PhD Open Days

Probing the nano-structure of Ionic Liquids gels using ^{129}Xe NMR spectroscopy: structure-properties relation

Chemistry

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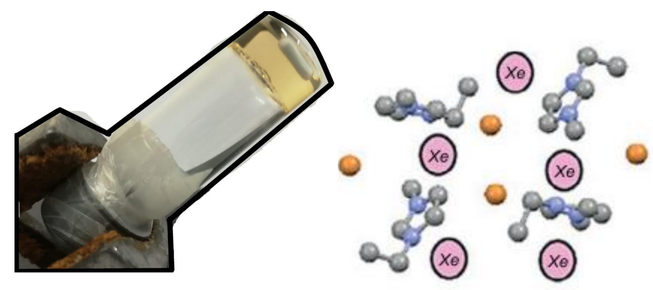
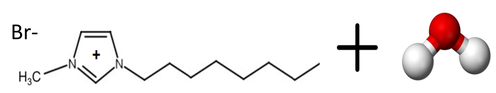
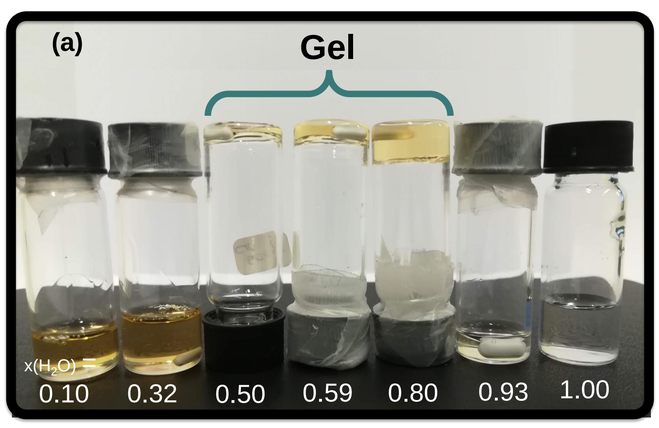


Liquid Crystalline Ionogels: $[C_{10}\,mim^+][Br^-] + H_2O$



Ionic liquids (ILs) are organic molten salts with melting points below 100 ºC. Given their tunable character and negligible vapour pressures, ILs are potentially suitable for a vast range of applications. The $[C_{10}mim^+][Br^-]$ is an imidazolium-based IL that turns into a high viscosity gel when a small quantity of water is added [1]. The ionogel exhibits a lyotropic liquid crystalline behaviour, displaying a set of mesophases that depend on the water concentration.



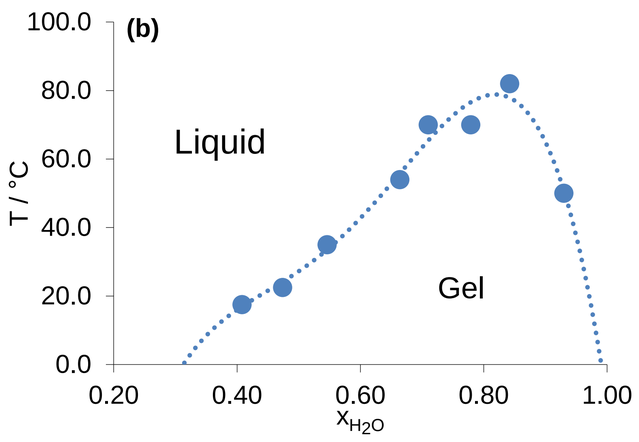
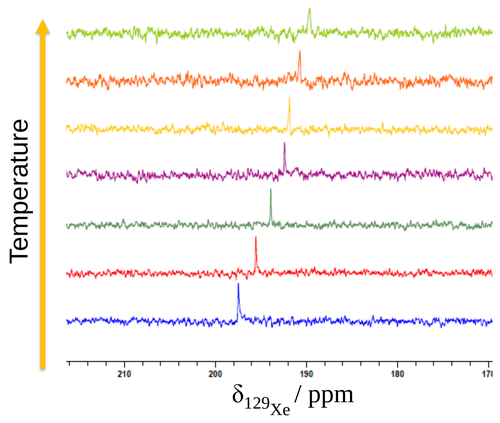


