

Solvent-free ionic liquids as *in-situ* probes for assessing the effect of ion size on the performance of electrical double layer capacitors

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Recently, there is a tremendous interest in increasing energy density of electrochemical capacitors for high-pulse applications, e.g., electric vehicles. In the electrical double layer capacitors (EDLCs), the charges are stored in the electrode/electrolyte interface using high-surface area materials [1]. Activated carbons are the most frequently utilized materials, because they are cheap and they can be produced with a large pore volume, enabling high values of capacitance [1]. However, a good matching between the electrode pore size and the dimensions of the ionic species is critical for an optimal performance of these systems [2-5]. In practice, it is difficult to figure the ideal dimensions of both partners forming the EDL, due to the facts that activated carbons are characterized by a broad pore size distribution and the ions are not all solvated by the same number of solvent molecules.

Moreover, the solvated or non-solvated state of the ions adsorbed in the EDL is not well established. So far, porous carbons have been tentatively used to establish a scale of ionic effective dimensions in aqueous and organic electrolytes, showing that a noticeable proportion of pores might be ineffective for the EDL formation depending on the kind of ions [3-5]. In this work, we propose to circumvent the uncertainty on ion size and their state in the EDL by the use of ionic liquids (ILs). Unlike other studies [7-9], our objective is not to establish the already proven properties of ILs as electrolytes, but to use them for investigating the effect of ion size on the electrosorption mechanism in nanoporous carbons. The great

advantage of ILs is their ionic nature in the absence of solvent, enabling the effective dimensions of the ions contributing to the formation of the EDL to be reasonably evaluated. Hence, ILs can be used as in-situ probe to explore directly the accessibility of the carbon porous texture during operation of a capacitor. For this purpose, we have prepared phosphonium-derived solvent-free ILs of increasing alkyl chain length.

The phosphonium-based ionic liquids, $[(C_6H_{13})_3P(ROCH_2)] [Tf_2N]$, were synthesized following the procedure described elsewhere [10]. In the formula, R stands for the different alkyl chains and Tf_2N for the bis(trifluoromethanesulfonyl)imid counteranion. The ILs will be referred to in the text as IL-3, IL-4, IL-7 and IL-12 for R=propyl, butyl, heptyl and dodecyl, respectively. The structure of the ILs is presented in Fig. 1 for clarity. The density and viscosity of ILs were measured with Mettler Toledo DA 110 M scale and micro Ostwald viscometer, respectively. Their conductivity was determined by impedance spectroscopy using a collector|electrolyte|collector stainless steel cell, previously calibrated with standard electrolytic solutions. The physico-chemical characteristics and dimensions of the ILs are given in Table 1.

The electrochemical performance of the composite carbon electrodes in IL electrolytic medium was tested with a two-electrode configuration using stainless-steel swagelok[®] cells. The activated carbon (AC, from Norit) used for manufacturing the electrodes is characterized by a BET specific surface area of 1653 m²/g, a large micropore volume (accounting 80 % of the total pore volume) and a well-developed mesoporosity which will favour the accessibility of ions to the micropores [6]. The electrodes are in the form of 1 cm² pellets obtained by pressing a mixture of carbon material (85 wt. %), acetylene black (5 wt. %) and polyvinylidene fluoride (PVDF, 10 wt. %). The capacitor device constituted of electrodes of comparable mass (10 to 15 mg), electrically isolated by a glassy fibrous separator, is assembled in a glove-box under argon. The capacitance properties are studied from 20 to

60°C by cyclic voltammetry (1–50 mV/s) and impedance spectroscopy in the frequency range from 100 kHz to 1 mHz, using a VMP-2 (Biologic, France). The capacitance values are expressed per mass of activated carbon in one electrode.

