Correlating Geometrical and Electronic Properties of Imidazolium-Based Cation-Iron Porphyrin Complexes to Ionic Liquid Biodegradability

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Experimental work focused on biodegradation of ionic liquids has suggested that long alkyl chain imidazolium-based ionic liquid cations can undergo hydroxylation in the presence of microbial community while the smaller cation resist any biotransformation. However, the molecular level details for such transformations have not yet been elucidated. Cytochrome P-450 has been identified and widely studied for its role in the oxidation of a wide variety of molecules in aerobic and anaerobic environments and can act as a possible enzyme implicated in the hydroxylation of ionic liquids. In order to determine the effect of cytochrome P-450 on the 1-n-alkyl-3-methylimidazolium [Cnmim]⁺ class of ionic liquids, a protein environment was modeled with cysteine ligated iron porphyrin (FePCys). Imidazolium cations $[C_n mim]^+$ (n=2,4,6,8, and 10) were considered as potential substrates that interact with different variants of FePCys. These variants may be oxygenated (FePOCys) or non-oxygenated referring to the enzymatic cycle of the P-450 enzyme in focus. All the systems considered ([Cnmim]+FePCys or [Cnmim]+FePOCys) were treated quantum mechanically for understanding the effect of the porphyrin receptor on the electronic environment of imidazolium cations considering their properties in the gas phase as the datum for the same. To include the regioselective and stereoselective aspects of the system, geometrical analyses were also conducted to identify key cationic orientations. Electronic properties such as frontier orbital energies i.e. Highest Occupied and Lowest Unoccupied energy levels (HOMO and LUMO) were obtained to determine the reactivity of these molecules. Additionally, the results of HOMO and LUMO locations, hydribization of molecular orbitals of FePCys and the cations, and FePOCys and the cations will be presented along with the thermodynamic properties such as binding energy and free energy change upon binding to aid in inferring the molecular mechanism of ionic liquid biodegradation.