect the outcome of the experiment. The frequency change when a crystal is exposed to a fluid from vacuum is calculated according to:\textsuperscript{177}

\[ \Delta f = -\frac{\sqrt{f_0}}{2\sqrt{\pi} t_q \rho_q} \sqrt{\rho_f \eta_f} \]  \hspace{1cm} (13)

where \( \rho_f \) and \( \eta_f \) are the density and viscosity of the fluid, respectively, and \( t_q \) is the thickness of the crystal. The corresponding change in dissipation, \( \Delta D \), is:

\[ \Delta D = \frac{1}{\sqrt{\pi f_0 t_q \rho_q}} \sqrt{\rho_f \eta_f} \]  \hspace{1cm} (14)

These equations were used in Paper V to discriminate between changes in adsorbed mass from changes in bulk properties of the solutions used.

### 3.2.2 Electrochemical measurements

A custom-built electrochemical setup was coupled to an A100 or an A200 QCM-instrument from Attana AB (Stockholm, Sweden). The electrochemical setup is described in more detail in Paper IV. The 10 MHz QCM-crystals were sputtered with a 150 nm thick gold layer.
(Attana AB, Stockholm, Sweden) and have an area of 15.9 mm$^2$. Gold was used as the working electrode and the quasi-reference electrode was a 0.15 or 0.25 mm thick Pt-wire. After complete assembly and injection of the studied fluid, the system was left to equilibrate overnight and the drift at the start of an experiment was at or below 0.2 Hz min$^{-1}$. The system was allowed to relax between applied potentials so that any surface change was permitted to stabilise. To convert observed frequency changes to changes in mass per area, the Sauerbrey equation (Equation 12) was used where the constant $C$ was equal to 0.23 Hz ng$^{-1}$ cm$^2$ for the crystals used.$^{171}$

3.2.3 Concentration measurements

A Q-Sense E4 QCM-D from Biolin Scientific (Gothenburg, Sweden) was used with gold plated AT-cut 5 MHz crystals for the concentration studies in Paper V. Coupled to the cell was a Q-Sense Flow module (QFM 401) and parts in contact with sample liquid were made from either titanium or Vitron®. The frequency and dissipation changes were monitored for six different concentrations of the IL (0.5, 1, 2, 3, 4, and 5 wt%) in oil. When the neat oil had stabilised in the cell, the IL-solution was injected until the frequency and dissipation changes plateaued, after which the system was rinsed with neat oil again and the procedure was repeated with a higher concentration of the IL-solution. Due to the large viscosity of the solutions only the 3$^{rd}$ overtone oscillated properly.
4 Materials

A MilliQ-unit (Millipore, Molsheim, France) was used to purify all water used in this thesis to a resistivity of 18.2 MΩ cm except in Paper II where reverse osmosis water was used. EAN and EtAN were synthesised by drop-wise addition of an ethylamine or ethanolamine solution to nitric acid under constant agitation. Ethylamine, ethanolamine and nitric acid were acquired from Sigma Aldrich (Munich, Germany). The reaction vessels were kept in an ice bath at temperatures below 283 K to prevent oxide formation. Excess water was removed by rotary evaporation for 2 h at elevated temperatures (313-323 K) followed by heating at 383 K in an oil bath under a nitrogen atmosphere for at least 12 h.

1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (EMIMFAP) was purchased from Merck in ultrapure quality and used as received. Luleå Tekniska Universitet (Luleå, Sweden) provided Trihexyltetradecylphosphonium bis(mandelato)borate (P_{6,6,6,14}BMB) and the polar oil, UCON OSP-46, was from Dow Corning. The water concentration of the neat ILs and [P_{6,6,6,14}][BMB] in oil were all measured using Karl-Fischer titration (Metrohm) and were below 0.1 wt% for EAN, 0.5 wt% for EtAN, 0.01 wt% for EMIMFAP and 0.5 wt% for P_{6,6,6,14}BMB in oil. Freshly cleaved mica was used as a surface for all AFM experiments. Figure 5 shows the ILs used in this work and physico-chemical properties are provided in Table 1.
Figure 5. Molecular structures of the ILs used in this work.
Table 1. Physico-chemical properties for EAN, EtAN, EMIMFAP, and P$_{6,6,6,14}$BMB at 298 K and 1 atm.

<table>
<thead>
<tr>
<th>Property</th>
<th>EAN</th>
<th>EtAN</th>
<th>EMIMFAP</th>
<th>P$_{6,6,6,14}$BMB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Clear, colourless</td>
<td>Clear, colourless</td>
<td>Clear, colourless</td>
<td>Clear, colourless</td>
</tr>
<tr>
<td>Molecular weight (g mol$^{-1}$)</td>
<td>108.1</td>
<td>124.1</td>
<td>556.2</td>
<td>795.0</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>13$^a$</td>
<td>-25.2$^a$ and 51$^c$</td>
<td>-1$^g$</td>
<td>&lt;-44$^j$</td>
</tr>
<tr>
<td>Density (g cm$^{-3}$)</td>
<td>1.21$^a$</td>
<td>1.39$^b$</td>
<td>1.71$^g$</td>
<td>1.01$^j$</td>
</tr>
<tr>
<td>Viscosity (Pa s)</td>
<td>0.032-0.04$^b$</td>
<td>0.15-0.16$^b$</td>
<td>0.07$^h$</td>
<td>7.18$^k$</td>
</tr>
<tr>
<td>Conductivity (S cm$^{-1}$)</td>
<td>26.9$^c$</td>
<td>9.35$^c$</td>
<td>0.05$^h$</td>
<td>10$^{-5}$$^j$</td>
</tr>
<tr>
<td>Diffusion coefficients (10$^{-11}$ m$^2$ s$^{-1}$)</td>
<td>EA$^+$ 3.9$^d$</td>
<td>N/A</td>
<td>EMIM$^+$ 2$^h$</td>
<td>P$_{6,6,6,14}^+$ 0.012$^l$</td>
</tr>
<tr>
<td></td>
<td>NO$_3^-$ 5.7$^d$</td>
<td></td>
<td>FAP$^-$ 1$^h$</td>
<td>BMB$^-$ 0.015$^l$</td>
</tr>
<tr>
<td>Electrochemical window (V)</td>
<td>2.7 vs. Pt$^e$</td>
<td>N/A</td>
<td>5 vs. Pt$^h$</td>
<td>N/A</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>26.3$^f$</td>
<td>60.9$^f$</td>
<td>12-14 for similar ILs$^i$</td>
<td>N/A</td>
</tr>
</tbody>
</table>

