Doctoral Thesis in Chemistry

Electro-Interfacial Composition Control by Ionic Liquid Technology

Nanostructure, Self-Assembly, and Friction

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Electro-Interfacial Composition Control by Ionic Liquid Technology

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Academic Dissertation which, with due permission of the KTH Royal Institute of Technology, is submitted for public defence for the Degree of Doctor of Philosophy on Friday the 1st March 2024, at 2:00 p.m. in F3, Lindstedtsvägen 26, Stockholm.
In loving memory of my late Grandmother,

XIULIAN GUO (1935-2021),

who inculcated integrity, bravery, and love for life in me.

**ABSTRACT**

Given the potential of ionic liquids (ILs) for batteries, supercapacitors and advanced lubricants, it is crucial to understand how electric fields affect the interfacial behaviour in IL-solvent systems and the intricate relationship between nanostructure and tribotronic properties. This thesis investigates the structural and compositional changes of ILs with different solvents at electrified interfaces.

The four papers constituting this thesis can be broadly divided into two studies. The first study outlines the electro-interfacial behaviour of various monocationic (MILs) and dicationic ILs (DILs) dispersed in propylene carbonate. Combining electrochemical quartz crystal microbalance, neutron reflectivity (EC-NR), and atomic force microscopy, a voltage-induced interphase transition from a self-assembled cation bilayer to a conventional electrical double-layer structure has been revealed in bis(oxalato)borate anion MILs. This interphase transition has not been observed in DILs, attributed to the dual charge centres reducing the segregation between polar and apolar domains of dications for self-assembly interaction.

The second study explores three MILs sharing the same phosphonium cation with varying orthoborate-based anions dissolved in 2-ethylhexyl laurate (2-EHL). EC-NR measurements reveal a solvent-rich interfacial corona layer and the subtlety of anion architecture in tuning electro-interfacial properties. Meanwhile, EC-NR has been used as a complementary probe to elucidate the nano-scale structural and compositional changes in the boundary films of IL/2-EHL systems with varying potentials, providing a direct link between the molecular controllability and macroscopic tribotronic performance studies.
This thesis contributes to the fundamental understanding of electro-interfacial behaviour and controllability of IL-solvent systems and offers valuable molecular insights for deploying these novel ILs as additives in advanced tribological and electrochemical contexts.

**Keywords:**

Ionic liquids, electrical double layer, self-assembly, electro-interfacial structure, tribotronics, supercapacitors, friction, lubrication
SAMMANFATTNING

Med tanke på potentialen hos jonvätskor (IL) för batterier, superkondensatorer och avancerade smörjmedel är det viktigt att förstå hur elektriska fält påverkar gränssytans beteende i IL-lösningsmedelssystem och det intrikata förhållandet mellan nanostrukturer och tribotroniska egenskaper. Denna avhandling undersöks strukturella och kompositionella förändringar av ILs med olika lösningsmedel vid elektrifierade gränssnitt.

Avhandlingen baseras på fyra artiklar och kan grovt delas i två bredare studier. Den första studien beskriver det elektro-interfaciala beteendet hos olika monokatjoniska (MILs) och dikatjoniska ILs (DILs) dispergerade i propylenkarbonat. Kombinationen av elektrokemisk kvartskristallmikro-balans, neutronreflektivitet (EC-NR) och atomkraftsmikroskopi har lett till avslöjande av en spänningsinducerad fasövergång från ett självassocierad katjonbilager till en konventionell elektrisk dubbelsiktsstruktur i MIL med bis(oxalato)boratanjon. Denna interfasövergång har inte observerats i DILs, vilket tillskrivs de dubbla laddningscentra som minskar segregeringen mellan polära och apolära domäner av dikationer för självvassoceringsinteraktion.

Den andra studien undersöker tre MIL som delar samma fosoniumkatjon med olika ortoboratbaserade anjoner löst i 2-ethylhexyllaurat (2-EHL). EC-NR-mätningar avslöjar ett lösningsmedelsrikt korona-skikt i gränssytan och hur anjonarkitekturen påverkar de elektro-interfaciala egenskaperna. Samtidigt har EC-NR belyst de nanoskaliga strukturella och kompositionella förändringarna i gränssikten i IL/2-EHL-system med varierande potentialer, vilket ger en direkt koppling av den
molekylära styrbarheten och makroskopiska tribotroniska prestandan.

Denna avhandling bidrar till den grundläggande förståelsen av elektro-interfacial beteende och styrbarhet hos IL-lösningsmedelssystem och erbjuder värdefulla molekylära insikter för att använda dessa nya IL som tillsatser i avancerade tribologiska och elektrokemiska sammanhang.

**NYCKELORD:**
Jonvätskor, elektriskt dubbelskikt, självassociering, gränsskikts-elektrostruktur, tribotronik, superkondensatorer, friktion, smörjning
LIST OF PUBLICATIONS

This thesis is based on the following papers:

I. Tuneable interphase transitions in ionic liquid/carrier systems via voltage control.


II. Anion architecture controls structure and electroresponsivity of anhalogenous ionic liquids in a sustainable fluid.


III. Dicationic versus monocationic non-halogenated ionic liquids in an organic solvent: nanostructure, and electro-intercalative crowding


IV. Tribotronic traction control through ionic boundary films: influence of cation architecture

CONTRIBUTION TO THE PAPERS

I. Methods development; all the reported measurements; analyses and data visualizations; original draft writing.

II. All the reported measurements; major part in analyses and data visualizations, except for the small-angle neutron scattering (SANS) measurements; major part of original draft writing.

III. Major part of the reported measurements, except for part of neutron reflectivity (NR) tests; major part in analyses and data visualizations, except for SANS measurements; major part of original draft writing.

IV. Part in reported measurements (NR works); NR data analyses and visualizations; part of original draft writing.

ADDITIONAL PUBLICATIONS

Papers not included in this thesis:

I. Molecular architecture effects on bulk nanostructure in bis (orthoborate) ionic liquids


II. Small-angle neutron scattering insights into 2-ethylhexyl laurate: a remarkable bio-ester

Hammond, O. S.; Morris, D. C.; Bousrez, G.; Li, S.; Campo, L. d.; Recsei, C.; Moir, M.; Glavatskih, S.; Rutland, M. W.; Mudring, A.-V. ACS Sustainable Chemistry & Engineering 2023, Accepted
NOMENCLATURE

Abbreviations

AC Alternating Current
AFM Atomic Force Microscopy
ANSTO Australian Nuclear Science and Technology Organisation
CE Counter Electrode
DILs Dicationic Ionic Liquids
EC-NR Electrochemical Neutron Reflectivity
EDL Electrical Double Layer
EIS Electrochemical Impedance Spectroscopy
EW Electrochemical Window
FOM Figure of Merit
FTO Fluorine-doped Tin Oxide
ILL Institut Laue-Langevin
ILs Ionic Liquids
MILs Monocationic Ionic Liquids
NR Neutron Reflectivity
PTFE Polytetrafluoroethylene
QCM Quartz Crystal Microbalance
RE Reference Electrode
SAILs Surface-active Ionic Liquids
SFA Surface Force Apparatus
SI Supplementary Information
SLD Scattering Length Density
TOF Time-of-flight
WE Working Electrode

Ionic Materials

[P_{4,4,4,14}][BOB] Tributyl(tetradecyl)phosphonium-bis(oxalate)borate
[P_{6,6,6,14}][BMB] Trihexyl(tetradecyl)phosphonium-bis(mandelato)borate
Trihexyl(tetradecyl)phosphonium-bis(oxalato)borate

Trihexyl(tetradecyl)phosphonium-bis(salicylato)borate

1,12-di(tributylphosphonium)dodecane

1,12-di(trihexylphosphonium)dodecane

1,12-di(trioctylphosphonium)dodecane

1,12-di(tributylphosphonium)dodecane dication

1,12-di(trihexylphosphonium)dodecane dication

1,12-di(trioctylphosphonium)dodecane dication

Bis(oxalato)borate anion

Bis(mandelato)borate anion

Bis(salicylato)borate anion

Propylene Carbonate

Non-deuterated 1,2-Propylene Carbonate

Perdeuterated 1,2-Propylene-\textit{d}_6 Carbonate

2-Ethylhexyl Laurate

Non-deuterated 2-Ethylhexyl Laurate

Perdeuterated 2-Ethylhexyl Laurate-\textit{d}_{40}

Melting point

Resonance frequency

Frequency change

Mass change

Density

Shear wave velocity

Surface area

Momentum transfer vector
\[ \theta \] Angle of incidence (and reflectance)
\[ \lambda \] Neutron wavelength
\[ n \] Neutron refractive index
\[ b \] Coherent scattering length
\[ F_f \] Friction force
\[ \Delta V \] Lateral voltage difference of photodiode
\[ k_{\phi} \] Torsional spring constant
\[ h_{\text{eff}} \] Effective height of the AFM tip
\[ k_N \] Spring constant of the cantilever
\[ L \] Cantilever length
\[ w \] Cantilever width
\[ G \] Shear modulus
\[ E \] Young’s modulus
\[ \dot{Z} \] Complex impedance
\[ Z' \] Real part of impedance
\[ Z'' \] Imaginary part of impedance
\[ \phi \] Diameter
\[ V_M \] Molecular volume
\[ \mu \] Friction coefficient
\[ \text{mol}\% \] Molar concentration
\[ \% \text{ w/w} \] Weight concentration

**Units**

\[ K \] Kelvin
\[ ^\circ C \] Degree Celsius
\[ \text{cP} \] Centipoise
\[ V \] Volt
\[ \text{Hz} \] Hertz
\[ \text{Å} \] Angstrom
\[ s \] Second
\[ \text{ng/cm}^2 \] Nanogram per square centimetre
\[ \text{nN} \] Nanonewton
\[ \text{g/cm}^3 \] Gram per cubic centimetre
\[ \mu \text{m}\cdot\text{s}^{-1} \] Micrometre per second
\[ \text{mV}\cdot\text{s}^{-1} \] Millivolt per second
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1. **Introduction**

Economic development has become increasingly inequitable and resource-intensive in recent years, exceeding the Earth’s finite capacity to sustain human well-being. The global emergencies of climate change, biodiversity loss, and pollution compel society to unite and collaborate in restoring and adapting to Earth’s capacity without surrendering hard-won development gains and respecting the legitimate aspirations of less affluent nations for improved living standards. In 2015, the United Nations introduced 17 sustainable development goals (SDGs) in the 2030 Agenda to address fundamental systemic obstacles to sustainable development. However, the realization of these SDGs is jeopardized by a series of escalating and interrelated environmental challenges. Traditional fossil fuels, such as oil, coal, and gas, continue to dominate global primary energy consumption (cf. Figure 1). Carbon dioxide (CO$_2$) emissions, primarily driven by global energy consumption, have continued to increase, reaching a new high of over 36.8 gigaton (Gt) in 2022. Addressing these challenges requires developing new materials, systems and technologies for energy storage and conversion, as well as reducing energy losses, for example in the generation and consumption of energy, all of which plays a crucial role.

As demand for electrification increases, ionic liquids (ILs)–innovative materials with unique and customisable physicochemical properties–have emerged as one of the critical enablers for sustainable chemistry, with applications spanning batteries, fuel and solar cells, supercapacitors, and lubrication. In particular, ILs, as versatile lubricants, excel in reducing friction and wear, contributing to a significant reduction in tribological contacts, which account for approximately 23% of total energy consumption. Furthermore, the remarkable electro-responsive behaviour of ILs has facilitated the development of advanced tribological systems using external electric fields, a concept termed “tribotronics”, making them promising additives for use in electric and hybrid electric vehicles. However,
the common use of halides in conventional ILs, including being part of one of the ions (especially anions) or as an impurity originating from the synthesis, poses challenges for commercialization due to their negative environmental impact, high production cost, and corrosion risk. Consequently, there is an increasing demand for innovative non-halogenated ILs to address these challenges.

![Figure 1. Development in global primary energy consumption by various sources since 1800. Data source: Energy Institute Statistical Review of World Energy (2023).](image)

This thesis focuses on the electro-interfacial structure and composition control in novel IL systems as part of the multidisciplinary project REFIT (cf. Figure 2), which aims to reduce friction through ionic technology. The nanoscale investigations conducted in this thesis offer essential molecular insights that hope to guide the development of more sustainable IL technologies for tribotronics and supercapacitors, thereby contributing to the following UN SDGs:

- Goal 7: Affordable and Clean Energy
- Goal 9: Industry, Innovation, and Infrastructure
- Goal 11: Sustainable Cities and Communities
- Goal 12: Responsible Consumption and Production
- Goal 13: Climate Action
1.1. Aim and scope

This thesis focuses on investigating the changes in solid-liquid interfacial composition and structure of various non-halogenated ILs dispersed in solvents under external electric fields by employing advanced surface characterization techniques. Considering their distinct interfacial electro-responsive behaviour, this study addresses various interfacial nanostructures formed by ILs at charged interfaces, including the conventional electrical double-layer (EDL) and self-assembled structures. In addition, this thesis identifies the influence of solvent and ion architecture on electro-interfacial properties. Furthermore, it investigates the correlation between the electro-interfacial structures and bulk organization of ILs, as well as their nanotribology and macro-scale tribotronic performance.

