

Ionic Liquid Media and Mesoscopic Effects on Hydrogen Bonding: NMR and DFT Study using Molecular Probe

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Ionic liquid media and mesoscopic effects on the state of H-bonding were studied by NMR and DFT methods. The proton sharing (positioning) in the H-bonds was monitored following the chemical shifts of picolinic acid *N*-oxide (PANO) used as the molecular probe dissolved in ammonium- and pyrrolidinium-based room-temperature ionic liquids (RTILs). Initially the relationships between ¹H and ¹³C NMR shifts and proton position in the O–H...O bridge were calibrated using traditional organic solvents and other H-bond complexes of pyridine *N*-oxide with acids increasing the H-bond strength. The reliable parameter for H-bond monitoring was proposed. The state of H-bond in ionic liquid media is largely governed by the bulk media dielectric properties. Some finer short-range order (mesoscopic) effects in RTILs can be also deduced. A drastic fall out of PANO/[BuMePyr][TfO] from the general dielectric scheme built using 'classical' solvents with increasing dielectric constant (from chloroform to water and culminating with formamide) can be explained by the extraordinary action of the triflate anion (CF₃SO₃⁻) being the conjugate base of one of the strongest 'superacids'. On a molecular level this effect indicates that the ionic liquid [BuMePyr][TfO] can act on H-bonded systems as a stimulant of proton transfer. In 'super-polar' media (formamide) the intramolecular H-bond system converts into intermolecular one forming the neutral H-bond complex of PANO with formamide molecule.