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Cold-Spray Ionization mass spectrometry: evidence of cooling effect in term of ion internal energy and application in deep eutectic solvent analysis

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The *Cold-Spray Ionization* (CSI) source is a variant of the *Electrospray Ionization* (ESI) source where the nebulizing gas is cooled by liquid nitrogen at a temperature of -40°C [1]. Thereby, the liquid emerging from the capillary is considerably cooled but the temperature of gaseous ions produce is not known. For the presented studies, CSI was used to characterize Deep Eutectic Solvents (DES) a new class of green solvents [2]. In this context, the evaluation of internal energy distribution of so-called “thermometer ions” has been first performed in CSI and compared to the distribution observed in ESI. The "Vibrational Temperatures" calculated from the mean internal energies of the dissociating benzhylpyridinium cations have been compared to the “Characteristic Temperatures” (T_{char}) referenced to be the temperature required for an ion population in thermal equilibrium leads to the same ion Survival Yields (*SY*) as experimentally observed with the same mass spectrometer (JEOL AccuTOF) [3,4]. The modelling of ion’s behavior in mass spectrometer, the calculation of $P(E_{int})$ and then T_{char} have been performed thanks to the software “Mass Kinetics” [5]. Results shows that the temperature of ions generated by CSI is approximately 100K cooler in comparison by the ones formed by ESI. This temperature difference should explain why the CSI mode allows the characterization of labile non-covalent complexes unobserved by ESI such as the Deep Eutectic Solvent (DES) [6]. Indeed, Deep Eutectic Solvent are a new generation of green solvent able to form non-covalent molecular networks by the combination of hydrogen bond acceptor (HBA) and donor (HBD) and electrostatic interaction. A previous study shows that it is possible to characterize the structural affinities of constituent molecules of DES by mass spectrometry and especially with the CSI method. The chosen DES is the Reline, a mix of choline chloride salt and two urea molecules. To complete this work, other DES having choline chloride salt as hydrogen bond acceptor were also analysed by CSI-MS, namely the assembly of choline chloride/thiourea (1:1) and choline chloride/glycerol (1:1). This work allowed to testify the ability of the CSI method to characterise DES in gaseous phase.

References

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