

I. Cyclic Voltammetry of p-methylphenyl thiocyanate (**1**) in the absence and in the presence of 4,4'-dimethylphenyl disulfide (**4**).

Figure 1a shows the voltammograms of **1** in the absence and presence of 4 % of the corresponding disulfide (**4**). Adding catalytic amounts of **4** allows consumption of **1** at the reduction peak of **4** through the catalytic process and only one peak is seen located at the reduction potential of **4**. When the scan rate is increased the catalytic process (Reaction 2) is diminished and two peaks appear, the catalytic peak and the peak corresponding to the direct reduction of **1** at the electrode (Figure 1b). At higher scan rates, the catalysis is totally eliminated and one can identify the peaks corresponding respectively to **4** and **1** (Figure 1c).

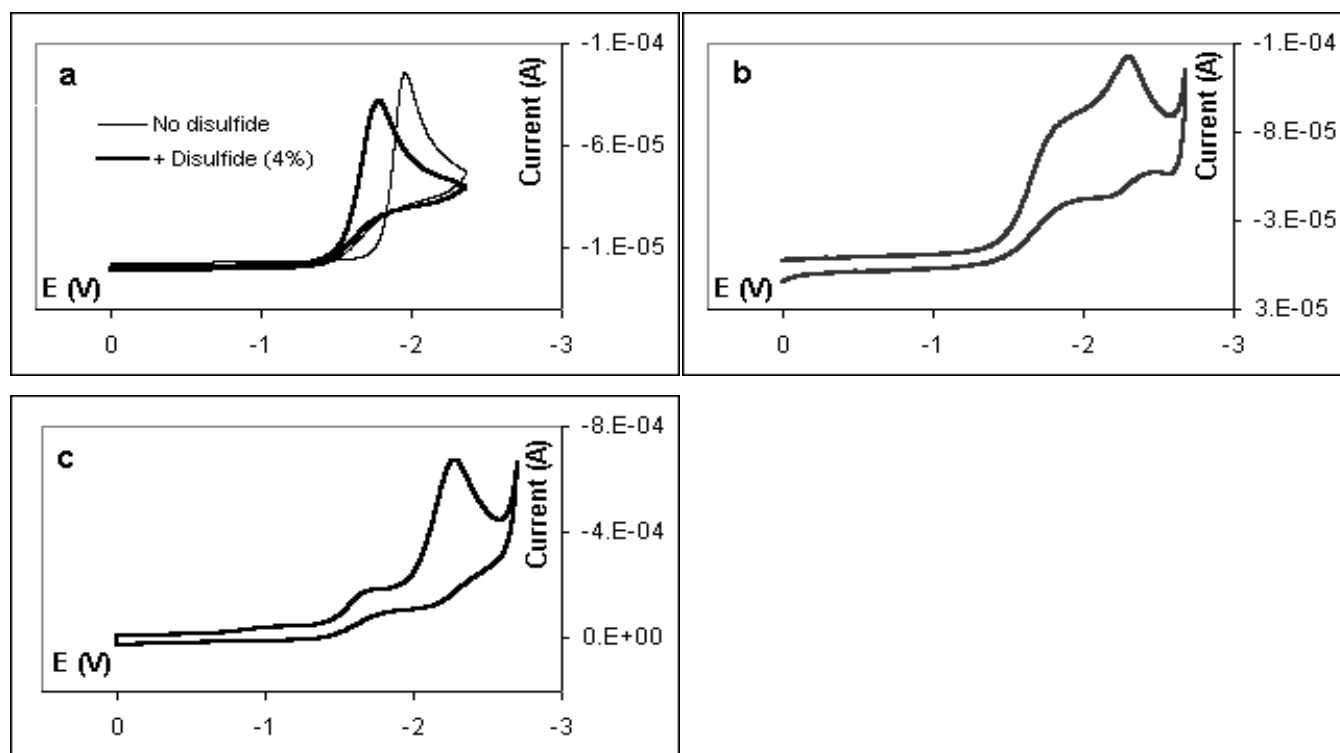


Figure 1: Cyclic voltammetry, in $\text{CH}_3\text{CN/TBAF}$ (0.1M) at glassy carbon electrode, temperature = 20 °C, of (—) **1** (2.55 mM) and (—) **1** (2.55 mM) + 4% of **4**, at (a) 0.2 V/s, (b) 2.4 V/s and (c) 10 V/s.

II. Cyclic Voltammetry of 4,4'-dimethylphenyl disulfide (**4**) and variation of its reduction peak width and peak potential with the scan rate.