This thesis comprises the research from four papers: Paper I and Paper III explore the electro-interfacial structures of ILs with varied monocationic and dicationic architectures in a polar aprotic organic solvent, revealing a novel interphase transition between self-assembling bilayer and conventional EDL interfacial structures. Paper II investigates the electro-interfacial properties of similar monocationic ILs with varying anion structures in a biodegradable
lubrication oil, highlighting their potential for practical application in tribological systems. **Paper IV** extends this research methodology to a dicaticonic IL in the same biodegradable oil and examines the relationship between electro-interfacial nanostructures and macroscopic tribotronic performance.

### 1.2. Structure

This thesis is outlined as follows: The **Scientific Contexts** section briefly introduces the ILs and their nanostructures at the electrified interface, along with the methods for characterizing interfacial composition and structure. The **Research Approaches** section details the materials, experimental setup, and procedures. The ensuing **Results & Discussion** section summarises appended Papers I-IV concisely and critically. Lastly, the **Concluding Remarks** section outlines the major findings of this thesis and discusses **Future Prospects** for further investigation.
2. SCIENTIFIC CONTEXTS

2.1. Ionic liquids

2.1.1. What are ionic liquids and what are their properties

Ionic liquids (ILs) are commonly referred to as “molten salts” since they consist entirely of cations and anions. They typically exhibit melting points ($T_m$) below 373 K. In contrast to traditional (crystalline) salts such as sodium chloride, which exhibit significantly higher melting points over 1000 K, the low melting temperature of ILs is attributed to both entropic and enthalpic effects. The anisotropic and bulky size of their constituent ions (cations and anions) result in a highly nonuniform molecular charge density, leading not only to diminished electrostatic forces but also van der Waals, steric, and specific (e.g., hydrogen-bonding and self-assembly) interactions. The significant configurational entropy arising from the high degree of freedom in their flexible side groups also contributes to the low melting point of ILs. Although ILs have been known for over one century, beginning with ethylammonium nitrate reported by Paul Walden in 1914, their potential as tailored materials with unique and tuneable physicochemical properties was not appropriately recognised until the past three decades. Extensive literature, including books and reviews, has discussed the properties of ILs. The following paragraphs will briefly introduce some key characteristics of ILs pertinent to this thesis.

Generally, ILs exhibit good thermal stability, characterized by high decomposition and vaporization temperatures. Most ILs begin to decompose at temperatures exceeding 200-300 °C, as determined by both ramped temperature and isothermal thermogravimetric analysis. Furthermore, ILs typically have an even lower vapour pressure than traditional low vapour-pressure molecular solvents such as glycerol, within the 100-120 °C range. These high thermal stabilities are attributed to the strong electrostatic interactions...
between ions, which are more pronounced than in other molecular liquids. ILs typically possess much higher viscosities than water and most common organic solvents, usually ranging from 20 to 40000 cP at room temperature, compared to the latter’s 0.2-100 cP range. The high viscosity of ILs is a result of the many intermolecular interactions possible within ILs (e.g., van der Waals forces and hydrogen bonding) and is significantly influenced by the nature of both cations and anions. While the high viscosity of ILs can negatively impact certain industrial applications, such as processes involving heat and mass transfer operations, it can be preferable when using ILs as lubricants in high temperature and pressure conditions.

Another critical characteristic of ILs is their electrochemical properties. Due to their superior stability at electrified interfaces and wide electrochemical windows, ILs have occupied a vital position in the field of electric storage and conversion devices, such as batteries, solar cells, supercapacitors, and electrocatalysis. Generally, the electrochemical window (EW, i.e., the range between maximum oxidation and reduction potentials) for ILs can be up to 6 V, offering a higher energy density. However, despite their high ionicity, pure ILs exhibit relatively low conductivities due to their low ion mobility. The conductivity of ILs significantly depends on the structures of anions and cations, and can be enhanced by increasing temperature and mixing appropriate solvents.

2.1.2. Classification by structure

Classifying ILs with a single, rigid definition is challenging as multiple labels are appropriate depending on their structural features, functional groups, constituted elements, and properties. Nevertheless, a broad classification incorporating protic ILs, aprotic, and other subclasses has been established based on the proton-donating (protic) and nonproton-donating (aprotic) characteristics derived from molecular solvent systems.

Figure 3 shows the representative ion structures employed in ILs. Recently, the IL family’s diversity has expanded beyond monovalent
IL (e.g., monocationic ILs, MILs) to divalent ion (e.g., dicationic ILs, DILs), oligomer ILs, and even poly(ionic liquid)s (PILs). Compared to their monovalent counterparts, multi-valent ILs exhibit larger molecular weights, additional charge carriers, and increased intermolecular interactions, providing enhanced thermal and electrochemical stability, especially at higher temperatures. With these advantageous traits, DILs have been found in diverse technological applications, including catalysis, batteries, supercapacitors, and lubricants.

**Figure 3.** Representative ion structure for commonly used ILs. (Reproduced from Fedorov et al.)

From Figure 3, we can find halides are widely used in anions, such as bis(trifluoromethylsulfonyl)imide ([NTf₂]-) and hexafluorophosphate [PF₆]-, which bring adverse effects on the environment due to toxic and corrosive risks, particularly under high temperature and pressure. To address these issues, a series of novel non-halogenated ILs has been synthesized and developed. Meanwhile, given their promising potential in applications in tribotronic as well as batteries and supercapacitors, it is vital to acquire an understanding of the effect of electric fields on the interfacial structure and composition control in neat ILs or IL/solvent systems, as well as the intimate
relationship between their nanostructures and macro-scale properties, such as tribological performance and supercapacitance.

This thesis mainly addresses the electro-interfacial composition control and behaviour for innovative phosphonium orthoborate-based MILs and DILs in diverse base solvents, including propylene carbonate (PC) and 2-ethylhexyl laurate (2-EHL). Long alkyl chain phosphonium cations are acknowledged to have enhanced thermal stability, while the chelated orthoborate anions demonstrate anti-wear properties. This combination makes them effective in reducing friction and wear, thereby enhancing device lifespan and reducing energy consumption.52-54

2.1.3. Ionic liquids-solvent mixtures

In numerous applications and processes, ILs are employed not solely as pure liquids but as additives with various carriers, including water, organic solvents, base oil, etc.55 As mentioned, adding solvent to ILs can markedly decrease viscosity while concurrently enhancing conductivity and capacitance.56-58 In this thesis, “solvent” refers to any neutral molecular liquid introduced into the IL. The unique properties and performance of IL-solvent mixtures, in contrast to neat form, present a crucial research area.13

Simulation and experimental studies have recently reported a relatively large solvent fraction at the electrified interface in IL-solvent systems.59, 60 The properties of the solvent, such as its polarity, size, and structure, strongly influence the electro-interfacial structure and dynamics of IL-solvent systems.61 Meanwhile, IL-solvent systems exhibit a non-monotonic dependence on IL concentration for various properties, such as differential capacitance, electrostatic screening length, and long-range force. This contradicts classical electrolyte theories, though it is a controversial topic with ongoing debates. For example, Bozym et al. recently reported a maximum in differential capacitance as a function of the quantity of solvent, contrary to the Gouy–Chapman-Stern (GCS) theory.62 In addition, Smith et al. have reported a non-monotonic variation of the electrostatic screening
length with concentration in IL-solvent systems, in contrast to the Debye–Hückel theory. The main reasons for these deviations from dilute-solution electrolyte theories in the IL-solvent systems can be attributed to the following reasons: i, the ion is usually large and bulky for ILs, which cannot be neglected like in the classical mean-field Poisson-Boltzmann model; ii, neutral solvent molecules can act as effective charge carriers when steric packing frustration is dominated in highly concentrated solutions. Recently, the ion aggregation model was proposed to provide an alternative explanation for the surprisingly large decay length of the long-range force in the IL systems. Considering the bulky and asymmetric size of ions, ILs are assumed to be dielectric solvents composed of a strongly correlated ionic network that participates in charge screening, with only a small percentage of the network effectively dissociated. Consistent with this model, Espinosa-Marzal and colleagues have shown that the trace amounts of water in ILs impact the long range interaction force.

### 2.2. Ionic liquids at electrified interfaces

#### 2.2.1. Electric double layer

ILs primarily manifest in the interfacial region as an electrical double-layer (EDL) model at an electrified surface. This model has been evolved by Helmholtz, Gouy, Chapman, and Stern since a century ago in the context of ordinary inorganic electrolytic solutions. In the classic EDL model, the first layer (Stern or Helmholtz layer) is close to the electrified surface, mainly occupied by the electrostatically attracted counter-ions. The secondary layer is a diffusive region consisting of an exponentially decaying excess of counter-ions.
Figure 4. A schematic overview of interfacial ion arrangements as a function of potential, where $\kappa_{\text{Cation}}$ corresponds to negative surface charge density and $\kappa_{\text{Anion}}$ corresponds to positive surface charge density. (Reproduced with permission from Ivaništšev et al. Copyright 2014 Elsevier)

Compared to conventional electrolytic solutions, the nature and structure of the EDL for IL systems are more intricate than anticipated, constituting an ongoing debate topic in research for the past two decades. Several recent excellent reviews have provided an overview of the current state of EDL structures at the IL-electrode interface. The EDL structures in various IL (or IL-solvent) systems have been extensively studied using both molecular dynamic simulations and experimental techniques, such as surface force apparatus (SFA), atomic force microscopy (AFM), quartz crystal microbalance (QCM), electrochemical impedance spectroscopy (EIS), sum frequency generation spectroscopy (SFG), and scattering experiments. In addition, theoretical frameworks have been developed to describe the tuneable interfacial arrangement and structure of ILs at the electrified surface as a function of potential. These frameworks primarily involve checkerboard, overscreening, and crowding structures. Systems with strong electrostatic interactions between ions, like short-chain imidazolium-based ILs, display a checkerboard-type arrangement of
cations and anions at the surface (cf. Figure 4D). At low surface charge densities, the counterion boundary layer may overcompensate the surface charge, leading to an excess of co-ions in the subsequent layer, and could repeat several layers until electroneutrality is reached. This overcompensation results in the overscreening of the multilayer structure (cf. Figure 4C, F). With a more pronounced surface charge, the monolayer of counterions becomes inadequate to compensate for the surface charge. This results in a crowding structure of counterions beyond one ion diameter (cf. Figure 4A, H).

2.2.2. Self-assembly in ionic liquids

A newly recognized group of ILs, known as surface-active ILS (SAILs), has recently garnered attention. Typically, SAILs consist of surfactant-like ions featuring a polar (charged) headgroup and one or more lengthy apolar alkyl chains. The inherent amphiphilicity of SAILs grants them exceptional properties combining those of ILs and surfactants, forming long-range ordered nanostructures with polar and non-polar domains. Consequently, this well-defined self-assembly structure facilitates SAILs in a variety of applications such as electrochemical devices, and lubricants. The self-assembled nano-organization of SAIL in bulk has been extensively studied, whereas the investigation on SAIL electro-interfacial self-assembly structure is still in its infancy.

Earlier measurements using SFA by Perkin et al. revealed a structural transition from a monolayer to a bilayer in imidazolium- and pyrrolidinium-based SAILs with cations of varying alkyl chain lengths. The friction coefficient in \([C_{10}C_1Pyrr][NTf_2]\) was remarkably low on the sliding interface between two bilayer polar domains. Recently, Zhang et al. synthesized catanionic SAIL and studied how their nano-organization and electrochemical behaviour could be tuned by ionic structure using AFM and small angle X-ray scattering. The non-halogenated ILs investigated in this thesis also include a series of surface-active cations, exhibiting the self-assembly nanostructures both at the interface and in the bulk phase with solvent molecules. Further details will be presented in Section 4.
2.3.3 Ionic liquids for tribotronics

Since ILs were acknowledged as innovative and versatile lubricants with outstanding tribological performance compared to traditional synthetic lubricating oils in 2001,25 numerous multidisciplinary studies spanning machine design, material science, and surface chemistry, have explored the tribological properties and application of ILs.8 In addition to the previously mentioned physicochemical properties, ILs, either in neat form or as additives into lubrication oils, have shown a promising anti-wear capability by forming a surface-protective film in boundary and mixed lubrication regimes.54,58

**Figure 5.** Schematics of electrochemical SFA (a) and AFM (b) instrument set-ups for electro-interfacial structure and friction measurements. SFA employs two macroscopic substrates in crossed-cylinder geometry with large radii of curvature (left). The surfaces comprised silver (Ag) layers that acted as mirrors and electrodes behind mica sheets, which served as dielectric spacers. The surfaces can be either polarized symmetrically or asymmetrically. AFM involves a sharp tip interacting with a planar substrate with an optical feedback system. The externally applied fields are usually introduced to the
metal-coated planar substrate, with the tip electrically isolated. However, both SFA and AFM can incorporate various electrical and electrochemical configurations, including working (WE), reference (RE), and counter (CE) electrodes. More details related to electrochemical AFM will be provided in the following sections. The interfacial sketches of IL between asymmetrical polarizations of two mica surfaces separated by distance D with a lateral force $F_l$ in SFA (c) and between a tip and substrate electrode in AFM (d). (Reproduced with permission from Bresme et al.12 Copyright 2022 Springer Nature)

Owing to their fascinating electro-responsiveness, ILs and their mixture with solvents have recently provided a new avenue for nanoscale lubricity control through the electrical polarization of contact surfaces.12 The ILs (or ions) can strongly interact with an electrified solid surface to form a lubricating tribofilm with tunable composition and structure under different polarization biases. In 2008, Glavatskih et al. introduced the term “tribotronic” to describe the active control of advanced lubrication systems using electric fields.10 Recently, SFA equipped with real-time control of surface charges (cf. Figure 5) has been developed to study IL-based electro-nanotribological systems.93, 94 In addition, the interfacial structure and nanotribological performance of IL-based tribofilms have been extensively investigated with electrochemical AFM.11, 59, 83, 95

2.3. Interfacial characterization techniques

This section introduces theoretical aspects of interfacial characterization techniques employed in this thesis for investigating diverse IL/solvent systems. Quartz crystal microbalance, neutron reflectometry, and electrochemical impedance spectroscopy have been utilized to examine electro-interfacial responsiveness and compositional control under different electric fields. Atomic force microscopy has been applied to analyze the electro-nanotribological performance of IL/solvent systems.

