

# Probing the Structure of Ionic Liquids and Ionic Liquid Crystals with $^{129}\text{Xe}$ NMR and Molecular Dynamics

Pedro Morgado<sup>S</sup>

*Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal*

Karina Shimizu

*Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal  
Instituto de Tecnologia Química e Biológica, ITQB2, Universidade Nova de Lisboa, Oeiras, Portugal*

João A. P. Coutinho

*Departamento de Química, CICECO, Universidade de Aveiro, Aveiro, Portugal*

Ana I. M. C. Lobo Ferreira and Luís M. N. B. F. Santos

*Centro de Investigação em Química, Departamento de Química e Bioquímica, Universidade do Porto, Porto, Portugal*

Luís P.N. Rebelo

*Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Oeiras, Portugal*

José N. Canongia Lopes

*Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal  
Instituto de Tecnologia Química e Biológica, ITQB2, Universidade Nova de Lisboa, Oeiras, Portugal*

and

Eduardo J.M. Filipe<sup>C</sup>

*Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal  
[efilipe@ist.utl.pt](mailto:efilipe@ist.utl.pt)*

A substantial part of the research effort in the field of ionic liquids (ILs) is dedicated to the study of their organization at the molecular level. The nano-structuration of these fluids gives rise to many of their peculiar properties, both in the pure state and in the interaction with other substances. Its understanding is thus fundamental to the rationalization of IL behavior. A wide range of techniques has been applied with that purpose, from X-ray and neutron diffraction to molecular simulations. Spectroscopic techniques, using appropriate probes, have also been applied to the study of the nano-structuration of ILs, with the advantage of their accessibility and non-destructive nature. The NMR active  $^{129}\text{Xe}$  nucleus is very sensitive to the local molecular environment around it, due to the large electron cloud and high polarizability of the xenon atom. Depending only on the solvent,  $^{129}\text{Xe}$  presents a range of chemical shifts over 250 ppm. Moreover, its small size as opposed to the usual spectroscopic probes (e.g. fluorescence, solvatochromic, etc), and the non-specific nature of its intermolecular interactions (only van der Waals forces) assures little perturbation of the liquid structure. In this work,  $^{129}\text{Xe}$  chemical shifts have been obtained, as a function of temperature, for solutions of Xe in a wide range of ionic liquids. Evidence is shown for the change of liquid structure with the increase of the alkyl chain length along a given IL family, for the mobility of Xenon around both polar and apolar domains, and for its preferential location in apolar regions. Molecular

dynamics simulations help to elucidate the NMR results [1]. Particular attention has been dedicated to ILs which display thermotropic liquid crystalline behaviour. It is shown that  $^{129}\text{Xe}$  spectroscopy is not only able to identify the isotropic liquid to liquid crystal transition, but is also able to provide insight on the differences between the molecular environments in both phases.

#### References

[1] P. Morgado, K. Shimizu, J.M.S.S. Esperança, P.M. Reis, L.P.N. Rebelo, J.N. Canongia Lopes, et al., Using  $^{129}\text{Xe}$  NMR to Probe the Structure of Ionic Liquids, *J. Phys. Chem. Lett.* 4 (2013) 2758–2762.