



Charge Storage on Ionic Liquid Electric Double Layer: The Role of the Electrode Material



Renata Costa, Carlos M. Pereira*, A. Fernando Silva*

Faculdade de Ciências da Universidade do Porto, Departamento de Química e Bioquímica, CIQUP-Physical Analytical Chemistry and Electrochemistry Group, Rua do Campo Alegre, s/n 4169 – 007 Porto, Portugal

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ABSTRACT

The influence of the electrode surface material, the ions chemical structure and the combination of both on differential capacitance curves plays an important role to a deeper understanding on the molecular level structure of electrical double layers (EDLs) involving ionic liquids (ILs).

The research work focused on the structure of ionic liquids on charged surfaces is technologically-important for the development of new applications and in the upward of the existing ones, such as electrodeposition or energy storage and conversion. Understanding EDL property will allow maximizing the specific capacitance, which in turn leads to higher energy and powering densities of the devices. The electronic interactions of 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [C₄MIM][FAP] ionic liquid with Hg, Au, Pt and GC were assessed in order to get a fundamental understanding of the electrical double layer microscopic structure and its intrinsic properties at electrode/IL interface. Ionic liquids containing the [FAP][−] anion exhibit a strong hydrophobic nature and wider electrochemical window than previously used ionic liquids and a good electrochemical stability. The magnitude and shape of C(E) curves revealed different orientations of the cation when the nature of the substrate is changed. The predominantly hydrophobic interactions of the imidazolium hydrocarbon chains with the Hg are translated by the camel shape type curve. In contrast, the low and nearly constant C(E) values obtained for Au electrode point to the interfacial structure being dominated by the electrostatic π -stacking of the imidazolium ring/electrode interaction with the aromatic ring adopting an orientation more parallel to the surface.

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1. Introduction

The bulk molecular structure of ionic liquids outcomes from a delicate balance between the long-range forces (Coulombic) and short-range forces (van der Waals, dipole-dipole, hydrogen bonding). The ion-ion interactions of ILs provide a fundamental understanding of the electronic structure and specific interactions that occur within the ionic liquid. The extent and strength of the intermolecular interactions between anions and cations (such as coulombic and hydrogen bonding interactions) are usually invoked to explain the physical properties and reaction dynamics of these Coulombic fluids [1].

Despite the behavior of room temperature ionic liquids (RTILs) near charged surfaces is receiving increasing attention,

there is still some controversy and lack of consensus in understanding how the pure ionic liquid is structured at charged and uncharged surfaces.

At electrified surfaces, the above mentioned interactions are additionally modulated by the applied potential.

Over recent years, the study of anion-cation interactions [2,3], nanostructural organization [4–7] and different conformations of anions [8] and cations [9] in both liquid phase and in the crystalline structure, have been the subject of considerable interest. Evidence of micro and nano heterogeneities emerged from theoretical studies involving molecular dynamics simulations performed by Wang et al. [10] and Pádua et al. [4] concerning the nanostructural organization were corroborated by Triolo et al. [11] and Bodo et al. [12] through X-ray measurements. The structural heterogeneity resulting from the aggregation of the alkyl side chains of the nonpolar substituent imidazolium cations plays an important role in the properties of the liquid making them distinguishable from the molecular solvents. The absence of solvent molecules in the molten salts with high melting temperatures and ionic liquids

* Corresponding author. Tel.: +351 22040613; fax: +351 220402659.
E-mail addresses: cmpereir@fc.up.pt (C.M. Pereira),
afsilva@fc.up.pt (A. F. Silva).

raises the challenge to develop models capable to describe the structural properties of interfaces constituted only by ions.

The IL/electrode interfacial structure models proposed until now range from the Helmholtz double layer and a multilayered structure, with the ions exhibiting a pronounced oscillatory structure close to the interface. Extensive work concerning simulation techniques was done to better comprehend the electrode–electrolyte interfaces, enlightening that the ions adopt a multilayered structure at the ionic liquid/graphite (planar) electrode interface. Kislenco et al. [13] performed molecular dynamics simulation in order to evaluate the structure of the electrical double layer in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄MIM][PF₆]) near a basal plane of graphite. It was found that near an uncharged surface the IL structure differs from its bulk structure exhibiting a well-ordered region. At the negatively charged graphene sheet was found to be composed by alternated cationic and anionic layers.

Increasing efforts have been made in the past few years to investigate the interfacial region at electrode/IL systems; however, information of ILs in contact with charged surfaces is still scarce. Considering the significant experimental and computer simulations progress in the study of electrode/ionic liquid interface, the EDL models proposed so far do not appropriately accommodate the influence of the chemical nature of ionic liquids and their interactions with the surface.

Ionic liquids containing the tris(pentafluoroethyl)trifluorophosphate [FAP][−] anion paired with imidazolium, pyrrolidinium and phosphonium cations exhibit a strong hydrophobic nature and wider electrochemical windows than [PF₆][−] or equivalent ionic liquids [14], making them ideal candidates as extraction solvents [15] and energy storage devices electrolytes [16].