2.3.1. Quartz crystal microbalance

The quartz crystal microbalance (QCM) is a surface-sensitive, in situ technique consisting of a quartz crystal sensor chip with conductive
electrode material coating on each side. It quantifies interfacial mass change. Due to its piezoelectricity, the quartz crystal exhibits a mechanical oscillation with resonance frequency driven by externally applied alternating electric fields via the coating electrode. The resonance frequency depends on the sensor chip design and the coupled mass of interfacial layers. Thus, the mass change of interfacial layers can be quantified through the measurable resonance frequency change using the Sauerbrey equation, expressed as:

\[ \Delta f = -\frac{2f_0^2 \Delta m}{\rho_q v} \frac{\Delta m}{A} = -C \frac{\Delta m}{A} \]  

(1)

Where \( f_0 \) is the resonance frequency of the quartz crystal, \( \rho_q \) the quartz crystal density, \( v \) the shear wave velocity of quartz. All these parameters are related to quartz crystal properties and could be unified as the constant \( (C) \). Additionally, \( \Delta m \) is the mass change, and \( A \) is the electrode area.

The Sauerbrey equation reveals a (reverse) linear relationship between the frequency change and mass change due to the absorbed amount. In other words, adding mass bound on the surface reduces the oscillation frequency and vice versa. QCM typically employs a sensor chip processed as an “AT-cut” to generate pure thickness shear mode oscillation, with the crystal’s two faces moving in an anti-parallel fashion. A standard AT-cut quartz crystal resonates in the MHz frequency range, detecting frequency changes below 0.01 Hz and ensuring a high mass change sensitivity in the ng/cm² range.

Although the Sauerbrey equation applies strictly to elastic and rigid absorbed layers, this approximation has been shown to be valid for IL/solvent systems. This is only true for constant fluid composition (i.e., viscosity and density of the bulk solution are unchanged). Thus, the slight frequency change observed in this thesis study, under the application of electric potentials, is attributed solely to ion exchange in the boundary layer. In this context, the Sauerbrey equation is a reasonable assumption for converting measured frequency change to mass change in ng/cm².
2.3.2. Neutron reflectometry

Neutron reflectometry, also known as neutron reflectivity (NR), has emerged as one of the powerful scattering techniques for investigating surfaces and interfaces.\textsuperscript{99} Despite the expanding growth of microscopy techniques, NR stands out as one of the few methods that simultaneously provides structural and compositional insights at the solid-liquid interface, encompassing the information of thickness (approximately from 5 to 5000 Å),\textsuperscript{100} density and interfacial roughness. Essential NR concepts will be briefly introduced here; further details on its principles and applications can be found in comprehensive books and reviews.\textsuperscript{101-105}

The principle involves measuring the reflection coefficient \( R \) of a neutron beam (\textit{i.e.}, the intensity ratio between the reflected and the incident beam) as a function of the incident angle and wavelength. Like the synchrotron beam, the fundamental components of neutron reflection comprise a radiation source, a wavelength selector (or choppers), a collimation system, the sample, and a detection system. Unlike X-rays interacting with electronic clouds, neutron-matter interaction directly involves neutron and atomic nuclei, providing several notable differences and advantages. With its short wavelength, NR achieves high resolution in the sub-nanometer range.\textsuperscript{106} Neutrons have an energy range of a few meV, much lower than the X-ray (keV), ensuring the non-destructive nature of NR.\textsuperscript{100} Moreover, neutrons exhibit high penetration due to weak absorption by other materials, making them suitable for studying buried interfaces that are inaccessible to many other techniques.\textsuperscript{99} Neutrons can interact with the magnetic moment of atoms, extending their polarised-NR capability for surface magnetism studies. Notably, neutrons are intrinsically sensitive to isotopes, facilitating contrast variation experiments where deuterium-labelled molecules create neutron contrasts in the system.\textsuperscript{100} These characteristics have rendered NR experiments vital for studying surfaces and interfaces over the past three decades.
NR is usually measured as a function of the momentum transfer vector $Q$, which is defined with the neutron wavelength and reflection angle as the following equation:

$$Q = \frac{4\pi \sin \theta}{\lambda}$$  

(2)

where $\theta$ represents the angle of incidence (and reflectance), and $\lambda$ is the neutron wavelength. Reflectivity measurements, based on the definition of $Q$, can be performed either by fixing $\lambda$ with varying $\theta$ or fixing $\theta$ with various $\lambda$. The former approach uses a wavelength selector (with the collimation system) to obtain a monochromatic and collimated neutron beam with fixed $\lambda$, and rotates the sample ($\theta$) and detector ($2\theta$) step by step. This monochromatic wavelength-based approach is widely utilized in nuclear reactor source beamlines. The latter method, known as the time-of-flight (TOF) model, is applicable in both spallation and reactor source beamlines equipped with a chopper system. The TOF model can cover a broad-spectrum $Q$ range at a fixed $\theta$ due to the varied $\lambda$ of a polychromatic beam. $Q$ is determined based on the arrival time of each neutron as a function of its wavelength. In this thesis, both modes of NR measurement have been applied depending on different instruments; the monochromatic mode is configured on SuperADAM at Institut Laue-Langevin (ILL) in Grenoble, France and the TOF mode is applied on Platypus at
The Australian Nuclear Science and Technology Organisation (ANSTO) in Sydney, Australia which will be given in more detail in Section 3.3.

The same law governs neutron reflection as light reflection, but the refractive index depends on the number of nuclei and their scattering strength. Therefore, the neutron refractive index \( n \) can be calculated using the coherent scattering length \( b \) of an isotope and its number density \( N \), expressed as:

\[
n = \sqrt{1 - \frac{\lambda^2}{\pi} N b} = \sqrt{1 - \frac{\lambda^2}{\pi} SLD}
\] (3)

The \( Nb \) represents the scattering length density (SLD). As mentioned previously, the coherent scattering length of a neutron for an element varies irregularly (either negative or positive) with the periodic table, contrary to the case of X-rays, which are always positive and proportional to the number of electrons. In particular, the coherent scattering length of hydrogen (H or \(^1\)H, -3.74 fm) is quite different value with an opposite sign than other constitutive organic elements (e.g., C, O, N), as well as from its isotopic deuterium (D or \(^2\)H, 6.67 fm). Thus, replacing hydrogen atoms in a molecule with deuterium atoms will significantly alter the refractive index without changing its physical properties. This essential and well-established strategy can be leveraged to achieve contrast match (i.e., enhance or render invisible) of specific constitutions in a complex system for neutron experiments. It is also possible to match the SLD of the solution with that of the solid substrate by adjusting the H/D ratio of the solution (i.e., using non-deuterated and deuterated solvents), giving a reflectivity profile that exclusively originates from the interfacial region.

2.3.3. Atomic force microscopy

Atomic force microscopy (AFM), a type of scanning probe microscopy (SPM), has proven highly versatile for surface analysis since its first demonstration in 1986. AFM provides high-resolution topographic imaging at the sub-nanometer scale in various environments and also contributes to the exploration of surface forces and nanotribological
studies. In this study, the lateral force measurements in contact mode were used to study the electro-nanotribological performance of IL/solvent systems under different external electric fields (cf. Section 4.1).

**Figure 7. Schematic representation of the operation principle of the AFM.**

The fundamental operational principle of a standard AFM with an optical feedback system involves scanning the AFM probe over the sample in a raster pattern. Figure 7 shows the general layout of the AFM system. The AFM probe, usually a sharp tip near the free end of a flexible cantilever, is controlled by a scanner with piezoelectric components, precisely adjusting the X-, Y-, and Z-positions relative to the surface. A laser focused on the rear of the cantilever reflects into a position-sensitive quartered photodiode. Changes in photodiode voltage indicate the deflection or twist of the cantilever (vertical or lateral movement, cf. Figure 7) in response to tip-sample interactions. Based on the nature of tip motion, the AFM operation mode can be divided into contact, tapping, and non-contact modes. The principles and detection mechanisms of these modes are well known, so they will not be overly described here; details can be found in the relevant
book\textsuperscript{113} or instrument manuals. The principles of friction and lateral force calibration involved in this thesis will be introduced below.

In the contact mode AFM, the cantilever slides back and forward with a scan line on the surface (\textit{i.e.}, perpendicularly to the cantilever axis). During the trace and retrace of sliding, the loaded cantilever twists in opposite directions, resulting in two different output signals from the photodiode (in terms of voltage) that reflect the lateral deflection. The difference of these output signals, $\Delta V$, can be converted to friction force ($F_f$) using the following equation:\textsuperscript{114,115}

$$F_f = \frac{\Delta V k_{\phi}}{2 h_{eff} \delta}$$

with $k_{\phi}$ denoting the torsional spring constant, $h_{eff}$ denoting the effective height of the AFM tip (corresponding to the height of the tip plus half the cantilever thickness), and $\delta$ denoting the lateral sensitivity of the AFM photodiode determined by the photodetector calibration.\textsuperscript{116} The torsional spring constant $k_{\phi}$ is determined using a hybrid method that has been recently developed, which combines the Sader method with an approximation based on the plate theory, expressed as:\textsuperscript{117}

$$k_{\phi} = \frac{k_N 4 L^2 G}{3 E} \left( 1 - \left( \frac{w \tanh \left( \frac{L}{w \sqrt{3(4 - E/G)}} \right)}{L \sqrt{3(4 - E/G)}} \right)^{-1} \right)$$

With $k_N$ denoting the cantilever’s spring constant, $L$ denoting cantilever length, $w$ denoting cantilever width, the $G$ and $E$ denoting shear, and Young’s moduli of cantilever material, respectively.

