

# Electrochemical Investigations of Lewis Acid Interactions with Ketones in a Room-Temperature Ionic Liquid

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## Introduction

Room-temperature ionic liquids have received much attention as solvent media for organic reactions (1, 2). An important class of reactions is those in which Lewis acids play an important role, such as Friedel-Crafts and isomerization reactions. In this work, the behavior of boron trifluoride and aluminum chloride in the 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF<sub>4</sub>) ionic liquid has been studied.

## Experimental

1-Ethyl-3-methylimidazolium tetrafluoroborate (97%) was obtained from TCI America. The melt was heated at 90°C under vacuum to remove volatile impurities. A cyclic voltammogram at platinum showed a reduction peak at -0.9V, indicating the presence of protons. Addition of basic alumina removed this peak and presumably the protons responsible for it.

Potentials are referred to a Ag/AgCl electrode, prepared by immersing a Ag/AgCl wire (Cypress Systems) in 0.1 M EMICl / EMIBF<sub>4</sub>.

## Results and Discussion

A cyclic voltammogram of 9-fluorenone in EMIBF<sub>4</sub> (Figure 1, light curve) shows two successive one-electron redox processes, similar to behavior observed in aprotic nonaqueous solvents (3). Upon addition of BF<sub>3</sub> etherate, the potential for the first reduction process shifts to a less negative value (Figure 1, dark curve), indicating complexation of the carbonyl oxygen by BF<sub>3</sub>. At the same time, the reduction process becomes less reversible, there being no oxidation current on the return sweep. Similar results are observed for 9-fluorenone in acetonitrile / tetraethylammonium BF<sub>4</sub> with BF<sub>3</sub> etherate.

The addition of aluminum chloride to EMIBF<sub>4</sub> ionic liquid results in formation of chloride ion, as seen by an oxidation process at +1.48V. Chloride ion is thought to be formed by interaction of aluminum chloride with BF<sub>4</sub><sup>-</sup>. Addition of 9-fluorenone to this solution results in a reduction peak at -0.85V, similar to that found for 9-fluorenone complexed by BF<sub>3</sub>. This finding shows that complexation of the carbonyl oxygen also occurs in this solution.

The behavior of benzophenone in the EMIBF<sub>4</sub> system has also been studied and will be discussed.

## Acknowledgement

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## References

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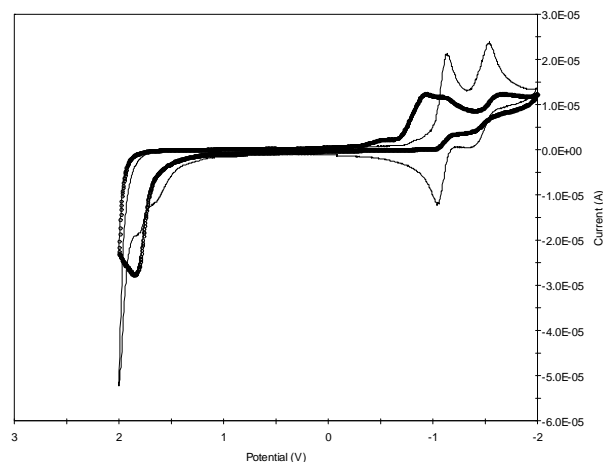


Figure 1. Effect of addition of BF<sub>3</sub> OEt<sub>2</sub> to 9-fluorenone in EMIBF<sub>4</sub>.