A Simple Hydrocarbon Electrolyte: Completing the Electron-transfer Series $[Fe_4S_4(SPh)_4]^{1-/2-/3-/4-}$

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Electrochemical properties of $\{[NBu^n{}_4][BF_4]\cdot 3\ \text{toluene}\}$ are described; the hydrocarbon medium allows, for the first time, the observation of all members of the $[Fe_4S_4(SPh)_4]^{n-}$ electron-transfer series, n = 1—4.

Tetra-n-butylammonium tetrafluoroborate, $[NBu^n{}_4][BF_4]$, forms a transparent, mobile solution (η = 1.5 ± 0.1 cP, 28 °C) when the crystalline salt (m.p. 162—163 °C) is stirred in toluene (B.D.H. Ltd.,'AnalaR'; freshly distilled under dinitrogen from liquid sodium). The liquid, Y, partitions from the excess of toluene as an immiscible lower layer ($\rho \simeq 0.98$, 22 °C). It is stable down to about 22 °C; near or below this temperature $[NBu^n{}_4][BF_4]$ separates as a solid crystalline phase free of toluene. The liquid is best prepared and manipulated between 25—30 °C.

The ^1H n.m.r. spectrum of neat Y shows resonances for $C_6H_5CH_3$ and $[N(n\text{-}C_4H_9)_4]^+$ protons alone: integration of the spectrum gives the molar ratio $[NBu^n{}_4]^+$: toluene as 1:3. ^{19}F N.m.r. spectroscopy shows a single resonance for the tetra-

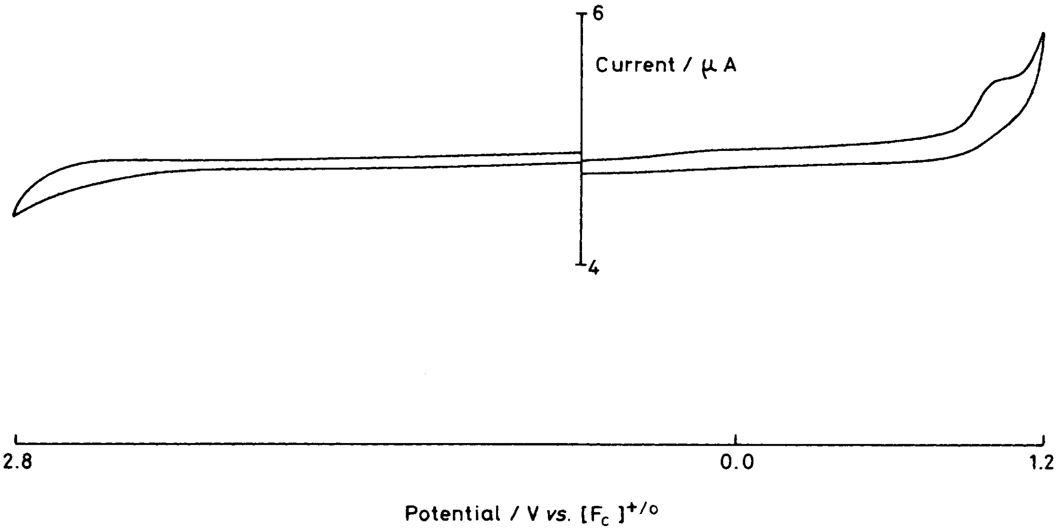

Figure 1. Background cyclic voltammogram of Y at 23 °C. The scan-rate is 0.1 V s^{-1} at a Pt-electrode of geometric area 0.034 cm^{2}.

hedral $[BF_4]^-$ ion. The nominal composition of Y is therefore $\{[NBu^n_4][BF_4]\cdot 3$ toluene$\}$ and this is supported by gravimetric measurements (removal of toluene at *ca.* 60 °C *in vacuo*).

Y can be usefully employed as an electrochemical medium with properties complementary to those of 'room temperature' molten salts,[1,2] to the more commonly employed 50% (v/v) dilutions of these with benzene or toluene,[3,4] and to conventional non-aqueous electrolytes.[5]

The specific conductance, κ of Y is $(1.2 \pm 0.1) \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at 25 °C: this conductivity is similar to those of room-temperature melts such as those based on *N*-(n-butyl)pyridinium tetrachloroaluminate and tetra-alkylammonium tetra-alkylborides,[1,2] but is less than that of the familar non-aqueous electrolyte, $\{0.2$ M $[NBu^n_4][BF_4]$–$CH_3CN\}$, for which κ was found to be $(8.8 \pm 0.1) \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, when measured under the same conditions.

Figure 1 shows a cyclic voltammogram recorded at a conventional microelectrode of Y alone. The electrochemical window is wide, *ca.* 4 V, even as conservatively estimated at high sensitivity. Charging currents are not excessive at moderate scan-rates: the capacitance, C_d, at bright platinum is $(41 \pm 2)\ \mu F\ cm^{-2}$ at 22 °C, which compares with $C_d = (23 \pm 2)\ \mu F\ cm^{-2}$ for $\{0.2$ M $[NBu^n_4][BF_4]$–$CH_3CN\}$, measured analogously at the same electrode.