2.3.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is extensively employed to extract information regarding the EDL structure and differential capacitance at the IL/electrode interface.\textsuperscript{118-120} In this study, complementary EIS measurements have been performed to validate the EDL structures of IL/solvent systems studied by EC-NR measurements.
EIS is usually acquired by applying a small AC voltage as an electrical stimulus to an electrochemical system and measuring the response from the system. The frequency of the applied AC voltage can be varied, typically ranging from millihertz to megahertz, to probe diverse electro-behaviors across different time scales. The measured impedance ($\tilde{Z}$), derived from the applied AC voltage and the corresponding AC current, is expressed as a complex function:

$$\tilde{Z}(\omega) = Z'(\omega) + iZ''(\omega)$$  \hspace{1cm} (6)

The Nyquist plot is commonly invoked to illustrate the frequency-dependent complex impedance, where $-Z''$ is plotted against $Z'$. Various electro-interfacial processes can be directly extracted from the Nyquist plots by fitting them with a suitable parameterised model function, known as an electrical equivalent circuit.\textsuperscript{121}
3. RESEARCH APPROACHES

3.1. Materials

In this work, various combination ILs of phosphonium-based mono- and di-cations with orthoborate-based anions were investigated. The ILs were supplied by collaborators from Luleå University of Technology and Stockholm University. The ILs were used without further purification. The structure and high purity of the ILs had been earlier verified using electrospray ionization mass spectrometry (ESI-MS) and multinuclear ($^{1}H$, $^{13}C$, $^{31}P$ and $^{11}B$) NMR spectroscopy.\textsuperscript{48,49} Table 1 lists the materials used in this thesis, and Figure 8 shows the molecular structure and dimension of the IL ions and solvents.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Abbreviations</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tributyl(tetradecyl)phosphonium-bis(oxalate)borate</td>
<td>[P$_{4,4,4,14}$][BOB]</td>
<td>III</td>
</tr>
<tr>
<td>Trihexyl(tetradecyl)phosphonium-bis(mandelato)borate</td>
<td>[P$_{6,6,6,14}$][BMB]</td>
<td>I, II</td>
</tr>
<tr>
<td>Trihexyl(tetradecyl)phosphonium-bis(oxalato)borate</td>
<td>[P$_{6,6,6,14}$][BOB]</td>
<td>I, II, III</td>
</tr>
<tr>
<td>Trihexyl(tetradecyl)phosphonium-bis(salicylato)borate</td>
<td>[P$_{6,6,6,14}$][BScB]</td>
<td>II</td>
</tr>
<tr>
<td>1,12-di(tributylphosphonium)dodecane-bis(oxalate)borate</td>
<td>[P$<em>{4,4,4}$-C$</em>{12}$-P$_{4,4,4}$][BOB]$_2$</td>
<td>III, IV</td>
</tr>
<tr>
<td>1,12-di(trihexylphosphonium)dodecane-bis(oxalate)borate</td>
<td>[P$<em>{6,6,6}$-C$</em>{12}$-P$_{6,6,6}$][BOB]$_2$</td>
<td>III</td>
</tr>
<tr>
<td>1,12-di(trioctylphosphonium)dodecane-bis(oxalate)borate</td>
<td>[P$<em>{8,8,8}$-C$</em>{12}$-P$_{8,8,8}$][BOB]$_2$</td>
<td>III</td>
</tr>
<tr>
<td>1,2-propylene carbonate</td>
<td>H-PC</td>
<td>I, III</td>
</tr>
<tr>
<td>1,2-propylene-$d_6$ carbonate</td>
<td>D-PC</td>
<td>I, III</td>
</tr>
<tr>
<td>2-ethylhexyl laurate</td>
<td>H-2-EHL</td>
<td>II, IV</td>
</tr>
<tr>
<td>2-ethylhexyl laurate-$d_{40}$</td>
<td>D-2-EHL</td>
<td>II, IV</td>
</tr>
</tbody>
</table>

The organic solvents employed in this thesis were 1,2-propylene carbonate (H-PC, anhydrous, 99.7%) and perdeuterated 1,2-
propylene-$d_6$ carbonate (D-PC, 99.5 atom% D) from Sigma Aldrich and Qmx Laboratories Ltd., respectively. In addition, a bio-degradable oil, 2-ethylhexyl laurate (H-2-EHL), was commercially obtained as Dehylub® 4003 from Emery Oleochemicals GmbH, and its perdeuterated form, 2-ethylhexyl laurate-$d_{40}$ (D-2-EHL), was synthesized by the National Deuteration Facility of ANSTO.122 PC was selected as the solvent because of its high dielectric constant and low viscosity, rendering it an ideal charge carrier. 2-EHL, recognized as a green ester-based biodegradable oil, proves useful in lubricant formulation owing to its low viscosity and high spreading properties.122, 123 Moreover, both D-PC and D-2-EHL offer a high SLD, allowing the matching of the bulk solution with the gold electrode in NR measurements to provide contrast with the adsorbed film.

**Figure 8.** Molecular structure and dimension of the IL ions and solvents.
3.2. Electrochemical quartz crystal microbalance measurements

A QCM (A100®, Attana AB) coupled to a custom-built electrochemical cell setup was used for characterizing electro-interfacial mass changes. The details of the electrochemical cell setup are available in Paper I. Briefly, the measurements were conducted using a two-electrode system due to the cell configuration constraints. A quartz crystal (10 MHz) sputter-deposited with a 150-nm thick gold layer served as a working electrode (WE), and a Pt wire (Ø = 0.15 mm) functioned as both the counter (CE) and quasi-reference electrode (RE). A custom-built potentiostat applied different potentials across the cell. Two multimeters (3000 FC series, FLUKE) monitored the applied potential across the cell and open circuit potential (OCP) decay during all experiments. The QCM crystal, sealed by an FFKM X-ring (Trelleborg) with internal Ø = 6.07 mm, determined the electrode surface area. Using wave velocity and density of quartz crystal (3340 m/s and 2650 kg/m³), the constant \( C \) of the Sauerbrey equation (Equation 1) was calculated as 0.23 Hz·ng\(^{-1}\)·cm\(^2\). Frequency changes were converted to mass changes in ng·cm\(^{-2}\). Notably, the Attana program reports the frequency reduction value, resulting in positive frequency changes with positive mass increases (overall frequency reduction), which is more intuitive.

Prior to each measurement, the QCM cell components (excluding the crystal) underwent 30 minutes of ultra-sonication in a 2% v/v Deconex Universal (VWR) solution with Milli-Q water (resistivity 18.2 MΩ·cm at 25 °C; total organic carbon (TOC) ≤ 5ppb). Subsequently, components were thoroughly rinsed with Milli-Q water and absolute ethanol before drying with filtered nitrogen. QCM crystals were immersed in a 2% v/v solution of Deconex® Universal in Milli-Q water for 30 minutes, then rinsed and dried with the same procedures as above.

After installing the cell with the injected solution in the QCM, the system was left to stabilise overnight to minimize intrinsic drift (< 1 Hz/min). The experimental system was maintained at 25°C. Each
measurement involved applying a potential for 5 minutes, following the removal of the applied potential, the decay of the cell potential to OCP was recorded for approximately 2-5 minutes, depending on the decay rate. Frequency was monitored throughout the experiment. For each curve corresponding to a potential response, the frequency change was referenced to the intrinsic drift baseline value immediately before the voltage change. Typically, the largest potential was applied first, followed by potential of equal magnitude but opposite bias. This cycle continued to the second-largest potential and so forth. This switched-bias potential application sequence was adopted to facilitate baseline re-establishment. The applied potential span was -0.8 V to +0.8 V, with a decrement of 0.2 V. Before changing potentials, the setup was allowed to fully relax for a minimum of 20 minutes until OCP decay approached zero monitored by multimeter, and the intrinsic drift (i.e., initial sensor frequency decay) baseline was restored.

3.3. Electrochemical neutron reflectivity measurements

Solution preparation

Prior to usage, all ILs were dried in a dynamic vacuum at 60°C for approximately 72 hours to eliminate volatile contaminations such as atmospheric water. To minimise ambient water contamination, the studied solutions were prepared in a polyethylene glove bag under a dry argon atmosphere (relative humidity < 10%). As mentioned earlier, to enhance measurement sensitivity for detecting changes at the interfacial region, the solution was prepared by weighing the respective IL and appropriate amounts of deuterated and non-deuterated solvents to achieve contrast-matching SLD of the bulk solution with the gold electrode. Table 2 presents the densities, molecular volumes and theoretical SLDs for the pure ILs, respective ions, and deuterated/non-deuterated solvents. Ion density and volume were estimated through atomistic simulation, as reported previously, while the density of the pure ILs was measured using a density meter (DMA™ 4500 M, Anton Paar). Theoretical SLDs of
different components were calculated using the National Institute of Standards and Technology (NIST) SLD online calculator with their chemical formula and mass density. Each solution was homogenized through ultra-sonication (maximum 10 minutes) and promptly utilized. The stability and water content of the IL solutions were evaluated using Fourier-transform infrared spectroscopy, both pre and post NR measurement. Figure 9 shows the representative IR spectra of 5% w/w [P_{6,6,6,14}][BOB]/2-EHL system employed in the EC-NR measurements and exhibited no discernible water peaks.

Table 2. Densities, molecular volumes and SLDs of IL, ion, and solvent.

<table>
<thead>
<tr>
<th>Species</th>
<th>( \rho ) at 25 °C (g/cm(^3))</th>
<th>( V_M ) (Å(^3))</th>
<th>SLD ((\times 10^{-6}\text{Å}^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[P_{4,4,4,14}][BOB]</td>
<td>1.014</td>
<td>961</td>
<td>0.49</td>
</tr>
<tr>
<td>[P_{6,6,6,14}][BOB]</td>
<td>0.997</td>
<td>1118</td>
<td>0.37</td>
</tr>
<tr>
<td>[P_{6,6,6,14}][BMB]</td>
<td>1.023</td>
<td>1291</td>
<td>0.50</td>
</tr>
<tr>
<td>[P_{6,6,6,14}][BScB]</td>
<td>1.019</td>
<td>1247</td>
<td>0.53</td>
</tr>
<tr>
<td>[P_{4,4,4-C_{12}}-P_{4,4,4}][BOB](_2)</td>
<td>1.057</td>
<td>1487</td>
<td>0.77</td>
</tr>
<tr>
<td>[P_{6,6,6-C_{12}}-P_{6,6,6}][BOB](_2)</td>
<td>1.027</td>
<td>1804</td>
<td>0.58</td>
</tr>
<tr>
<td>[P_{8,8,8-C_{12}}-P_{8,8,8}][BOB](_2)</td>
<td>1.015</td>
<td>2010</td>
<td>0.45</td>
</tr>
<tr>
<td>[P_{6,6,6,14}]^*</td>
<td>0.880</td>
<td>914</td>
<td>-0.40</td>
</tr>
<tr>
<td>[P_{4,4,4,14}]^*</td>
<td>0.877</td>
<td>757</td>
<td>-0.42</td>
</tr>
<tr>
<td>[P_{4,4,4-C_{12}}-P_{4,4,4}]^{2+}</td>
<td>0.882</td>
<td>1079</td>
<td>-0.39</td>
</tr>
<tr>
<td>[P_{6,6,6-C_{12}}-P_{6,6,6}]^{2+}</td>
<td>0.882</td>
<td>1396</td>
<td>-0.37</td>
</tr>
<tr>
<td>[P_{8,8,8-C_{12}}-P_{8,8,8}]^{2+}</td>
<td>0.893</td>
<td>1692</td>
<td>-0.37</td>
</tr>
<tr>
<td>[BOB]^-</td>
<td>1.521</td>
<td>204</td>
<td>3.84</td>
</tr>
<tr>
<td>[BMB]^-</td>
<td>1.376</td>
<td>375</td>
<td>2.71</td>
</tr>
<tr>
<td>[BScB]^-</td>
<td>1.411</td>
<td>333</td>
<td>3.10</td>
</tr>
<tr>
<td>H-PC</td>
<td>1.205</td>
<td>141</td>
<td>1.53</td>
</tr>
<tr>
<td>D-PC</td>
<td>1.258</td>
<td>143</td>
<td>5.87</td>
</tr>
<tr>
<td>H-2-EHL</td>
<td>0.860</td>
<td>604</td>
<td>-0.08</td>
</tr>
<tr>
<td>D-2-EHL</td>
<td>0.971</td>
<td>602</td>
<td>6.70</td>
</tr>
</tbody>
</table>
Electrochemical NR cell and gold electrode preparation

In this thesis, electrochemical NR (EC-NR) measurements utilized a custom-made electrochemical NR cell (cf. Figure 10), the design of which has been described previously in studies by collaborators.59, 82 The working electrode (WE) was a thin, amorphous gold film (approximately 170 Å), coated onto a 10 mm thick (50 × 50 mm, w × l) polished silicon (100) block (Sil’tronix Silicon Technologies). A pre-deposited adhesion layer of either titanium or chromium was applied to the silicon surface. A short, insulated copper wire was affixed to a corner of the gold surface using conductive epoxy CW 2400 (Chemtronics) and then cured at 120°C in an oven for 20-30 minutes; it allowed a potential to be applied. Subsequently, the gold surface was rinsed with filtered absolute ethanol, dried with nitrogen gas, and exposed to UV/ozone for 10 minutes to remove organic residues.

To accommodate space limitations in the NR electrochemical cell, a two-electrode system was used for the presented measurements. The counter/reference electrode (CE/RE) was a conductive glass coated with fluorine-doped tin oxide (FTO, Sigma Aldrich). A 0.5 mm thick PTFE gasket separated the CE/RE from the WE and enclosed the IL/solvent solution. Prior to assembly, all cell components, including the conductive glass and gasket, underwent a 30-minute ultrasonic treatment in 2% v/v Hellmanex® with Milli-Q water (at room
temperature). Subsequently, they were rinsed thoroughly with Milli-Q water and filtered with absolute ethanol before nitrogen drying. Cell assembly was performed in a polyethylene glove bag with a dry argon atmosphere (relative humidity < 10%) to minimize ambient water contamination. After assembly, the prepared solutions were introduced into the cell using an adaptor and a glass Luer syringe.

**Figure 10.** The layout of the EC-NR cell. (A) and (I) aluminium outer shell. (B) PTFE seat. (C) gold-coated silicon as WE. (D) PTFE gasket. (E) conductive glass as CE/RE. (F) Kalrez gasket. (G) PTFE spacer with adapters. (H) PEEK plate. (Reproduced with permission from Pilkington et al.\textsuperscript{82} Copyright 2018 AIP Publishing.)

