

## **Modelling ionic liquids at electrochemical interfaces**

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# **1. Proposal**

## **1.1 Introduction and motivation**

Ionic liquids are room-temperature molten salts, composed mostly of organic ions that may undergo almost unlimited structural variations. The scientific and technological importance of ionic liquids now spans a wide-range of applications [1]. For example they can be used as solvent for the textile industry, as lubricants or as fluids for thermal engines; due to their solvent potential they may even be at the origin of emerging technologies in such fields. Here we will focus on the electrochemical applications of ionic liquids only. These can be separated in two main families: electrodeposition on the one hand and energy storage and conversion on the other hand. For the former, ionic liquids allow for the development of processes that are otherwise impossible in water; for example the electroplating of aluminium in order to protect steel from corrosion [2]. As for the very-active field of electrochemical storage of energy, many synthesis routes involve the use of ionic liquids [3]. They are also used in replacement of the conventional organic solvents as electrolytes in battery [4], fuel cell or supercapacitor [5] devices, allowing for their operation under a large electric potential window. In particular, it is worth underlining the case of electrical double layer capacitors (EDLC), which have attracted much attention in recent years [6]. The discovery of nanoporous electrode materials with enhanced performances when using an ionic liquid with ion sizes matching the pore size opens the way for a widespread use of supercapacitors in many contexts where high power electrical output is required [7]. As an extension, the behavior of the ionic liquids at charged interfaces even allows to forecast the development of electroactuators [8] which could be used as artificial muscles, sensors, and even energy generators in turbulent flows or sea-tide.

## **1.2 State of the art**

The considerable amount of experimental results, some of them somewhat unexpected, has spurred the interest of the theoreticians community. Despite the underseen simulation work of Heyes and Clarke [9], the interface between electrodes and ionic liquids had barely remained explored until the last decade. Then several studies have focused on the structure of ionic liquids on charged surfaces [10, 11], showing that the ions exhibit a pronounced oscillatory structure close to the interface. In parallel, the development of a mean-field theory based on the Poisson-Boltzmann lattice-gas model showed that it is compulsory to account for the finite volume occupied by the ions, resulting in a dramatic departure from the Gouy-Chapman law for the capacitance-potential curves [12]. It is worth noting that the latter work has actually preceded experiments, and that numerous studies have reported differential capacitance results in qualitative agreement with the mean-field theory since then [13, 14].

In a second step, simulation studies have focused on a better understanding of the existence of particular capacitance-potential curve shapes, such as e.g. the « bell-shaped » or « camel-shaped » ones. In particular, the roles of the anisotropy of size between the ions or of the charge distribution inside a given ion have been addressed [15, 16, 17, 18]. It was also shown that for the particular case of the interface between the molten salt LiCl

and an aluminium electrode, a potential-induced ordering transition of the adsorbed layer was at the origin of a peak of the capacitance [19, 20]. Such a situation has also been reported for imidazolium ionic liquids systems in experiments based on in situ STM [21, 22]. Lately, the adsorption on atomically corrugated electrodes was shown to induce a systematic increase in the differential capacitance compared to the case of electrodes [23, 24].

The technologically-important case of porous electrode has also recently been investigated. Simulations involving slit-like pores [18] or carbon nanotubes [25, 26] provided a first insight of the structure of ionic liquids in confined environment. But it is the correct introduction of polarization effects by the metallic walls which could allow for a complete understanding of the formation of a superionic state [27, 28]. The mechanism at the origin of the enhanced capacitance in nanoporous electrodes was then fully understood from molecular dynamics simulations involving realistic carbon materials and taking into account the polarization in an appropriate way [29]. In order to underline the current vigor of the simulation community in this field, we may mention the following example: the existence of a capacitance varying with an oscillatory behavior depending on the pore size was simultaneously reported by three different groups in the same week [30, 31, 32]!

### 1.3 Objectives

The main objective of this meeting is to discuss the recent advances on the understanding of the ionic liquids/electrode interface. A particular focus will be given on the case of supercapacitors, which has attracted most of the attention in recent years. The relative contributions from the various approaches to the problem, such as molecular dynamics, electrolyte theory (A. Kornyshev), thermodynamic modelling (R. van Roij), etc will be put into perspective. There are many experimental groups working on this topic and we expect some of them to participate in the meeting and to provide their feedback on what they have learnt from simulations and what they expect to learn in the next years. In parallel, simulators should be able to propose new experiments that could be performed in order to confirm/infirm theoretical results.

As an extension of this meeting, we would like to propose a full workshop for the next CECAM call. Such a workshop could remain focussed on the specific case of ionic liquids, but it would also be of interest to extend the scope to the case of other electrolytes, e.g. to the modelling of the liquid / electrode interface.

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