

Innovations in the Study of Adsorbed Reactants by Chronocoulometry

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► Two new methods for obtaining values of the charge in the electrical double layer in the presence, as well as absence, of adsorbed reactants are described. Application of the methods allows smaller amounts of adsorbed reactants to be determined or demonstrated to be absent. The methods are used to establish that, at most, 0.3×10^{-10} moles per sq. cm. of Co(en)_3^{+3} or Co(en)_3^{+2} are adsorbed on mercury electrodes from 0.1*F* ethylenediamine-1*F* KCl solutions.

ELECTROACTIVE SUBSTANCES that are adsorbed on electrode surfaces can be studied in the adsorbed state by means of a new electrochemical technique that has been previously described (1, 4, 5). The technique involves measurement of the charge that flows across the electrode-electrolyte interface when the potential of the electrode is changed from a value where no current is flowing to a value where a faradaic current does flow. This technique has been called by various names (1, 4, 5) but "chronocoulometry" seems the most aptly succinct.

When there is no adsorption of the reactant and the experimental conditions are adjusted so that the faradaic current that flows upon application of the potential step is limited by semi-infinite linear diffusion—i.e., the potential is well out on the diffusion plateau of the corresponding polarogram for the system under study—the charge time behavior can be calculated from the integrated Cottrell equation (4).

$$Q = \frac{2nFAC\sqrt{Dt}}{\sqrt{\pi}} + Q_{d.l.} \quad (1)$$

where Q is the amount of charge in coulombs that has passed at time, t , since the application of the potential step; C and D are the concentration and diffusion coefficients of the reactants, respectively; A is the electrode area (although Equation 1 was derived for a plane electrode, it is obeyed at spherical electrodes when measurement times are kept sufficiently short—e.g., < ca. 0.5 second); n and F have their usual significance; and $Q_{d.l.}$ is the charge consumed by the electrode-electrolyte

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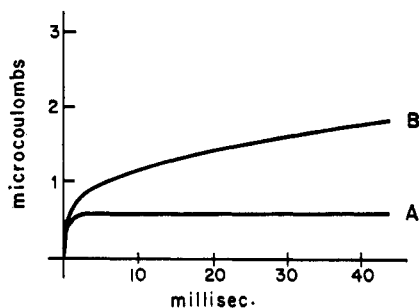


Figure 1. A. Charge-time curve for potential step from -200 to -800 mv. vs. S.C.E. in 1*F* NaNO_3 . B. Repeat of A with 1*mM* $\text{Cd}(\text{NO}_3)_2$ in 1*F* NaNO_3 .

Electrode area was 0.032 sq. cm.

double-layer capacitance when the potential is changed from its initial to its final value.

According to Equation 1, plots of Q vs. $t^{1/2}$ are straight lines having intercepts on the Q axis equal to $Q_{d.l.}$ (1).

NO ADSORPTION OF REACTANT. In the absence of the specific adsorption of reactant or product, $Q_{d.l.}$ can be obtained from a blank experiment performed in reactant-free supporting

electrolyte. Curve A in Figure 1 shows the Q - t behavior obtained when the potential is changed from -200 to -800 mv. vs. S.C.E. in a 1*F* NaNO_3 solution. The step change in Q of about $0.55 \mu\text{-coulomb}$ is equal to $Q_{d.l.}$. When the solution was made 1*mM* in $\text{Cd}(\text{NO}_3)_2$, as an example, and the experiment repeated, the Q - t behavior in curve B in Figure 1 resulted. The corresponding plots of Q vs. $t^{1/2}$ are shown in Figure 2. The fact that the two Q intercepts in Figure 2 are identical demonstrates that Equation 1 accounts for the observed Q - t behavior and that, within experimental error (ca. $\pm 3 \mu\text{coulombs per sq. cm.}$), cadmium ion is not specifically adsorbed on the mercury electrode in 1*F* KNO_3 .