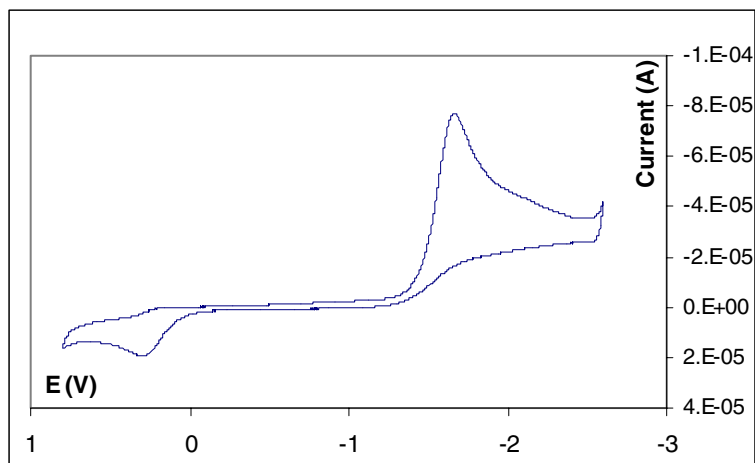


Figure 2: cyclic voltammogram of **4** (3 mM). In CH₃CN/TBAF (0.1M) at a glassy carbon electrode; $\nu = 0.2$ V/s.

Figure 2 represents the CV of p-tolyl disulfide at $\nu = 0.2$ V/s. A single irreversible reduction peak is observed at -2.35 V vs $E_{Fc/Fc^{++}}^o$. By scanning towards the positive potentials, the same anodic peak corresponding to the oxidation of p-toluenethiolate anion is observed. The height of the reduction peak corresponds to the exchange of two electrons per molecule by comparison with the peak height of the monoelectronic reversible wave of ferrocene recorded under the same condition.¹ The peak width ($E_p - E_{p/2}$) is 140 mV and the corresponding transfer coefficient (α) is 0.33. The variations of the peak potential and the peak width with $\log(\nu)$ for compound **4** are reported in Figure 3. Figure 3a shows the variation of the peak width with the scan rate. This is what is expected when a simple ET mechanism is involved and differs from what is seen for **1** and **2**, which show unusual but predictable behaviors (variation of E_p and ($E_p - E_{p/2}$) width ν) based on the autocatalytic mechanism involved.

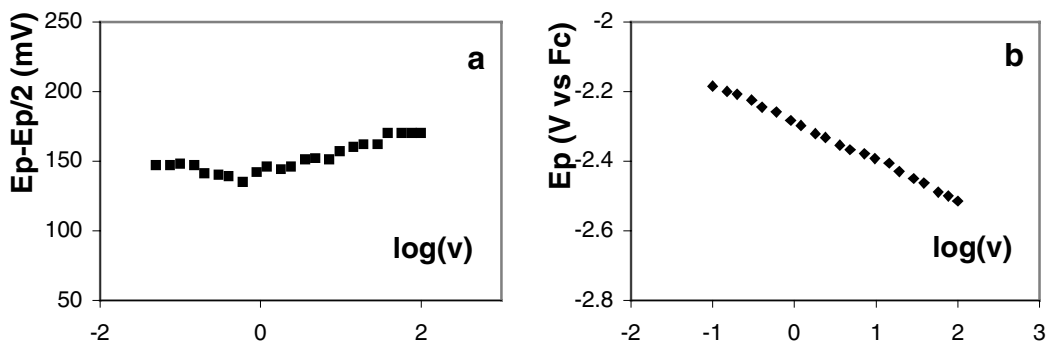


Figure 3: variation of (a) the peak with $(E_p - E_{p/2})$ and (b) the peak potential E_p with the scan rate for **4** (1.38 mM) in $\text{CH}_3\text{CN/TBAF}$ (0.1M) at a glassy carbon electrode. Temperature = 20 °C.

III. Convolution analysis for 1 and 2.

The background-subtracted voltammograms are convoluted to yield convoluted current I vs E plots. I is related to the voltammetric current i through the convolution integral (eq 1).

$$I = \pi^{-1/2} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \quad (1)$$

The limiting current I_l is defined as $I_l = nFAD^{1/2}C^0$, where n is the overall electron consumption per molecule, A the electrode area, D the diffusion coefficient, and C the bulk substrate concentration. I_l is independent of scan rate and has been used to calculate D ($4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for both **1** and **2**).²

The background subtracted linear scan voltammetry and the corresponding convolution curve for the reduction of **2** (0.69 mM) at $v = 20 \text{ V/s}$ are illustrated in Figures 4a and 4b.

For a totally irreversible system (when the dissociative electron transfer is concerted or when the dissociation of the reduction product is fast) I_l can be related to the rate constant of the heterogeneous electron transfer k_{het} through eq 2.

