Chronopotentiometric Studies of Adsorption on a Mercury Electrode

DeWitt A. Payne
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Chronopotentiometry, or voltammetry at controlled current is one of the many methods used for studying reactions at electrodes. It consists of applying a constant current through a solution and measuring the potential of one of the electrodes with respect to a standard reference electrode.

If one assumes that the only mass transfer process involved is diffusion, that is, if the solution is at a uniform temperature and is not being mechanically stirred, then the concentration of the various reactive species in the solution can be calculated by solving the basic diffusion equations with suitable boundary conditions. Let i_o be the current passed through the cell, n be the number of electrons involved in the reaction, F be Faraday's constant, D_O be the diffusion constant for the substance reacting at the electrode, and C_o be the concentration of the reacting species.

Then: $$i_o = n F D_o \left(\frac{\partial C_o(x,t)}{\partial x} \right)_{x=0}$$

also: $$D_o \left(\frac{\partial C_o(x,t)}{\partial x} \right)_{x=0} + D_R \left(\frac{\partial C_R(x,t)}{\partial x} \right)_{x=0} = 0$$

Where C_R is the concentration of the substance being produced, and D_R is the diffusion constant for tha t substance. Initial conditions are usually assumed to be: $C_R(x,0) = 0$, $C_o(x,0) = C^o$, $C_o(x,t)$ and $C_R(x,t)$ approach C^o and 0 respectively as x approaches infinity.

$$\lambda = \frac{i_o}{nFD_o}$$ Solving these equations one obtains;

$$C_o(x,t) = C^o - \frac{2\lambda D_o^{\frac{1}{2}} t^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \exp\left(\frac{-x^2}{4D_o t}\right) + \lambda x \operatorname{erfc}\left(\frac{x}{2D_o^{\frac{1}{2}} t^{\frac{1}{2}}}\right)$$

$$C_R(x,t) = \frac{2\lambda D_o t^{\frac{1}{2}}}{D_R^{\frac{1}{2}} \pi^{\frac{1}{2}}} \exp\left(\frac{-x^2}{4D_R t}\right) - \frac{\lambda x D_o}{D_R} \operatorname{erfc}\left(\frac{x}{2D_R^{\frac{1}{2}} t^{\frac{1}{2}}}\right)$$

Substituting these expressions into the Nernst equation one obtains! setting $x=0$

$$E = E^{0} + \frac{RT}{nF} \ln \frac{f_O D_R^{1/2}}{f_R D_O^{1/2}} + \frac{RT}{nF} \ln \frac{C^{0} - P t^{1/2}}{P t^{1/2}}$$

$$P = \frac{2 i_O}{\pi^{1/2} n F D_O^{1/2}}$$

The potential becomes infinite when $t^{\frac{1}{2}} = C^{0}/P$. This time t is called the transition time and hereafter will be referred to as τ.

In actua l practice E does not become infinite, but increases rapidly to the point where a new reaction begins. This transition is usually sharp enough to be easily measured. Interestingly enough, $i \tau^{1/2} = \frac{\pi^{1/2} n F D_O^{1/2} C^{0}}{2}$

which is a constant for any one solution.

One may also study both the oxidation and reduction of a species by oxidizing for a time less than or equal to the transition time and then reversing the current and running to the cathodic transition time. We now have:

$$C_R(0,t_1) = \frac{2\lambda D_O t_1^{1/2}}{D_R^{1/2} \pi^{1/2}} \exp\left(\frac{-x^2}{4 D_R t_1}\right) + \cdots$$

$$\left(\frac{\partial C_R(x,t')}{\partial x}\right)_{x=0} = \lambda' = \frac{i_O'}{nFD_R} \qquad C_R(x,t) \to 0 \text{ as } x \to \infty$$

Solving, one obtains:

$$C_R(x,t') = 2\theta \left[\frac{D_R(t_1+t')}{\pi}\right]^{1/2} \exp\left[\frac{-x^2}{4D_R(t_1+t')}\right] - \theta x \operatorname{erfc}\left[\frac{x}{2 D_R^{1/2}(t_1+t')^{1/2}}\right]$$
$$-2(\theta+\lambda')\left(\frac{D_R t'}{\pi}\right)^{1/2} \exp\left(\frac{-x^2}{4D_R t'}\right) + (\theta+\lambda') x \operatorname{erfc}\left[\frac{x}{2 D_R^{1/2} t'^{1/2}}\right]$$

$$\theta = \frac{i_O}{nFD_R}$$

solving for $C_R(0,\tau') = 0$ $\qquad \tau' = \frac{\theta^2}{(\theta+\lambda')^2 - \theta^2} t_1$

when $\theta = \lambda'$ $\tau' = \frac{1}{3} t'$

These equations have been confirmed for many systems by various experimenters. However, there are certain systems which change the boundary conditions. Specifically, a reactive substance can be specifically adsorbed on the surface of the electrode.

