Heterogeneous and Homogeneous Electron Transfer Kinetics of the [CeCl$_6$]$^{3-/2-}$ Redox Reaction in the 1-Butyl-3-methylpyrrolidinium Bis(trifluoro-methylsulfonyl)imide Ionic Liquid

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The coordination of f-block elements complexed with chloride has been studied for many years, but the reports are restricted mainly to the octahedrally coordinated trivalent species, [LnCl$_6$]$^{3-}$. However, cerium, which is one of the most abundant of the early f-block elements, is an exception because it is the only lanthanide element that has a stable tetravalent oxidation state in solution. As a result, Ce^{4+} is often used as a surrogate of convenience for actinide species such as Pu^{4+} and Th^{4+}.

In a previous investigation, we reported the coordination of Ce^{4+} and Ce^{3+} in the 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid.[1] As a continuation of this study, we have examined the heterogeneous electron transfer kinetics of the [CeCl$_6$]$^{2-/3-}$ redox reaction, as well as the homogeneous kinetics of the reaction of [CeCl$_6$]$^{2-}$ with Cl$^-$ in this ionic liquid. This investigation was conducted by using electrochemical impedance spectroscopy (EIS) and electronic absorption spectroscopy (UV-Vis). As shown in Fig. 1, EIS measurements indicate that the [CeCl$_6$]$^{2-/3-}$ redox reaction is quasireversible in this ionic liquid. The standard heterogeneous rate constant, k^0, of this reaction was found to be 1.2×10^{-4} cm s^{-1} at 303 K with an activation energy of 28.1 kJ mol^{-1}. In addition, the mass transport of [CeCl$_6$]$^{3-}$ and [CeCl$_6$]$^{2-}$ was investigated with rotating-disk electrode voltammetry (RDEV). At 323 K, the average diffusion coefficients for [CeCl$_6$]$^{3-}$ and [CeCl$_6$]$^{2-}$ were found to be 8.0×10^{-8} and 6.8×10^{-8} cm^2 s^{-1}, respectively.

Figure 2 illustrates absorption spectra that were recorded over a period of 90 min for electrogenerated Ce^{4+} in the ionic liquid containing a 10-fold excess of Cl$^-$ at 125°C. At short times, these spectra show bands at 257 and 376 nm consistent with those [CeCl$_6$]$^{2-}$. However, an absorption band at 331 nm characteristic of [CeCl$_6$]$^{3-}$ becomes apparent at longer times. The pseudo first-order homogeneous rate constant for this reaction, k', was found to be 1.57×10^{-2} s^{-1} at this temperature. An investigation of k' over the temperature range 333 – 398 K gave an activation energy of 88.0 kJ mol^{-1} for this reaction.
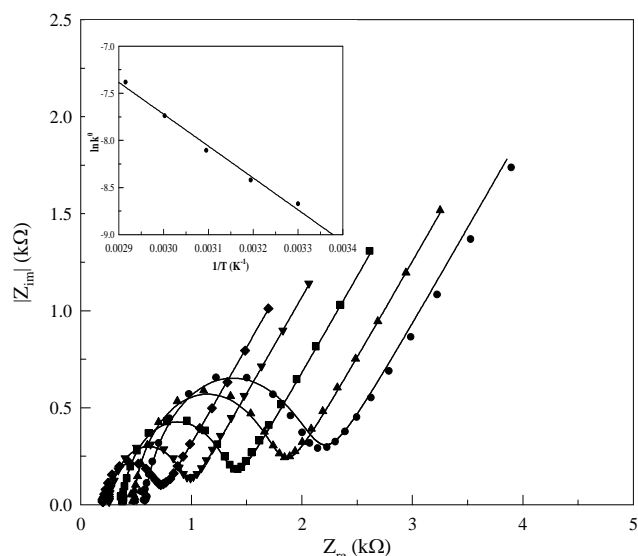
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Figure 1. Complex plane impedance plots recorded at a GC electrode in BuMePyroTf$_2$N containing 20 mM [CeCl$_6$]$^{3-}$ + 20 mM [CeCl$_6$]$^{2-}$ at (●) 303 K, (▲) 313 K, (■) 323 K, (▼) 333 K, and (♦) 343 K. The solid lines represent the fitted Randles-Ershler equivalent circuit model. Inset: variation of $k^{0'}$ with the inverse of the absolute temperature.
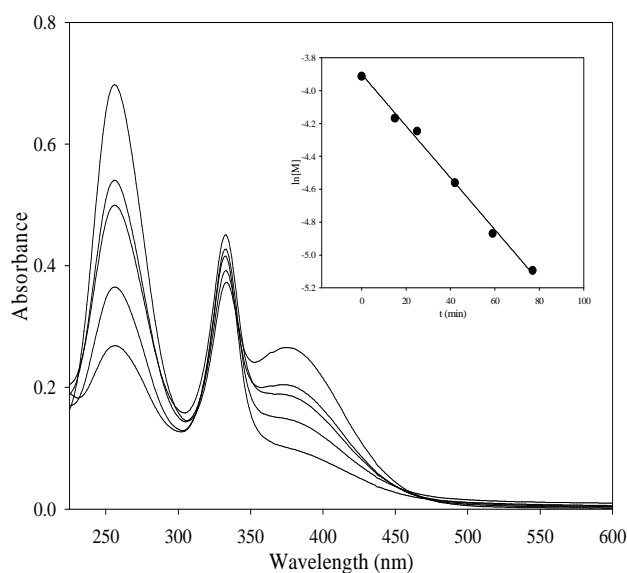

Figure 2. Absorption spectra as a function of time for a 1.08 mM solution of [CeCl$_6$]$^{2-}$ in BMPyroTf$_2$N containing 11.9 mM Cl$^-$ ion at 398K. The cell path length was 1.0 mm. Inset: plot of the [CeCl$_6$]$^{2-}$ concentration versus time.

Reference

1. Chou, L.-H.; Cleland W. E., Jr.; and Hussey, C. L., *Inorg. Chem.*, **51,** 11450-11457 (2012).