

Chronocoulometry: Application to the Study of
Adsorption at an Electrode Solution Interface

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Introduction

Chronocoulometry is a term used to describe a technique, developed jointly at North American Aviation Science Center and California Institute of Technology,^{1,8} in which the charge-time behavior of an electrode in a solution is observed. The electrode, initially at some potential E_i where no current flows, has applied to it either a linear potential ramp or a potential step which results in the passage of charge across the electrode interface. If the resultant potential excursion is sufficient to bring the electrode potential into a region where a faradaic current flows, the charge passed will include coulombs required to charge the electrical double layer, Q_{dl} , as the potential changed from E_i to a final potential, E_f , and the faradaic charge passed, Q_F , from time the potential excursion is initiated at $t=0$ until the measurement is made at some later time, t . Thus, the total charge passed, Q_t , will be

$$Q_t = Q_F + Q_{dl} \quad (1)$$

The prime assumption in what follows is that the Q_{dl} is essentially time independent, while Q_F is a function of time. If Q_t is measured as a function of time, and $Q_F(t)$ is known, then the terms may be separated by plotting Q_t against the proper function of time. In addition, if Γ moles/cm² of a species Ox are adsorbed at E_i and react at E_f , an additional amount of charge, $nF\Gamma$, will pass. If we assume that this charge will likewise be time independent, then

$$Q_t = Q_F + Q_{dl} + nF\Gamma \quad (1')$$

Q_F then arises from a faradaic reaction where the reactant must diffuse to the electrode to result in charge passage. Q_{dl} and $nF\Gamma$ represent charge which arises from non-diffusing - hence time independent - sources. Q_{dl} must be determined, then, by an independent procedure to permit evaluation of $nF\Gamma$. For instance, consider an electrode in a supporting electrolyte with species Ox, at a potential E_i , when no faradaic current flows. The surface charge density, Q_{E_i} may be determined by using an extruded mercury drop or dropping mercury electrode. Now, consider the solution containing only Red at a concentration in solution or in an amalgam equal to Ox. An electrode potential E_f is impressed. E_f is such that the reaction $Ox + ne \rightarrow Red$ would occur and the surface concentration of Ox would be zero. (This is the condition that would prevail at the electrode surface at E_f in an experiment where only Ox is initially in solution and the potential is changed to E_f , with the charge-time behavior recorded.) The charge density, Q_{E_f} is measured. However, since

$$Q_{dl} = Q_{E_f} - Q_{E_i}$$

then Q_{dl} is known regardless of how the potential is varied from E_i to E_f in the chronocoulometric experiment.

This ability to separate the faradaic and double layer charge, either by time-independence of Q_{dl} or by direct measurement of surface charge density, makes chronocoulometry particularly useful.

Chronocoulometry has been applied to the study of electrode kinetics,^{4,5,9-11} to a study of a catalytic reaction and other reactions in solutions¹¹⁻¹⁴ and to studies and determinations of the extent of the adsorption of a species which undergoes reaction at the electrode surface.^{3,4,6-8,15,17} It is principally to this latter problem that the remainder of the paper is addressed. In particular, we shall consider the use of double-potential step chronocoulometry as a technique which permits an "insitu" double layer correction even in the presence of extensive adsorption.^{19,20}

Double Potential Step Chronocoulometry

Consider the redox couple, with standard potential E^0 ,



An electrode at a potential E_i , sufficiently anodic of E^0 so no current flows, is in a solution containing excess supporting electrolyte and Ox. At $t=0$, the potential is stepped to a value E_f sufficiently cathodic of E^0 so that the surface concentration of Ox is immediately driven to zero. Reaction 2 then proceeds to the right at a rate limited by diffusion of Ox to the electrode. After a time, τ , the potential is stepped back to E_i , which is sufficiently anodic so that the concentration of Red at the electrode surface is driven to zero. Again, the current is limited by the rate of diffusion of Red back to the electrode surface. The Q - t behavior is observed.

Initially we consider neither Ox nor Red adsorbed. The faradaic charge during the forward step is given by the integral of the Cottrell equation

$$i(t) = nF\sqrt{D_{\text{Ox}}} C_{\text{Ox}} / \sqrt{\pi t}$$

and, adding in Q_{dl} , we obtain

$$Q(t < \tau) = \frac{2nF\sqrt{D_{\text{Ox}}} C_{\text{Ox}} \sqrt{t}}{\sqrt{\pi}} + Q_{dl} \quad (3)$$

where the symbols have their usual significance. For $t > \tau$, the charge Q_f may be obtained by integration of current-time equations derived by Kambara. This yields

$$Q(t > \tau) = \frac{2nF\sqrt{D_{\text{Ox}}} C_{\text{Ox}}}{\sqrt{\pi}} (\sqrt{t} - \sqrt{t-\tau}) \quad (4)$$

Equation (4) contains no Q_{dl} term because the electrode potential is back at its initial potential at $t > \tau$.