Since we want to investigate the effect of alkyl chain length on the capacitor performance, all the measurements have been carried out with pure ILs. As a consequence, the electrochemical characteristics of the capacitors are slightly resistive at room temperature, being this fact linked to the relatively high viscosity and low conductivity of these electrolytes (Table 1). For this reason, electrochemical measurements were also performed at 60°C, allowing the viscosity to decrease below 100 cP.

Fig. 2 shows the impedance spectra of the capacitors at two temperatures for the different electrolytes tested. Increasing temperature from ambient to 60°C results in a remarkable decrease of the equivalent series resistance (ESR) for all ILs, e.g., the ESR of IL-3 is 17 and 9 Ω at 25 and 60 °C, respectively. At high temperature, the viscosity of ILs decreases enhancing the mobility of ions and their penetration in the bulk of the carbon electrode. For comparison, the impedance spectra of AC based capacitors in aqueous and organic media show that the ESR at 60 °C in IL-3 is slightly higher than the value obtained with the same carbon in organic medium at room temperature.

Fig. 3 shows the cyclic voltammograms of the capacitors built with the different electrolytes, at room temperature and 60 °C. As expected, the performance of the capacitors increases significantly with temperature due to an enhanced diffusion of ions towards the pores of the carbon electrode. It is noteworthy that an increase of alkyl chain length results in a decrease of capacitance. Since the same trend is observed at both temperatures, it seems reasonable that the size of the cation is crucial for the development of the EDL. However, other factors affecting the EDL capacitance should be taken into account, such as viscosity or conductivity. These two parameters are of the same order for all the electrolytes studied (Table 1). This

leads to think that the differences in the overall capacitance are unlikely due to differences in the diffusion of the cations inside the pores of the electrode. Moreover, if capacitance would be only related to viscosity, one would expect a variation in the order: IL-7 > IL-3 > IL-4 ~ IL-12 according to data from Table 1, whereas the data indicate a link with the ions dimensions. The dimensions of the ions constituting the ILs were evaluated using a computer model (MS Modelling v3.2.0.0) which is a modified version of the Allinger's MM2 force field [11]. The results of the optimized structures showed that the ions do not present a spherical shape. For this reason, only the largest dimension of the ionic species was estimated. As expected, the cation size increases with the length of the alkyl chain, from 0.8 to 2 nm (Table 1), being much larger than the estimated for the counteranion, bis(trifluoromethylsulfonyl)imid (0.64 nm). Taking into account the series dependence of the overall capacitance of a two-electrode cell [1], we assume that this value is controlled by the electrode where the cations are sorbed, since the counteranion has a much smaller size than the former, and is kept constant for all the ionic liquids.

Accordingly to the size of the cations herein calculated, the pores smaller than 0.8 nm are not accessible to any of the electrolytes tested. In agreement with the pore size distribution of the activated carbon obtained from the N₂ adsorption data, this represents 39% of the overall porosity which cannot contribute to the formation of the EDL, and thus to the capacitance of the negative electrode. It can then be concluded that the porosity of this electrode is under-used from an electrochemical point of view. Micropores between 0.8-2 nm still represent 42% of the total porosity, although they would be all accessible only in the case of IL-3. As long as the alkyl chain increases (the largest dimension of the cation), the volume of pores accessible to the electrolyte is smaller and the capacitance value decreases. The volume fraction of AC corresponding to micropores larger than the cation size was estimated by applying the DFT model to the nitrogen adsorption data, and represented versus the capacitance values (Fig. 4).

The figure shows almost a proportional dependence of capacitance with the so-defined accessible volume, confirming the outstanding role of the relationship between pore size and cation size on the formation of the EDL. Considering that activated carbons are constituted of slit-shape pores, among the two extreme orientations of the cations chains versus the pore walls, i.e. parallel or perpendicular, our results indicate that the perpendicular position is preferred. A similar situation has already being reported for the intercalation of quaternary ammonium derivatives in lamellar hosts [12], where the ions are perpendicular to the layers presenting their positive charges close to the negative ones located on these layers.