At the concentrations required for electrochemical measurements, (mM), Y is a good solvent for both neutral and ionic compounds, particularly salts of $[NBu^n_4]^+$. Figure 2 shows a set of cyclic voltammograms for ferrocene, $[F_c]$, dissolved in Y, which were recorded under the same conditions as for the background. The current–potential responses are qualitatively the same for $[F_c]$ in Y as they would be for the diffusion-controlled, reversible, one-electron oxidation of this complex in any indifferent electrolyte under uncompensated conditions. The magnitude of the peak-current-function†[6] for ferrocene is (0.35 ± 0.02) A cm mol^{-1} V$^{-\frac{1}{2}}$ s$^{\frac{1}{2}}$ in Y; this compares with (1.14 ± 0.02) A cm mol^{-1} V$^{-\frac{1}{2}}$ s$^{\frac{1}{2}}$ in $\{0.2$ M $[NBu^n_4][BF_4]$–$CH_3CN\}$ at the same electrode.

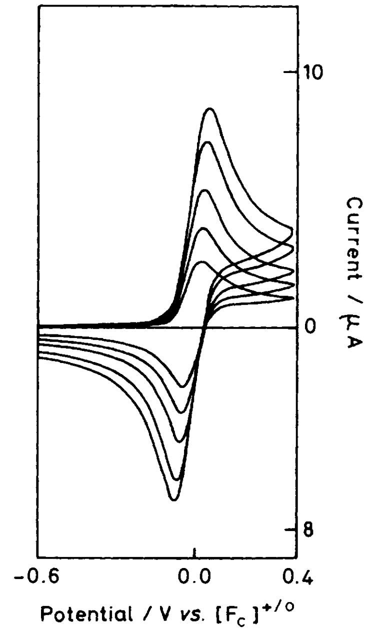

Figure 2. Cyclic voltammetry of ferrocene at 23 °C in Y at a Pt-electrode of geometric area 0.034 cm^{2}. Scan-rates are 0.3, 0.2, 0.1, 0.05, and 0.02 V s^{-1}. Concentration of ferrocene is 1.54 mM.

Electrogenerated intermediates frequently attack solvent molecules in a non-aqueous electrolyte; thus one of the attractions of performing electrochemistry in ionic liquids such as the tetrachloroaluminate family of room-temperature molten salts is that the participation of reactive solvent molecules is circumvented. Unfortunately, those liquids based upon $[AlCl_4]^-$ are notoriously susceptible to moisture: they require stringent preparation and handling procedures.[1,2] The tetra-alkylammonium tetra-alkylboride salts form a family of room-temperature liquids which are hydrolytically stable and are of low nucleophilicity, but these advantages are somewhat offset by the facile oxidation of the tetra-alkylboride anions.[2] This severely narrows the electrochemical window. In contrast

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† Peak-current-function referred to here is i_p (area)$^{-1}$ $[F_c]^{-1}\nu^{-\frac{1}{2}}$ where i_p is the peak-current (A), $[F_c]$ the bulk concentration of ferrocene (mol cm^{-3}), ν (*cf.* ref. 6) the potential scan-rate (V s^{-1}) and the area is in units cm^{2}.

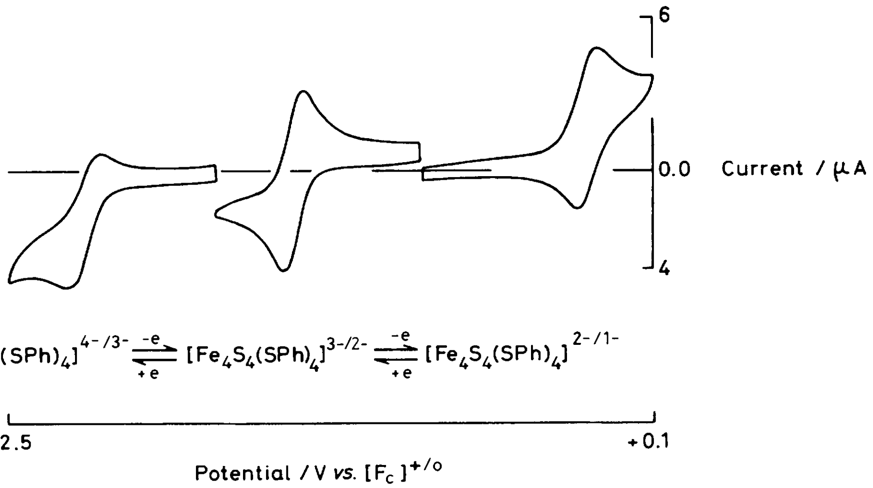

Figure 3. Electron-transfer series $[Fe_4S_4(SPh)_4]^{4-/3-/2-/1-}$ in Y at 23 °C. The scan-rate is 0.1 V s^{-1} at a Pt-electrode of geometric area 0.034 cm^2. Concentration of cluster is 3.8 mM.

