

Tetrabutylammonium salt/phenol-based deep eutectic solvents: Structure elucidation from combined Infrared and DFT calculations.

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Abstract

Deep Eutectic Solvents (DESs) are a new class of solvents with promising properties for a large number of applications such as gas separation and sequestration, electrochemistry, catalysis and the extraction of natural compounds for cosmetic or pharmaceutical applications.[1-4] These solvents are usually prepared by mixing two components, one hydrogen bond donor (HBD) and an hydrogen bond acceptor (HBA) and are characterized by a significant depression in their melting point compared to those of the neat constituents. As reported in many recent publications on DESs, hydrogen bonding is believed to be the key intermolecular force leading to the melting point depression observed during the DESs formation.[5] Nevertheless, anion-cation interactions as well as steric effects could also play a significant role. Therefore, efforts are still needed to identify the solvation mechanisms at work at a molecular level that govern the structure–property relationships in this class of solvents.

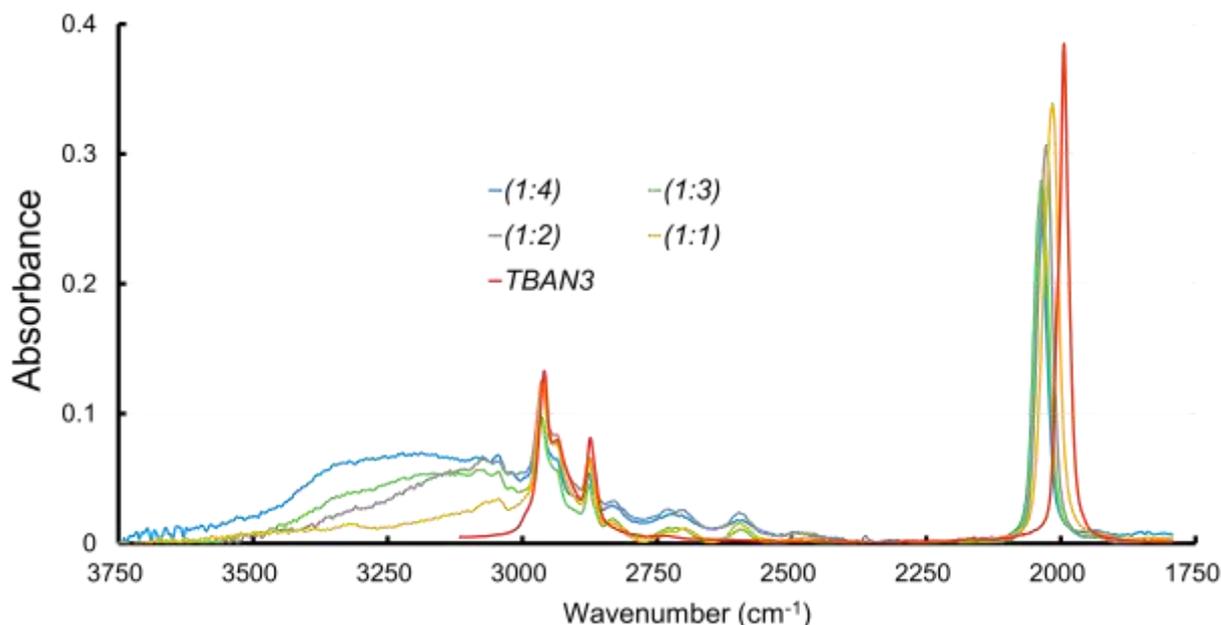


Figure 1: ATR-IR spectra of the TBAN₃-Phenol DES with various HBA-HBD ratios 1:1, 1:2, 1:3 and 1:4. The spectrum of the neat TBAN₃ salt is reported for comparison.

In this study, a series of new DESs composed of phenol as the HBD and tetrabutyl ammonium (TBA) salts with different anions as HBA were prepared and investigated by ATR-IR spectroscopy and DFT calculations in order to get insights into the local order existing in these DESs. In particular, a characteristic vibrational mode of the azide anion (N₃⁻) in the TBAN₃-Phenol DES with various HBA-

HBD ratios displays significant shifts in frequency in comparison with that measure for the neat TBAN₃ salt (see figure 1). Similarly, the OH stretching mode of phenol is significantly shifted in the DESs in comparison with that reported for neat phenol. These frequency shifts were interpreted by DFT calculations as related to specific hydrogen bonding interactions between the azide anion and phenol molecules. Thus, such solvation effects are believed to be responsible for the formation of a liquid phase at room temperature in these ammonium salt/phenol-based DESs.

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