**Electrochemical NR measurements and data reduction**

Specular neutron reflectivity \((R)\), the intensity ratio between the reflected and the incident beam, was experimentally determined by varying the momentum transfer vector \((Q)\). (see **Equation 2**) In this thesis, the presented NR measurements were conducted using both the Platypus time-of-flight neutron reflectometer at ANSTO\textsuperscript{125} and the SuperADAM reflectometer at ILL\textsuperscript{126,127}

For Platypus (\textbf{Paper II, IV}), two incident angles, 0.65° and 3°, were used to cover the Q range from the critical edge to the background
A constant $\Delta Q/Q$ resolution, approximately 5%, was maintained throughout all measurements. Slits were used to precisely define the beam size, ensuring a consistent beam footprint within the region covered by the gold-solution interface. For SuperADAM (Paper I, II, III), the wavelength was held constant at 5.21 Å, and the angle of incidence was adjusted, yielding a Q range of 0.005 - 0.21 Å⁻¹ with a resolution of $\Delta \lambda/\lambda = 0.005$. NR measurements were conducted with the electrochemical NR cell positioned horizontally for Platypus and vertically for SuperADAM.

Initial NR measurements were usually performed in the air to obtain substrate parameters (i.e., SLD, thickness and roughness of substrate layers) for subsequent NR fitting of the solution data. This involved directing the neutron beam through the Au surface, reflecting it at the Si interface, and then passing the reflected neutron beam through the Au surface once more before reaching the detector. For EC-NR measurements with the solution, the direction of the neutron beam was reversed. The beam passed through the Si block, reflected at the Au-solution interface, passed through the block again, and exited toward the detector. Once the cell was mounted on the beamline, an Autolab PGSTAT204 potentiostat (Metrohm) was connected to apply external potentials across the cell, continuously monitoring and recording the voltage and current. NR measurements were conducted after maintaining each applied potential for 30 minutes to establish equilibrium conditions. Surface charge density was estimated based on the effective electrode surface area (defined by the PTFE gasket, 42 × 42 mm²) and the integrated current change during the equilibrium time.

Standard data reduction procedures were applied, including background subtraction, detector efficiency calibration, over-illumination correction (specifically for data collected from SuperADAM), and subsequent normalization to reflectivity using the direct beam. Datasets from the two incident angles collected by Platypus were combined to generate a unified NR profile. The error bars in reflectivity data presented were computed from a Poisson
distribution, with the count error equal to the square root (or standard deviation) of the counts measured at each Q position.

**NR Data fitting and analysis**

Reduced data were fitted using the GenX software package\textsuperscript{128, 129} to derive SLD profiles based on best fits to NR profile with lowest figure of merit (FOM) values. The fitting process employed a slab model with constraints on thickness, roughness, and SLD between super- and subphases of multiple layers.\textsuperscript{99, 130} Due to the comparable roughness of the gold surface relative to the IL (ion) dimensions (cf. Figure 8), a “micro-slabbing” method, also known as “slicing”, was applied to fit the gold-innermost-layer interfacial region.\textsuperscript{83, 131} Briefly, this method sliced the gold-innermost-layer interface into multiple 1 Å thick layers without roughness. The SLD of each micro-slab was determined from the normal distribution of the volume fraction of gold and the innermost layer, ensuring a smooth transition in this region. Instead of fitting the gold roughness, the thickness of this interfacial region was fitted and fixed after the first applied potential, along with the SLD of the bulk solution. Other substrate-related parameters, including the SLD, thickness, and roughness of the substrate layers of the electrode block, were determined either from the reflectivity of the block measured in air (cf. Figure 11) or directly fitted at the first applied potential with a pre-characterized block as the reference (depends on beamtime constraints, refer to Paper II, III methods for more details), and were fixed for all applied potentials.

Beyond the mentioned parameters, the thickness, roughness, and SLD values of the interfacial layers were allowed to vary for fitted datasets. Simulations were independently performed for each potential, with no pre-defined structures assumed. Typically, the roughness of each layer was restricted not to exceed 30% of its thickness, and the SLD of each layer was constrained within the range of possible component species. Initially, a one-layer slab model was used for fitting, and additional layers were introduced if the FOM value decreased significantly.
Figure 11. (a) Representative normalized NR curve for the gold block characterised in the air before the EC-NR measurements of 5% w/w [P\textsubscript{6,6,6,14}][BOB]/2-EHL solution. The circular points represent the experimental data, while the solid line represents the best fit to the data. (b) The appropriate SLD profile of the best fit. (Reproduced from SI of Paper II.) The characterisation of blocks in the air for other systems can be found in the SI of the appendix papers.

3.4. Cyclic voltammetry and electrochemical impedance spectroscopy

Cyclic voltammetry (CV) measurement is widely employed to determine the stable electrochemical window (EW) of studied systems. In particular, post NR measurements, CV was performed across the cell solution to identify the occurrence of any Faradaic events during the NR experiment, evaluating the charge transfer reversibility in the studied potential range (cf. Figure 12a for one representative CV test). The Autolab PGSTAT204 potentiostat (Metrohm) was chosen to perform the CV test of the EC-NR cell within the specified potential range at a scan rate of 10 mV·s\textsuperscript{-1}.

Complementary EIS measurements were conducted across the studied solutions (off-line) using a sealed TSC surface measuring cell (rhdi instruments GmbH & Co. KG) with the potentiostat equipped with the FRA32M module, which is specially designed for EIS. A gold-coated silicon chip (University Wafer, Inc.), prepared similarly to the NR and AFM gold electrode surface, served as the WE. A glassy carbon
electrode, enclosed in PEEK, with an active electrode surface diameter of 6 mm, served as the CE. A silver wire acted as the *pseudo*-RE. The liquid area of the WE was determined by an FFKM O-ring with an internal diameter of 6 mm. Before each EIS measurement of the studied solution, test cell components were thoroughly cleaned with acetone, isopropanol, and ethanol, followed by overnight drying at 60°C in a vacuum oven. Subsequently, the cell components were transferred into a glove bag under a dry nitrogen atmosphere (relative humidity < 10%) for assembly and filling with the prepared solution, thus minimizing ambient water contamination.

The applied potentials of WE were referenced to the *pseudo*-RE with the first anodic scan direction and followed by the cathodic direction. After the stabilisation of 30 minutes for each applied potential, impedance measurements were conducted across a frequency range of 0.01 Hz to 100 kHz, using an AC voltage with a 10 mV(rms) amplitude and automated current ranging. The acquired impedance data were analysed using RelaxIS 3 software provided by the same company. The representative Nyquist plots and the related equivalent electric circuit model are shown in Figure 12b.

**Figure 12.** (a) Representative CV profile for the NR cell of 2 mol% [P₄,₄,₄-C₁₂-P₄,₄,₄][BOB]₂ in PC solution after EC-NR measurements, with the scan rate of 10 mV·s⁻¹. (b) Representative EIS Nyquist plots (-Z” against Z’) for 2 mol% [P₄,₄,₄-C₁₂-P₄,₄,₄][BOB]₂ in PC solution for different applied potentials. The inset is the equivalent electric circuit used to model experimental EIS data. (Reproduced from SI of Paper III.) The CV and EIS measurement results for other systems can be found in the SI of appendix papers.
3.5. Electro-nanotribological measurements

Electro-nanotribological measurements utilized a JPK (Santa Barbara, CA) AFM equipped with a JPK ECCell™ electrochemical cell. Contact mode was used to measure the electrochemical friction between a sharp Si AFM tip (nominal radius ~7 nm; AC204TS, Olympus) and a gold-coated silicon wafer in IL/solvent solutions. The thermal noise method determined the normal spring constants of AFM tips (~2.2 N/m). Measurements were performed in a two-electrode system, with the potential of the gold-coated electrode (WE) controlled relative to a platinum (Pt) wire serving as the CE/RE.

Before the measurements, cell parts (Pt wire, O-ring, and screws) were sonicated in 2% v/v Hellmanex®, rinsed with Milli-Q water and filtered absolute ethanol before drying with nitrogen. Other parts were thoroughly cleaned with isopropanol (IPA) and absolute ethanol and dried with nitrogen. The AFM tip and deposited gold surface were only rinsed with absolute ethanol and irradiated in an ultra-violet (UV) ozone cleaner (PCE-44-LD; MTI Corporation) for 10 minutes.

Friction measurements covered a 500 nm scan size at scan rates of 1, 6, and 12 µm·s⁻¹. The slow scan axis was disabled, resulting in the cantilever moving with one-coordination trace and retrace. For each scan, the normal force (presented in terms of vertical voltage deflection in the system) was increasingly loaded in discrete steps from zero to maximum value and then back until the AFM tip was separated from the surface. The lateral voltage difference Δ𝑉 for each normal force was averaged over ten trace and retrace cycles and converted to friction using Equation 4. Based on Amonton’s law, the friction coefficient μ was extracted from the gradient of the friction force against the normal force in the linear region. External potentials were applied using the Autolab PGSTAT204 potentiostat (Metrohm). To achieve equilibrium, friction measurements were performed after maintaining each applied potential for 30 minutes.
4. RESULTS & DISCUSSION

4.1. Electro-interfacial properties of ionic liquids in propylene carbonate: effect of voltage and ion structure

QCM and EC-NR studies on [P$_{6,6,6,14}$][BMB] and [P$_{6,6,6,14}$][BOB] with PC systems: a distinct tuneable interphase transition

Electrochemical QCM can measure the changes in interfacial films by monitoring frequency changes under different applied potentials. These interfacial changes are linked to ion exchange and rearrangements of various structures. In Figure 13, QCM measures the resonance frequency change over time under different potentials for the 20% w/w [P$_{6,6,6,14}$][BMB]/PC solution (negative potentials) and 20% w/w [P$_{6,6,6,14}$][BOB]/PC solution (positive potentials). The data for positive potentials in the [P$_{6,6,6,14}$][BMB]/PC system and negative potentials in the [P$_{6,6,6,14}$][BOB]/PC system are detailed in Paper I. When the gold surface is polarised (i.e., under applied potentials), the IL/PC solutions usually show an abrupt initial response followed by a gradual decay towards a plateau value. The initial response and plateau value vary with the magnitude of the applied potentials, typically exhibiting opposite dependences on the potential sign.

![Image](image_url)

*Figure 13. QCM resonance frequency changes as a function of time for 20% w/w [P$_{6,6,6,14}$][BMB]/PC with negative potentials (a) and 20% w/w*
In Figure 14a, the abrupt initial frequency change values are plotted against applied potentials for the reference PC system and the two 20% w/w IL solutions. Both the PC and the [P6,6,6,14][BMB] solution exhibit a linear response to the potential, with the PC showing a slightly stronger dependence. Because of its large dipole moment, a net response in PC orientation to the applied potential is anticipated, detectable here as a slight change in the resonant frequency. The abruptness of this change reflects the small size of the PC molecules and their rapid adaptation to the local electric field. The comparable linear behaviour of the [P6,6,6,14][BMB] system suggests a similar solvent response, indicating a significant solvent presence in the [P6,6,6,14][BMB] interfacial film and a less screened surface charge by presented ions at the interface. In the [P6,6,6,14][BOB] solution, this solvent response is undetectable at negative potentials and very weak at positive potentials. One possible reason for this observation is the smaller size of [BOB]- anions, compared with [BMB]- anions (cf. Figure 8), allowing them to pack more efficiently at the interface alongside any (self-assembled) cations, resulting in a reduced proportion of PC at the electrode interface. The diminished response is also likely a result of the increased charge dissociation of the [P6,6,6,14][BOB], influencing both the absolute IL amount in the interfacial film and the extent of electric field screening. In other words, the PC in the film is locally oriented by the discrete charges of the dissociated ions, rendering the electrical potential less significant.
Figure 14. (a) Initial frequency change with different applied potentials for pure PC, 20% w/w [P$_{6,6,6,14}$][BMB]/PC and 20% w/w [P$_{6,6,6,14}$][BOB]/PC. (b) mass changes converted from plateau frequency change as a function of applied potentials for pure PC, 20% w/w [P$_{6,6,6,14}$][BMB]/PC and 20% w/w [P$_{6,6,6,14}$][BOB]/PC. The error bars represent the data’s maxima and minima values for three independent experiments. (Reproduced from Paper I)

The second observed feature in Figure 13 was a gradual decay over time, reaching a plateau and resulting in a frequency (or mass) change opposite to the solvent response. Plateau frequency changes were converted into mass changes using Sauerbrey’s equation (Equation 1) and plotted against applied potentials in Figure 14b. Negative potentials exhibit an expected mass decrease for the IL systems. This results from the different molecular densities (density sequence: $\rho_{\text{cation}} < \rho_{\text{IL}} < \rho_{\text{PC}} < \rho_{\text{anion}}$, cf. Table 2). At negative potentials, solvent molecules (PC) and co-ions (i.e., [BMB]: or [BOB]: anions) are effectively expelled from the electrified surface, with their volume replaced by less-dense cations and/or IL ion pairs. At positive potentials, both 20% w/w [P$_{6,6,6,14}$][BMB]/PC and 20% w/w [P$_{6,6,6,14}$][BOB]/PC systems show a non-symmetrical and complex variation, indicating different mechanisms, to be discussed later in more detail.