$^a$From ref$^{149}$, $^b$From ref$^{36}$, $^c$From ref$^{30}$, $^d$From ref$^{37}$, $^e$From ref$^{179}$, $^f$From ref$^{180}$, $^g$From ref$^{181}$, $^h$From ref$^{182}$, $^i$From ref$^{183}$, $^j$From ref$^{184}$, $^k$From ref$^{185}$, $^l$From ref$^{186}$, $^m$From ref$^{187}$
5 Results and discussion

5.1 The effect of temperature and Li\(^+\) on the interfacial layer

This section describes how the interfacial layer and dynamic properties of EAN (a common IL) respond to elevated temperatures (Paper I and III). Colloidal probe AFM and rheology were used to measure normal and friction forces as well as the viscosities of EAN. Additionally, in Paper II the addition of a lithium salt to EAN and EtAN was investigated using a similar approach. Both these ILs have been well characterised previously in terms of their bulk properties and structure, therefore they are good model molecules for fundamental research.\(^{11, 36, 37, 146, 149, 178}\)

Rheological measurements were performed on all solutions between 298 and 353 K (293 to 393 K for neat EAN, Paper III). The Arrhenius plots for the obtained data are shown in Figure 6 and reveal a linear dependence, indicating Arrhenius type behaviour (single activation energy). The shear viscosities were greatly reduced with increasing temperature and the data for the neat ILs is in good agreement with previous studies.\(^{36, 37, 178}\) In EtAN, the terminal hydrogen on the EAN cation has been replaced by a hydroxide group. This changes the properties significantly since the hydroxide groups disrupt the solvophobic interaction between the alkyl chains on the cation, resulting in a weaker nanostructure. However, the introduction of the hydrogen group allows for extra hydrogen-bonding and EtAN therefore forms denser hydrogen-bonding networks.\(^{26, 146}\) This affects the dynamic properties and the shear viscosity, for example, is four times higher for neat EtAN compared to neat EAN (Figure 6).\(^{36}\)
Figure 6. Shear viscosities as a function of temperature and salt concentration for a) EAN and b) EtAN. Note that the shear viscosities for neat EAN, 0.5 wt% LiNO₃ in EAN and 1 wt% LiNO₃ in EAN cannot be distinguished from each other.

The addition of Li⁺ to EAN had a negligible effect on the viscosity for low lithium ion concentrations (≤ 1 wt%) but at larger concentrations the viscosity increased (Figure 6a). At 10 wt% LiNO₃ in EAN and 298 K the viscosity was 70 mPa s compared to ~40 mPa s for neat EAN. This is presumably due to larger solid-like structures being formed as Li⁺ incorporates itself into the polar domains of EAN at higher concentrations and interacts strongly with nitrate ions. The weaker bulk structuring of EtAN influences the viscosity behaviour when Li⁺ is added. Even at small concentrations there was a
measureable difference in shear viscosity and at 10 wt% LiNO\textsubscript{3} in EtAN the viscosity was 2.5 times larger than for neat EtAN (Figure 6b). A recent article demonstrated that the bulk structure of EAN is largely unaffected with the addition of Li\textsuperscript{+} whereas EtAN’s bulk structure changes from a clustered morphology to a bicontinuous sponge.\textsuperscript{44} It was proposed that Li\textsuperscript{+} has easier access to the polar domain of EtAN compared to EAN because of the added hydroxide groups at the cation alkyl chains, facilitating the change in structure. It is therefore likely that a similar process explains the viscosity dependences observed here. However, it does not describe how these changes apply to the surface properties. AFM force and friction measurements were therefore performed as a function of temperature (EAN only) and LiNO\textsubscript{3} concentration.

5.1.1 Normal forces

Force measurements were conducted at different approach rates for neat EAN at 298 K (Figure 7). A repulsive force was encountered, which increased with decreasing separation and increased rate. These solutions have a large viscosity compared to many molecular liquids and, together with the rate-dependence, suggested that the repulsive forces have a fluid dynamic origin. The force curves in Figure 7 were analysed using Equation 7, which includes a correction factor for slip. Good fits were obtained using the bulk viscosity of EAN and a slip length of 18-20 nm (\textit{Paper I}). According to Equation 9, the introduction of a slip length suggests one of two things. Either there is a thick boundary layer with small differences between bulk and interfacial viscosity or a thin boundary layer with a large change in viscosity. At present there are no means to distinguish the two, however, the fluid dynamic force clearly masks other possible surface forces.
EAN forms well-defined layers at a surface, similar to the oscillatory solvation forces discussed in Chapter 2.2.1. Rather than squeezing out layers of “spherical” uncharged molecules from contact (Figure 3), these forces arise from squeezing out layers of ion-pairs. The discrete thicknesses are therefore related to the ion-pair diameter, which in EAN’s case is ~0.5 nm. However, the viscosity is high for EAN compared to many molecular liquids. The use of a probe also increases the effect of viscosity (Equation 7) but at elevated temperatures the shear viscosity is negligible (Figure 6). The temperature was thus increased to 323 and 353 K, respectively, to investigate the effect of temperature on the interfacial structure. Analogous force curves to those in Figure 7 were obtained and the force data in Figure 8 demonstrates that fluid dynamics no longer dominates. Instead, solvation forces are measured independent of the approach velocities used (force curves for more approach rates can be found in Paper I).