It is convenient, however, to consider the net charge, Q_r , passed during the interval $t > \tau$, $Q_r = Q(\tau) - Q(t > \tau)$. Thus

$$Q_r = \frac{2nF\sqrt{D_{\text{Ox}}} C_{\text{Ox}}}{\sqrt{\pi}} [\sqrt{t-\tau} + \sqrt{\tau} - \sqrt{t}] + Q_{dl}$$

Thus, plots of $Q(t < \tau)$ vs. $t^{1/2}$ and Q vs. $\Theta = (\sqrt{t-\tau} + \sqrt{\tau} - \sqrt{t})$ will a) be linear, b) have identical slopes ($2nF\sqrt{D_{\text{Ox}}} C_{\text{Ox}} / \sqrt{\pi}$) proportional to C_{Ox} , and c) have identical intercepts equal to Q_{dl} .

If Ox is adsorbed to the extent of Γ moles/cm² and reacts at E_f , then

$$Q(t < \tau) = \frac{2nF\sqrt{D_{\text{Ox}}} C_{\text{Ox}}}{\sqrt{\pi}} \sqrt{t} + Q_{dl} + nF\Gamma \quad (5)$$

A plot of $Q(t < \tau)$ vs. $t^{1/2}$ will have the same slope as in the absence of adsorption, but the intercept will now be $Q_{dl} + nF\Gamma$. However, during the forward step more Red is formed at the surface, and starts to diffuse away than in the absence of adsorbed Ox - i.e., Red is formed both from Ox which was adsorbed on the electrode surface and which diffuses to the electrode. This, qualitatively, will make the slope of the reverse step larger than in the absence of adsorption of Ox, hence larger than the forward slope, which is unaffected by adsorption.

Specifically, defining Q_r as before,^{19,20}

$$Q_r = \frac{2nF\sqrt{D_{\text{Ox}}} C_{\text{Ox}}}{\sqrt{\pi}} [\Theta] + nF\Gamma \left[1 - \frac{2}{\pi} \sin^{-1} \sqrt{\frac{\tau}{t}} \right] + Q_{dl} \quad (6)$$

This differs from Eq. 4 only by the term $nF\Gamma [1 - 2/\pi \sin^{-1} \sqrt{\tau/t}]$, arising from reoxidation of initially adsorbed Ox. Q_{dl} here is the true double layer charging term in the presence of adsorption.

Equation (6) may be simplified by approximating $(1 - 2/\pi \sin^{-1} \sqrt{\tau/t})$ with a linear function of the form $a_1(\Theta/\sqrt{\tau}) + a_0$ to give

$$Q_r = \frac{2nF\sqrt{D_{\text{Ox}}} C_{\text{Ox}}}{\sqrt{\pi}} \left(1 + \frac{a_1 nF\Gamma}{Q_c} \Theta + a_0 nF\Gamma \right) + Q_{dl} \quad (6')$$

where Q_c is the charge which has diffused at $t=\tau$, $(2nF/D C_{ox} \sqrt{\tau})/\sqrt{\pi}$. Hence, from the intercepts of $Q(t < \tau)$ vs. $t^{1/2}$ and Q_r vs. Θ plots, $nF\Gamma$ may be attained.

$$nF\Gamma = \frac{Q_c - Q_r}{1 - a_r} \quad (7)$$

when Q_c and Q_r are the intercepts in the Q-axis of the $Q(t < \tau) - t^{1/2}$ and $Q_r - \Theta$ plots. The constants a_0 and a_1 , although dependent on the experimental time-ratios used, can be made close to zero and unity, respectively. In short, the intercept of the $Q_r - \Theta$ plot is quite close to the true Q_{dl} required.

Further,

$$\frac{S_r}{S_f} = 1 + \frac{a_1 nF\Gamma}{Q_c} \quad (8)$$

where S_r and S_f are the slopes of the reverse and forward plots, respectively, (Q_c , experimentally, is $Q(t=\tau) - Q_c$). This may be used to establish an internal check on the procedure. Further, the double layer charging term is given by

$$Q_{dl} = \frac{Q_r - a_0 Q_c}{1 - a_0} \quad (9)$$

Figure 1 shows, qualitatively, the Q-t behavior expected without (a) and with (b) adsorption.