$$\ln k_{het} = \ln D^{1/2} - \ln \frac{I_l - I(t)}{i(t)} \quad (2)$$

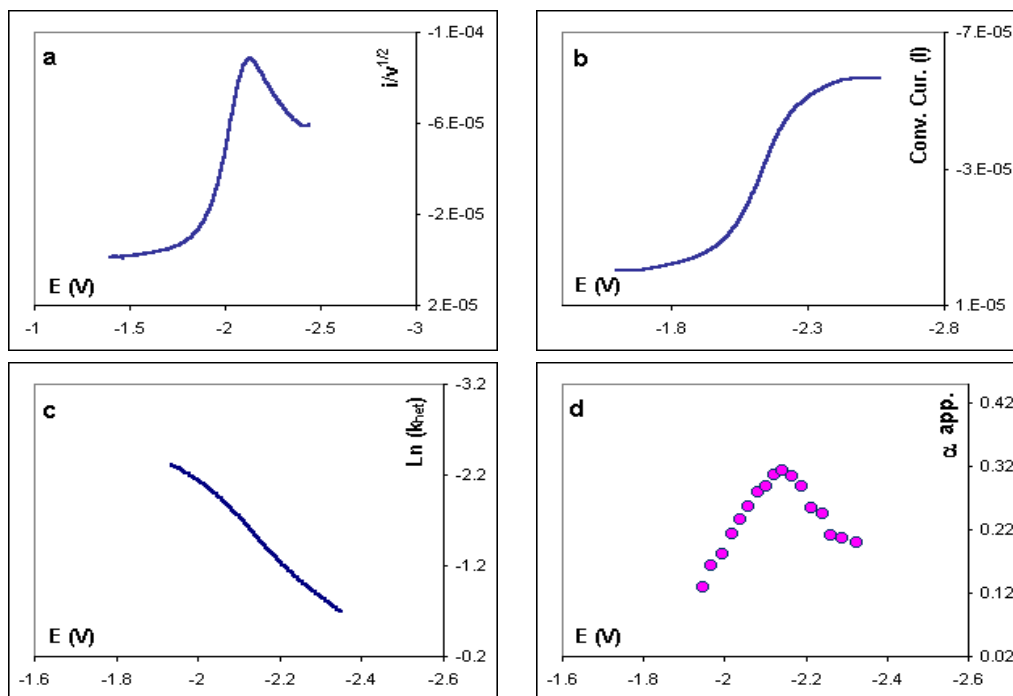


Figure 4: Convolution analysis for **2** (0.69 mM) in CH₃CN/TBAF (0.1M) at $\nu = 20$ V/s, Temperature = 20 °C, (a) background subtracted LV, variation of (b) convolutive current, (c) heterogeneous ET constant and (d) apparent transfer coefficient with potential.

The $\ln k_{het}$ vs E plot obtained by application of eq 2 for $\nu = 20$ is shown in Figure 4c. Systems following a single ET mechanism show either a linear or a parabolic pattern.^{3,4} Figure 4c shows that the $\ln k_{het}$ vs E plot for **1** is neither linear nor parabolic which suggests that the ET reduction mechanism is not following a single mechanism through the whole potential range. Values of $\ln k_{het}$ on Figure 4c also indicate a slow electron transfer as suggested earlier from the cyclic voltammetry study.

Apparent values of transfer coefficient (α_{app}) can be obtained from the $\ln k_{het}$ vs E data by using eq 3. α_{app} is related to α through the double-layer correction⁵ whose properties, to the best of our knowledge, are yet unknown for the glassy carbon electrode. However, it has been previously showed that uncorrected transfer coefficient values provide a reasonable representation of the process, as these values do not differ much from the true ones.⁶

$$\alpha_{app} = -\frac{RT}{F} \frac{\partial \ln k}{\partial E} \quad (3)$$

Differentiation is accomplished by linear regression of the experimental data within small E intervals (18 to 24 mV). The α_{app} vs E plot is shown in Figure 4d, definitively showing that the electrode process is not ruled by a simple ET mechanism.

References.

- (1) Ferrocene was used as an internal reference. It was added and a run towards positive potentials was performed before each cathodic scan.
- (2) The working electrode is a 3 mm diameter glassy carbon disc; n was determined by coulometry and is equal to 2 electrons per molecule.
- (3) Antonello, S.; Maran, F. *J. Am. Chem. Soc.* **1997**, *119*, 12595.
- (4) (a) Antonello, S.; Maran, F. *J. Am. Chem. Soc.* **1999**, *121*, 9668. (b) Antonello, S.; Musumeci, M.; Wayner, D. D. M.; Maran, F. *J. Am. Chem. Soc.* **1997**, *119*, 9541. (c) Donkers, R. L.; Workentin, M. *J. Phys. Chem. B* **1998**, *102*, 401. (d) Donkers, R. L.; Maran, F.; Wayner, D. D. M.; Workentin, M. *J. Am. Chem. Soc.* **1999**, *121*, 7239. (e) Antonella, S.; Frmaggio, F.; Moretto, A.; Toniolo, C.; Maran, F. *J. Am. Chem. Soc.* **2001**, *123*, 9577.

- (5) α is related to α_{app} by the equation $\alpha = \alpha_{\text{app}} / (1 - \partial\phi^{\#} / \partial E)$, where $\phi^{\#}(E)$ is the difference between the potential of the bulk solution and the potential at which the substrate is located when the electron transfer takes place.
- (6) (a) For the mercury electrode, where the double-layer correction is better defined, α_{app} has been shown to be smaller than α by only 3%.^{3,4c}