



# Viscous origin of ionic liquids at the molecular level: A quantum chemical insight



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## ABSTRACT

The viscosity of selected families of ionic liquids has been assessed at the molecular level as a function of the intermolecular interactions using Density Functional Theory together with Atoms-in-a-Molecule and Natural Bond Orbitals approaches. Large ion clusters were studied, with the energetics and topology of interactions being related with experimental viscosity data to infer nanoscopic mechanisms controlling the viscous behavior. The reported results exhibit important information on the molecular basis controlling viscosity, which would allow advancing in the development of low-viscous ionic liquids, through a judicious selection of ion pairs considering their interactions and molecular structure.

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## 1. Introduction

Thermophysical properties of fluids are of great relevance for the industry due to technical and economic reasons [1–5]. Efficient process design and integration [6], energy savings [7] and low environmental impact products and processes [8] require accurate knowledge of thermodynamic behavior (e.g. physical properties) of the used materials. Among the various different thermophysical properties required by the industry, viscosity ( $\eta$ ) may be considered as one of the key properties for most of the industrial processes [9]. For instance, relatively large viscosity values increases the fluid pumping requirements and thus that poses a techno-economical bottleneck for industry although the functionality of the materials is satisfactory. The number of fluids commonly used in the chemical and related industries is roughly around 1000 [10]. According to new environmental regulations elsewhere all around the world, the use of traditional solvents in new processes and in new products are subject to several critiques due to their both poor physical properties and undesired associated environmental impacts. Ionic liquids (ILs) have been pointed out as very attractive alternative materials to these conventional fluids in the recent years due to two major reasons: (i) the large number of possible anion–cation combinations results in several alternative room temperature ionic liquids (roughly  $10^6$  probable ILs, only considering pure ILs) [10], and (ii) tuneable properties through the selection of various ions [11].

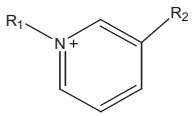
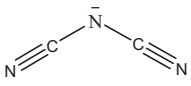
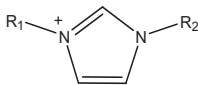
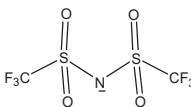
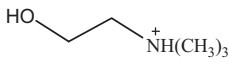
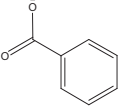
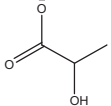
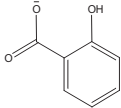
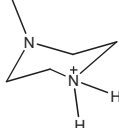
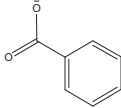
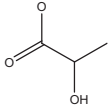
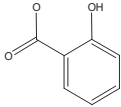
Unfortunately, some ILs yield viscosities two or even three orders of magnitude larger than the conventional organic solvents (viscosity ranges from 0.2 to 10 mPa s) [12]. These phenomena could be considered as a drawback of ILs when compared with traditional solvents from an industrial viewpoint [13]. However, not all ILs have huge viscosities [14], low viscous ILs may be selected from the pool of possible ILs. However, the large number of ion pair combinations makes it almost impossible to test all sort of probabilities via systematic experimental studies on the viscosity as a function of ion type. Therefore, computational tools could be quite useful to predict ILs viscosity [15,16]. From a molecular point of view, ILs viscous origin seems to be very related to the intermolecular hydrogen (H) bond network, intermolecular interactions in general, between involved ions [17–20]. Therefore, a deep and detailed analysis of the intermolecular interactions in relationship with viscosity data is essentially required for the development of a roadmap for ILs that are integrated both from structure and property point of view [21–24].