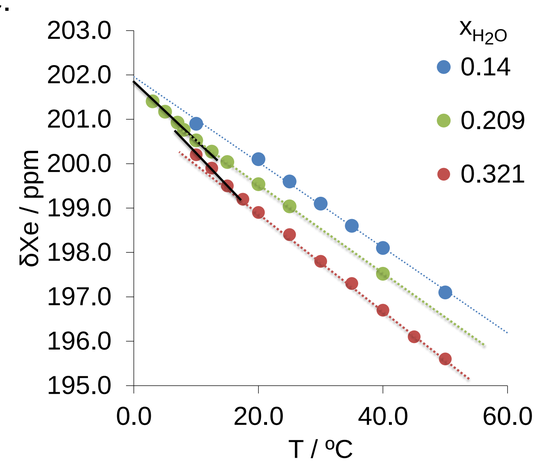
Figure 1 – $[C_{10}mim^+][Br^-]$ + water mixtures (a) samples; (b) Gel-Liquid transition temperatures as a function of the water molar fraction.

^{129}Xe Nuclear Magnetic Resonance spectroscopy: Xenon as a molecular probe

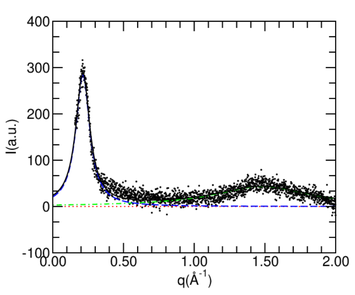
Xenon can be used as molecular probe due to its quasi-inertness and high sensitivity to its immediate environment. Since the ^{129}Xe isotope is detectable in nuclear magnetic resonance (NMR), yielding a sharp signal, ^{129}Xe NMR spectroscopy has been widely used to provide structural information in a broad range of systems, in particular ionic liquids. [2]

In this work, ^{129}Xe NMR spectroscopy was performed to explore the bulk structure of $[C_{10}mim^+][Br^-]$ + water mixtures. Xenon gas was bubbled in the solutions and the ^{129}Xe chemical shift was measured in a range of temperatures between 0.0 and 100.0 ºC.

