

Electrochemical Studies of Fluorenone in Ionic Liquids and Aprotic Solvents

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The electrochemical behavior of 9-fluorenone in acetonitrile / tetraethylammonium tetrafluoroborate (TEA BF₄) solutions has been explored by additions of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIm BF₄) and the proton donor 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). The effect of EMIm BF₄ addition was found to be consistent with complexation of the dianion of 9-fluorenone by the EMIm cation, causing a positive shift of the second reduction process. Addition of HFIP as proton donor, on the other hand, caused the formation of a single reduction process near the first fluorenone reduction process.

Introduction

As presented in a previous report, 9-fluorenone undergoes two successive one-electron reductions in 1-ethyl-3-methylimidazolium tetrafluoroborate EMImBF₄ (1). The potential separation between these processes is 300 mV, which is considerably less than the 700 mV found in acetonitrile / 0.1M tetraethylammonium tetrafluoroborate (TEA BF₄). For dinitrobenzene reduction in BMImBF₄, ion-pairing with the imidazolium cation has been proposed to account for similar peak potential shifts (2). It is also possible that proton donation by the imidazolium ring (3) also plays a role in the reduction process. The purpose of the present work is to assess the relative importance of these effects in the electrochemical reduction of ketones, specifically 9-fluorenone.

Experimental

Acetonitrile (anhydrous) was obtained from Aldrich Chemical Corp. TEA BF₄ was purchased from Sachem. EMIm BF₄ was prepared by metathesis of EMIm Cl and NaBF₄. Potentials are reported with respect to a Ag/AgCl reference electrode (ESA / Cypress Systems). All experiments were carried out in a Vacuum Atmospheres glovebox.

Results and Discussion

In order to study ion-pairing effects, EMIm BF₄ was gradually added to a solution of 9-fluorenone in AN/TEABF₄. As EMIm BF₄ was added, the reduction process at more negative potential underwent a shift to more positive potentials, stopping at a 1:1 molar ratio of EMIm BF₄ : fluorenone (Figure 1). The resulting peak separation was very similar to that seen for 9-fluorenone in neat EMIm BF₄ (1). These results support the complexation of the 9-fluorenone dianion by the imidazolium ring. This complexation has been noted for dinitrobenzenes in BMIm BF₄ (2), although the two reduction processes in this case are actually merged into one process. Similar behavior has also

been reported for the complexation of 1,4-dinitrobenzene by urea (4). A case with behavior more similar to the 9-fluorenone : EMIm cation complexation has been reported for the hydrogen-bonding interaction between ethanol and tetrachloro-1,4-benzoquinone initially dissolved in benzonitrile (5). In this case, the second reduction process for the quinone also underwent a positive shift while maintaining its reversible nature as a separate process.

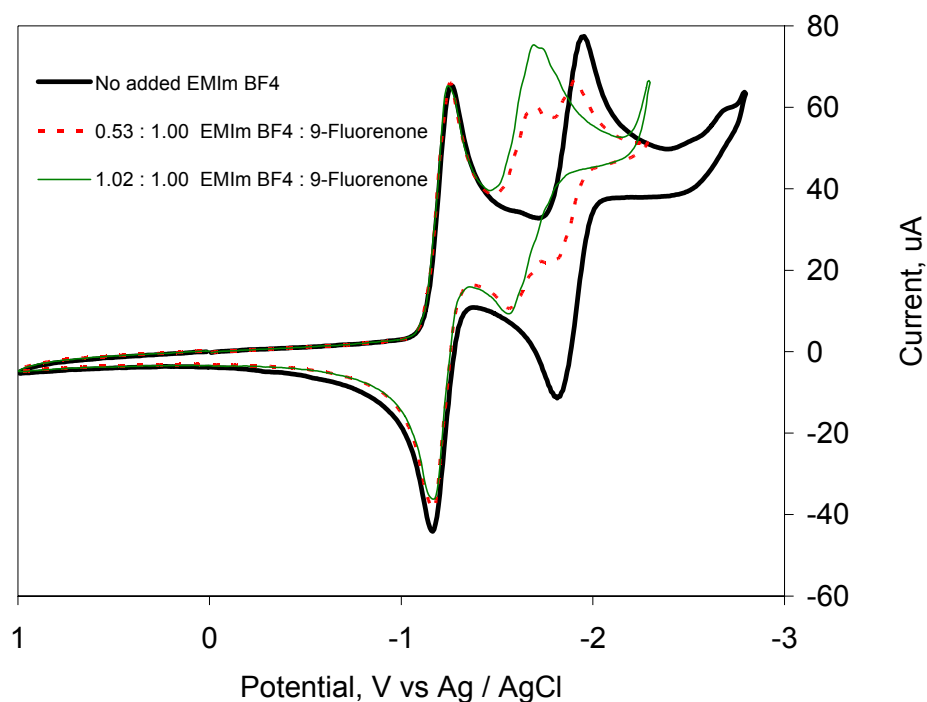


Figure 1. Cyclic voltammograms of 20 mM 9-fluorenone in AN / TEA BF₄ at 1 mm diameter glassy carbon electrode, 100 mV/s.

