

Mechanism of solvation dynamics in prototypical ionic liquid/molecular solvent mixtures: combining experimental and theoretical studies

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This last decade, ionic liquids have attracted the attention of the scientific community because of their unique properties such as environment friendly replacing volatile solvents, high conductivity and thermal stability. Therefore ionic liquids have been used for many applications in various fields like solvents for organic synthesis, exchange media in supercapacitors^[1] and electrolytes in dye sensitized solar cells.^[2] In order to decrease their intrinsic viscosity and to facilitate diffusion processes, they are often mixed with conventional solvents. However, the information concerning the molecular rearrangements occurring after the turbulence in solute-media interaction (e.g. the charge redistribution within the excitation of the solute or formation of the reaction intermediate) is still scarce.

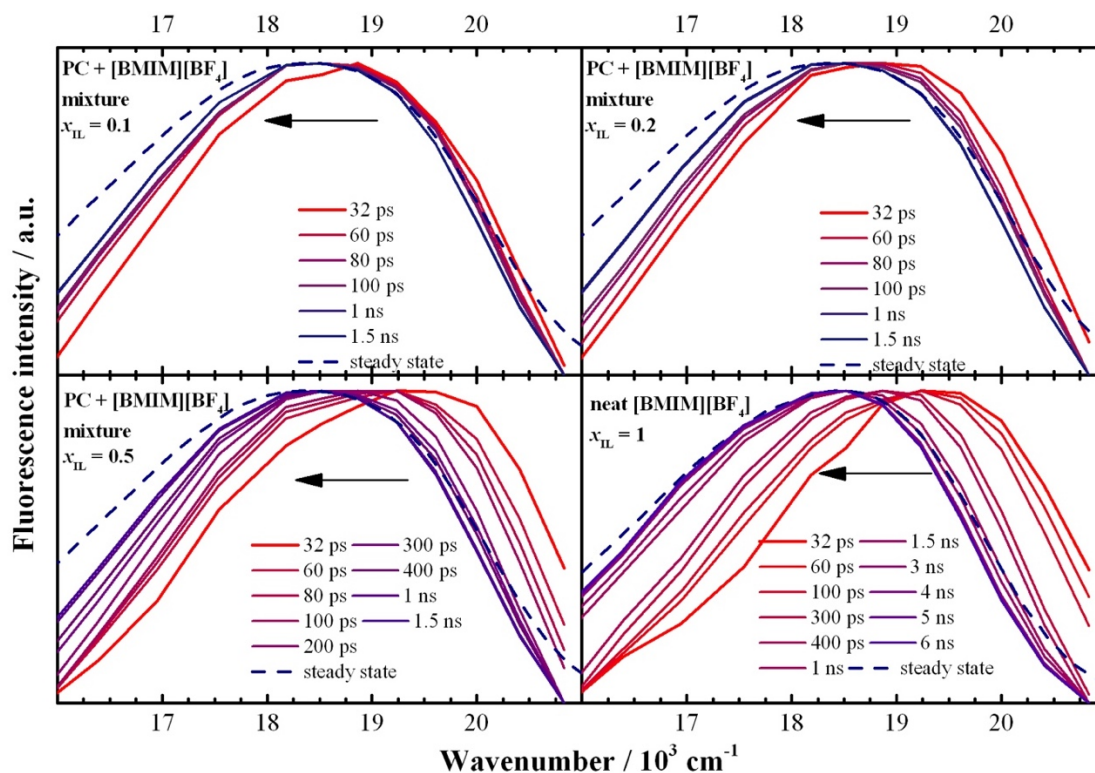


Figure 1. C153 fluorescence time-resolved spectra in [Bmim][BF₄]/PC mixtures

We present here a study combining experimental and theoretical data on the solvation dynamics in [Bmim][BF₄]/PC mixtures for various ionic liquid molar fractions, using the fluorescent probe coumarin 153 (C153). The C153 fluorescence decays, recorded with both fluorescence upconversion (FU) and time-correlated single photon counting (TCSPC) techniques, were used to reconstruct the time-resolved emission spectra and thus access the dynamic solvation response (Fig. 1). The combination of these two time-resolved fluorescence techniques allowed us to obtain an overview of the full solvation response, from the ultrafast time-scale, starting from ~200 fs to 200 ps for FU, up to ~ 5 ns for TCSPC. Multi-exponential model functions were required to fit the experimental curves. The resulting parameters clearly show the existence of very different time scales related to different regimes of solvation dynamics.

Like in the [Bmim][TFSI]/PC mixtures, studied previously,^[3] a long component was found to be largely dependent on the viscosity of the mixture. Fluorescence anisotropy measurements were performed at the emission maximum. Contrary to predictions by hydrodynamic theory, the dependence of the rotational time on the viscosity exhibits a large degree of non-linearity. This phenomenon is majorly ascribed to the non-ionic nature of the coumarin probe molecule.

Molecular Dynamics (MD) simulations performed on C153 in neat ionic liquid and mixtures are used to interpret the experimental solvation responses by characterizing the rearrangement of the solvent (here the ionic liquid and the molecular solvent) induced by the electronic excitation of the probe. These MD simulations give a mechanistic understanding of the rearrangements occurring in the solvation shell after photoexcitation. The response was calculated within both linear response and multiple vertical excitation methods and compared to experimental data.

To sum up, both experimental and theoretical results confirm the largely multi-component dynamics of these ionic liquid/molecular solvent mixtures.

Analysis of the structural properties of the coumarin's solvation shell, in the ground and the excited state as well as for its time evolution after vertical excitation, determines the dominating role of ionic/molecular species and motions. The governing influence of the Bmim⁺ cation on the solvation was suggested and verified.

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References:

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