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Solubility of Carbon Dioxide in Methoxy and Nitrile-Functionalized Ionic Liquids

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Abstract : Global warming and climate change are significant environmental concerns, which require immediate global action in carbon emission mitigation. The capture, sequestration, and conversion of carbon dioxide to other products such as methane or ethanol are ways to control excessive emissions. Ionic liquids have shown great potential among the materials studied as carbon capture solvents and catalysts in the reduction of CO2. In this study, ionic liquids comprising of a methoxy (-OCH3) and cyano (-CN) functionalized imidazolium cation, [MOBMIM] and [CNBMIM] respectively, paired with tris(pentafluoroethyl)trifluorophosphate [FAP] anion were evaluated as effective capture solvents, and organocatalysts in the reduction of CO2. An in-situ electrochemical set-up, which can measure controlled amounts of CO2 both in the gas and in the ionic liquid phase, was used. Initially, reduction potentials of CO2 in the CO2-saturated ionic liquids containing the internal standard cobaltocene were determined using cyclic voltammetry. Chronoamperometric transients were obtained at potentials slightly less negative than the reduction potentials of CO2 in each ionic liquid. The time-dependent current response was measured under a controlled atmosphere. Reduction potentials of CO2 in methoxy and cyano-functionalized [FAP] ionic liquids were observed to occur at ca. -1.0 V (vs. Cc+/Cc), which was significantly lower compared to the non-functionalized analog [PMIM][FAP], with an observed reduction potential of CO2 at -1.6 V (vs. Cc+/Cc). This decrease in the potential required for CO2 reduction in the functionalized ionic liquids shows that the functional groups methoxy and cyano effectively decreased the free energy of formation of the radical anion CO2●⁻, suggesting that these electrolytes may be used as organocatalysts in the reduction of the greenhouse gas. However, upon analyzing the solubility of the gas in each ionic liquid, [PMIM][FAP] showed the highest absorption capacity, at 4.81 mM under saturated conditions, compared to [MOBMIM][FAP] at 1.86 mM, and [CNBMIM][FAP] at 0.76 mM. Also, calculated Henry's constant determined from the concentration-pressure graph of each functionalized ionic liquid shows that the groups -OCH3 and -CN attached terminal to a C4 alkyl chain do not significantly improve CO2 solubility.

Keywords : carbon capture, CO2 reduction, electrochemistry, ionic liquids
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