The results of 20% w/w [P$_{6,6,6,14}$][BMB]/PC reveal two consequences of using larger [BMB]- anions. Firstly, as implied in Figure 14a, the solvent molecules (i.e., PC) are more polarisable by the electrified interface due to the lack of separation of charges of adsorbing ions.
Secondly, the self-assembly is potentially constrained due to its lower dissociation compared to [P_{6,6,6,14}][BOB], resulting in the predominant structure of the EDL being an intrinsic checkerboard interfacial structure. Based on the ion-exchange density difference approach described in the preceding paragraph, a positively polarized surface overall replaces [P_{6,6,6,14}]^{+} cations (and possibly PC) with intermediate-density IL ion pairs, essentially nullifying the mass change at positive potentials. This explains the less pronounced mass change observed for [P_{6,6,6,14}][BMB]/PC at positive potentials. This observation explains previous neutron data, where the SLD changes are consistent with the replacement of cations by ion pairs.\(^{59}\)

While the asymmetry with potential was initially unexpected, the [P_{6,6,6,14}][BMB] data can be explained by simple ion exchange within the framework of a checkerboard structure. The scenario is more complicated for 20% w/w [P_{6,6,6,14}][BOB]/PC under positive potentials. The ion-exchange density difference approach works well in the regions of negative and small positive potentials (-0.8 V to +0.4 V), where the denser [BOB]^{-} anions (and possibly polarized PC) are expelled, and the void volume formally replaced by neutral IL ion pairs, leading to a reduced mass for negative potentials and a mass increase with positive potentials (i.e., sparser [P_{6,6,6,14}]^{+} cations exchanged by IL ion pairs). A notable mass reduction occurs at intermediate to large positive voltages, exhibiting an opposite trend and making this approach inapplicable (cf. Figure 13b and 14b +0.6 V). A distinct negative mass change is observed in all repeated measurements. Notably, the error bars seem large in this region due to averaging three curves, each with steep changes; however, the trend is reproducible (cf. SI of Paper I). A new explanation for this anomalous mass change must be sought, taking into account molecular architectures and ion-packing behaviours.

Due to the smaller structure of [BOB]^{-} anions and the high dissociation of IL ions,\(^{123}\) [P_{6,6,6,14}]^{+} cations are more likely to form a bilayer structure at the electrified surface, especially at negative potentials, akin to a SAIL (surface-active IL). On negatively and slightly positively
polarized (up to ~0.4 V) surfaces, the polar heads of the [P_{6,6,6,14}]^+ cations are electrostatically drawn to the interface. The non-polar tails extend outward, near the non-polar tails of a subsequent [P_{6,6,6,14}]^+ cation layer, resulting in a bilayer formation at the interfacial region. At sufficiently high positive external potentials, the bilayer structure of cations becomes untenable due to the low cation density (cations are repelled) that cannot support a self-assembly structure. This triggers an interphase transition to a more energetically favourable EDL arrangement with an anion-rich interfacial layer. This interphase transition from a highly dense bilayer structure to a sparser, thinner EDL structure is expected to cause a significant mass reduction at higher positive voltages. Figure 15 proposes a schematic illustrating the distinct electro-interfacial behaviours for [P_{6,6,6,14}][BMB] and [P_{6,6,6,14}][BOB] in PC systems.

Figure 15. Proposed model for the EDL of two IL/PC systems on electrodes as a function of the potential. (a) The schematics for ions and solvent molecule. Electro-interfacial structures for (b-d) 20% w/w [P_{6,6,6,14}][BMB]/PC system and (e-g) for 20% w/w [P_{6,6,6,14}][BOB]/PC system. (Reproduced from Paper I)

This observation has important and far-reaching implications. It affects the dynamics observed in capacitive systems, will lead to apparent hysteresis behaviour, and finally will also lead to a history-dependent OCP value. While the QCM technique is now proven, its use is confined to our group, so it would be reassuring if another technique could verify the phenomenon. Hence, EC-NR was employed to elucidate interfacial structuring and compositional changes at the electrified gold surface. Figure 16a shows the NR curves for the 20%
w/w [P$_{6,6,6,14}$][BOB] in d-PC on a gold electrode surface at three different potentials (0 V, -1.5 V, +0.5 V). The prominent Kiessig fringes reveal a significant SLD contrast between the interfacial region and the gold electrode. The NR profile would lack distinctive features in the absence of structured layers at the gold interface (shown as the dashed line). The reflectivity difference for both polarized potentials (compared to 0 V) was calculated and is presented as inset asymmetry plots. An oscillatory function was observed across the entire Q range for both polarized potentials, suggesting a systematic electroresponsivity of the IL at the gold interface.

**Figure 16. (a)** Experimental neutron reflectivity, $R$, of 20% w/w [P$_{6,6,6,14}$][BOB] in d-PC at the gold electrode surface for different applied potentials (applied order as indicated in the legend) as a function of the momentum transfer vector $Q$. The symbols show the experimental data, whilst the solid lines represent the simulated reflectivities obtained from the best fit to the data. For clarity, the curves have been offset on the y-axis. For comparison, the dashed line represents the simulated NR curve for the same gold surface and bulk IL-PC solution that would be predicted without an absorbed, structured layer. The inset shows asymmetry plots $\Delta R = [R^V(QZ) - R^0(QZ)] / [R^V(QZ) + R^0(QZ)]$, highlighting the difference of reflectivity between polarized potentials and 0 V. **(b)** Corresponding model SLD profiles obtained from the best fits to the reflectivity curves as a function of distance Z, where the gold-solution interface is located at Z = 0. (Reproduced from Paper I.)

Figure 16b shows the SLD profiles derived from the best fit to the reflectivity curves as a function of the distance from the gold surface.
(Z = 0). The SLD profiles generally reveal a broad interfacial region with relatively low SLDs for all applied potentials, indicative of the increased ion density at the gold interface. The thickness and average SLD of the interfacial region vary with different applied potentials. At 0 V and -1.5 V, a one-layer model adequately captures the features of the reflectivity curves, and adding another layer did not provide a noticeable improvement in fit quality (i.e., provide a lower FOM). The two-layer model afforded a better fit for +0.5 V, consisting of a significant SLD drop close to the electrode interface, followed by a broader layer with higher SLD. Similar to the QCM, the SLD profiles cannot yield an unambiguous absolute composition due to an unknown solvent composition. Nevertheless, the changes in composition can be easily followed. At 0 V, the relatively low SLD of the boundary layer indicates a high cation concentration at the gold interface. The depth of the SLD minimum is notably lower at the negative potential, indicating a surface enrichment of cations. Moreover, the slightly decreased thickness of the boundary layer at -1.5 V aligns with a more well-defined, condensed cation layer at the interface, which is needed to counteract the negative surface potential. The thickness of the layer under neutral and negative potentials is approximately double the maximum length of the [P6,6,6,14]+ cation (cf. Figure 8 and 16b), suggesting a bilayer structure of cations. The SLD profile undergoes a significant change after reversing the potential bias to +0.5 V. The depth of the SLD minimum increases. In addition, the SLD profile presents a significantly reduced thickness for the first layer, comparable with the size of [BOB] anion at the positive potential. Together, these changes in the SLD profile can be inferred as an interfacial structure transition from the self-assembled bilayer cation domain to an anion-rich interfacial layer, contributing to the previously mentioned substantial mass reduction over +0.5 V in QCM.

**Exploring the electro-interfacial self-assembly structure in the mono- and di-cationic ILs in PC with EC-NR measurements**

Our collaborators recently synthesized novel MIL (monocationic ILs) [P4,4,4,14][BOB] with shorter side alkyl chains and DILs (dicationic ILs).
These DILs share the same bis(oxalato)borate ([BOB]−) anion paired with diverse phosphonium-based dications with a -C_{12}- linkage spacer and three alkyl side chains of varying lengths ([P_{n,n,n}-C_{12}-P_{n,n,n}]^{2+}, n=4, 6, 8). To the best of the author’s knowledge, despite the extensive use of DILs in various chemistry areas, most research has primarily focused on their synthesis and physicochemical properties.\textsuperscript{133-135} Limited attention has been given to investigating the microscopic structure and dynamics of DILs. Using EC-NR, Paper III firstly explores the impact of the DIL structural variations in cations due to the spacer and the length of the alkyl side chains on interfacial structuring and electro-responses.

**Figure 17.** SLD profiles for 2 mol\% IL ([P_{4,4,4,14}]([BOB]) (a), [P_{4,4,4}-C_{12}-P_{4,4,4}]([BOB]) (b), [P_{6,6,6}-C_{12}-P_{6,6,6}]([BOB]) (c), [P_{8,8,8}-C_{12}-P_{8,8,8}]([BOB]) (d) in PC solution, obtained from the best fits to the NR measurements at different applied potentials as a function of distance z, where the gold-solution interface
is located at \( z = 0 \). The legend indicates the potential applied order. The dashed line represents the SLD profile for the same gold surface and bulk IL-PC solution that would be predicted without an absorbed, structured layer. (Reproduced from Paper III.)

**Figure 17** shows the SLD profiles of these IL at 2 mol% in PC. The associated NR data and fitted parameters are available in the SI of Paper III. Their SLD profiles generally reveal a broad interfacial region with consistently low SLD values for all applied potentials, suggesting a considerable surface excess due to the higher density of ionic constituents. Complementary EIS (electrochemical impedance spectroscopy) measurements of the same systems (conducted offline), presented in the SI of Paper III, affirm the existence of the structured interfacial layers through the observation of two resistor-capacitor (RC) models in the equivalent electric circuit, which correspond to the EDL and bulk in lower and higher frequency regions, respectively.\(^{36, 59}\)

![Neutral Checkerboard, Anion-rich Checkerboard, Cation-rich Checkerboard](image)

**Figure 18.** Schematics of neutral, anion-rich, and cation-rich checkerboard structures of ion arrangements at different polarised electrified interfaces.

\([P_{4,4,4,14}]\text{[BOB]}\) exhibits a similar electro-responsive behaviour with the \([P_{6,6,6,14}]\text{[BOB]}\) mentioned earlier (Paper I), suggesting a voltage-induced interphase transition phenomenon. At neutral and negative potentials, the thickness of the interfacial layer (~ 40 Å, cf. black and blue lines in **Figure 17a**) is roughly twice the maximum length of the \([P_{4,4,4,14}]^+\) cation (cf. **Figure 8**), indicating the presence of a self-assembled cation bilayer structure at the interface. Reversing the potential bias to +0.25 V results in a significant change in the SLD profile, with a substantial thickness reduction in the innermost layer, comparable to the dimension of [BOB]- anion. This implies a very different interfacial structure – once again similar to a checkerboard structure of an anion-rich interfacial layer (cf. **Figure 18**). In
comparison to $[P_{6,6,6,14}]^+$, the shorter tri-butyl chains of $[P_{4,4,4,14}]^+$ cation lead to a smaller head group area with a higher charge density, promoting its charge condensation (with anions) and the formation of the self-assembled bilayer structure. This interphase transition in SAILs $[P_{4,4,4,14}][BOB]$ and $[P_{6,6,6,14}][BOB]$ can be tuned by external electric fields, facilitating a higher charge density and more robust tribotronic boundary film in the specific potential regions.

In contrast to the monocationic analogues, a one-layer slab model provided the best fit for the DIL with short alkyl side chains ($[P_{n,n,n}-C_{12}-P_{n,n,n}][BOB]$, $n=4, 6$) under all potential conditions. The thickness of the interfacial layer for these systems is comparable to the dimensions of dications (cf. Figure 8). The geometry of the dications allows for forming a “bilayer” of cations through single-layer adsorption, for example, with one end of the dication on the surface and the other pointing towards the solution. (Strictly, self-assembly would be possible via bending the alkanes into a U-shape such that both the cations of the dication are confined to the same layer, with the loops intercalating. This would also be of approximately the right thickness. However, the steric challenges for intercalation of loops would be large, so this possibility has been excluded.)

\[\text{Figure 19. (a-c)}\text{ Schematics showing structure and composition change of interfacial layers under neutral and polarized potentials for 2 mol}\%\text{ $[P_{4,4,4}-C_{12}-P_{4,4,4}][BOB]_2$ or $[P_{6,6,6}-C_{12}-P_{6,6,6}][BOB]_2$ in PC solution. The semi-transparent region over the dashed line represents the bulk solution. (Reproduced from Paper III.)}\]

Unlike their monocationic analogue forming a self-assembled bilayer structure, the dications with two phosphonium charge centres connected by the alkyl chain spacer ($-C_{12}H_{24}^-$) appear to pack with a
higher proportion of other constituents (e.g., [BOB]- anion and H/D-PC), resulting in a relatively higher SLD in the innermost layer. Related to this phenomenon, it has been noted in a previous study that DILs (different cationic groups and shorter spacer) are less prone to form bilayers than MILs.\textsuperscript{137} This could be due to two charged sites leading to less pronounced segregation of dications' polar (charge centre) and apolar (alkyl side chain and/or spacer) domains.\textsuperscript{13, 136} However, the interfacial layer of DIL/PC systems still show electro-responsive behaviour, presenting a higher proportion of dications (lower SLD) at the negative potential and more anions at the positive potential (higher SLD). \textbf{Figure 19} illustrates the schematics of the proposed interfacial structuring of these DILs in PC at the gold electrode interface for different applied potentials.

