



Short communication

Structural ordering transitions in ionic liquids mixtures



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ABSTRACT

Differential capacitance curves for the electrical double layer (EDL) of mixtures of imidazolium-based ionic liquids (ILs) with a common cation (1-ethyl-3-methylimidazolium, $[C_2MIM]^+$) and two different anions (bis(trifluoromethylsulfonyl)imide, $[Tf_2N]^-$) and tris(pentafluoroethyl)trifluorophosphate $[FAP]^-$) were obtained. Sharp peaks in the differential capacitance curves were observed for a small range of mixtures compositions at positive charge densities. The appearance and position on the potential scale of the peaks were found to be dependent on the mixture composition and temperature. The occurrence of these phenomena is interpreted as corresponding to an abrupt change in the EDL structure arrangement as a result of a complex interplay of electrostatic interactions and steric effects. The use of the non-structured mercury electrode allowed to decouple the eventual potential induced restructuring occurring at the double layer from the well-known surface reconstruction effects often reported for ionic liquids in contact with single crystal face electrodes.

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1. Introduction

Electrified interfaces research involving ionic liquids is still intense [1–3]. Structure-potential relationships at EDLs of ILs are of paramount importance since they control most of the observed experimental phenomena and applications [4]. Many studies have addressed possible potential induced restructuring of EDL as a result of the interplay of electrostatic interactions and steric effects resulting from the complex structure of the ions of the ILs [5,6].

Theoretical simulations have indicated the occurrence of three main processes at the EDL upon electrode charge variation: ion layering, crowding and overscreening of the surface charge, with the overscreening being considered as a distinctive aspect of the EDL structure in ILs [7]. The results of recent simulation studies point to transitions between those structures which occur via formation of monolayer of counter-ions.

Differential capacitance is a fundamental property of the electrified interface, it is expected that this property should be sensitive to such structural changes and transitions occurring at the interface as reported in ILs in contact with single crystal gold [8,9] and bismuth [10] electrodes. Characteristic features in differential capacitance and voltammetric curves associated with restructuring of the EDL have also been reported for $Au/[HPO_4]^{2-}$ [11] and $Pt/[HPO_4]^{2-}$ [12] aqueous electrolyte interfaces.

Non surface structured Hg/ILs have the advantage in allowing to decouple features associated with potential induced surface reconstruction, known to occur with single crystal face electrodes with

features related to restructuring occurring on the adjacent layer at the electrode, as shown for thiourea [13–15] and uracil [16] and isoquinoline [17]. In this work we correlate the maxima obtained in the differential capacitance with structural transitions occurring at the electrode interface composed by ionic liquids mixtures with a common cation.

2. Materials and methods

The hydrophobic ionic liquid $[C_2MIM][FAP]$ was purchased to Merck and $[C_2MIM][Tf_2N]$ to Io-li-tec 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 $80 \pm 5^\circ C$ 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 $18.2 M\Omega \cdot cm$.

IL mixtures were prepared in defined molar ratios by stirring the required masses using a high-precision balance (MettlerToledo) with an uncertainty of ± 0.0001 g. After preparation, the ionic liquid mixtures were placed back under vacuum to eliminate contamination by air moisture during this procedure.

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Electrochemical experiments were carried out in a water jacketed three-electrode cell and the temperature was kept constant by the use of a thermostated bath. The experiments were performed inside a N_2 -filled glove box to prevent oxygen and moisture interference. The working electrode used was a hanging mercury electrode (model 663 Metrohm VA stand), the counter electrode was made of glassy carbon, and a silver wire was used as a quasi-reference electrode. Differential capacitance curves were extracted from impedance data accordingly the method described elsewhere [18].

3. Results and discussion

We report differential capacitance curves for mixtures of two ILs with a common cation and widely different anions.

Fig. 1 a) and b) show C(E) curves for mixtures with two $[C_2MIM]^+$ based ILs containing anions $[FAP]^-$ and $[Tf_2N]^-$.

As expected for liquids containing the same cation and practically with the same concentration [19], at large negative potentials, the C(E) curves are coincident.

By contrast adding small amounts of $[C_2MIM][FAP]$ liquid to the pure $[C_2MIM][Tf_2N]$ causes “large” effect on C(E) curves for potentials above -1.0 V vs. Ag. The C(E) curves in the presence of $[FAP]^-$ are close to those obtained for $[C_2MIM][Tf_2N]$.