SPECIFIC ADSORPTION OF REACTANT. When reactant adsorption does occur an additional term must be added to Equation 1 (1).

$$Q = \frac{2nFAC\sqrt{Dt}}{\sqrt{\pi}} + Q_{d.l.} + nF\Gamma \quad (2)$$

where Γ is the amount of adsorbed reactant in moles per sq. cm. Now a Q vs. $t^{1/2}$ plot gives an intercept on the Q -axis that exceeds the $Q_{d.l.}$ value by $nF\Gamma$

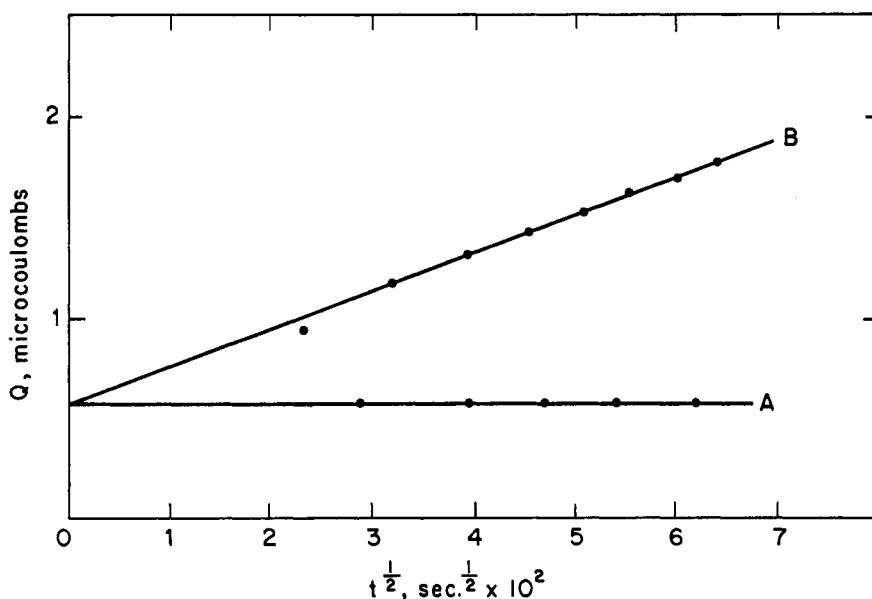


Figure 2. A, charge vs. $t^{1/2}$ plot of curve A in Figure 1. B, charge vs. $t^{1/2}$ plot of curve B in Figure 1

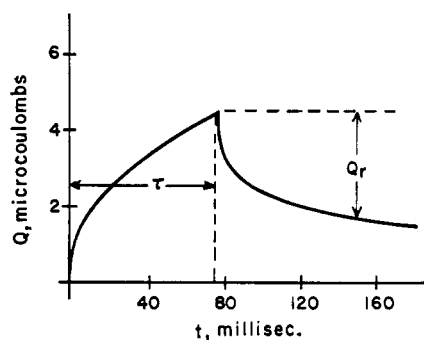


Figure 3. Charge-time curve for double potential-step chronocoulometry with 1mM $\text{Cd}(\text{NO}_3)_2$ in 1F NaNO_3

The potential was stepped from -200 to -800 to -200 mv. vs. S.C.E. Electrode area was 0.032 sq. cm.

so that the magnitude of Γ can be determined. Two examples of such plots have been published (1, 9).

When reactant adsorption occurs, the values of $Q_{d.l.}$ obtained in blank experiments which are performed in the absence of the adsorbable reactant are not rigorously applicable to Equation 2. The difference, if any, between the double-layer capacitance (and therefore the charge on the electrode) in the absence and presence of reactant should be measured to obtain the correct value of $Q_{d.l.}$ for insertion in Equation 2.

Described in this paper are two innovations in the chronocoulometric procedure that allow correct values for $Q_{d.l.}$ to be obtained in the presence of adsorbed reactants.