Figure 7. Force measured as a function of apparent separation for neat EAN at three approach rates.
Figure 8. Force profile for neat EAN at a) 323 K and b) 353 K. The data is averaged from 25 force curves and error bars are shown in the inset (zoomed in).

Two discrete steps were measured irrespective of temperature. The outermost step in Figure 8 (for both 323 and 353 K) is about 0.5 nm in width and can be ascribed to an ion-pair of EAN being squeezed out but the innermost step is only about half that size. This smaller step has been observed previously for this experimental setup and has been ascribed to an effect of a cation layer being squeezed out of the contact, likely from the silica colloidal probe since the EAN cation interacts strongly with mica. A fluid dynamic analysis was also performed on these force curves (Paper I), with an identical approach to that used at ambient temperature. The fits were good
and included a slip length that was independent of temperature. This demonstrated that the boundary layer formed from EAN was largely unaffected within this temperature range but small differences were detected in the solvation forces. For 323 K the steps were more vertical and the layers were removed at higher forces compared to at 353 K, suggesting a slight loss of order and compressibility due to increased thermal motion.

Remarkably, another force dominated at temperatures above 373 K. In Figure 9, the measured force is plotted on a logarithmic scale as a function of apparent separation at 393 K. The solvation forces measured at short separation were unaffected by the increase in temperature but there was a repulsive force extending approximately 10-12 nm away from the surface. The logarithmic scale on the y-axis revealed a linear dependence with separation, indicating an EDL force. At lower temperatures long-range forces were also measured but were rate-dependent fluid dynamic interactions. Furthermore, they decreased with increased temperature due to a reduction of EAN’s viscosity. At 393 K the viscosity of EAN is even lower so fluid dynamic interactions are negligible. The experimental force data at 393 K was fitted to Poisson-Boltzmann theory using the values in Figure 9 and the constant potential approximation. Figure 9 demonstrates that a good fit could be obtained from the force data with a decay length of 6.5 nm. This can be translated to a concentration of free ions at less than 1 mM and strongly suggests that the microscopic association behaviour of EAN changed. EDL forces have been measured only very recently for a few ILs and has been controversial due to the general view that ILs are largely un-associated ions, meaning such interactions should be screened because of the high ionic strengths (Equation 4).
Figure 9. Measured force vs. apparent separation for neat EAN at 393 K. The graph includes a fit to an electrical double layer force using the values included in the plot and the constant potential approximation.

The ionicity of ILs has been investigated and discussed in several previous studies, using a so-called Walden plot (Chapter 2.1). A Walden plot was therefore constructed (Figure 10) based on the viscosity values in Paper III and conductivity and density values extracted from the literature. Previous Walden plots for EAN have revealed a linear dependence between the logarithmic molar conductivity and the logarithmic inverse viscosity for modest changes in temperature, which is consistent with the data in Figure 10. However, starting at around 343 K, the relationship deviates from linearity and this deviation becomes more pronounced with increasing temperature. The deviation indicated that the conductivity of EAN is lower than expected from the Walden rule, which is likely due to a change in ion association.
Examples of ion associations include the formation of neutral ion-pairs, ionic clusters and aggregates. All of these could explain the deviation but they cannot be individually distinguished based on the Walden plot. More importantly, although revealing a deviation, the fraction of ion association suggested from the Walden plot is much smaller than what is suggested from the decay length in Figure 9. No absolute value can be extracted from the plot but the magnitude of the deviation is relatively small. This indicates a modest change in EAN’s association behaviour whereas the force data suggests a large change. However, the approaches are not directly comparable because the force data is based on a measurement of quasi-static thermodynamics whereas the Walden plot is derived from dynamic properties. Dielectric spectroscopy has previously been used to investigate the ionicity of EAN. The first study indicated that 92% of the ions were dissociated, with the remaining ion association attributed to the hydrogen-bonds between anions and cations (EAN hydrogen-bonds extensively). In the second study there was no evidence of such formations at all and the discrepancy remains unclear but both studies were performed in a limited temperature range: 288-353 K and 278-338 K, respectively. Other studies have suggested the formation of larger EAN clusters but they were
ascribed to the proximity of a liquid-air interface. These AFM force measurement were carried out at 393 K, which is well below the boiling point of EAN. They were also performed in a sealed liquid cell, meaning there was no gas phase that could have caused this effect. Furthermore, an increase in temperature has been suggested to destabilise any associated structure but that is not commensurate with the data in Figure 7, Figure 8, and Figure 9 since these figures clearly show that the largest temperature induces the change in association. The microscopic association behaviour of EAN is thus unclear but clearly different at 393 K when compared to lower temperatures.

The effect of adding Li+ to EAN and EtAN on the boundary layer was studied at ambient temperature only. Previous data for neat EAN demonstrated that fluid dynamics were strong at this temperature due to the large viscosities (Figure 6 and Figure 7). The approach rate was thus greatly reduced in these AFM force measurements to suppress the influence of fluid dynamics (Chapter 3.1.3). In Figure 11, forces were measured for solutions of EAN and EtAN, with and without the addition of LiNO3. Solvation forces were present for both EAN and EtAN solutions but differed markedly in “appearance” when Li+ was introduced.
The data for neat EAN (Figure 11a) was similar to the force curves in Figure 8 and Figure 9 as well as previous studies. Two steps were observed at apparent separations of 0.3 and 0.8 nm. The width of the outermost step correlated with a layer of EAN ion-pairs being squeezed out of contact, whereas the innermost step corresponds to a layer of EAN cations removed from the colloidal probe.