Since the interfacial effects of ionic liquids at charged surfaces are very relevant for electrochemical applications of ionic liquids, following the ion arrangement at the interface is fundamental in order to give a comprehensive understanding of how nanostructuration observed in the bulk will affect the EDL structure.

The high-energy X-ray reflectivity results obtained by Mezger et al. [17] considering ionic liquids with [FAP][−] anions in contact with charged sapphire substrate point to an interfacial molecular layering structure. AFM studies have shown that the molecular structure and, consequently, the interfacial properties of ionic liquids at charged surfaces can be modulated not only by changing the surface potential, but also by varying chemical composition of the ionic liquids [18]. From AFM results obtained with pyrrolidinium and imidazolium [FAP][−] ILs at Au(111) surface, it was possible to conclude that ILs are strongly adsorbed onto solid surfaces with several IL layers presenting oscillating ion density profiles at the electrode surface [19].

The multilayer type model is the most common accepted model to describe the IL/electrode structure, however some authors advance another possible arrangement of the ions at the interface such as the monolayer type structure [20]. Baldelli's description of the charge arrangement of the cation and anion at the interface resembles the classical Helmholtz picture of an ionic monolayer at a charged surface, e.g., ionic liquids are organized into one ion layer thick [20].

To accomplish a better understanding of charged solid–electrolyte interfaces, a systematic study was followed in order to discriminate the contribution of the ion–ion and ion–electrode material interactions on the electrochemical performance of systems containing [FAP][−] ionic liquids. The novelty of this work is based upon the proposal of an interfacial structure for each electrode studied based on the shape of the differential capacity curves.

2. Experimental

2.1. Reagents

The hydrophobic ionic liquid [C₄MIM][FAP] was purchased to Merck with the highest purity grade available (higher than 99%).

The IL purification procedure included the washing of the ionic liquid several times consecutively using ultra-pure water with continuous stirring in order to dissolve and remove water soluble impurities. To reduce the water content to the lowest minimum, before electrochemical study, the IL was heated for several hours at 80 ± 5 °C under vacuum and (≈10 Pa) with stirring. The water content, according to Karl-Fisher titration (831 KF coulometer Metrohm) was below 30 ppm.

Before each experiment all glass material was washed with concentrated sulfuric acid followed by abundant washing with ultra pure water and finally with boiling ultra-pure water. The ultra-pure water was obtained by filtration through Milli-Q deionized water purification system with a volume resistivity of not less than 18.2 MΩ cm.

The experiments were performed in a three electrode electrochemical cell assembled. Mercury electrode (Metrohm 663 VA Stand), Au, Pt or GC were used as working electrode. Autolab 302 N potentiostat EcoChemie equipped with a frequency analyzer (FRA) was used in the electrochemical studies. The cell is surrounded by a glass jacket allowing water circulation to keep the temperature of the system at a required value. A silver wire was used as pseudo-reference electrode and glassy carbon was used as auxiliary electrode. The IL was purged with pure Nitrogen to remove dissolved oxygen for at least 30 min. During the experiments, N₂ was kept over the electrolyte without disturbing the electrochemical measurements.

As mentioned in the literature, an important factor in the use of solid electrodes is the dependence of the electrode response (in terms of activity, stability and reproducibility) relatively to the surface conditions. Consequently, the surface requires a specific pre-treatment in order to obtain reproducible results. The characteristic voltammogram obtained indicates the perfectness of solid surfaces, cleanliness of the cell used and quality of the reference electrode.

The polycrystalline Au, Pt and CG used in the characterization of ionic liquids were acquired to Metrohm (0.0314 cm²) and consist in a polished hard disk imbedded PEEK cylinder. Before each study, the electrodes were polished with 1 micron diamond paste (Buehler) during 2 minutes and washed with abundant ultra-pure water to remove any diamond paste trace remaining in the electrode surface. Subsequently, the Au electrode treatment proceeded with electrochemical cleaning in a perchloric acid solution (Aldrich, 70%) with concentration of 0.1 M until a stable electrochemical profile is reached. For Pt electrode the surface was electrochemically cleaned in 0.5 M H₂SO₄ aqueous solution. The first step of cleaning consisted in holding the Pt electrode at +2.0 V vs. SCE for 2 min in order to anodically dissolve any organic trace residues. The following step consisted in cycling the electrode between −0.23 and +1.10 V vs. SCE at 100 mV/s, stopping after 10–20 cycles at the positive limit (+1.10 V) vs. SCE. The voltammetric profiles of the Pt electrode were in good agreement with the previously reported voltammograms [21].

The electrocapillary curve was obtained by measuring the lifetime of a set of 10 Hg drops falling at a constant potential within the ideal polarizability window estimated by cyclic voltammetry measuring the time at which the drop falls. The applicability of the technique to determine the pzc and the extraction of the capacitance values is described in our previous work [22,23].

The size of the ions was estimated using ChemBio3D Ultra 13.0 modeling program (Perkin Elmer).

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