DOUBLE POTENTIAL-STEP CHRONOCOULOMETRY. An attractive possibility for solving the problem of a truly rigorous double-layer charge correction is to eliminate any net double-layer charging by performing the experiment so that the electrode ends up back at its initial potential—the charge in the double layer will then be the same as it was at the start of the experiment (assuming there are no complications from slow achievement of equilibrium), and no value for $Q_{d.l.}$ will be needed. A double potential-step chronocoulometric procedure that achieves this objective is the following.

Consider the generalized redox couple



which has a polarographic half-wave potential, $E_{1/2}$. In a solution of Ox containing no R the electrode potential is adjusted to some value, E_i , which is sufficiently anodic of $E_{1/2}$ so that no faradaic current flows. The potential is then stepped to a new value, E_f , sufficiently cathodic of $E_{1/2}$ that the concentration of Ox at the electrode surface is zero and Reaction 3 proceeds at a rate limited by the diffusion of Ox to the electrode. At some later time, τ , the

potential is stepped back to E_i and Reaction 3 proceeds in reverse at the electrode at a rate limited by the diffusion of R (which had been produced from $t = 0$ to $t = \tau$) back to the electrode. A typical coulomb-time curve that resulted from the procedure described is shown in Figure 3. Such curves can be analyzed with the aid of the following equations.

For times less than τ , the coulomb-time behavior is given by Equation 1. For times greater than τ , Q can be calculated by integrating the equation derived by Kambara (6) for the current flowing during square-wave electrolysis with a reversible couple. The result is Equation 4.

$$Q(t > \tau) = \frac{2nFAC\sqrt{D}}{\sqrt{\pi}} \times [t^{1/2} - (t - \tau)^{1/2}] \quad (4)$$

where D and C are the diffusion coefficient and concentration, respectively, of Ox and the other symbols have the same meanings as in Equation 1.

There is no term in Equation 4 corresponding to the double-layer charge because for $t > \tau$ the electrode is at its initial potential again and no net charging of the double layer has occurred. A plot of $Q(t > \tau)$ vs. $t^{1/2} - (t - \tau)^{1/2}$ must pass through the origin if neither reactant, Ox , nor product, R , are specifically adsorbed. Such a plot for the Q - t curve in Figure 3 is shown in Figure 4.

An even more revealing procedure is to measure the coulombs that flow after τ with respect to Q_r , the value of Q at τ . Then Q_r , the coulombs that are ac-

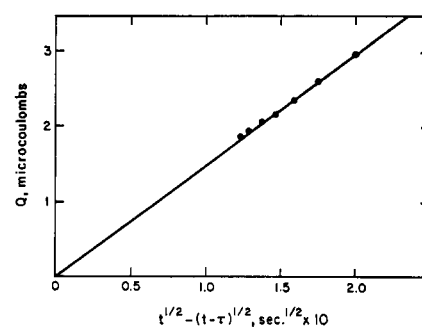


Figure 4. Charge vs. $t^{1/2} - (t - \tau)^{1/2}$ plot for curve in Figure 3

cumulated following the second potential step, is given by

$$Q_r = Q_r - Q(t > \tau) \quad (5)$$

Since

$$Q_r = \frac{2nFAC\sqrt{D}\tau}{\sqrt{\pi}} + Q_{d.l.} \quad (6)$$

it follows that

$$Q_r = \frac{2nFAC\sqrt{D}}{\sqrt{\pi}} \times [\tau^{1/2} + (t - \tau)^{1/2} - t^{1/2}] + Q_{d.l.} \quad (7)$$

The equation for Q_r includes the double-layer charging term, $Q_{d.l.}$, which corresponds to the charge needed to change the potential of the electrode back to its initial value. The absolute value of $Q_{d.l.}$ in Equations 6 and 7 should be identical because the electrode potential is stepped between the same two