In summary, the sieving effect of the carbon host in the formation of the electrical double layer was clearly demonstrated by using solvent-free ILs of increasing cation dimensions. Taking into account the textural properties of carbon evaluated by gas adsorption and the size of the electrolytes calculated by molecular modelling, it was proved that the overall porosity of the carbon electrode is underused.

Contrarily to previous papers reporting that pores within the range of 0.8-2 nm together with a moderate amount of mesopores [1, 2, 5] mainly contribute to the EDL formation, our results indicate that there is not an optimum pore size of the electrode material. Hence, the performance of capacitors can be only optimized if the porosity of the carbon electrode and the dimensions of the chosen electrolyte match to each other. The dependence of capacity values with cations dimensions confirms that the perpendicular position of the chains is preferred. This information is of extremely relevant importance for a fundamental understanding of the EDL formation in porous carbons.

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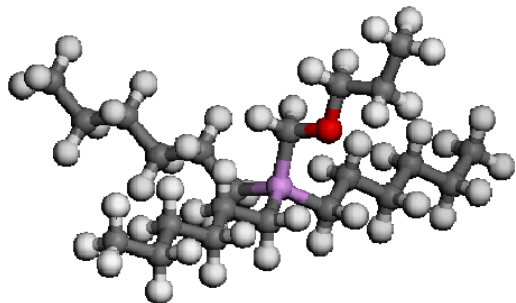
Table 1. Dimensions and physico-chemical characteristics of the series of phosphonium-derived ILs at 25 °C.

Nomenclature	Density [g/cm ³]	Viscosity [cP]	Conductivity [mS/cm]	Largest dimension (Å) *
IL-3	1.122	106.4	0.51	8.5
IL-4	1.112	132.9	0.33	8.9
IL-7	1.074	97.6	0.32	11.5
IL-12	1.044	133.5	0.12	15.8

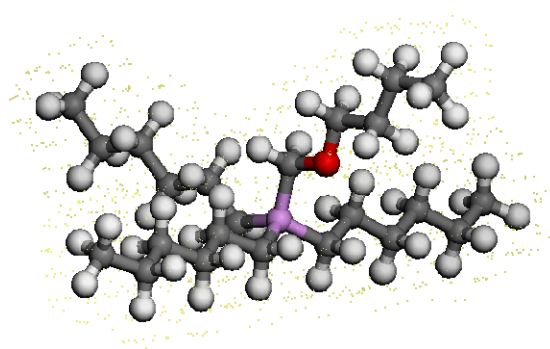
* Computed from the MS modelling software

Figure 1. Molecular structure of the phosphonium-based cations obtained from the MS-modelling software.

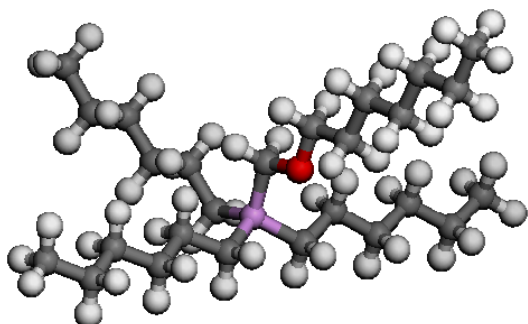
IL-3



IL-4



IL-7



IL-12

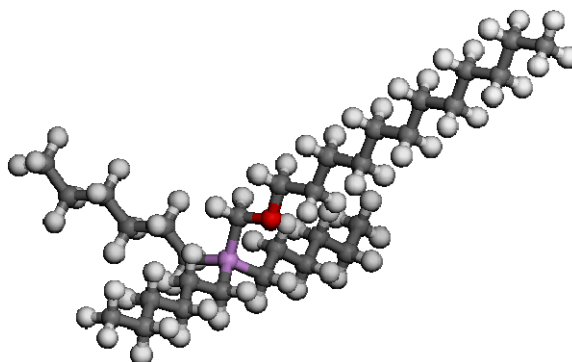


Figure 2. Nyquist plots of supercapacitors built from AC and phosphonium-based ILs at: A) room temperature; B) 60 °C. Inset: Impedance spectra of the carbon electrodes in acidic (H_2SO_4 , 1 mol.L⁻¹) and organic media (TEABF₄, 1 mol.L⁻¹ in acetonitrile). Frequency range from 100 kHz to 1mz.

