PREFACE/FOREWORD

Interfaces of ionic liquids

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Preface

Interfaces of ionic liquids

Guest Editors

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The physics of ionic liquids has been ‘hot’ during the past decade, with many attracted to study these remarkable substances which challenge our classical understanding of the liquid state [1–5]. However, in comparison with high temperature molten salts, these purported wonder-fluids are very cold; their melting points, being around room temperature, are many hundreds of degrees lower than that of a typical metal halide. And herein lies both the technological and fundamental interest in ionic liquids, which have together fuelled the current furore. The development of customizable ambient-temperature liquid salts opens the way for many potential applications, from electrolytes to carbon sequestration to lubrication; whilst disentangling the complex web of inter-ionic interactions significant in ionic liquids—including hydrogen bonding, dipole interactions, dispersion interactions, as well as Coulomb interactions—has brought together physicists from erstwhile distant fields.

The interaction of ionic liquids with a solid surface is of particular interest due to electrochemical applications with ionic liquids as electrolytes [6]. Traditional theories for electrolyte-electrode interfaces, resting upon the assumption of dilute solution conditions, are not fit for purpose in the domain of highly concentrated ionic liquids [5], and a central focus in the field of ionic liquid interfaces is the refinement of alternative models. The interest of ionic liquids in electrochemistry has recently been boosted by the need for new electricity storage devices. Unlike batteries which involve redox reactions inside the electrodes, Electrochemical Double Layer Capacitors (EDLCs) are a family of devices in which the charge is stored at the electrode/electrolyte interface through reversible ion adsorption at high-surface-area porous carbon electrodes [7]. Their development has generated a great deal of fundamental research to examine the underlying molecular phenomena, especially from the ionic liquids simulation community. This reflects here in the numerous papers covering this topic. A first objective is to design EDLCs with a larger energy density. In their contribution, Han et al [8] propose an extension of the seminal mean-field theory developed by Kornyshev [2] to take into account the asymmetric character of ionic species. They include a parameter which accounts for the anion/cation volume ratio and show that a smaller anion leads to a larger peak in the differential capacitance at positive polarization. Breitsprecher et al investigate the impact of a variety of ionic characteristics (density, ion size and valency in [9] and ion shape and charge localization in [10]) on the structure they adopt at an electrode surface and on the differential capacitance. This is made possible through the use of coarse-grained models, which are not intended to represent specific ionic liquids but rather to provide reference data for systematic interpretation of the experimental results.

Still on the topic of EDLCs, Li et al [11] study the performance of a new family of ionic liquids, in which the cation is doubly charged. In this paper, they show that these dicationic ionic liquids have different adsorption profiles compared to the monocationic ones. As for the differential capacitance, they observe that there is a transition from camel-shape to bell-shape as the dication chain length increases. A drawback of these liquids is, nevertheless, their slow dynamic properties. In a second paper, Li et al [12] show that this can be overcome by adding an organic solvent, which results in an increase of the conductivity without impacting the capacitance.

Indeed, an important feature of EDLCs is that they have large power densities, i.e. they can be charged/discharged in a few seconds. It is therefore very important to understand the dynamics at the interfaces. In their contribution, Van Aken et al [13] combine electrochemical experiments with molecular dynamics simulations, with the objective of studying the diffusion of several ionic liquids adsorbed at onion-like carbon electrodes. By varying the size of the cation, they show that ones with a smaller size have larger diffusion coefficients, thus allowing the corresponding EDLCs to be operated at faster rates. Jiang et al [14] use
an original molecular dynamics simulation setup to study the charging of the double-layer under constant current conditions. They observe an interesting effect; the presence of pronounced oscillations in the cell potential during the initial stage of charging. They show this is caused by the sequential growth of the space charge layers with net charges of alternating signs near the electrode wall. Jiang et al [15] use a different method; time-dependent classical density functional theory. In this case, the charging occurs under constant voltage condition. They observe that the kinetics follow an exponential behavior in excellent agreement with the equivalent-circuit model, provided that the distance between the electrodes is large enough.