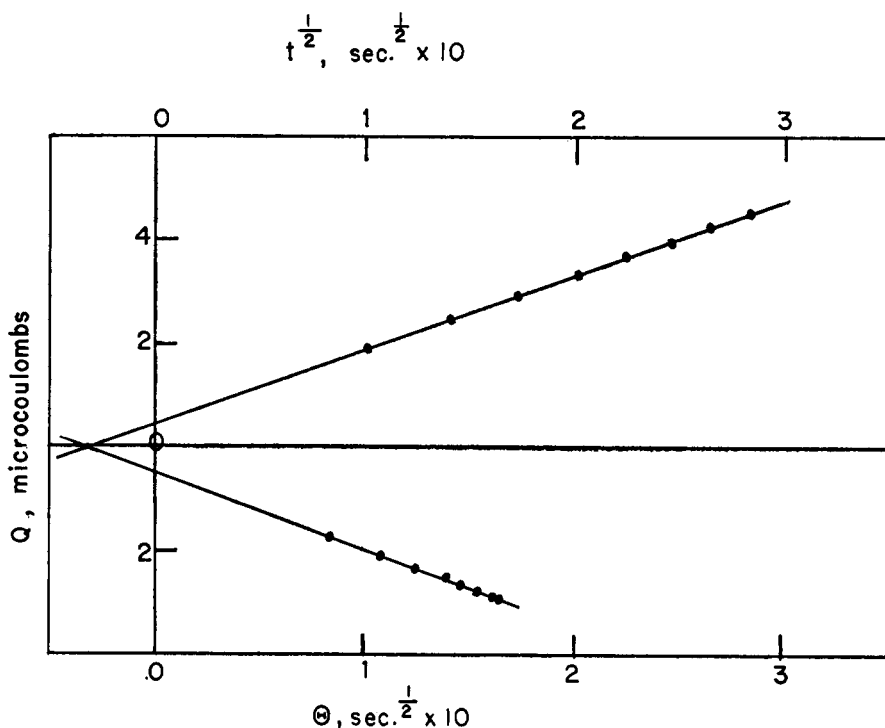


Figure 5. Charge vs. $t^{1/2}$ and charge vs. Θ plots for curve in Figure 3

Table I. Charge on Extruded Mercury Drops in 1F NaNO₃

Change in drop area = 0.032 sq. cm.	
E , mv. vs S.C.E.	Q , $\mu\text{coulomb}$
-200	+0.34
-800	-0.27
$\Delta Q = 0.61 \pm 0.10 \mu\text{coulomb}$	

potentials, only in opposite directions, in the two parts of the experiment. Now, if the value of Q obtained for times less than τ is plotted vs. $t^{1/2}$ as before and, on the same graph, $-Q$, is plotted vs. $[\tau^{1/2} + (t - \tau)^{1/2} - t^{1/2}] = \Theta$, the result should be two straight lines of equal slope that intersect each other at the $Q = 0$ axis. Each line should intersect the $t = 0$ axis the same distance from the origin at $Q = Q_{d.l.}$. The absence of electroactive adsorbed reactant or product is strongly indicated for any system which gives Q and Q_r plots that meet all of these criteria. (It is assumed that the absolute values of the coulombs measured are commensurate with the quantity of potentially adsorbed reactants—i.e., 25–100 $\mu\text{coulombs}$ per sq. cm.)

Such plots of Q vs. $t^{1/2}$ and Q_r vs. Θ for data of Figure 3 are shown in Figure 5. The agreement between the experiment and the expected behavior in the absence of adsorption is excellent (equal slopes, equal Q -axis intercepts, intersection of the lines at the $Q = 0$ axis).