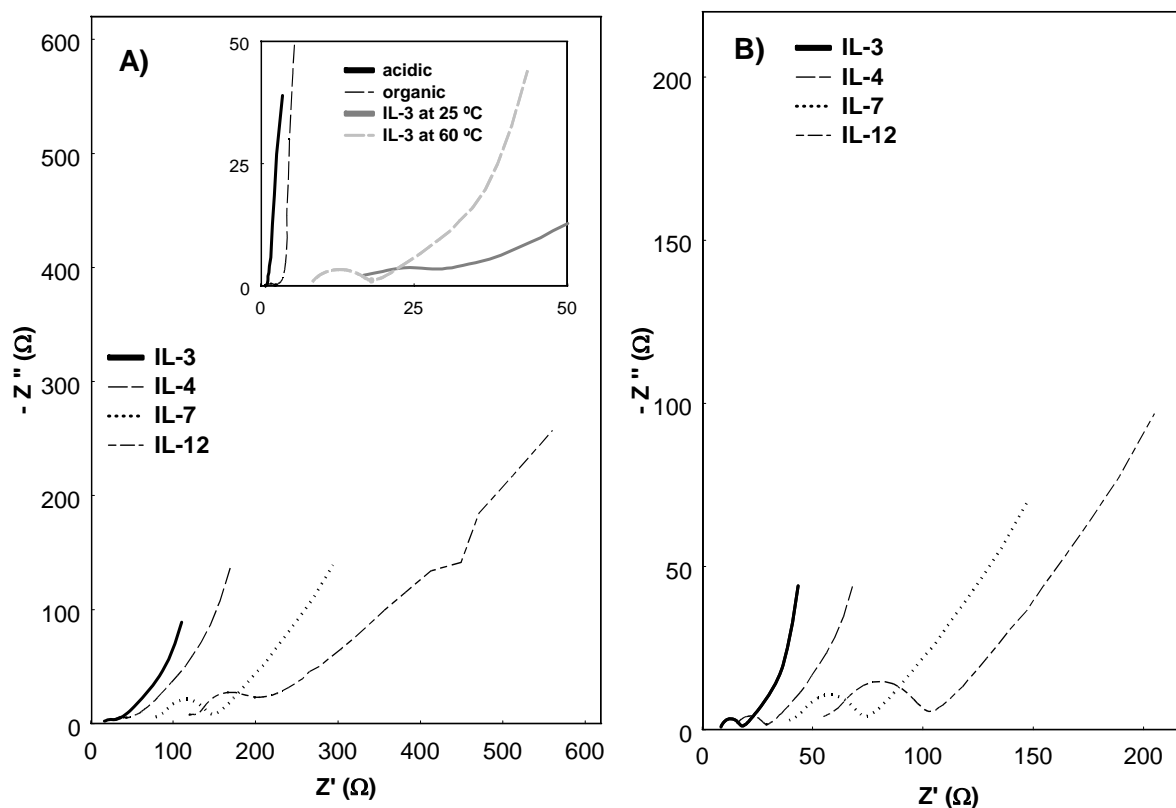


Figure 3. Voltammetry characteristics (2mV/s) of the activated carbon AC in the solvent-free solutions of the different ionic liquids, at: A) room temperature; B) 60°C.