Compared with the shorter alkyl side chain DILs, the bulkier [P\textsubscript{8,8,8-C\textsubscript{12}-P\textsubscript{8,8,8}}][BOB]\textsubscript{2} demonstrates more pronounced electro-responsive behaviour. Once again, a one-layer slab model effectively describes the neutral and positive potential conditions (\textit{cf. Figure 17d}), whereas a two-layer slab model was required to fit the negative potential data adequately. (\textit{cf. FOM plot in SI of Paper III}). [P\textsubscript{8,8,8-C\textsubscript{12}-P\textsubscript{8,8,8}}][BOB]\textsubscript{2} also exhibits overall lower SLDs for the interfacial region than other DILs, indicating greater adsorption of the dications, presumably related to a lower bulk solubility.

At 0 V, the [P\textsubscript{8,8,8-C\textsubscript{12}-P\textsubscript{8,8,8}}]\textsuperscript{2+} dication displays a thick interfacial layer characterized by a relatively disordered boundary region with large roughness (\textbf{Figure 17d} black line), potentially arising from a certain level of dication intercalation. The depth of the SLD minimum at the gold interface is relatively lower for the negative potential, indicating a higher proportion of dication. In addition, the stratified SLD profile at -1 V is commensurate with a well-defined, intercalative dication bilayer structure at the interface to compensate for the negative surface charge (\textit{cf. Figure 17d} blue line). This may be due to the larger cation volume preventing surface neutralization by a full monolayer and requiring a crowding adsorption behaviour. The SLD profile undergoes a significant change upon reversing the potential bias to
The depth of the SLD minimum increased, suggesting the relative enrichment of [BOB]- anions at the positively electrified interface to neutralize the positive surface charge. The SLD profile reveals a notable reduction in the thickness of the boundary layer (from ~33 Å at 0 and -1 V to ~20 Å at +0.25 V). However, this reduced thickness is still considerably larger than the anion dimensions, suggesting the presence of cations in the interfacial layer (i.e., an anion-rich checkerboard structure, see Figure 18) but reoriented to a more surface-parallel arrangement. The more gradual transition of the layer to the bulk SLD, shown in Figure 17d red line, suggests a certain roughness or disorder of the layer, as depicted in Figure 20c.

Considering the dimensions of the anion and the fact that the surfaces are net positive charged, it is reasonable to assume that the remaining ion pairs (or triples) in the EDL are oriented to optimize the local electrostatic interactions within the surface plane.

Figure 20. (a-c) Schematics showing structure and composition change of interfacial layers under neutral and polarized potentials for 2 mol% [P_{8,8,8-C_{12}}-P_{8,8,8}][BOB] in PC solution. The semi-transparent region over the dashed line represents the bulk solution. (Reproduced from Paper III.)

The complementary electro-nanotribological measurements were preliminarily conducted between a sharp Si tip and an electrified gold thin film in the same concentration as EC-NR measurements of 20% w/w [P_{6,6,6,14}][BOB] and 2 mol% [P_{8,8,8-C_{12}}-P_{8,8,8}][BOB] in PC (20.4% w/w) at several applied potentials (OCP, 0, -0.5 and +0.25 V). The OCP for [P_{6,6,6,14}][BOB]/PC and [P_{8,8,8-C_{12}}-P_{8,8,8}][BOB] /PC systems were -0.24 V and -0.12 V, respectively. The lateral friction was measured during loading and unloading between 0 to 140 nN, and the potentials were applied by alternating bias as presented in the legend. Three
different scan speeds (1, 6, and 12 µm·s⁻¹) were performed for both studied systems. For clarity, the friction forces are only shown as a function of loading force with the intermediate speed (6 µm·s⁻¹). However, the scan speed did not significantly affect the friction coefficient (cf. Figure 21 insets). With applied potential, the magnitude of the friction was found to vary, whereby the neutral and negative bias led to larger frictions and a positive led to a friction reduction.

**Figure 21.** Friction force as a function of normal load in a solution of (a) 20% w/w \([P_{6,6,6,14}][\text{BOB}]\) and (b) 2 mol% \([P_{8,8,8-\text{C}_{12}}-P_{8,8,8}][\text{BOB}]_2\) in PC on electrified gold thin film with different applied potentials during loading measured as a scan speed of 6 µm·s⁻¹. The dashed lines represent linear fits to loading datasets to get corresponding friction coefficients (µ). The insets show the friction coefficients for three different scan speeds.

Meanwhile, the friction coefficients extracted from the gradient between friction and normal load are plotted as a function of applied potentials in Figure 22. For \([P_{6,6,6,14}][\text{BOB}]/\text{PC}\) systems, the friction coefficient is comparable for both neutral and negative potentials and decreases pronoucnedly at positive potential (cf. Figure 21a and 22). This trend is consistent with changes in the electro-interfacial structure observed through QCM and EC-NR measurements, providing further evidence of the interphase transition from a cation bilayer domain to an anion-rich interfacial structure. The \([\text{BOB}]^-\) anion has been well recognized for lowering shear strength at the interface and
reducing friction.\textsuperscript{52, 138} For the $[\text{P}_{8,8,8}\text{-C}_{12}\text{-P}_{8,8,8}]\text{[BOB]}_{2}/\text{PC}$ system, the magnitude of the friction coefficient varied approximately linear with applied potentials, as shown in Figure 22. This result is consistent with the interfacial structure observed from the NR SLD profile for 2 mol\% $[\text{P}_{8,8,8}\text{-C}_{12}\text{-P}_{8,8,8}]\text{[BOB]}_{2}$ in PC (cf. Figure 17d and 20), which shows crowding adsorption of dications at the negatively electrified surface and a higher proportion of anions at the interface under the positive potential.

\textbf{Figure 22.} Friction coefficient ($\mu$) as a function of applied potential during loading at a scan speed of 6 $\mu\text{m}\cdot\text{s}^{-1}$ for the solution of 20\% w/w $[\text{P}_{6,6,6,14}]\text{[BOB]}$ and 2 mol\% $[\text{P}_{8,8,8}\text{-C}_{12}\text{-P}_{8,8,8}]\text{[BOB]}_{2}$ in PC on electrified gold thin film.
4.2. Electro-interfacial properties of ionic liquids in a biodegradable oil: effect of voltage and anion architecture

This section will describe the work of Paper II about the EC-NR measurements for studying the electro-responsive interfacial behaviour of three MILs with different anion structures dissolved in a biodegradable oil, 2-EHL (2-ethylhexyl laurate), which is of more practical utility in a lubricant formulation than PC. It allows the effect of solvent polarity to be investigated on electro-interfacial responsivity. The investigation of a mixed system comprising two MILs in 2-EHL under similar conditions with EC-NR will also be introduced.

Figure 23. SLD profiles for 5% w/w (a) [P$_{6,6,6,14}$][BMB], (b) [P$_{6,6,6,14}$][BOB], and (c) [P$_{6,6,6,14}$][BScB] in 2-EHL solutions, obtained from the best fit to the NR measurements at different applied potentials as a function of distance Z, where
the gold-solution interface is located at \( Z = 0 \). The legend indicates the potential applied order. The dashed lines represent the SLD profile for the same gold surface and bulk IL/2-EHL solution that would be predicted without an adsorbed, structured layer. (d) The SLD values \( \times 10^{-6} \text{Å}^{-2} \) and dimensions for the different molecular constituents of the solutions. (Reproduced from Paper II.)

In Figure 23, SLD profiles derived from the best fit to reflectivity curves are presented for 5% w/w \([P_{6,6,6,14}][A]\) in 2-EHL solutions (where A=BMB, BOB or BScB) at different applied potentials. The layer parameters obtained from fitting, including thickness, roughness, and SLD values, for these profiles are detailed in the SI of Paper II. Unlike the majority of the PC results in the preceding section, a two-layer slab model consistently provided the best fit for all investigated ILs and potential conditions. These models show an ion-rich innermost layer with a compact structure, succeeded by a diffuse, solvent-rich (i.e., 2-EHL-rich) outer layer with an SLD value close to that of the bulk. Such a solvent-rich layer is also inferred as a corona or shell around the high aspect ratio aggregates observed in bulk by SANS measurements of the same study (Paper II).

In the PC solvent systems (Section 4.1 and recently reported \([P_{6,6,6,14}][BMB]^{59}\)), no such solvent-rich layers were observed, even when the models were adjusted to accommodate multiple layers. The existence of a solvent-rich outer layer in IL/2-EHL systems studied here can be ascribed to the much larger size of the solvent, which is comparable with the cation alkyl chain length and the distinct structural features of 2-EHL. Unlike PC, a cyclic carbonate ester, 2-EHL exhibits a configuration where the polar ester linkage is partially separated from the apolar alkyl tails, oriented parallel and away from the oxygen-rich “head group”.\(^{122, 123}\) This “surfactant-like” structure introduces some degree of self-assembly or interpenetration with the long alkyl chains of \([P_{6,6,6,14}]^+\) cations, resulting in the formation of the diffuse solvent-rich (secondary) layer.

The distinct electro-responsive behaviour of the ion-rich innermost layer in these systems depends on the nature of the specific anion. SLD profiles of 5% w/w \([P_{6,6,6,14}][BMB]\) in 2-EHL (cf. Figure 23a) indicate
that \([\text{BMB}]^-\) is the least electro-responsive anion, attributed to its limited dissociation.\(^{123}\) This weak responsivity aligns with previous findings regarding \([P_{6,6,6,14}][\text{BMB}]\) on gold in other polar solvents,\(^{59,82}\) which has been attributed to the fact that \([\text{BMB}]^-\) exhibits a lower diffusion coefficient than \([\text{BOB}]^-\) and \([\text{BScB}]^-\) anions.\(^{139}\) In contrast to the low electro-response of the innermost layer, the outer solvent-rich layer demonstrates a relatively prominent response under various bias potentials, despite its predominantly solvent composition. In comparison with 0 V, the thicker outer layer with a higher SLD at negative potentials suggests the formation of a dispersed structure containing more 2-EHL, attributed to the increased proximity of the cation polar group to the surface and the resulting inclination of the longer alkyl tails towards the bulk to interpenetrate more efficiently with the 2-EHL.

5\% w/w \([P_{6,6,6,14}][\text{BOB}]\) in 2-EHL displayed the most pronounced electro-response (cf. Figure 23b), aligning with its behaviour in PC, as discussed in Section 4.1. This substantial response can be attributed to the high ion dissociation and diffusion,\(^{123,139}\) leading to a significant potential induced rearrangement from a random adsorbed film to an electrically conditioned checkerboard structure (cf. Figure 24). Compared to 0 V, the decreased SLD of the innermost layer at -0.5 V indicates a higher content of \([P_{6,6,6,14}]^+\) cations. At +0.25 V, the thickness of the innermost layer is roughly halved, suggesting ion exchange from a cation-rich layer, probably with multiple cation orientations, to an anion-rich interfacial layer (cf. Figure 18). This anion-rich layer leads to a more organized checkerboard structure with lower solvent content, decreasing the innermost layer SLD. The increased outer layer thickness with a lower SLD compared to 0 and -0.5 V suggests the accumulation of expelled \([P_{6,6,6,14}]^+\) cations in the solvent-rich layer. This solvent layer also implies a continued cation presence in the innermost layer for interpenetration interactions with 2-EHL. This structural transition seems irreversible, as indicated by the consistently low thickness and SLD of the innermost layer at the subsequent -1 V potential. The thin innermost layer with significantly lower SLD implies that ongoing ion exchange into the boundary layer.
occurs while preserving the electrical ordering in a checkerboard structure. This irreversibility or hysteresis with potential demonstrates that the interfacial states can be “flipped” from one to another and suggests that significant reversing potentials need to be applied to “un-flip” them. This would have rather large implications and lead, for example, to a history-dependent OCP.

Figure 24. Schematics showing structure and composition change of interfacial layers under neutral and polarized potentials for 5% w/w [P₆,₆,₆,₁₄][BOB] in 2-EHL solution. The innermost layer is ion-rich, and the outer layer is solvent-rich. The schematics from left to right are arranged according to the applied voltage order.

5% w/w [P₆,₆,₆,₁₄][BScB] in 2-EHL exhibits a somewhat limited electro-response under applied potentials (cf. Figure 23c), which may be related to the weaker manifestation of IL aggregate structures observed in bulk SANS measurements (see Paper II). In 2-EHL, this more prominent association between cations and anions could lead to a somewhat diminished self-assembly/interpenetration interaction between the [P₆,₆,₆,₁₄]⁺ cations and 2-EHL molecules, resulting in an outer solvent-rich layer with the SLD more closely matching that of the bulk solution. At +0.25 V, the rise in SLD and thickness of the innermost layer can be ascribed to the attraction of [BScB]⁻ anion (or ion pair due to the strong ion binding). This situation is mirrored at large negative potentials (i.e., -1 V), where the reduction in SLD and increase in thickness of the innermost layer reflects the attraction of [P₆,₆,₆,₁₄]⁺ cations. Furthermore, compared to the neutral potential (0 V), the decreased thickness of the outer solvent-rich layer at polarized potentials suggests a more compact arrangement of counter ions to
compensate for the excess surface charge. The behaviour of the [BScB]- system is thus intermediate between that of [BOB]- and [BMB]-, but more closely resembles [BMB]-.