It may be worth emphasizing the fundamental assumption upon which this analysis of double-potential step chronocoulometry, in the absence of reactant or product adsorption, is based: (1) The potential steps are assumed to be ideally sharp; that is, the potentiostat can instantaneously supply whatever output current and voltage may be needed and there is essentially no uncompensated resistance. (2) The integral capacity of the electrode is assumed to depend only on potential and not on the previous history of the electrode. For example, even though an amalgam is being formed after the first potential step, the electrode is assumed to have the capacitance of pure mercury when the potential is stepped back to its initial value where the surface concentration of dissolved metal in the amalgam is zero. In cases when amalgam formation does not occur (for example, both forms of the redox couple are soluble in the solution phase), it is assumed that all electrode reactions proceed reversibly (in all senses) at diffusion limited rates. (3) Any adsorption and desorption of the constituents of the supporting electrolyte (that could affect the double-layer capacitance) are assumed to occur in times much shorter than the times of measurement.

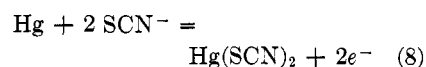
CHRONOCOULOMETRY WITH SPECIFICALLY ADSORBED REACTANT. If the reactant but not the product is adsorbed, and the double potential-step chronocoulometric technique is applied to the system, the $Q-t^{1/2}$ plot will have a larger intercept on the Q -axis than the $Q_r-\Theta$ plot. The two lines will then intersect each other above, rather than on, the t -axis. It is to be expected that the $Q_r-\Theta$ plot might deviate from linearity in cases where reactant but not product is adsorbed because the concentration profile of product at the electrode surface at time τ will differ from that resulting when no reactant is adsorbed. A detailed examination of this point (3) has shown that only small errors (5–10%) in the slopes and intercepts result if a least-squares straight line is forced through the data points. The magnitude of such errors can be calculated (they vary with measurement times), and appropriate corrections applied. In such cases the difference between the two Q -axis intercepts is the best measure of the amount of adsorbed reactant because the $Q_r-\Theta$ plot continues to have a corrected Q -axis intercept equal to $Q_{d.l.}$. Details of the application of this double potential-step chronocoulometric technique to systems where reactant adsorption occurs will be published soon. It is worth emphasizing here, however, that this method of determining adsorbed reactants suffers least of all from the model-building needed to begin to correct for the double-layer charging contribution in chronopotentiometric or faradaic-impedance measurements. The double potential-step chronocoulometric approach automatically supplies the correct double-layer charge (assuming the product of the reaction is not adsorbed) as part of the experiment in which the adsorbed reactant is determined.

INTEGRATION OF CURRENT FLOWING INTO EXTRUDED MERCURY DROPS. Whenever hanging mercury drops are employed as working electrodes, a very simple procedure can be followed to obtain the correct value of $Q_{d.l.}$ for insertion in Equation 2. The absolute value of the charge on the hanging drop can easily be measured by keeping the potentiostat and current integrator in the circuit while a new drop is extruded. The experiment is performed twice: first, in a homogeneous solution of the reduced half of the redox couple with the electrode potential maintained at the value to which it is stepped in the cathodic chronocoulometric experiment; then, in a homogeneous solution of the oxidized half of the couple with the electrode potential maintained at the initial potential to be used in the chronocoulometric experiment. The difference between the two charges measured is the value of $Q_{d.l.}$ that will be observed when

the potential is stepped between the same two potentials and a faradaic reaction occurs. (Note that in drop extrusion experiments the two potentials must be chosen so that essentially no faradaic current is flowing.)

The data in Table I were obtained by drop extrusion in a 1F NaNO₃ solution. The difference between the two values of the charge matches, within experimental error, the value obtained when the potential was stepped between the same two potentials (Figure 1).

An example of a system in which measurement of the double-layer charging correction by the drop extrusion technique is absolutely essential is the chronocoulometric anodic oxidation of mercury in the presence of thiocyanate ion (2). The electrode reaction is



The specific adsorptions of both thiocyanate and mercuric thiocyanate on the electrode produce very large changes in the electronic charge on the electrode. The adsorption of $\text{Hg}(\text{SCN})_2$ is so extensive that the positive charge on the electrode is actually smaller at +0.300 than at -0.200 volt vs. S.C.E. Clearly, in such circumstances, the charge values obtained in the absence of the reactants are worthless in trying to correct for double-layer charging when the electrode reaction is occurring.

