

## Imidazolium/Imidazolate $\pi^+$ - $\pi^-$ stacked ions pair simulations in chloroform

Chiara Valsecchi, Jessé G. Neumann, Hubert K. Stassen

Grupo de Química Teórica, Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Goncçalves 9500, 91540-180 Porto Alegre - RS, Brazil

## Abstract:

Bulk ionic liquids (ILs) have been widely studied by experimental and computational methodologies, due to their enormous variety of potential applications [1, 2, 3]. The imidazolium (Im) group and its derivates have been of large interest, among the large spectrum of organic cations that might compose/form ILs, also for the possibility of tailoring the ILs thermodynamic and physical properties by alkyl substitutions at different locations [2, 4]. The supermolecular structure of neat ImILs, and consequently their properties, are directly linked to the three-dimensional arrangement of cations and anions. The interplay of the three intermolecular forces, electrostatics, dispersive, and hydrogen bonding, controls the organization of the ImIL in the gas and the liquid phases [4, 5, 6, 7]. More recently, it became of interest to understand cation-anion contact ion pairs when the IL is dissolved in other solvents [8, 9] and to characterize the structure and intermolecular interactions in these intimate ion pairs. The structure of contact ion pairs containing the imidazolate anion and a variety of six methyl substituted 1,3dimethyl-imidazolium cations in chloroform solution were studied by molecular dynamic simulations in the present work. These ionic liquids were studied under the condition of infinite dilution, that means, only one ion pair. This study focused on determining the importance and the effect of different methylations at the cation's imidazolium ring. The novelty of the work also consists in the fact of having an organic molecule, the imidazolate, as counter-ion, instead of the common chloride or hexafluoroborate. The formation of a stable contact pair in chloroform along the entire simulation period was demonstrated by radial and spatial distribution functions (Figure 1). The cations are localized preferentially above or below the anion's plane ring, reflecting contributions of  $\pi^+$ - $\pi^-$  stacking interaction between the two aromatic planar ions. The most acidic hydrogen at position C2 of the imidazolium cation exhibits the strongest structural correlations with the imidazolate anion, at distances within the range of hydrogen bonding. The structural correlations was in general weakened by methylations at all the cation's ring positions., The difference in the free energy of association for the methylation at the cation's C<sub>2</sub> has been determined in the order of 13 kJ/mol from potential of mean-force calculations, favoring the ion pair containing the protonated C<sub>2</sub> atom.



12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil



Figure 1. SDFs of the six different functionalized cations studied around the imidazolate anion (at the center, view from the C4 and C5 side). Upper row: cations with hydrogen at C2 of the imidazolium ring; lower row: the corresponding cations with a methyl group at C2. The SDFs depict the same isodensity surface for all the pairs.

Key-words: Imidazolium Ionic Liquid, Contact Pair, Methyl group substitution Click here to enter text.

Support: This work has been supported by CNPq and CAPES

## **References:**

- [1] P. Wasserscheid, Nature, 439, 797 (2006).
- [2] A.A. Pádua, M.F. Costa Gomes, J.N. Canongia Lopes, Acc. Chem. Res. 40, 1087– 1096 (2007).
- [3] M. Smiglak, J.M. Pringle, X. Lu, L. Han, S. Zhang, H. Gao, D.R. Mac-Farlane, R.D. Rogers, Chem. Commun. 50, 9228–9250 (2014).
- [4] R.M. Lynden-Bell, M.G. Del Po polo, T.G. Youngs, J. Kohanoff, C.G. Hanke, J.B. Harper, C.C. Pinilla, Acc. Chem. Res. 40, 1138–1145 (2007).
- [5] J. Dupont, J. Braz. Chem. Soc., 15, 341-350 (2004).
- [6] M.N. Garaga, M. Nayeri, A. Martinelli, J. Mol. Liq., 210, 169-177 (2015).
- [7] R. Hayes, G.G. Warr, R. Atkin, Chem. Rev., 115, 6357–6426 (2015).
- [8] K. Fumino, P. Stange, V. Fossog, R. Hempelmann, R. Ludwig, Angew. Chem. Int. Ed., 52, 12439–12442 (2013).
- [9] M. Zanatta, A.L. Girard, N.M. Simon, G. Ebeling, H.K. Stassen, P.R. Livotto, F.P. dos Santos, J. Dupont, Angew. Chem. Int. Ed., 53, 12817–12821 (2014).