Introducing small concentrations of Li$^+$ to EAN changed the force response slightly (Figure 11c). The width of the innermost layer appeared to be unaffected but the strength of the barrier was

**Figure 11.** Force profiles for a) EAN, b) EtAN, c) EAN + 1 wt% LiNO$_3$, d) EtAN + 1 wt% LiNO$_3$, e) EAN + 10 wt% LiNO$_3$, and f) EtAN + 10 wt% LiNO$_3$. 
increased. This could indicate that Li$^+$ is mixed into the layer or that surrounding Li$^+$ induces better packing of the layer. The steps further out however, broadened to about 0.8 nm in width compared to 0.5 nm for neat EAN. Li$^+$ is known to interact strongly with nitrate ions due to its localised charge and so the enlargement is likely an effect of lithium incorporating itself into the polar domain of EAN, forming larger ionic structures. The addition of Li$^+$ thus changed the near surface composition, indicating that Li$^+$ had positioned itself close to the surface. An alternative explanation for the increased strength of the innermost layer is the replacement of EAN cations with Li$^+$ but the width of the layer remained constant so this is unlikely. At higher lithium concentrations the outermost steps were unaffected in terms of width but the strengths of the barriers increased (Figure 11e). A hindrance component in the measured force, from an apparent separation of 0.8 nm into apparent contact, was also observed and could be a result of the much increased viscosity of the solution at this lithium concentration (Figure 6).

As shown in Figure 11b, the force profile for neat EtAN demonstrated two steps before apparent contact. Each step had a width of 0.55-0.6 nm and was consistent with the ion-pair diameter of EtAN. The viscosity of EtAN is larger than that of 10 wt% LiNO$_3$ in EAN (Figure 6) but no “viscous hindrance” was detected, suggesting a more intricate explanation for the behaviour observed in Figure 11c, which was likely related to the addition of salt. Furthermore, the final “half-step” measured for neat EAN was clearly missing. This could suggest that EtAN cations have less affinity for the surface(s), implying that weaker solvophobic forces are largely responsible for the layering on silica in that case. The rheology measurements in Figure 6 demonstrated that the viscosity of EtAN is strongly affected by the addition of Li$^+$ and a similar dependence is found here. At 1 wt% LiNO$_3$ in EtAN (Figure 11d), the steps have broadened and are of
similar width to what was observed for Li⁺ in EAN. However, at an apparent separation of 1.4 nm there is a continuous force component, similar to what was found for 10 wt% LiNO₃ in EAN (Figure 11c). Since this compression was absent from neat EtAN it suggests a possible interplay between increased viscosity and the addition of salt, which could affect the local viscosity or cause local rearrangements. The force profile in Figure 11d also revealed that there could be a small step at an apparent separation of 0.4 nm but the resolution was insufficient to be certain.

Larger lithium concentrations in EtAN revealed a similar behaviour to 1 wt% LiNO₃ in EtAN (Figure 11f), with negligible changes in step height and width. The (viscous) force component increased slightly in range and the small step observed close to contact for 1 wt% LiNO₃ in EtAN was absent. However, there was a weak step at an apparent separation of 3.2 nm, indicating an increased ordering since that step was missing for neat EtAN and lower salt concentrations. The interfacial layer for EtAN thus appeared to be more sensitive to structure changes with the addition of Li⁺, presumably due to the weaker bulk nanostructure for neat EtAN when compared to neat EAN.

### 5.1.2 Friction forces

The measured force curves for EAN as a function of temperature revealed that increased thermal motion reduced viscosity but solvation forces were still present (Figure 8, Figure 9 and Figure 11a). Furthermore, the addition of water has been shown to have little effect on the nanostructure for EAN in bulk and at the solid-liquid interface. Lithium ions introduced changes in the near surface structure at low concentrations but not the adsorbed layer, meaning a boundary layer was present, preventing direct contact between the two surfaces.
To investigate the robustness of EAN’s boundary layer frictional forces were measured as a function of load at three temperatures (Figure 12). The load was increased step-wise from zero to a maximum pre-set value and then decreased until the two surfaces were no longer in contact. The hysteresis on loading/unloading was small overall and the data points were therefore averaged out for clarity. The friction dependence at room temperature was similar to previous observations, with two regions separated by a transition. There is an energetic penalty in squeezing out the near surface layer because of solvophobic interactions between the cation alkyl chains, which causes this transition.

**Figure 12.** Frictional forces for EAN as a function of load at three temperatures.

Increasing the temperature leaves the regions unaffected but reduces the absolute friction force. The transition onset from one region to the other was comparable at all temperatures and corresponds to the final step in the solvation forces measured for 323 and 353 K (Figure 8). There was no such transition for the step at an apparent separation of ~0.8 nm, which was presumably due to the measured friction forces being very small at that load. Equation 5 was used to extract a friction coefficient from the linear high load region which
was largely independent of temperature. This data was also consistent with the observation that the steps in Figure 8 appear to be largely insensitive to rate and temperature, decisively demonstrating that the boundary layer properties for EAN were preserved in the studied temperature range.

