

Studies of Adiponitrile as an Electrochemical Solvent

Graham T. Cheek
572M Holloway Road, Stop 9b
United States Naval Academy
Annapolis MD 21402

Introduction

Electrochemical investigations have been greatly enhanced by the use of nonaqueous solvents, enabling the study of many electrochemical processes over a very broad potential range (1). The use of nonaqueous solvents such as acetonitrile, however, occasionally has some disadvantages, such as the typically low boiling points of these solvents, restricting their use to room temperature applications. The rather high polarity of acetonitrile, and its wide potential range, gives some hope that the higher nitriles may allow higher temperature operations while maintaining good electrochemical properties. Some general considerations concerning the use of adiponitrile [NC(CH₂)₄CN] as a general electrochemical solvent have been presented (2); however, adiponitrile has been mostly confined to work with capacitors (3) and Li-ion batteries (4). The present abstract represents work involving the use of adiponitrile as an electrochemical solvent for some common redox systems such as ferrocene and 9-fluorenone. Recent work involving 9-fluorenone has been carried out in acetonitrile (5) and the ionic liquids 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate [BMPY TfO] (6) and 1-ethyl-3-methylimidazolium tetrafluoroborate [EMI BF₄] (7), providing useful comparisons (8) to the present work.

Experimental

Adiponitrile and 9-fluorenone were obtained from Aldrich Chemical Co., and tetraethylammonium tetrafluoroborate [TEA BF₄] was purchased from Southwestern Analytical Chemicals (SACHEM). Ferrocene was obtained from Strem Chemicals Inc. Voltammograms were taken with a PAR283 potentiostat using PowerSuite™ software. Potentials are reported with respect to a Ag/AgCl (0.1M EMICl in EMI BF₄) reference electrode (Cypress Systems). Vitreous carbon electrodes were obtained from Cypress Systems. All experiments were carried out in a Vacuum Atmospheres drybox.

Results and Discussion

As shown by the background curve in Figure 1, adiponitrile has a useful potential range of approximately +2.0V to -2.4V vs Ag/AgCl after drying over 3A sieves for one day. The electrochemical behavior of 9-fluorenone has been found to be similar to that in acetonitrile (5), involving two successive one-electron transfers. Although the second process is not as reversible in adiponitrile as it is in acetonitrile at 100 mV/s, increasing the scan rate to 5 V/s results in essentially reversible behavior for the second process. It is planned to discuss the reasons for these results in the presentation.

Ferrocene undergoes a one-electron redox process in adiponitrile; however, the peak separation with 0.12 M TEA BF₄ is 270 mV/s at 100 mV/s. Addition of 0.38 M TEA BF₄ lowers this separation to 160 mV. Similar results are found for 9-fluorenone, evidently due to the less polar character of adiponitrile compared to acetonitrile.

These results indicate that adiponitrile, in addition to its applications in power sources (3,4), is useful as a convenient, inexpensive electrochemical solvent for general studies over its very wide liquid range of 2°C to 295°C (2).

References

1. R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York (1969).
2. P. G. Sears, J. A. Caruso and A. I. Popov, *Journal of Physical Chemistry*, **71**(4), 905 (1967).
3. A. Brandt, P. Isken, A. Lex-Balducci, A. Balducci, *Journal of Power Sources*, **204**, 213 (2012).
4. A. J. Gmitter, I. Plitz, G. G. Amatucci, *J. Electrochem. Soci.*, **159**(4), A370 (2012).
5. D. S. Canby and G. T. Cheek, *ECS Trans.*, **3**(35), 609 (2007).
6. G. T. Cheek, *ECS Trans.*, **35**(16), 17 (2011).
7. G. T. Cheek, D. S. Canby, and E. Sanders, *ECS Trans.*, **2**(23), 1 (2007).
8. D. Canby, E. Sanders, and G.T. Cheek, *J. Electrochem. Soc.*, **160**(7), G3159 (2013).

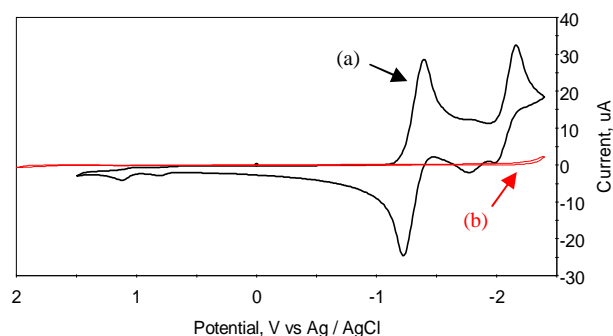


Figure 1. Cyclic voltammogram of 38 mM 9-fluorenone in adiponitrile (0.44 M TEA BF₄) at 1mm diameter vitreous carbon, 100 mV/s [(a), black curve].

Background scan, also at 100 mV/s [(b), red curve].