

Bioelectrocatalytic Reactions in Room Temperature Ionic Liquids

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The goal of our research is to develop new technology platforms utilizing novel enzymatic methods and processes for the modification of lipids to produce value-added products. Our approach to developing these new processes and products follows the established principles of green chemistry by using non-toxic catalysts, inherently benign solvents, and high-atom-economy synthetic routes. Accordingly, we developed the first enzyme-catalyzed reactions to be performed in mixtures of room temperature ionic liquids and supercritical carbon dioxide. More recently, we have demonstrated the first example of a bioelectrocatalytic reaction, involving hemin, to be carried out in room temperature ionic liquids.

The direct electrochemical reduction of hemin, protoporphyrin(IX) iron(III) chloride, ligated with strong or weak heterocyclic bases, was investigated in the ionic liquids (IL), 1-butyl- and 1-octyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆] and [omim][PF₆]), using cyclic voltammetry and chronocoulometry. Hemin complexed with N-methylimidazole (NMI) or with pyridine had $E_{1/2}$ values slightly (4 to 59 mV) more positive in IL (without electrolyte) than in methanol (1.0 M electrolyte) using a gold electrode. NMI-ligated hemin had a lower $E_{1/2}$ than pyridine-ligated hemin in either IL, consistent with the stronger electron donor characteristic of NMI. [Bmim][PF₆] solutions consistently yielded $E_{1/2}$ values 30 mV more negative than [omim][PF₆] solutions.

The diffusion coefficients D_o of hemin in the IL ranged between 1.50 and $2.80 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, while the heterogeneous electron-transfer rate constants k_s ranged between 3.7 and $14.3 \times 10^{-3} \text{ cm s}^{-1}$. Cyclic voltammetry of hemin adsorbed to a gold surface through 4,4'-bipyridyl disulfide linkages showed a large positive shift in the oxidation wave, indicating that adsorption stabilizes the reduced hemin state. The surface concentration Γ_o of the adsorbed hemin was determined to be $1.21 \times 10^{-10} \text{ mol cm}^{-2}$, indicating the presence of one or more complete monolayer of hemin.

These findings suggest that while hemin is electrochemically active in IL, its behavior is modified by ligand field strength and surface adsorption phenomena. These studies are foundational in establishing the technical feasibility of employing bioelectrocatalysis in unconventional solvents to produce specialty lipids as new products.