Friction measurements were also performed as a function of lithium concentration for both EAN and EtAN (Figure 13). The hysteresis on loading/unloading was small for all solutions and the data was therefore averaged between loading and unloading. Note that a different source of silica probe was used in this study, which prevents direct comparison of neat EAN in Figure 12 and Figure 13. Nevertheless, the trends were similar and the onset of the transition correlated to the innermost barrier in Figure 11a. At 1 wt% LiNO₃ in EAN the onset was shifted to lower loads, correlating with the step at 1.1 nm instead of the innermost barrier in Figure 11c. The transition was also less steep than for neat EAN, suggesting a more compressible layer. Presumably this was caused by the larger ionic structures formed in the near surface layer. At larger loads the friction force was comparable between neat EAN and 1 wt% LiNO₃. This indicates that the adsorbed layer was unaffected, as suggested from the force curves (a and c in Figure 11). The frictional forces for 10 wt% LiNO₃ in EAN were markedly different compared to neat EAN. There were two transitions that correlated well to the steps in Figure 11e. The friction force was larger than for neat EAN at low loads, seemingly due to the larger salt concentration inducing more order in the ionic structures. At larger loads the friction force was also higher than for either neat EAN or 1 wt% LiNO₃ in EAN, suggesting a different (if any) adsorbed layer on the surface. The friction coefficient also increased by ~30%.
The frictional forces for EtAN solutions, with and without added Li$^+$ are shown in Figure 13b. Neat EtAN demonstrated a behaviour similar to neat EAN, with two separate regions and a sharp transition. The friction coefficient extracted from the linear region at large loads was higher than that measured for neat EAN. Interestingly, the load at the transition point correlated with “apparent contact” in Figure 11b, indicating that a larger applied load was needed to reach zero separation.

For 1 wt% LiNO$_3$ added to EtAN, the absolute friction force was significantly lower than for neat EtAN at large loads and the sharp
transition observed for neat EtAN was much less pronounced, presumably due to the changed surface composition. The force profile in Figure 11d revealed a possible step at 0.4 nm and since the applied load matches the transition point in Figure 13b it seems likely that this step is significant. The changed friction behaviour suggests that the boundary layer was modified, especially at large loads. Increasing the salt concentration in EtAN revealed that the friction forces were similar to 1 wt% LiNO₃ in EtAN at large loads but deviated at lower loads. The transition point was at a much lower load, corresponding to the step before the (viscous) hindrance started, demonstrating a change in surface composition.

Finally, a negligible amount of salt was added to EtAN to investigate the sensitivity towards the addition of Li⁺. The measured friction data showed that even 0.001 wt% LiNO₃ in EtAN was enough to change the boundary layer, meaning EtAN’s interfacial structure was incredibly sensitive to Li⁺ (Paper II).

5.2 Electro-responsiveness of the interfacial layer

The resonance frequency of a QCM-crystal is sensitive to differences in a fluid’s density and viscosity, adsorption or desorption of a solute molecule or changes in fluid composition at or near the surface due to external influences. Some of these points are illustrated in Paper V and the complexity of decoupling frequency responses arising from adsorption/desorption and changes in a fluid’s density and viscosity are discussed. The response of the QCM is generally registered as a function of time and the sensitivity decays exponentially away from the crystal surface.¹⁷⁰ This section describes how the surface composition of a neat IL (EMIMFAP, Paper IV) or two concentrations of an IL (P₆,₆,₆,₁₄BMB, Paper V) dissolved in a polar oil responded to polarisation.
5.2.1 Mass change as a function of potential

Figure 14 shows a (typical) graph of frequency change plotted against time for neat oil (solid, thin line) and oil + IL (solid, thick line) when exposed to a potential. Neat oil demonstrated no change in response from an applied potential at \( t=0 \) regardless of sign and magnitude. Conversely, there was a marked change in frequency with the addition of \( \text{P}_{6,6,6,14}\text{BMB} \) to the oil. The response revealed a significant change immediately upon polarisation that eventually reached a plateau, after which no changes were recorded. This implied that the IL caused the response and, since the bulk concentration was low, that an enriched layer was adsorbed to the surface. Neat EMIMFAP demonstrated a similar behaviour to \( \text{P}_{6,6,6,14}\text{BMB} \) in oil and always responded to polarisation (Paper IV). The relaxation of the system upon extinguishing the applied potentials reversed the frequency changes with a comparable value. Positive polarisation always resulted in a positive frequency change, which increased as the magnitude of the potential increased and negative polarisations demonstrated a reverse behaviour. These trends were observed for both neat EMIMFAP and \( \text{P}_{6,6,6,14}\text{BMB} \) dissolved in oil.

![Graph showing QCM responses](image)

**Figure 14.** Typical QCM responses, where a frequency change was observed for IL + oil upon polarisation (thickest line) and relaxation (thinnest line) and no change recorded for neat oil (intermediary line). The potentials were applied or turned off at \( t=0 \).
Sauerbrey’s equation was used to transform frequency changes at the plateaus to changes in mass (Equation 11). To facilitate data interpretation from all potentials, the mass change was plotted against applied potential, as shown in Figure 15 (EMIMFAP) and Figure 16 (P_{6,6,6,14}BMB). Only negative potentials are shown between 0 and -2 V for EMIMFAP. The results revealed a net mass loss which increased with increasing magnitude of the potential. Conversely, positive potentials (not shown) demonstrated a mass gain. For P_{6,6,6,14}BMB, potentials were explored between 0 and ±1.5 V. Figure 16 displays the mass changes against the magnitude of the potential for 3 and 5 wt% P_{6,6,6,14}BMB in a polar oil. The graph includes the response from applying a potential as well as turning it off. Good reversibility was achieved for both negative and positive potentials. The results also demonstrated an increasing response with a larger magnitude of potential. Moreover, the changes for both concentrations were similar except at large positive potentials where 5 wt% increased more rapidly. The zero response was shifted to positive potentials in Figure 16, suggesting that the BMB anion was less surface active than the P_{6,6,6,14} cation at zero applied potential. The responses for 3 and 5 wt% at negative potentials overlapped, indicating that the adsorption of the P_{6,6,6,14} cation had reached saturation. The lesser surface activity for the BMB anion, however, suggests that saturation had not been reached, thus explaining the deviation.
Figure 15. Recorded mass changes as a function of negatively applied potentials for neat EMIMFAP.

