

Spectroelectrochemical study of multi-electron transfer in ionic liquids

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Abstract:

Multi-electron transfer processes of organic compounds have been studied in both aqueous and non-aqueous media. More limited studies have been carried out in ionic liquids. Significant shifts in redox potentials have been observed for compounds such as 1,4-dinitrobenzene (DNB) where two one-electron waves have been observed in acetonitrile but a single two-electron wave in ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate (BMImPF₆).

In order to study this process in more details, visible spectroelectrochemistry was combined with conventional cyclic voltammetry. Obtaining good spectroelectrochemical data was complicated by the high resistance and viscosity of the ionic liquid which greatly extended the time required to obtain complete reduction. Because the second potential E⁰ (E⁰₂) for DNB was close to or positive of the first potential E⁰ (E⁰₁), there was no region where only the radical anion was present. As results, chemometric methods were used to determine spectra of the radical anion (DNB⁻) and dianion (DNB²⁻). The analysis was complicated because of the instability of the DNB²⁻ species due to the long electrolysis time, and additional spectra that might be due to protonated species. Spectra for these species were deduced from the slow scan rate data.

With the determination of all spectral species, it was possible to determine the redox potential, E⁰₁ and E⁰₂. Much lower stability of the DNB²⁻ was observed in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (BMImNTF₂), and the voltammetric wave was irreversible. The effect of ion pairing on the redox potentials was investigated, and the electrochemical & spectroelectrochemical behavior of DNB in acetonitrile and ionic liquids was compared.