In this work, we pointed out fundamental background of the viscous origin and ion pair structure relation from molecular viewpoint by handling a set of ILs. At molecular level, Density Functional Theory (DFT) simulations along Atoms-in-a-Molecule (AIM) [25] and Natural Bond Orbitals (NBO) [26] theories are very useful tools to characterize, by means of a topological analysis of the electronic density, energetic viewpoint as well as intermolecular forces. Thus, other goal is to characterize intermolecular interactions in selected ILs through AIM and NBO theories, and to establish relationships with the viscosity data. A set of short-listed 14 ILs, with cations pertaining to pyridinium (Py) [27], imidazolium (Im) [24], cholinium (CH) [28,29] and piperazinium (concretely methyl-piperazinium,

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**Table 1**  
Molecular structure of selected compounds along their viscosity values ( $\eta$ ). Units are in mPa.s.

<i>Pyridinium based ILs</i>			
[BPy][BF <sub>4</sub> ]	70.5 <sup>a,b,c</sup>		[BF <sub>4</sub> ] <sup>-</sup>
[B3MPy][BF <sub>4</sub> ]	75.9 <sup>a,b,c</sup>		
[O3MPy][BF <sub>4</sub> ]	172.0 <sup>a,b,c</sup>		
[B3MPy][NCN <sub>2</sub> ]	18.4 <sup>a,b,c</sup>	[BPy]: R <sub>2</sub> = butyl, R <sub>1</sub> = H [B3MPy]: R <sub>1</sub> = butyl, R <sub>1</sub> = methyl [O3MPy]: R <sub>1</sub> = octyl, R <sub>1</sub> = methyl	
<i>Imidazolium based ILs</i>			
[BMIm][BF <sub>4</sub> ]	53.3 <sup>a,b,d</sup>		[BF <sub>4</sub> ] <sup>-</sup>
[BMIm][PF <sub>6</sub> ]	120.0 <sup>a,b,d</sup>		
[BMIm][Tf <sub>2</sub> N]	28.5 <sup>a,b,d</sup>		
[EMIm][Tf <sub>2</sub> N]	19.6 <sup>a,b,d</sup>	BMIm: R <sub>1</sub> = butyl, R <sub>2</sub> = methyl EMIm: R <sub>1</sub> = ethyl, R <sub>2</sub> = methyl	
<i>Choline based ILs</i>			
[CH][BE]	1096.73 <sup>a,b,e</sup>		
[CH][LA]	643 <sup>a,b,f</sup>		
[CH][SA]	1192.31 <sup>a,b,e</sup>		
<i>Piperazinium based ILs</i>			
[MP][BE]	693 <sup>g,h,i</sup>		
[MP][LA]	1404.3 <sup>a,h,j</sup>		
[MP][SA]	899 <sup>g,h,i</sup>		

<sup>a</sup> From experimental measurements.

<sup>b</sup> Obtained at 313 K.

<sup>c</sup> From Ref. [27].

<sup>d</sup> From Ref. [24].

<sup>e</sup> From Ref. [28].

<sup>f</sup> From Ref. [29].

<sup>g</sup> From molecular dynamics simulations.

<sup>h</sup> Obtained at 303 K.

<sup>i</sup> From Ref. [30].

<sup>j</sup> From Ref. [31].

MP) [30,31] families were investigated in combination with [BF<sub>4</sub>]<sup>-</sup>, [PF<sub>6</sub>]<sup>-</sup>, [NCN<sub>2</sub>]<sup>-</sup>, [Tf<sub>2</sub>N]<sup>-</sup> (bis((trifluoromethyl)sulfonyl)imide), lactate [LA], benzoate [BE] and salicylate [SA] anions (see Table 1). These ILs were selected due to the availability of the experimental data from previous studies, considering several groups of classic (imidazolium- and pyridinium-based ILs) and new generation (cholinium- and piperazinium-based) cations paired with anions selected with the same criteria. Moreover, on-going studies under

development in our laboratory on the application of these ILs to technologies such as carbon nanosystems [32], fuels dearomatization [30], or behavior under electric fields [33], are strongly dependent on an accurate characterization of the molecular origin of their viscous behavior.

The reported results have shown analytical relationships between the molecular structure, nanoscopic interactions between involved ions, and the macroscopic viscosity data.

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