

Ionic Liquids as a solvent for Bioelectrocatalysis.
Examining Specific Cation and Anion Effects on
Electrode-Immobilized Cytochrome *c*

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Immobilized Cytochrome *c* on mercaptothiol self-assembled monolayers exhibit a characteristic Fe(III)/Fe(II) redox signal that is lost when exposed to ionic liquids composed of a butylimidazolium cation combined with either hexafluorophosphate or bis(trifluoromethylsulfonyl)imide anion. In this study it was shown that exposure to the aqueous solubilized ionic liquid components, butyl-, hexyl-, and octyl- imidazolium cations and bis(trifluoromethylsulfonyl)imide anion, resulted in partial loss of the electrochemical signal. Spectroscopic measurements, including both absorbance and fluorescence, showed that signal loss due to the cationic liquid component followed a different mechanism than that of the anionic component. Although a portion of the signal was recoverable, irreversible signal loss also occurred in each case. The source of the irreversible component is suggested to be the loss of protein secondary structure through complexation between the ionic liquid components and the protein surface residues. The reversible electrochemical signal loss is likely due to interfacial interactions imposed between the electrode and the cytochrome heme group. Microperoxidase-11 was also used as a simple model protein to explore the influence of the amount of exposed surface residues.