Clearly, the anion architecture significantly influences electro-interfacial behaviour. The smaller [BOB]- anion exhibits a predominantly isotropic distribution of its negative charge, whereas [BMB]- and [BScB] display more charge distribution anisotropy, along with aromatic rings contributing to both greater and more directional intermolecular interactions.51 All of these structural features lead to a lower sensitivity of [BMB]- and [BScB] to the effect of electric fields. Moreover, the larger O-B-O bond angle in the [BScB]- anion (cf. Figure 23d), featuring two six-membered heterocycles, integrating aromatic groups (as opposed to tethered, as in the case of [BMB]- anion) seems to lead to a strong ion pairing and diminishes the ability to form extended structures in bulk.

Figure 25. SLD profiles for 2.5% w/w [P6,6,6,14][BMB] and 2.5% w/w [P6,6,6,14][BOB] mixture in 2-EHL solutions, obtained from the best fit to the reflectivity curves as a function of distance Z, where the gold-solution interface is located at Z = 0. The legend indicates the potential applied order. The dashed line represents the SLD profile for the same gold surface and bulk ILs/2-EHL
solution that would be predicted without an adsorbed, structured layer. (Reproduced from Paper II.)

$[P_{6,6,6,14}][BMB]$ and $[P_{6,6,6,14}][BOB]$ have both demonstrated promising capabilities in modifying friction and serving as anti-wear agents,$^{123,138}$ but their electro-responsive behaviours are clearly distinct. It is therefore of interest to investigate how a mixed system would behave in terms of interfacial structuring and electro-responses under competitive conditions. **Figure 25** shows the SLD profiles for a mixture of 2.5\% w/w $[P_{6,6,6,14}][BMB]$ and 2.5\% w/w $[P_{6,6,6,14}][BOB]$ in 2-EHL at a gold electrode interface at different applied potentials. For all potential conditions, the mixed system’s SLD profiles again exhibit an ion-rich innermost layer and a solvent-rich outer layer, attributed to the self-assembly interaction between $[P_{6,6,6,14}]^+$ cation and 2-EHL.

Meanwhile, the SLD profiles under applied potentials show a relatively weak electro-responsive behaviour, more closely resembling the characteristics of $[P_{6,6,6,14}][BMB]$. Especially upon reversing the potential bias to $+0.25$ V, the SLD profile exhibits a reversible behaviour, restoring the thickness and composition of the interfacial layer, which is quite different from the irreversible interphase behaviour seen for the pure $[BOB]$ system. While $[P_{6,6,6,14}][BMB]$ generally dominates the hybrid interfacial layers due to its higher interfacial preference, the reduced SLD and thickness of solvent-rich layer compared to pure IL/2-EHL system (*cf. Figure 23a, b and 25*) implies a slightly enriched cation content in the outer layer. These interfacial structure changes in the mixture system suggest that at least some $[BOB]$- anions lead to a rather different orientation of the cation tails and break the regular EDL packing.
4.3. Correlating macroscopic IL tribological tests and nanoscale structure

From previous sections, the phosphonium orthoborate-based ILs have shown the electro-tuneability of interfacial structure and composition both in PC and 2EHL. Extending these molecular controls to the macrotribotronic performance and controllability is thus meaningful. Recently, our constellation has developed electro-tribological measurement systems, an elastohydrodynamic (EHD) rig, and more recently, a mini traction machine (MTM) coupled to external electric field control. This realises in situ macroscopic tribotronic friction capability for the first time. Figure 26 shows the traction behaviour for MIL ([P_6,6,6,14][BOB]) and DIL ([P_4,4,4-C_{12}-P_{4,4,4}][BOB]_2) in 2-EHL at different applied potentials (Paper IV). The tribotronic traction coefficient of MIL can extensively respond to the external electric fields, consisting of its electro-interfacial composition and structure changes indicated by EC-NR measurements (cf. Figure 23b). However, DIL displays poor electro-responsive traction behaviour.

Figure 26. Traction behaviour under various external electric fields for MIL and DIL in 2-EHL with different weight percentages (% w/w). (Reproduced from Paper IV.)
EC-NR has been used to understand this poor electro-responsivity of tribotronic friction performance via electro-interfacial structure and composition. The fitted SLD profiles of EC-NR curves for 3.5% w/w \([P_{4,4,4\cdot C_{12}\cdot P_{4,4,4}}][BOB]_2\) in 2-EHL solution under different applied potentials are illustrated in Figure 27, which shows ion-rich layers with low SLD for all potential conditions close to the surface, followed by an additional solvent-rich layer under polarized potentials (i.e., -0.5, +0.25 and -1 V). These stratified ion-rich layers in \([P_{444\cdot C_{12}\cdot P_{444}}][BOB]_2\)/2-EHL system exhibit much lower interfacial SLDs compared to the MIL \([P_{6,6,6,14}][BOB]/2\)-EHL described in the previous section, which had the same molar concentration of anion in 2-EHL. Once again, the two charged sites of \([P_{4,4,4\cdot C_{12}\cdot P_{4,4,4}}]^+\) dications lead to less pronounced segregation of its polar and apolar domains, preventing the self-assembly/interpenetration interaction between cation and 2-EHL that occurs in monocationic systems, and leading to higher-content ion packing on the gold surface.

![Figure 27](image)

**Figure 27.** SLD profiles obtained from the best fit to the NR data as a function of distance \(Z\), where the gold-solution interface is located at \(Z = 0\). The legend indicates the potential applied order. The dashed line represents the predicted
Furthermore, the changes in SLD profiles under different potentials of \([\text{P}_{4,4,4}^-\text{C}_{12}^+\text{P}_{4,4,4}]\)[BOB] are less pronounced than \([\text{P}_{6,6,6,14}]\)[BOB], which could be attributed to the increased adsorption and stratification of DILs. This weak electro-interfacial behaviour probably accounts for the poor electro-responsivity of the traction coefficient observed in Figure 26. At -0.5 V, the second layer exhibits increased thickness and higher SLD, indicating the enrichment of \([\text{P}_{4,4,4}^-\text{C}_{12}^+\text{P}_{4,4,4}]^+\) cations with a more diffused structure with a higher 2-EHL content. Notably, the D-2-EHL has the highest SLD \(6.70 \times 10^{-6} \text{ Å}^{-2}\). The reduced thickness and SLD of the first layer at +0.25 V indicate an anion-rich interfacial structure due to the large dissociation and mobility of the [BOB]- anion. Reversing the potential to -1 V increases the thickness and SLD of the secondary layer, indicating the re-aggregation of \([\text{P}_{4,4,4}^-\text{C}_{12}^+\text{P}_{4,4,4}]^+\) cations at the boundary to compensate for a more negatively charged surface. However, the consistently low thickness of the first layer suggests the maintenance of the anion-rich interfacial structure from +0.25 V. Such irreversible electro-responsiveness is possibly consistent with the continuously increasing traction coefficient at -1 V in Figure 26 and is similar to the previously mentioned hysteretic interfacial electro-response observed for \([\text{P}_{6,6,6,14}]\)[BOB] in 2-EHL, which could be attributed to an interphase transition.
5. Concluding Remarks

This thesis details our endeavours to investigate the electro-interfacial behaviour and composition of the phosphonium orthoborate-based ILs in different solvents at electrified interfaces and how this electro-tunability of IL boundary layers, in turn, can be utilised for controlling tribotronic friction.

The first main section, comprised of Paper I and III, explores the interfacial electro-responsiveness of various innovative monocationic (MILs) and dicationic ILs (DILs) dispersed in the polar aprotic solvent, propylene carbonate (PC), using multiple techniques, including quartz crystal microbalance (QCM), neutron reflectivity (NR), atomic force microscopy (AFM). The interfacial structures of ILs can be modified as a function of applied potential, and the electro-responsiveness to different polarities is strongly dependent on the nature and structure of the ionic species as well as solvent composition. A voltage-induced interphase transition from a self-assembled bilayer to the typical electrical double-layer (EDL) structure has been revealed in bis(oxalato)borate anion ([BOB]⁻) based MILs. This interphase transition phenomenon results in non-linear electro-response, a history-dependent open circuit potential (OCP), and the ability to alter properties significantly with small voltage changes if targeted. The pronounced electro-nanofriction reduction in [P₆,₆,₆,₁₄][BOB] (where [P₆,₆,₆,₁₄]⁺ represents trihexyl(tetradecyl)phosphonium) within the PC system under positive potential has validated this observation.

Despite the alkyl spacer chain and the alkyl corona of the dications, the DILs ([Pₙ,ₙ,ₙ-C₁₂-Pₙ,ₙ,ₙ][BOB]₂, n=4, 6) exhibit lower self-assembly ability in PC systems than their monocationic counterparts. This lack of self-assembly ability could be attributed to the dual charge centres of the cation diminishing the segregation between its polar and apolar domains, rendering them unlikely to be effective additives for the multilayer-based ionic lubrication and supercapacitor. However, [P₈,₈,₈-C₁₂-P₈,₈,₈]²⁺ dications display intercalation interactions between
their long tri-octyl side chains, resulting in a second level of self-assembly. This also provides an additional control parameter that can be used in the future to promote surface-active behaviours through crowding assembly.

A biodegradable oil, 2-ethylhexyl laurate (2-EHL), has been selected as alternative solvent to dissolve a series of MILs which share the same \([P_{6,6,6,14}]^+\) cation with a variety of anions, \([\text{BOB}]^-\), bis(mandelato)borate (\([\text{BMB}]^-\)), and bis(salicylato)borate (\([\text{BScB}]^-\)) (Paper III). The “surfactant-like” feature of 2-EHL introduces some degree of intrinsic self-assembly and/or interpenetration with the \([P_{6,6,6,14}]^+\) cation through the intermolecular interaction with their long alkyl chains, resulting in the formation of the diffuse solvent-rich outer layer. However, different anion architectures tune this solvent corona layer and control the distinct electro-interfacial behaviours among these MILs. The \([P_{6,6,6,14}][\text{BOB}]/2\text{-EHL}\) system exhibited the most electro-response with ion exchanges under different electric fields and an irreversible interfacial structure change. Conversely, the subdued electro-response of \([P_{6,6,6,14}][\text{BScB}]\) and \([P_{6,6,6,14}][\text{BMB}]\) in 2-EHL systems can be ascribed to their lower dissociation and solubility properties, leading to a reduced ability to rearrange in response to the field. Meanwhile, EC-NR measurements of the \([P_{4,4,4-C_{12}}P_{4,4,4}][\text{BOB}]_2/2\text{-EHL}\) system reveal strong adsorption of DILs to the surface, but poor interaction with 2-EHL molecules due to low self-assembly ability of dications, leading to a much worse macroscopic tribotronic frictional performance (Paper IV).

Together, the results thus offer valuable insights into molecular-scale mechanisms by which electric fields modify and control the interfacial behaviour of non-halogenated IL systems and how ion architectures can influence electro-interfacial composition and structure. More practically, this work provides enormous implications for understanding the interfacial behaviour of formulated ionic liquids in electrical applications from tribotronics to supercapacitors and paves the way for the rational design of ILs for high-charge density energy storage devices and sustainable lubricant additives.
6. FUTURE PROSPECTS

In this work, various surface characterisation techniques have been developed to investigate IL interfacial composition control and the responsive behaviour under external electric fields. These newly developed systematic analytical methodologies can be extended to other ILs, given their intrinsic ionic nature and the vast compositional variety of available cations and anions. Beyond that, future works, related to the deployment of phosphonium orthoborate-based ILs in applications such as supercapacitors and tribotronics, can be concluded in the following aspects:

1. The interphase transition occurring in surface-active ILs (SAILs) possibly explains some IL systems' electro-irreversibility and hysteretic open circuit potential (OCP), which appear to confuse the community. Different potential sequences could be applied to further study their slow electro-interfacial dynamics.

2. Perdeuterated IL or partially deuterated ionic species, including cation or anion as well as long alkyl chain, can be utilized to provide more structural details (e.g., head-tail-tail-head bilayer formation) in neutron reflectivity (NR) measurements.

3. With the development of atomic-scale roughness metal surfaces and polarised NR analytical methods, electrochemical NR capability could be extended to more practical surfaces for tribotronic contact, such as stainless steel and alloy.

4. Water contamination from the environment is unavoidable during practical lubricant applications. Thus, extending the studied systems with different humidity controls is necessary to understand how the water influences the electro-interfacial composition, tribotronic friction, and potential corrosive risk.

5. Future investigations could apply additional characterisations, including comprehensive electrochemical tests and molecular dynamic simulations, to explore the potential applications of SAILs in multi-layer-based supercapacitor energy storage devices.
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