Two papers in this special issue study the structure of ionic liquids at electrode surfaces using an atomic force microscope. Hoth et al [16] investigated the interaction of a pyrrolidinium-containing ionic liquid with Au(111) held at a constant surface potential of 2 V. Quite remarkably, they record oscillations in tip-surface force corresponding to 12 anion and cation layers away from the surface. The authors go on to set out a model for the oscillatory forces between the AFM tip and surface, incorporating decay length and periodicity values inherent to the liquid (rather than the confining surfaces), and incorporate the spring instability to explain the observed jumps in the force profile. An analogy between the atomic friction stick-slip (a laterally oscillating potential) and the jumps in normal force due to a normal oscillatory potential is particularly useful. A second probe-surface interaction study by Li et al [17] also shows liquid layering for imidazolium-containing ionic liquids near a HOPG surface. Steps in force profiles are compared for the various ion structures. Notably, some attractive forces appear, usually superimposed on the oscillatory profile.

The effect of dissolved salts in ionic liquids at interfaces is the topic for two papers. Borisenko et al [18] reveal how LiCl salt can have quite dramatic effects on the Au(111)-ionic liquid interface. Unlike in pure ionic liquids, the gold herringbone reconstruction is not completed; the surface appears to dissolve at negative potentials in the presence of LiCl. It is proposed that Li+ ions act as supporting electrolytes to allow an unusual Au reduction to Au-. This work is of great relevance for electrochemical applications of metal-ionic liquid interfaces with dissolved Lithium salts, and shows that the behaviour of mixed electrolytes is not trivial to estimate and can deviate substantially from both pure ionic liquid or salt-in-water behaviour. A second paper by Mamusa et al [19] investigates the effect of adding electrolytes, this time on the colloidal stability of nanoparticles in ionic liquid. Ion-specific effects are observed with respect to the dissolved salt; whilst the particles are dispersed in the presence of Na+ ions, Li+ ions cause the particles to aggregate into clusters.

The interaction between ionic liquids and clay surfaces is the topic of two further papers in this issue. There is dual interest in studying clays as model surfaces; firstly, they are accessible experimentally as atomically smooth sheets over macroscopic areas and with regular (known) charge density, so prove ideal for comparison between theory and experiment. Secondly, they can be delaminated in many liquids to give dispersions of nano-platelets with useful properties. Molecular dynamic simulations of ammonium-based ionic liquids intercalated between montmorillonite sheets is investigated by Duarte et al [20]. Layering of the ions in planes parallel to the montmorillonite surfaces is observed, and whilst shorter alkyl-chain cations give rise to no order in the layers, the longer alkyl chain cations lead to alkyl-alkyl aggregation into bilayers with interdigitated chains. Payal et al [21] study the ion orientations of imidazolium-based ionic liquids in the region near mica surfaces. Intricate details of the ion orientations, disorder, and arrangement are revealed. A key finding of this work is the comparison of asymmetric and symmetric Imidazolium-based ionic liquids with similar total alkyl content; the former are more disordered, with chains pointing away from the surface (for long chains) or in plane (for short chains), whereas the latter are substantially more ordered with the longer chains pointing almost directly perpendicular to the surface.

A great deal of research in the field of physics of ionic liquids has reported substantial ion-specific effects, and note the ‘designer’ nature of ionic liquids resulting from our ability to select ions leading to particular desirable characteristics. Whilst this prospect is undoubtedly on the horizon, the link between structure and properties is not yet well resolved. Addressing this, and teasing apart the various molecular interactions using quantum mechanical simulations, in particular the role of different anions, was the aim of Matthews et al [22]. Anions and cations interact by way of in-plane H-bonding and inter-planar
The authors go on to rationalise how these interactions could explain viscosity and surface interactions including lubrication.

The effort to discover the structural and dynamic aspects of ionic liquids at interfaces over recent years has united researchers from diverse backgrounds and involved substantial cross-disciplinary collaboration. Electrochemists, colloid scientists, tribologists, surface scientists and molten salt physicists are all taking part using the tools of experiment, theory and computer simulation. This broad cross-disciplinary collaboration is represented well by the contributions in this special issue.

References