Figure 2 shows $Q - t^{1/2}$ and $Q_r - \Theta$ plots for 1 mM Cd(II) in 1 F KNO₃ and 0.8 F KNO₃ + 0.2 F KSCN.^{19,20} A potential step from -200 to -950 mV vs. the SCE was applied. The points labelled Blank in A and B refer to coulombs required to charge the double layer in the Cd(II) - free base solutions. A summary of data is given in Table I. It is seen that a) the amount of Cd(II) adsorbed decreases as the initial potential is made more cathodic and b) the amount of Cd(II) adsorbed rises to a maximum and decreases with increasing thiocyanate concentration.

Figure 3 is a plot of $nF\Gamma$ vs. E obtained chronocoulometrically for Zn(II) in 0.05 F NaSCN + 0.95 F NaNO₃. This system is of interest because the potential range for E is such that complete desorption can be achieved at potentials prior to the Zn(II) reduction wave.^{22,23} Also included in this figure,²⁴ is the amount of specifically adsorbed thiocyanate, as determined by Parsons. The straight line in the figure is a plot of the slope of the forward Q-t plot vs. [Zn(II)]. The slope should be, and is, proportional to the concentration of Zn(II).

Figure 4 is Γ vs. electronic charge,¹⁸ rather than potential, for thiourea in 1 M NaNO₃ obtained by Case and Anson. The thiourea does not react, but give rise to an anodic depolarization wave. The open circles are chronocoulometric data, the circles are from classical capacity measurements of Parsons and Symons²⁵ and the triangles from Schapink et al.²⁶ This is the first instance where a direct comparison between chronocoulometry and classical methods can be made, and the agreement is overwhelming!

Using essentially a coulometric method, evidence for the validity of the assumption regarding the rapidity of the reaction of adsorbed material has been obtained.²⁷

The chronocoulometric procedures appear to offer real advantages in adsorption and kinetic studies. With the aid of sophisticated data acquisition systems, rapid and precise measurements of parameters can be carried out.^{28,29} It is hoped that others will attempt to apply to their problems what we consider a very useful approach to studying electrode processes.

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Table I

Data Summary for Adsorption of Cd(II) from Thiocyanate Solutions

$nF\Gamma_0 \mu\text{C}/\text{cm}^2$ Potential steps from -200 to -300 to -400 } to -900 mV vs. S.C.E.

| [SCN ⁻] | .05 F | | | 0.1 F | | | 0.2 F | | |
|---------------------|-------|------|------|--------|------|------|-------|------|------|
| [Cd(II)] | .05 F | | | 0.1 F | | | 0.2 F | | |
| $E_i =$ | -200 | -300 | -400 | -200 | -300 | -400 | -200 | -300 | -400 |
| 0.2 | ~ 0 | ~ 0 | ~ 0 | 17.3 | 10.8 | 6.4 | 14.7 | 10.6 | 6.9 |
| 0.5 | 13.9 | 11.2 | 5.8 | 22.9 | 17.9 | 11.8 | 20.5 | 14.9 | 10.1 |
| 1.0 | 21.2 | 17.1 | 9.3 | 22.7 | 21.8 | 17.5 | 21.1 | 19.2 | 14.0 |
| | 0.5 F | | | 0.75 F | | | 1.0 F | | |
| 0.2 | 12.1 | 10.8 | 4.9 | 9.4 | 7.5 | 5.8 | 8.3 | 5.1 | 3.3 |
| 0.5 | 18.4 | 14.2 | 9.8 | 15.7 | 12.8 | 9.8 | 12.7 | 10.1 | 8.0 |
| 1.0 | 24.4 | 16.1 | 13.4 | 18.4 | 16.9 | 15.6 | 15.6 | 14.1 | 10.1 |

