

Preferential Solvation of *p*-Nitroaniline in Binary Mixture of Chloroform and Hydrogen Bond Acceptor Solvents: The Role of Specific Solute-Solvent Hydrogen Bonding

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ABSTRACT: Solute-solvent H-bonding in binary solvent mixtures, may increase the local concentration at specific sites resulting in location specific preferential solvation. In order to study location specific preferential solvation Preferential solvation of solvatochromic probe *p*-nitroaniline (PNA) has been studied in binary mixtures of chloroform with different hydrogen bond acceptor (HBA) solvents using spectroscopic transition energy (E_T). Analyses of solvatochromic shifts of absorption spectra of PNA in different neat solvents as a function of solvent polarity parameters reveal the major contribution from solvent dipolarity/polarizability and HBA basicity in the solvation of PNA. The event of preferential solvation in the chloroform-HBA binary mixtures and the preference of one solvent above other in the solvation shell have been attributed to the hydrogen bond donor and acceptor ability of the solvent mixtures. HBA solvents form strong hydrogen bond with the amino group while chloroform forms hydrogen bond with the nitro group of PNA. This specific functional group recognition increases the local concentration at specific sites resulting in location specific preferential solvation and synergistic preferential solvation. Solvents with comparable polarity have been found to show significant synergistic behavior as a result of the formation of stronger solvent-solvent hydrogen bonded S_1 - S_2 species. These propositions were found to be supported by theoretical solvation models, calculated HOMO-LUMO energy gaps, effect of deuterated solvent on the extent of PS, and from ^1H NMR spectral analyses.

