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Local structure and electrochemical properties of TEMPO in ionic liquids via polarizable MD simulations

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PURPOSE OF THE ABSTRACT

2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) and its derivatives are promising metal-free redox agents used as mediators in the oxidation of alcohols, amines, and cellulose. They find broad application in energy storage devices such as supercapacitors, dye-sensitized solar cells, and redox-flow batteries.

The electrochemical properties of TEMPO can be controlled by an accurate choice of a solvent for a reaction. Ionic liquids (ILs) seem to be potential candidates not only because of their high conductivity, good stability, and low flammability but due to their unique tunable properties. For example, the TEMPO/TEMPO+ redox potential can be increased when an anion with low basicity, such as bis(trifluoromethane)sulfonimide, is chosen. [1] Thus, a systematic analysis is necessary to obtain a complete understanding of the observed effects on the molecular level aiming to establish clear structure-property relationships.

In the present work, we study the solvation of TEMPO and TEMPO+ in imidazolium, pyrrolidinium, and phosphonium-based ionic liquids with tetrafluoroborate, dicyanamide, methylsulfonate, and bis(trifluoromethane)sulfonimide anions by means of classical molecular dynamics (MD) simulation with the polarizable force field. [2-3] Including explicit polarization effects provides a more detailed and realistic description of the ionic fluids being a state-of-art tool in exploring their properties such as affinity to the solute.

Analysis of the microstructure reveals important differences in the local environment of TEMPO and TEMPO+ in the IL solution (Figure 1). The TEMPO radical acts as a hydrogen bond acceptor, showing preferable interaction of its nitroxyl group with hydrogen atoms of the head group of the IL cations. On contrary, the TEMPO+ cation plays the role of a donor forming doubly ionic hydrogen bonds with the IL anions. Such a strong solvent rearrangement upon the oxidation of TEMPO has an impact on its electrochemical properties, including reaction free energies and reorganization energies that we evaluate in the frame of Marcus theory. The effect of the basicity of the anion, the nature of the cation, and the length of its side chain on the above-mentioned properties is discussed.

FIGURES

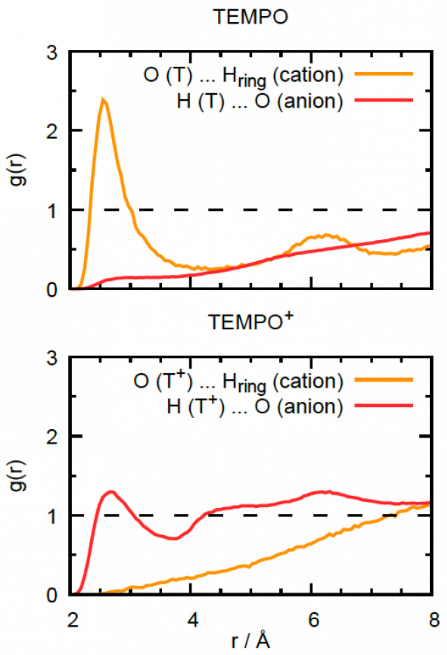

FIGURE 1

RDF around TEMPO/TEMPO+ in [C8C1im][NTf2]

Radial distribution functions around TEMPO (top) and TEMPO+ (bottom) atoms in 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid

FIGURE 2

KEYWORDS

TEMPO | ionic liquids | electron transfer | solvation

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