If there is adsorbed material, several things can happen. The adsorbed material could be reduced first, then the material which diffuses up to the electrode. This, however, should give a double wave, that is, two definite transition times, one exhibiting $i\tau_1 = \text{constant}$ the other $i\tau_2^{1/2} = \text{const.}$

If both adsorbed and diffusing material are reduced at the same time, then: $i\tau_{obs} = Q_{ads} + B\tau_{obs}^{1/2}$

The reverse current case is also affected by adsorption. If, for example, the product of the oxidation is completely adsorbed, then $t_1 = \tau$. As t_1 gets longer all the product cannot be adsorbed and some diffuses away. If t_1 gets long enough, the amount adsorbed becomes negligeable and the relationship approaches ideality.

Various compounds and complexes were tested to see if they were adsorbed on a mercury electrode, and were reduced at a potential convenient for study of the mechanism of electrode reactions and adsorption. The compounds studied were: cadmium EDTA complex, mercuric EDTA, Mercuric thiocyanate, and mercuric acetate.

Chronopotentiometry was done with several different apparatuses. The basic electronics were the same for all versions, though. This

consisted of a DeFord follower amplifier used to drive either a Varian G-10 recorder or a Textronix oscilloscope. Input was form an S.C.E. with the working electrode grounded and potential measured with respect to ground. A Philbrick * 300 volt stabilized power supply was used to power the follower. Current source was three 45 volt radio batteries. Current was controlled by a wide range decade resistance box. This provided essentially constant current provided the resistance of the cell was much less than the resistance of the box. Measurement of the current was made with a short in place of the cell as it was often impossible to read the meter during the time the current was on the cell, as the response time of the meter was far too slow for short transition times. The current was switched by a mercury wetted contact relay with a switching time on the order of a few milliseconds. When the scope was used, the voltage drop across the relay coil on switching was used to trigger the sweep. For very fast times, a delayed sweep triggering time base was used so the scope would not trigger until just before the relay actually closed.

Input to the follower was from one of several different cell arrays. The hanging drop mercury electrode of HDME, which consisted of a 250 ml. beaker with the lip cut off and a teflon cap. In the cap were holes for an S.C.E., the capillary from the mercury stand tube, an auliliary electrode, the working electrode from which the drop was hung, the cup support, by which the cup which caught and carried the drops from the stand tube to the holder was maneuvered, a fourth electrode for controlling the oxidation of the auxiliary electrode, and also holes for nitrogen to deareate the solution.

Current was fed to the working and auxiliary electrodes. The cell used with the mercury button electrode was an H cell with the S.C.E. in one arm and the other apparatus in the other arm. The two arms were separated by a fritted glass disk.

The mercury button electrode was made from a Beckman platinum button electrode. The electrode was placed in a sodium mercury amalgam for a few minutes. The surface of the electrode was reduced by the sodium and the mercury was then absorbed. The electrode was then placed in water to remove the last of the sodium, and then in clean mercury, in which it was stored while not in use. To use the electrode, the excess mercury was shaken off and the electrode washed with distilled water and then placed in the cell for use.

Cd^{++} and $CdY^{=}$ were studied with the HDME apparatus. Cd^{++} gave sharp waves, but $i\underline{T}^{\frac{1}{2}}$ was constant over a large range of i and $\underline{T}$, indicating that Cd^{++} was not adsorbed.

i	$\underline{T}$	$i\underline{T}^{\frac{1}{2}}$
.085 ma	2.20 sec.	126
.110	1.20	120
.150	.60	116
.218	.275	114
.320	.114	108
.500	.050	112
.710	.027	116

It was not possible to get meaningful data from chronopotentiometry of $CdY^{=}$ because the reduction potential was too close to the reduction potential of water; hence, the wave was not well defined enough to interpret.

It was then decided that it would be advantageous to use an Hg^{++} complex for furthe r study, as this would seem to be more likely to be adsorbed, and would also have a convenient potential for study if one could be found to be adsorbed. The forst of these

complexes to be studied was $HgY^{=}$.