Black curve (thick line) : no added EMIm BF₄
 Red curve (dotted line) : 0.53 : 1.00 EMIm BF₄ : 9-Fluorenone
 Green curve (thin line) : 1.02 : 1.00 EMIm BF₄ : 9-Fluorenone

In a similar fashion, the proton donor 1,1,1,3,3,3- hexafluoro-2-propanol (HFIP) was added to 9-fluorenone in acetonitrile / TEABF₄. At the 1:1 HFIP : 9-fluorenone point, the second 9-fluorenone reduction peak had shifted to a more positive value; however, further HFIP addition to the 2.5 : 1 point gave only one reduction peak (Figure 2). This behavior is consistent with an ECE process for 9-fluorenone reduction, the chemical step being protonation of the radical anion by HFIP. This pathway seems reasonable in light of the known proton-donating capabilities (pK_a 18.9 in DMF) of HFIP (6).

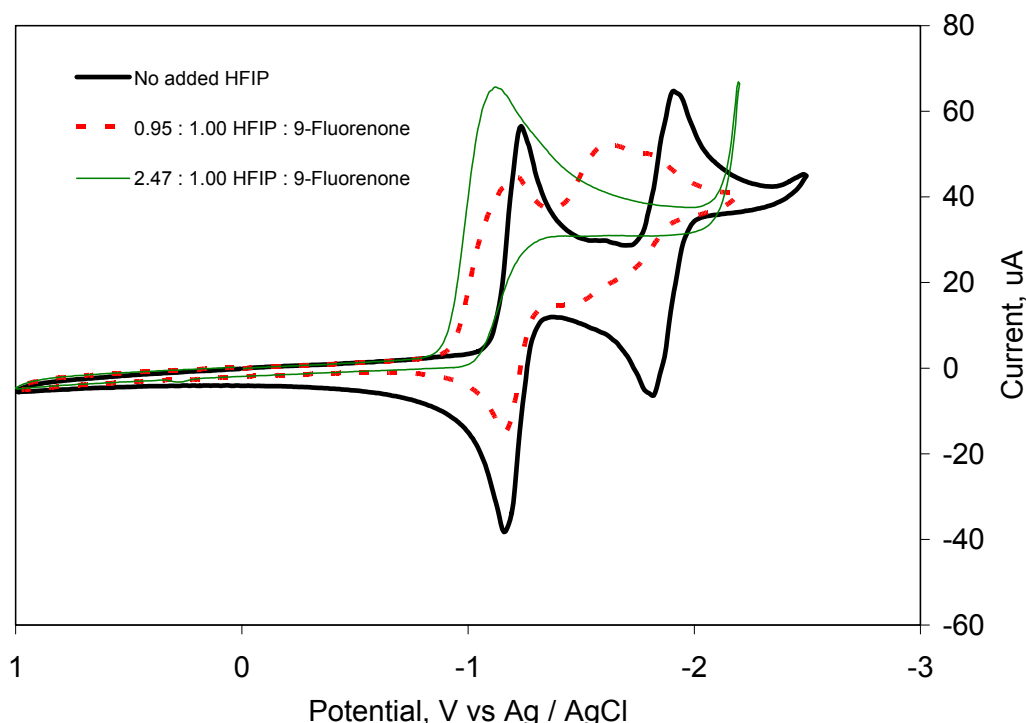


Figure 2. Cyclic voltammogram of 19 mM 9-fluorenone in AN / TEA BF₄ at 1 mm diameter glassy carbon electrode, 100 mV/s.

Black curve (thick line) : no added HFIP
 Red curve (dotted line) : 0.95 : 1.00 HFIP : 9-Fluorenone
 Green curve (thin line) : 2.47 : 1.00 HFIP : 9-Fluorenone

Conclusions

From the results of the present study, it appears that there is a specific complexation of the 9-fluorenone dianion by the EMIm imidazolium ring. Addition of the proton donor HFIP also causes a peak shift at low concentrations, but further additions result in a single reduction process, which is not observed for 9-fluorenone reduction in EMIm BF₄.

Acknowledgements

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References

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