NONADSORPTION OF $\text{Co}(\text{en})_3^{+3}$ AND $\text{Co}(\text{en})_3^{+2}$. There has been disagreement in the literature regarding the reported specific adsorption of the triethylenediamine complexes of cobalt(II) and (III) at mercury electrodes (1, 7, 8). The major source of suspicion in all of the previously reported experiments has been the methods employed to correct for double-layer charging. Inasmuch as the two methods described here appear to be better in this respect than those previously used, we have applied the two methods to the $\text{Co}(\text{en})_3^{+3}$ – $\text{Co}(\text{en})_3^{+2}$ system.

Table II contains the charge data obtained by mercury drop extrusion in a supporting electrolyte of 0.1F ethylenediamine in 1F KCl with and without $\text{Co}(\text{en})_3^{+3}$ or $\text{Co}(\text{en})_3^{+2}$.

The fact that the charge on the drop at both potentials in Table I is the same, within experimental error, whether or not the complexes are present is evidence against the specific adsorption of either complex. This is confirmed by the $Q-t^{1/2}$ and $Q_r-\Theta$ plots in Figure 6 which resulted from performing a double-step chronocoulometric experiment with a 2mM $\text{Co}(\text{en})_3^{+3}$ solution. The two intercepts on the Q axis in Figure 6 are equal and coincide with the measured value of $Q_{d.l.}$ in Table II. The slopes of the two straight lines are equal and the lines intersect each other on the time axis. Thus, the two plots

Table II. Integrated Charge on Extruded Mercury Drops

Supporting electrolyte: 0.1 <i>F</i> ethylenediamine in 1 <i>F</i> KCl change in drop area = 0.032 sq. cm.		
<i>E</i> , mv.	<i>vs.</i>	
S.C.E.	<i>Q</i> , μ coulomb	
Electrolyte alone	-700	-0.22 \pm 0.05
Electrolyte + 2 <i>mM</i> Co(en) ₃ ⁺²	-700	-0.24 \pm 0.05
Electrolyte alone	-250	+0.40 \pm 0.05
Electrolyte + 2 <i>mM</i> Co(en) ₃ ⁺³	-250	+0.37 \pm 0.05
<i>Q</i> _{d.i.} = 0.61 \pm 0.10 μ coulomb		

come very close to meeting all of the criteria that denote the absence of adsorption of reactant or product.

An interesting point, raised by a reviewer, asks what behavior would be expected if both Co(en)₃⁺³ and Co(en)₃⁺² were adsorbed in equal amounts. In such circumstances the slopes and intercepts of the two lines in Figure 6 would be equal to each other but the absolute values of both intercepts would exceed the values obtained for *Q*_{d.i.} by drop extrusion in Table II.

The data in Table II and Figure 6 can be reproduced with the present apparatus with a precision of about $\pm 0.10 \mu$ -coulomb which corresponds to an uncertainty of $\pm 3 \mu$ coulombs per sq. cm. in Γ . Taking this into account it seems safe to assert that not more than 3μ -coulombs per sq. cm. (0.3×10^{-10} mole per sq. cm.) of Co(en)₃⁺³ or Co(en)₃⁺² are adsorbed in 1*F* KCl-0.1*F* ethylenediamine at -0.25 and -0.70 volt *vs.* S. C. E., respectively.

CONCLUSIONS

The power of the double potential-step chronocoulometric technique to establish the absence of electroactive reactant or product adsorption at levels well below the double-layer charge is amply demonstrated by the data in Figures 4 and 6. The technique also shows considerable promise in the presence of reactant adsorption—its chief virtue being that the double-layer charge correction in the presence of the reactants can be obtained from *Q*_r intercept. Applications of this technique to several additional systems, with and without adsorption, are in progress.