Figure 16. Observed mass changes as a function of applied potential for 3 and 5 wt% P_{6,6,6,14}BMB in a polar oil. The graph reveals the mass changes both when applying the potential and turning it off.
Based on the results from both these studies, a simple physical model was proposed to explain the mass changes self-consistently for both EMIMFAP and P$_{6,6,6,14}$BMB. (In Paper IV a simpler model was proposed consistent with the observations, however, this approach was incapable of explaining the data in Paper V so a refined model was developed which satisfactorily explained the observations in both papers.) The model takes into account both electroneutrality and the density of the species. When a surface is polarised it will expel the coions from the adsorbed layer but this creates voids that must be filled. The interfacial region is already neutralised so statistically these vacancies will be replaced by equal numbers of cations and anions to preserve electroneutrality. For EMIMFAP, the density of the FAP anion is larger than that of the EMIM cation and the contrast is therefore provided from density differences ($\rho_{\text{anion}} > \rho_{\text{IL}} > \rho_{\text{cation}}$). The expulsion of FAP anions (negative potentials) and subsequent filling of empty spaces with bulk IL would result in a net mass loss and vice versa if the EMIM cation is expelled. The physical model works equally well for P$_{6,6,6,14}$BMB, where the P$_{6,6,6,14}$ cation is heavier than the BMB anion but the density is lower due to the sheer size of the cation ($\rho_{\text{anion}} > \rho_{\text{IL}} > \rho_{\text{cation}}$). This means that at positive potentials the P$_{6,6,6,14}$ cation is replaced by the denser bulk and results in a net mass gain and vice versa for negative potentials. The QCM thus responds to a similar density contrast for both ILs but of course with different density values (Table 1).

Applying a potential caused an imbalance of negative and positive ions in the interfacial region for EMIMFAP and P$_{6,6,6,14}$BMB in oil. Extinguishing the applied potential thus required coions to migrate back to the surface to restore electroneutrality. This process was also monitored for each potential. Figure 17 shows the mass change plotted as a function of $t^{1/2}$ for EMIMFAP. The responses were linear with $t^{1/2}$, demonstrating a diffusion driven process. In Figure 17, the
gradient was twice as steep when extinguishing the positive potential compared to the negative potential. A previous study found the self-diffusion coefficients for EMIM$^+$ and FAP$^-$ to be $2 \times 10^{-11}$ and $1 \times 10^{-11}$ m$^2$ s$^{-1}$, respectively.$^{183}$ This reflects their difference in size and the factor of two ratio between the relaxation gradients therefore were consistent with the ratio from literature values. The relaxation is clearly driven by the coion migrating back to the surface since the steepest ratio was observed for turning off the positive potential, where the faster cation would be diffusing back to the surface. This observation thus fully agrees with the physical model described earlier.

Figure 17. Mass change monitored as a function of $t^{1/2}$ for EMIMFAP upon relaxation from applied potentials of $\pm 1$V.

In Chapter 5.1 the selectivity of lithium ions for the surface, despite their very low concentration, was demonstrated using a surface force approach. This affinity depended strongly on the nature of the cation with which it competed, as demonstrated by the fact that only small changes in the cation structure dramatically changed the surface selectivity. This would tend to indicate that the size of the ions, in comparison to the area per charge on the surface, was important. The addition of a lithium salt to EMIMFAP in the QCM measurements
fulfilled two objectives. Firstly, since this approach was completely novel, there was no guarantee that the observed changes in mass signal were not caused by impurities. The addition of small amounts of a lithium salt thus modelled the effect of impurities and indirectly demonstrated the hypothesis that the observed mass changes were indeed due to diffusion based ion exchange of the IL constituent ions. The non-monotonicity of the data in Figure 18 shows how an impurity would likely affect the data in a competitive fashion. Indirectly it supports the affinity argument of small ions since upon the applied potential the mass change initially corresponds to an increased surface population of large anions, but the gradient suddenly reversed sign, as the much lighter, and much scarcer nitrate ions diffused to the surface.

Figure 18. Mass response against time for EMIMFAP + 0.1 wt% LiNO₃ at +1 V applied potential.

The relaxation behaviour was also investigated for P₆,₆,₆,₁₄BMB in oil. A plot displaying mass change as a function of $t^{1/2}$ is shown in Figure 19a. The data revealed a linear relationship for this system, demonstrating the relaxation to be diffusion dependent. The mass change was faster for negative potentials at ±750 mV, suggesting that the self-diffusion coefficient was slightly faster for the anion. In a
previous study, diffusion NMR revealed that the self-diffusion coefficients for [P$_{6,6,6,14}$]$^+$ and [BMB]$^-$ were similar but that the anion diffuses faster (Table 1). The trend observed in Figure 19a was therefore consistent with the measured self-diffusion coefficients and with the observations for the neat IL in Figure 17.

**Figure 19.**

a) Mass changes recorded for 5 wt% P$_{6,6,6,14}$BMB in oil upon relaxation from ±750 mV applied potentials. The response was plotted as a function of $t^{1/2}$. b) Linear slopes were extracted from all investigated potentials ($k$-values) and then plotted as a function of applied potential in the main graph. Note that the absolute values are used on the x-axis.
A larger range of potentials were also explored upon relaxation for this system and in Figure 19b the $k$-values (extracted linear slope from each potential) are plotted as a function of both positive and negative potentials. The response increased (almost) linearly with increasing potential irrespective of sign. This indicated that more coions were affected at increased potential, which therefore introduced a larger concentration gradient. As a consequence, the rate of diffusion increased and explains the steeper slopes in Figure 19b. Furthermore, the ratios between these slopes were consistent with the observation made from Figure 19a. Moreover, the proposed physical model describing the coion being expelled upon polarisation was strengthened by the relaxation data from both ILs.