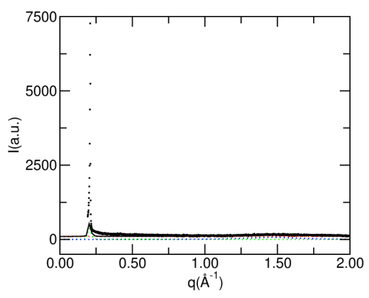




X-ray diffraction



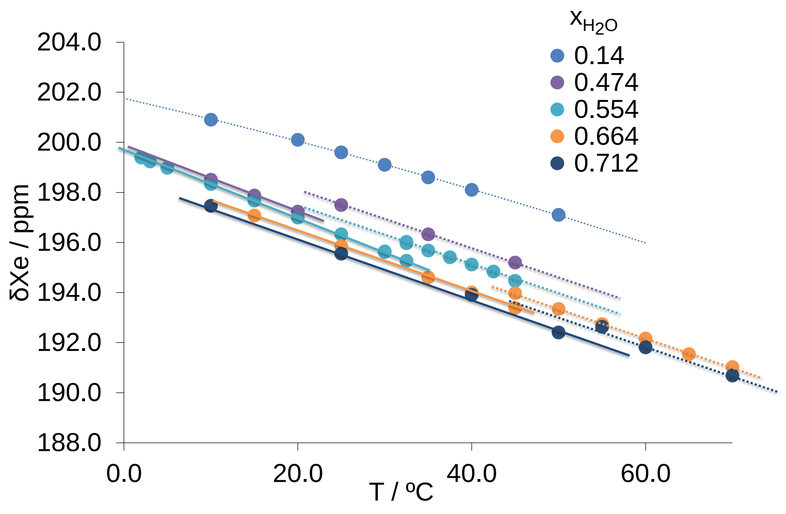
x_{H_2O} = 0.10



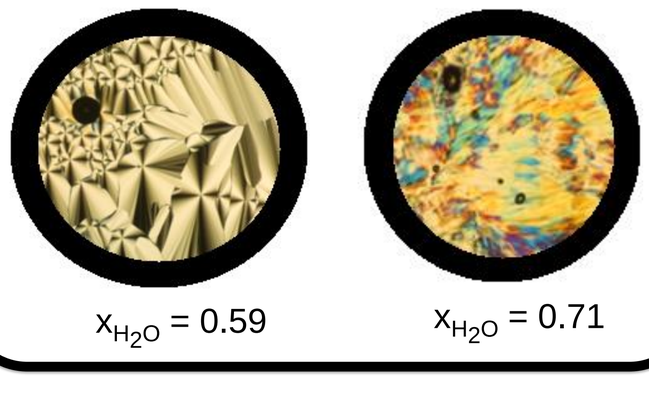
x_{H_2O} = 0.80

Methodology:

- **^{129}Xe NMR Spectroscopy**
- X-ray Diffraction
- Polarized Optical Microscopy
- Molecular Dynamics Simulations



Polarized Optical Microscopy



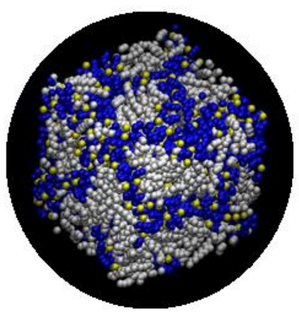
x_{H_2O} = 0.59

x_{H_2O} = 0.71

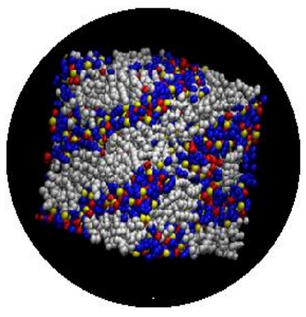
Molecular Dynamics Simulations

- Atomistic molecular dynamics simulations of the $[C_{10}mim^+][Br^-]$ + water systems were performed, starting from random configurations;
- Simulations have predicted the formation of a bicontinuous structure for the pure IL system. Lamellar and hexagonal structures were predicted for systems with concentrations within the liquid crystalline gel range.

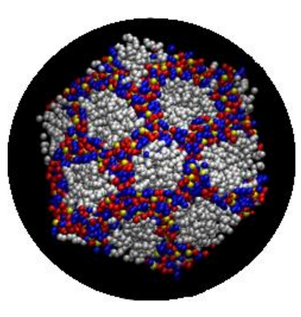
Cation ring (blue); cation tail (White); anion (yellow); water (red).



x_{H_2O} = 0.00



x_{H_2O} = 0.50



x_{H_2O} = 0.75

^{129}Xe NMR spectroscopy is sensible to the water content and structure of the samples. Furthermore, when following the ^{129}Xe chemical shift (δ_{Xe}) as a function of temperature it was found that:

- The gelification of the samples provokes in slightly change on the slope of the δ_{Xe} vs. T curve.
- A gel-gel transition was detected for the samples with x_{H_2O} between 0.47 and 0.71.

^{129}Xe NMR spectroscopy combined with other methodologies have provided important insights over the liquid bulk structure, phase transitions and gelification phenomena of the $[C_{10}mim^+][Br^-]$ + water systems.

References:

[1] M. A. Firestone, J. A. Dzielawa et al., Langmuir, 18, 2002, 7258-7260.
[2] P. Morgado et al., J. Phys. Chem. Lett., 4, 2013, 2758−2762.

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