EXPERIMENTAL

The electronic apparatus was a modified version of that previously described (1). Solid state operational amplifiers (Geo. A. Philbrick Researchers, Inc., Dedham, Mass., Model SP656) were used for the potentiostat,

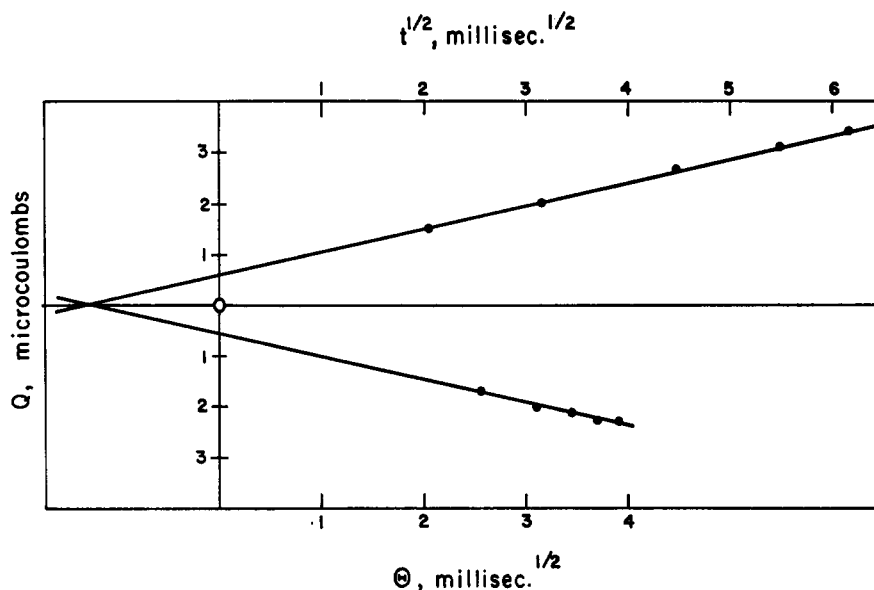


Figure 6. Charge vs. $t^{1/2}$ and charge vs. θ plots for double potential-step chronocoulometry with 2*mM* Co(en)₃⁺³ in 1*F* KCl - 0.1*F* ethylenediamine

The potential was stepped from -250 to -700 to -250 mv. *vs.* S.C.E. The electrode area was 0.032 sq. cm.

current measuring amplifier, and current integrator. Coulomb-time curves were recorded with a Tektronix Model 564 storage oscilloscope and the data were read directly from photographs of the traces.

The hanging drop mercury electrode was a commercially available assembly (Brinkmann Instruments, Inc.). With this electrode it was frequently observed that when a used drop was dislodged and a new drop extruded a rather high resistance (10-100 kilohms) appeared within the capillary. This resistance apparently was the result of a break in the mercury column within the capillary. The resistance could usually be eliminated by abruptly changing the electrode potential once or twice. This high resistance was often present during the drop-extrusion experiments but the time scale of these experiments was sufficiently long (1-2 seconds) that the measured charge on the drops was not affected.

In the drop-extrusion experiments the most reproducible results were obtained if the drop was expanded from a small initial volume to a much larger final volume rather than from zero volume to a final volume. Therefore, the drop-extrusion experiments were performed by increasing the drop area from 0.014 to 0.046 sq. cm. The values for *Q*_{d.i.} obtained in this way were then applied to chronocoulometric data obtained with hanging drops having an area of 0.032 sq. cm.

In order to be certain that adsorption equilibrium was maintained during the drop-extrusion experiments it was established that the measured values of the charge did not depend on the rate of drop extrusion or upon whether or not

the solution was stirred during the extrusion of the drop.

All solutions were prepared with triply distilled water and solutions were deaerated with high purity nitrogen that was further purified by passage through a vanadous washing tower and hot copper turnings. Reagent grade chemicals were not further purified.

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