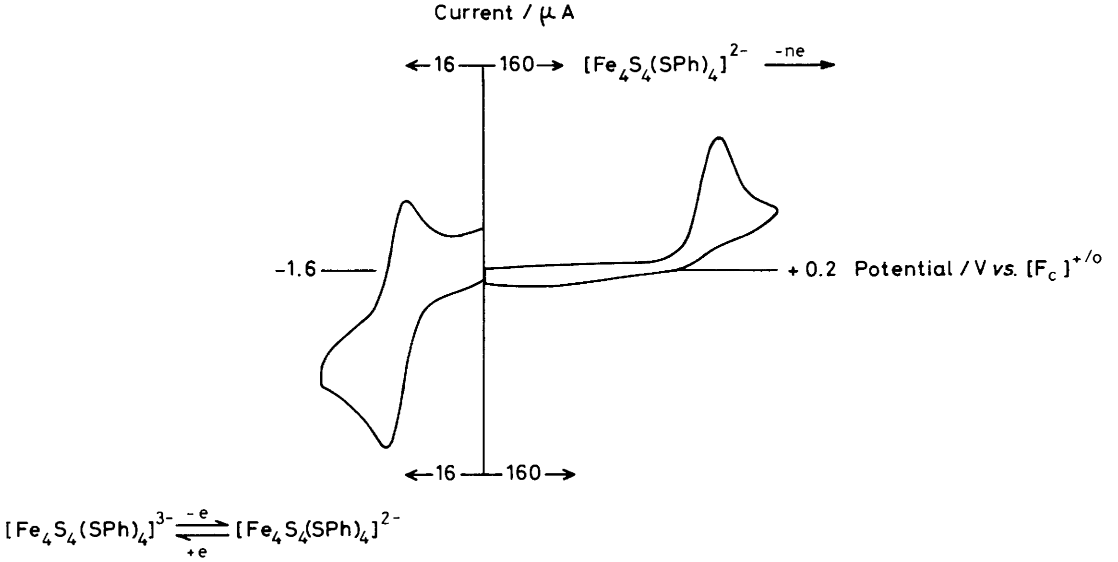

Figure 4. Multi-electron oxidation of $[Fe_4S_4(SPh)_4]$ in {0.2 M $[NBu_4][BF_4]$–CH_3CN} at 22 °C. The scan-rate is 0.1 V s^{-1}. Concentration of cluster 1.01 mM.

Y is hydrolytically stable, is convenient to prepare from readily available components, is comparatively easy to handle and possesses a wide electrochemical window. More importantly, as a hydrocarbon electrolyte it provides an inert electrochemical medium. This is illustrated by the following example.

Hitherto, the electrochemical oxidation of the iron–sulphur cluster $[Fe_4S_4(SPh)_4]^{2-}$ in a wide range of non-aqueous media has only been observed as a rather poorly defined irreversible process; related aryl and n-alkyl thiolate, and halido-clusters suffer similarly.[7—9] In all cases, chemical oxidation results in cluster degradation. Figure 3 shows the cyclic voltammetry of $[Fe_4S_4(SPh)_4]^{2-}$ in Y: the reversibility of the $[Fe_4S_4(SPh)_4]^{2-/1-}$ couple is evident and, for the first time, the complete 4-membered electron-transfer chain for the tetraphenylthiolate cluster is observed. The stability of the mono-anion is comparable to that of the tetra-anion, $t_{\frac{1}{2}} \sim 0.1$ s. For comparison, the oxidation of the dianion in {0.2 M $[NBu^n_4][BF_4]$–CH_3CN} is shown in Figure 4 (note the current scale). In this medium the complex undergoes a multi-electron oxidation process which probably involves adsorption at the electrode. Holm, Spence, and co-workers recently observed the reversible one-electron oxidation of the cluster $[Fe_4S_4(SBu^t)_4]^{2-}$ in a dimethylformamide electrolyte,[9] and they suggested that the singular observation by cyclic voltammetry of the 2−/1− couple was almost certainly a consequence of the electron-releasing property of the tertiary-alkyl substituents. Contrary to this, the above results suggest that steric protection from solvent attack afforded by the bulky Bu^t groups is at least a contributing factor in the stabilisation of the analogue of the biological high potential ferredoxin, HP_{ox}.

Other aspects of Y are as follows. The liquid has a cut-off in the visible u.v. region of the spectrum at about 350 nm; at longer wavelengths it is transparent, and thus spectroelectrochemistry in this medium should be possible proximate to room temperature.

The formation of a simple, single solvent, *two-phase* liquid system with toluene may be attractive for electrosynthesis particularly where ionic reactants (soluble in Y) are converted into neutral products (soluble in the electrolyte-free toluene phase).

One final point: electrochemistry in Y should be capable of spanning the complete ultra-microelectrode—macroelectrode domain, and thus provide a link with studies of electroactive species in toluene alone, which can *only* be performed at ultra-microelectrodes.[10]

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