CAPSULES
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Determination of Diffusion Coefficients with Chronocoulometry

Key Terms
Chronocoulometry, Diffusion coefficient determination, Anson Plot, BAS 100 Series

The current response at an electrode is dependent upon the rate of mass transport of the electroactive species to the electrode surface. Therefore, accurate knowledge of the diffusion coefficient is required for most electrochemical studies. The procedure for the determination of the diffusion coefficient by chronocoulometry is described in this capsule. Ferrocene in acetonitrile with 0.2 M $LiClO_4$ was the system chosen to demonstrate this method. The potential waveform for chronocoulometry is shown in Figure 1. The initial potential, where no electrolysis occurs, and final potential, where complete electrolysis occurs, are obtained from a cyclic voltammogram (Figure 2). The potentials chosen were 0.000 V and + 0.700 V respectively. The chronocoulometric response (Figure 3) is the total charge passed (Q), vs. time (t) from initiation of the step.

The response is described by:

$$Q_t = \frac{2nFACD^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{dl} + nFA\Gamma_o$$

where Q_{dl} is the capacitive charge. Γ_o is the surface excess of reactant, and the other terms have their usual meaning. The area of the electrode (A) was 7.94 x 10^{-2} cm^2 (Capsule 133) and the ferrocene concentration was 2.40 x 10^{-6} mole cm^{-3}. A plot of Q vs. $t^{1/2}$ (Anson plot, Figure 4) transforms the data into a linear relationship whose slope is $2nFACD^{1/2}/\pi^{1/2}$. Note: Be sure to convert to appropriate units. The slope is reported as $\mu c/ms^{1/2}$.

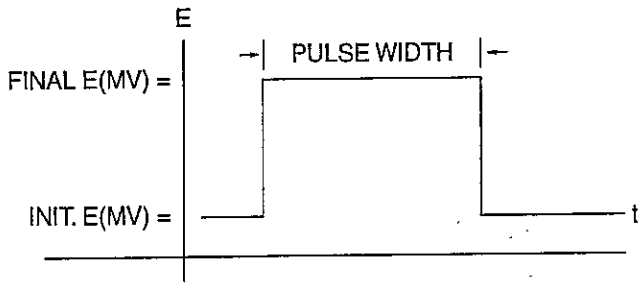

Figure 1. *Potential excitation for chronocoulometry.*

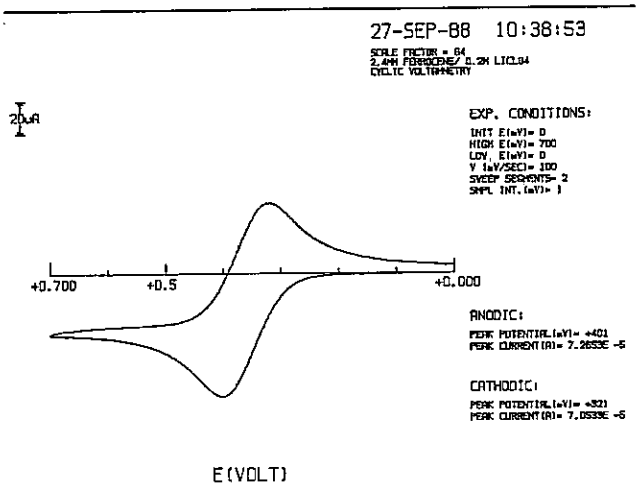

Figure 2. *Cyclic voltammogram for the oxidation of 2.40 mM ferrocene in acetonitrile 0.2 M $LiClO_4$ at a glassy carbon electrode.*

The diffusion coefficient of ferrocene in acetonitrile with 0.2 M $LiCLO_4$ determined from the Anson Plot is 2.3 x 10^{-5} cm^2 s^{-1}. This value agrees with the reported value of 2.4 x 10^{-5} cm^2 s^{-1} (1).

References

1. *T. Kuwana, D.E. Bublitz, and G. Hoh, J. Am. Chem. Soc. 82(1960) 5811.*

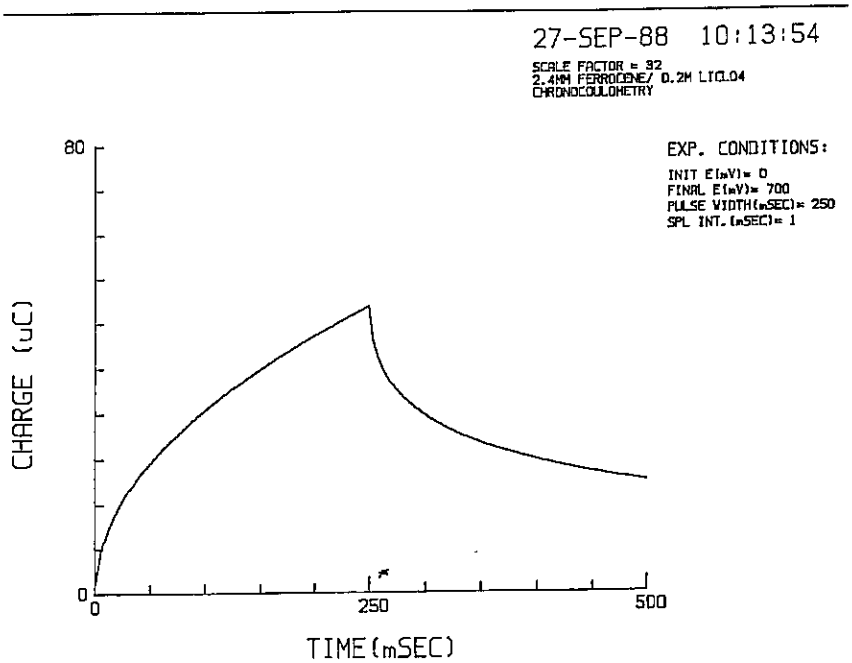

Figure 3. *Chronocoulometric response for 2.40 mM ferrocene in acetonitrile with 0.2 M $LiClO_4$.*

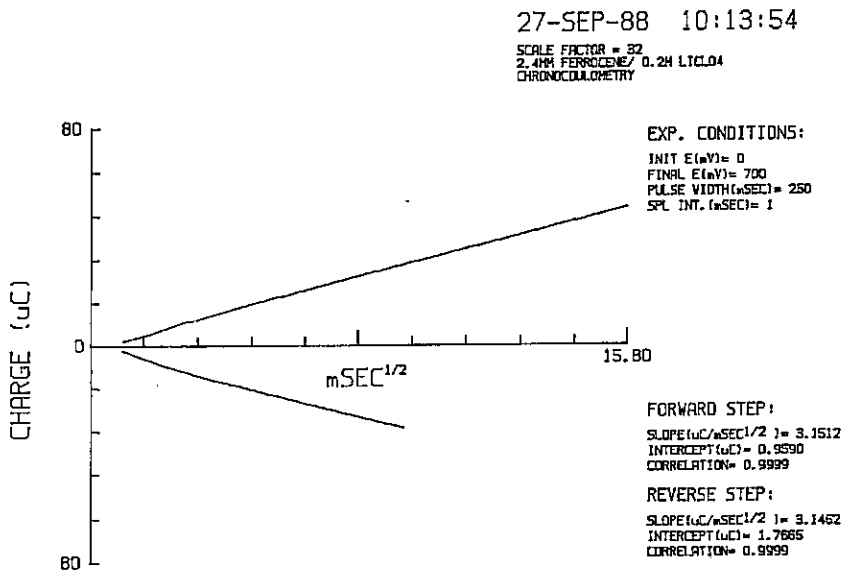

Figure 4. *Anson plot of data shown in Figure 3.*