$HgY^{=}$ produced confusing results on the HDME until it was discovered that in neutral KNO_3, which was being used for an electrolyte, $HgY^{=}$ has a polarographic maximum which made the transition times ridiculously long. It was also discovered that increasing the pH to 10 made the maximum disappear. Further work was done in pH 10 KNO_3 solution. Chronopotentiograms were made with the HDME, but the results were difficult to interpret as there was a double wave. Addition of more EDTA failed to make this wave disappear, even though the EDTA was probably in excess. Neither wave exhibited constant $i\underline{T}$ or $i\underline{T}^{\frac{1}{2}}$ behavior.

As these results were impossible to interpret accurately, it was decided to do reverse current chrono with a mercury electrode in EDTA solution. This was done by first oxidizing the mercury electrode, and then reducing until a transition time is reached. This was done for various lengths of oxidizing time, though with the current low enough so that the anodic transition time was never approached, and the ratio of anodic to cathodic time was calculated. It was decided that the fact that the cathodic chrono had been done in KNO_3 might have had something to do with the results, so a mercury button electrode was used and work done in pH 5 acetate buffer.

cathodic time	anodic time	ratio
.90 sec	3.06	3.41
1.28	4.00	3.13
1.60	5.08	3.18
1.83	6.15	3.36
2.30	7.10	3.08
3.02	10.04	3.45
4.32	15.07	3.48
4.73	14.96	3.16

Cathodic chrono was then done on $HgY^{=}$ with the button electrode in acetate buffer. The double wave essentially disappeared and $i\underline{T}^{\frac{1}{2}}$ became relatively constant over a large range of transition times. Hence, $HgY^{=}$ is not adsorbed in significant quantities.

The next compound to be investigated was $Hg(SCN)_2$. It was decided to try this compound because it existed in solution as an uncharged molecule, and the other compounds studied were all charged. Initial results of reverse current chrono seemed to indicate adsorption.

anodic	cathodic	ratio
3.18 secs	1.23 secs	2.58
4.08	1.59	2.57
5.10	1.92	2.65
6.05	2.28	2.65
7.00	2.62	2.78
8.02	2.95	2.72
8.16	2.80	2.91
9.04	3.21	2.82
10.05	3.60	2.79
11.20	3.90	2.87
15.11	5.14	2.94

However, when cathodic chrono was done to confirm this, $i\underline{T}^{\frac{1}{2}}$ remained constant over a wide range of $\underline{T}$. It was hypothesized that the concentration of KSCN in the reverse current experiment was too high, and the $Hg(SCN)_2$ produced was precipitating out on the electrode instead of being adsorbed. When reverse current chrono was repeated, it was found that careful reduction of the mercury electrode beforehand gave a relatively constant value close to 3.0 for the reverse current chrono over a range of anodic times from 1 to 15 seconds.

Hence, it was possible to say that $Hg(SCN)_2$ is almost certainly adsorbed in significant quantities.

$Hg(OAc)_2$ was the next compound to be studied. Cathodic chrono was done on a mercuric acetate solution with the mercury button electrode.

i	τ	$i\tau^{\frac{1}{2}}$
.01 ma	245.6 sec	157.6
.015	41.25	96.4
.02	21.90	93.5
.025	14.07	93.7
.030	10.32	96.3
.040	5.10	90.5
.050	2.85	84.5
.100	1.16	107.6
.200	.28	105.8
.400	.086	117.2
.800	.029	135.3

The increase of $i\underline{T}^{\frac{1}{2}}$ as $\underline{T}^{\frac{1}{2}}$ gets smaller is suspicious, but a plot of $i\underline{T}$ vs. $\underline{T}^{\frac{1}{2}}$ reveals the intersept at $\underline{T}^{\frac{1}{2}}=0$ is no more than 1 or 2 micro coulombs, which is not significant enough to be useful.

It would appear that none of the studied compounds were adsorbed in large enough quantities to be detected by these techniques. In fact, this is a large disadvantage of these techniques, they are not terribly sensitive. Under optimal conditions, one could probably detect adsorption of quantities as small as 5 microcoulombs on a mercury button. The big problem with cathodic chrono is that one must go to ridiculously fast transition times to detect small amounts of adsorption. On most systems, though, as the transition time gets

shorter, it is less well defined. Unless the couple is very reversible, it is ridiculous to go to times as short as 25 milliseconds, which is not very fast considering that it usually takes currents over a milliamp to get to times that short, and that is still 25 microcoulombs. 5 microcoulombs is only 20% of that and if that is the last possible point obtainable, one can't really detect the adsorption.

The selection of compounds was done somewhat haphazardly. Two were selected because they were uncharged, $Hg(SCN)_2$ because SCN^- is supposed to be adsorbed on mercury. It might be wise to look at the electronic structures of compounds which are and aren't adsorbed and try to see why they are and aren't. One would then have an easier time finding compounds which are adsorbed.