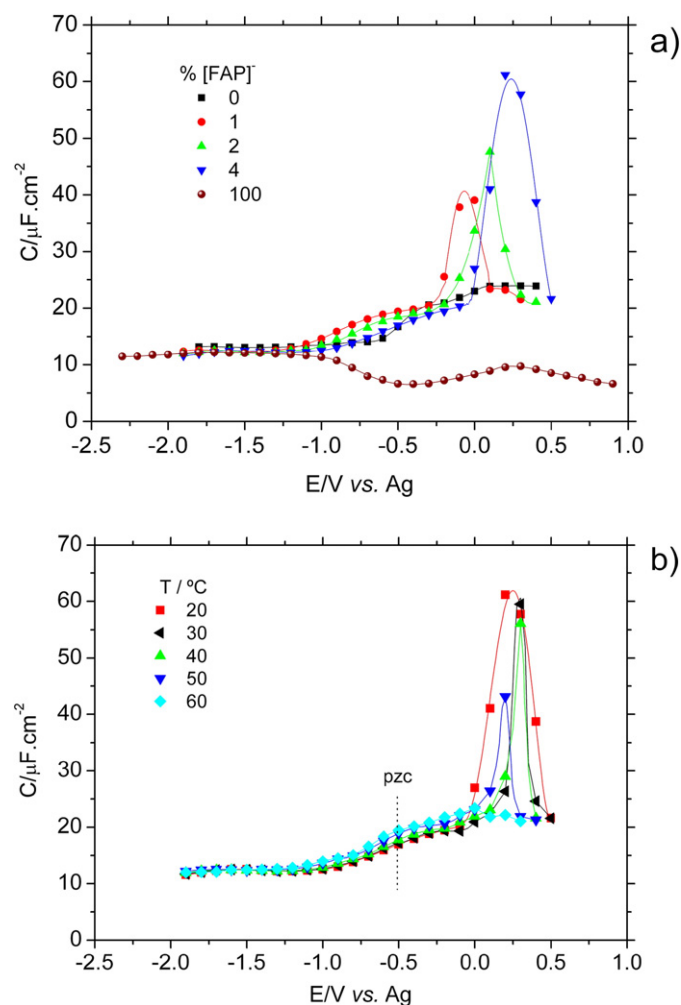


Fig. 1. Differential capacitance curves measured at Hg/ $[C_2MIM][Tf_2N]$ and $[C_2MIM][FAP]$ mixtures and at constant temperature (20 °C), b) Effect of temperature on C(E) curves for a mixture containing 1% $[FAP]^-$.

The difference in size and shape between cations and anions and, between the $[Tf_2N]^-$ and $[FAP]^-$ anions present in the mixture, results in a difference in their local charge distribution as counterions near the mercury electrified surface contributing to the asymmetry observed in the C(E) curves.

More relevant is the appearance of large capacitance peak which is $[FAP]^-$ concentration dependent and shifts towards more positive potentials with increasing concentration. For clarity no peaks are observed up to 40% $[FAP]^-$ anion concentration. Changing the temperature of the IL liquid causes also a shift of the peak position towards more positive potentials. For temperature above 60 °C no peak is observed within the available potential window.

It seems clear that the introduction of $[FAP]^-$ anion in the IL mixture causes significant changes on the EDL composition at positive potentials which approaches the interfacial composition against the pure $[C_2MIM][Tf_2N]$, i.e., the interfacial competition between $[FAP]^-$ and $[Tf_2N]^-$ is disadvantaged for $[FAP]^-$. The appearance of differential capacitance peaks has been associated to film formation and phase transitions. Indeed, Herman et al. [13,20] proposed the formation of stoichiometric thiourea/bromide film at the Hg interface. Potential induced surface orientation of compact film was identified to occur with isoquinoline [17]. In the case of $Au(111)/[HPO_4]^{2-}$ [11] and $Pt(111)/[HPO_4]^{2-}$ [12] it was proposed the formation of a surface film between $[HPO_4]^{2-}$ anion in the presence of Na^+ and also K^+ for $Pt(111)$.

Disorder/order transitions driven by change the applied potential have been suggested to be the origin of the peak in the differential capacitance for molten LiCl adsorbed at the (100) surface of metallic aluminum electrode [21,22]. Several simulation studies or theoretical approaches to the structure of ILs predict the possibility of structural transitions which may be detected by maxima in the differential capacitance [23–25].

Kirchner et al. [26] using molecular dynamics found structural transitions to occur from multilayer to monolayer structure at the surface with counter-ion being densely packed.

More recently, Ivaništšev et al. [7] showed the relevance of the interplay of the short range electrostatic interactions and steric effects on several interfacial phenomena such as ion layering, crowding and overscreening in the first interfacial layer. Ivaništšev et al. [7] also showed the appearance of differential capacitance peaks related to the transformation of an ionic bilayer structure closely related to a monolayer structure. The authors anticipate that experimental findings of the formation of the compact structure would be found for an ionic liquid with very large ions, specifically adsorbed halides or multivalent counter ions.

The data reported in Fig. 1 a) and b) are consistent with potential driven transition in the adsorbed layer of $[Tf_2N]^-/[FAP]^-$ anions at the interface. The transition is not only dependent of the coexistence of both anions but also dependent on the relative amount of both species. The hypothesis of the formation of a surface compact film would possibly lead to an abrupt decrease on C(E) curve at positive potentials when compared to the pure IL. Potential driven disorder/order transition as those reported on Au (100) are unlikely to occur at positive potentials [27].

According to Kornyshev and Qiao [1], phase transitions at the electrochemical interface affects, among other properties, the differential capacitance causing singular features. Capacitance peaks may appear when lateral arrangements of ions/molecules along the interface occur. Furthermore, Kornyshev and Qiao indicate that structural transitions in ionic liquids may occur even when ions may not be specifically adsorbed on the electrode. Merlet et al. [6] using molecular dynamics simulations discovered that structural transitions are associated with differential capacitance maxima.

Structural transitions from multilayer to monolayer have also been suggested by Ivaništšev et al. [3] for pure ionic liquids at high charge densities could explain the appearance of the peaks reported

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