5.2.2 Capacitance effect on the potential

Additionally, the potential decay was recorded as a function of time between the gold surface and Pt-wire upon relaxation. Figure 20 shows the measured potential as a function of $t^{1/2}$ for three different voltages during EMIMFAP relaxation. The lowest potential is also shown in the inset for clarification. All potentials revealed an exponential decay with $t^{1/2}$, which was indicated by a fitted line for each voltage, demonstrating a diffusion dependence similar to the mass relaxation. A similar approach was performed on data of the monitored potential vs. $t$ but this demonstrated a poor fit. At $t=0$ the potential values corresponded to that of the applied potential and the discharge equation for capacitors was therefore applicable to these results:

$$V = V_0 \cdot \exp \left[ -\frac{t}{RC} \right]$$

where $V$ is the observed potential, $V_0$ is the starting potential, $t$ is time, $R$ is the resistance and $C$ is the capacitance. Still, the data in Figure 20 revealed a $t^{1/2}$-dependence rather than an exponential decay vs. $t$. However, this was resolved by recognising the $t^{1/2}$-
dependence in charge transport (Figure 17 and Figure 19). Furthermore, the capacitance at \( t=0 \) is equal to \( Q_0/V_0 \), where \( Q_0 \) is the equivalent surface charge. The equation thus reads as:

\[
V = V_0 \cdot e^{\left(-\sqrt{tV_0}/RQ_0\right)}
\]  

(15)

Exponential decay data plotted in Figure 20 therefore revealed the capacitance charge on the surface at \( t=0 \), normalised to the resistance over the cell.

![Figure 20](image)

**Figure 20.** Recorded potential as a function of \( t^{1/2} \) upon relaxation for EMIMFAP at three different voltages: -0.2 V (squares and inset), -0.8 V (points) and -1.2 V (triangles). Note that the absolute values are used on the y-axis.

The same approach was used for P\(_{6,6,6,14}\)BMB in oil and Figure 21 displays the result for three negative voltages. Recorded potentials were plotted as a function of \( t^{1/2} \) and demonstrated a large initial drop in potential that resulted in a poorly fitted exponential decay, irrespective of magnitude and polarity. The neat EMIMFAP behaved as an ideal capacitor but the relaxation observed in Figure 21 indicated the involvement of another process, which was caused by the oil having a lower conductivity than P\(_{6,6,6,14}\)BMB. This difference in conductivity means an increase in resistance for the capacitive current, *i.e.* an IR-drop over the cell, resulting in an immediate drop.
in potential. In the inset of Figure 21 the first data point was therefore excluded from the exponential fit. The system then demonstrated the behaviour of an ideal capacitor with good fits and the surface charge could then be extracted at \( t=0 \), analogously to EMIMFAP.

![Figure 21](image)

**Figure 21.** Observed potentials for 5 wt% P\(_{6,6,6,14}\)BMB in oil plotted versus \( t^{1/2} \) at -0.5 V (triangles), -1 V (squares), and -1.5 V (points). The data point at \( t=0 \) is discarded from the fit in the inset. Note that the absolute values are used on the y-axis.

### 5.2.3 Quantitative analysis of the surface composition

Consequently, two independent methods were used to approach the charge, which allowed for a quantitative analysis. The mass change values in Figure 15 and Figure 16 were converted to “mass charge” using the difference in densities between the bulk IL, cation and anion (Paper V). (Values for EMIMFAP were recalculated using ref\(^{98}\).) “Capacitance charges” were extracted from each potential by the combination of Equation 15 with the data in Figure 20 and Figure 21. Figure 22 and Figure 23 show plots displaying the changes in “mass charges” on the surface against the “capacitance charges”. Note that a QCM responds to changes in resonance frequency and so it is not the total mass being measured but the changes in adsorbed mass. The data in Figure 22 reflects the enrichment of EMIM cations
as the magnitude of the negative potential was increased. Previous studies have proposed that the imidazolium ion adsorbs with the aromatic ring parallel to surfaces.\textsuperscript{199-201} Additionally, since the size of an EMIM cation is known the charge density of one monolayer of EMIM cations could be estimated at 50-60 µC cm\textsuperscript{-2}.\textsuperscript{151} This value can change if the ring adopts another conformation or if the alkyl chains point away from the surface. For example, a simulation study found that at large negative potentials the aromatic ring adsorbed perpendicularly to the surface to maximise the charge interaction.\textsuperscript{113} The maximum change in mass charge measured for EMIMFAP in Figure 22 was \textasciitilde15 µC cm\textsuperscript{-2} but there were also two different regions. At low surface charge (points) the slope was less steep than for larger surface charges (triangles) in terms of the change in mass charge. This could suggest that the cation changed conformation on the surface. Furthermore, the charge density of a cation monolayer is larger than what was measured here but the amount of cations on the surface prior to polarisation is unknown. It is therefore feasible to conclude that the cations were close to forming a full monolayer on the surface.