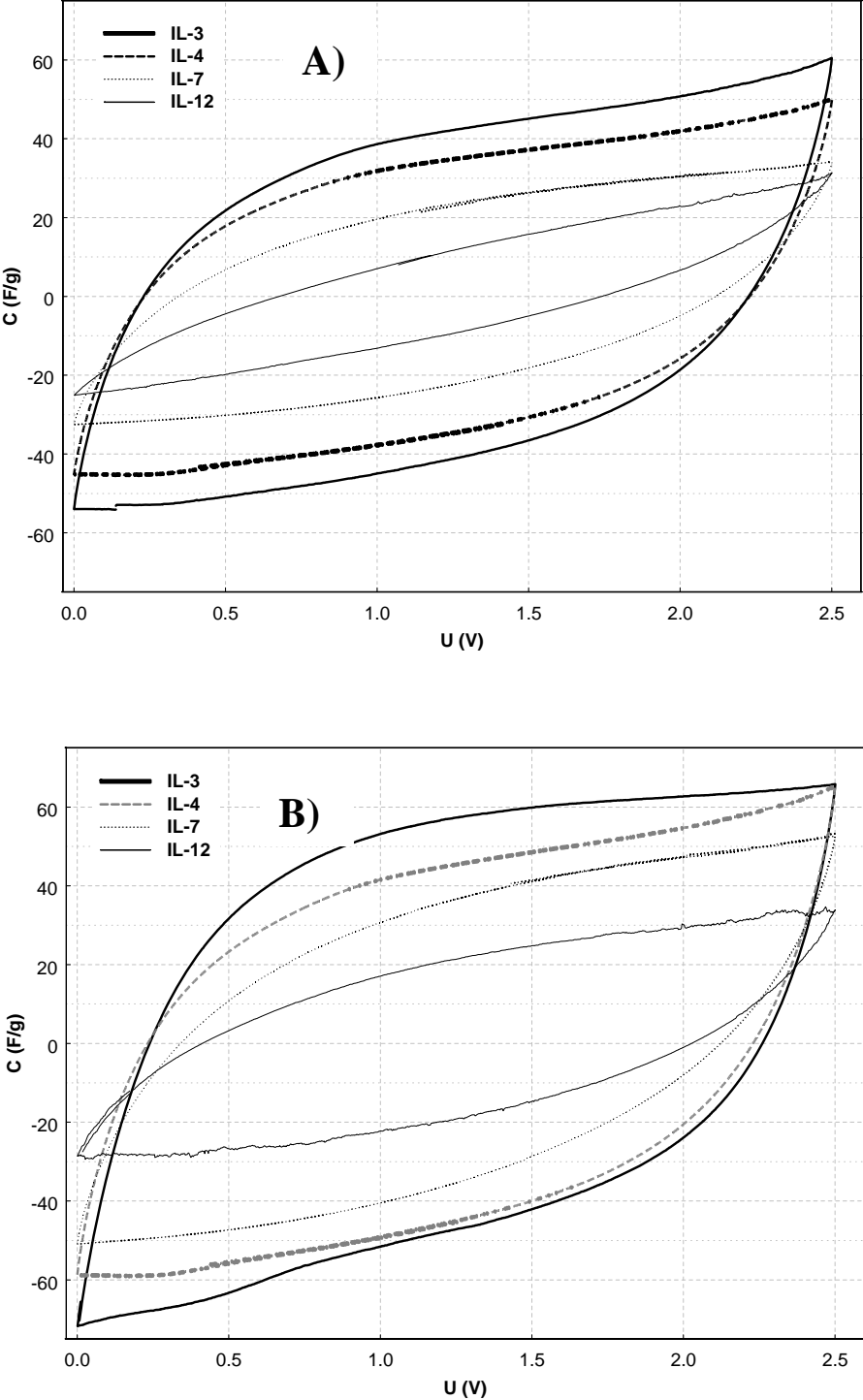


Figure 4. Relationship between the cation size or the accessible micropore volume of the AC electrode and the capacitance values.