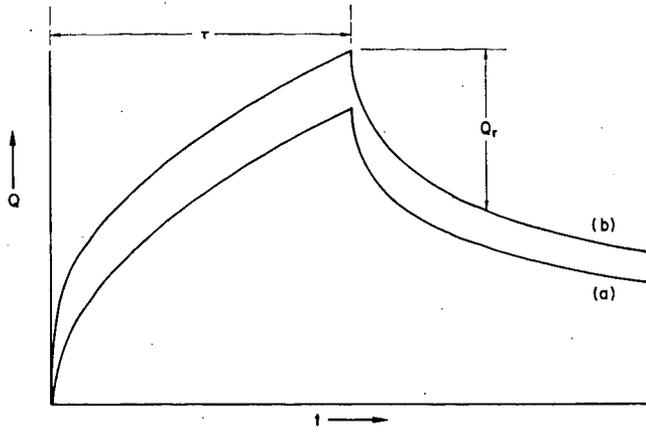


Fig. 1

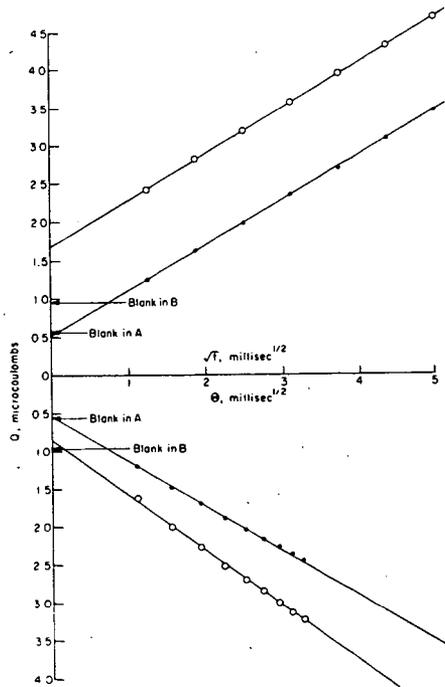


Fig. 2

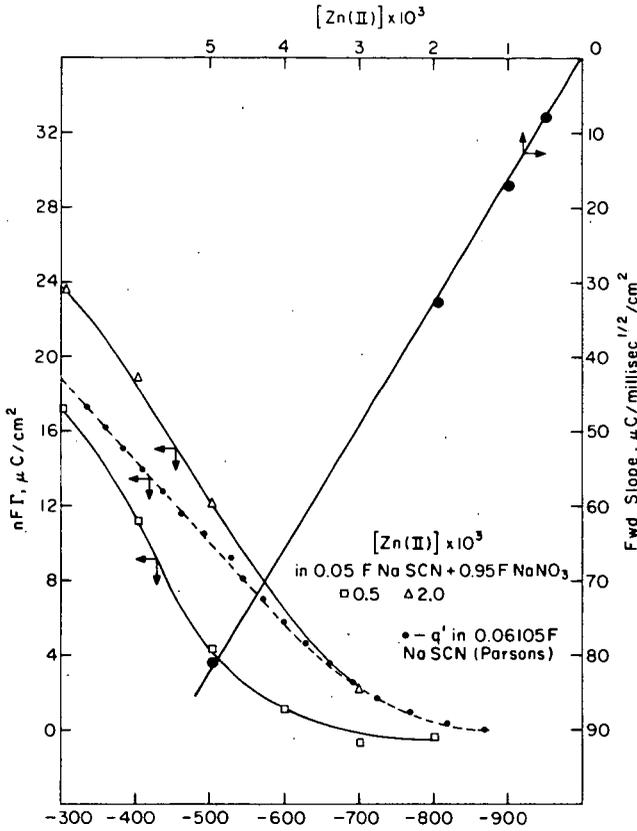


Fig. 3: E_i , mV vs SCE

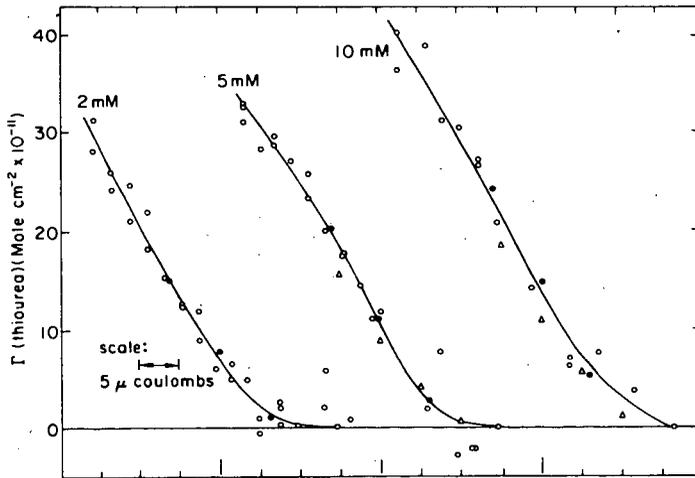


Fig. 4: q (microcoulombs cm^{-2})