Figure 22. Changes in “mass charge” as a function of “capacitance charge” for EMIMFAP. The two different regions were fitted to separate straight lines.
For $P_{6,6,6,14}$BMB in a polar oil both positive and negative potentials were explored. At positive “capacitance charges” the anion was attracted to the surface. The surface area per anion was estimated at 65 Å² ($13 \, \text{Å} \times 5 \, \text{Å}$) by assuming that the anion adsorbed flat to the surface. This resulted in a charge density of 25 µC cm⁻² for a full monolayer of BMB anions but any configuration change of the BMB anion would increase that value. In Figure 23, the data for 3 and 5 wt% $P_{6,6,6,14}$BMB in oil deviated and the maximum value for 3 and 5 wt% were 24 and 48 µC cm⁻², respectively. This suggested that (at least) a full monolayer of BMB anions was formed for 5 wt% $P_{6,6,6,14}$BMB in oil. However, similarly to the EMIM cation, it is likely that the BMB anion has changed configuration (Figure 5). Furthermore, the reduced surface activity of the BMB anion suggested that they had not fully populated the surface for 3 wt% $P_{6,6,6,14}$BMB in oil. Rather there was some residual oil in the layer which somewhat obscured the bulk density and skewed the calculation. It is therefore not 5 wt% that deviated from expected behaviour but rather 3 wt%.

**Figure 23.** Demonstrating the changes in “mass charge” against “capacitance charge” for 3 and 5 wt% $P_{6,6,6,14}$BMB in a polar oil.
The changes in “mass charge” were very similar for 3 and 5 wt% P_{6,6,6,14}BMB in oil at negative surface potentials and reached a maximum of -25 µC cm^{-2}. Negative surface charges would attract the P_{6,6,6,14} cation but it was difficult to predict the projected surface area of the P_{6,6,6,14} cation due to its sheer size and complexity. However, since the volume of the P_{6,6,6,14} cation is more than a factor of two larger than the BMB anion a good assumption would be that the charge density of a full monolayer of P_{6,6,6,14} cations is lower than for BMB anions (Paper V). This, together with the identical responses in “mass charge” changes for both weight fractions, indicated that a full monolayer of P_{6,6,6,14} cations was formed on the surface. These results thus demonstrate that it is possible to tune the surface composition when polarising a system consisting of either neat IL or an IL dissolved in a polar oil.
6 Conclusion

In this thesis the effects of temperature, added salt and applied potentials on the interfacial layer of ILs have been studied. A major outcome of this work was the development of a novel method to study the electro-responsiveness of ionic liquids (ILs) at the solid-liquid interface using an electrochemical quartz crystal microbalance. Potentials were applied across different liquids and the responses monitored in real-time. Non-charged systems were unresponsive but neat IL or IL dissolved in a polar oil responded consistently to polarisation, where positive polarisations resulted in mass gains and vice versa. The electro-response for the studied systems was understood by considering both charge neutrality and the density of the species, which enabled the extraction of changes in charge occurring at the surface. By varying the magnitude of the applied potential it was demonstrated that the IL surface composition could be controlled. Thus providing an opportunity to optimise surface phenomena such as friction.

The time dependent behaviour of the mass changes upon relaxation was also considered. It could be demonstrated that the changes were diffusion limited and the relative diffusion coefficients of the anion and cation could be extracted from the measurements. Consequently, this novel tool not only provides a means to quantify the amount of charge, and its response to the changes in potential, but also the ability to study the potential induced kinetics in the near surface region. Moreover, by monitoring the diffusion limited potential decay an independent measure of the surface charge could be determined. This unique approach therefore enables quantitative analysis of surface compositions at different potentials for neat ILs and ILs dissolved in oils.
Additionally, the technique enabled surface selectivity and ion kinetics to be studied upon polarisation by adding a small amount of a lithium salt to a neat IL. By monitoring the response it could be demonstrated from the non-monotonic behaviour that, albeit strongly outnumbered by the IL, the smaller ions of the lithium salt diffused to the surface and replaced the larger IL. This demonstrated that the surface selectivity was sensitive to ion chemistry. Using atomic force microscopy, the surface selectivity was also explored for two other ILs, with similar ion compositions. Measured normal and lateral forces revealed that the addition of a lithium salt affected the interfacial structure differently depending on the ion composition. This was associated with the nanostructure of the ILs. Knowledge about the chemistry and kinetics of ions at the solid-liquid interface can therefore provide a path to tune systems to specific surface properties.

The effect of temperature on the interfacial structure of an IL was also studied using a surface force approach. By increasing the temperature from 298 to 353 K it was shown that both normal and lateral forces were temperature dependent. However, the change in forces were due to the significant reduction in viscosity and not a modification of the interfacial structure of the IL, which was largely preserved. Consequently, the boundary lubrication properties were maintained and indeed resilient towards elevated temperatures. Conventional base oils require additives to display such a behaviour, which highlights the potential of ILs as lubricants for use with mechanical components operating at a range of temperatures.
Remarkably, measured normal forces at 393 K for this IL revealed a repulsive double layer force, which was not detected at lower temperatures. The appearance of such a force indicates that the IL no longer behaved as a system consisting mostly of free ions, which supports a few reported studies in the literature. However, the microscopic association behaviour of this IL is switched on at a high temperature, which is opposite to the current working model and demonstrates the complexities of ILs. It also emphasises the difficulties of categorising ILs into a group with a common set of properties.

This work aimed to investigate the behaviour of ILs at the solid-liquid interface and the sensitivity of their surface compositions to external influences. The outlined results demonstrated that 1) the surface composition of ILs can be quantified as different potentials are applied, 2) the changes are not instantaneous and conformation changes of molecules at the surface affect the response, 3) the charge densities of the involved ions greatly affect the interfacial structure and competition exists in a two-component system and 4) the interfacial structure of an IL was maintained within the studied temperature range. The discipline has come a long way since Walden’s discovery a hundred years ago but further investigations at a fundamental level are required to understand the properties and behaviours of ILs at surfaces.
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8 References


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