A Quantitative Study of Desorption in the Zinc(II)-Thiocyanate System

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Chronocoulometric studies had indicated that Zn(II), adsorbed at the Hg-solution interface in thiocyanate solutions, desorbs as the potential from which the experiment is initiated is made progressively more cathodic. As it was recognized that this "desorption effect" could have an appreciable effect on adsorption studies as carried out, for instance, by chronopotentiometric means, an effort was made to study this desorption quantitatively.

The amount of Zn(II) adsorbed in thiocyanate solutions decreases rather linearly as the initial potential in a chronocoulometric experiment is made more cathodic, until, at about -850 mV vs. SCE, there is no adsorbed Zn(II).[1] Biased chronopotentiometric measurements yield qualitatively similar results.[2] An initial potential can therefore be chosen at which a large amount of Zn(II) is adsorbed and complete desorption can be obtained just prior to the Zn(II) reduction wave (at about -1.0 V).

Chronocoulometry. An electrode, at an initial potential, E_0, at which an oxidant O is adsorbed to the extent of Γ moles/cm^2 or $nF\Gamma$ coulombs/cm^2, is stepped to a potential E_1, at which the species O desorbs. Only O is initially present in the solution and E is such that no faradaic current flows. We assume that the desorption is instantaneous and is complete. After a time, a, the potential is stepped to E_2, at which the reaction

$$O + ne \rightarrow R \tag{1}$$

takes place at its diffusion limited rate.[3] The charge-time behavior for $t > a$ is given by

$$Q(t > a) = \frac{2nF\sqrt{D_O}\,{}^*C_O}{\sqrt{\pi}}\sqrt{t-a} + \frac{2}{\pi}nF\Gamma\tan^{-1}\sqrt{\frac{t-a}{a}} + \Delta q_{O2} \tag{2}$$

where ${}^*C_O$ is the bulk concentration of O and Δq_{O2} is the charge consumed in charging the double layer from E_0 to E_2. The other symbols have their usual electrochemical significance. The E-t function and a Q-t response are shown in Figure 1a. If a = 0, Equation 2 reduces to the familiar chronocoulometric equation for the presence of adsorption.[3,4]

$$Q(t) = \frac{2nF\sqrt{D_O}\,{}^*C_O}{\sqrt{\pi}}\sqrt{t} + nF\Gamma + \Delta q_{O2} \tag{3}$$

Qualitatively, the longer the time, a, that the electrode potential is at E_1, the greater the curvature in a plot of Q vs. $(t-a)^{1/2}$.

Chronopotentiometry. An electrode, biased at E_0, at which the species O is adsorbed, has impressed on it a constant current density, i_o. It is assumed that desorption takes place linearly with time in the double layer charging region, that desorption is complete prior to any faradaic reaction occurring, and that the faradaic reaction starts immediately upon completion of the desorption. (Only one chronopotentiometric wave is observed.) The resulting i_o-τ behavior is given by

$$i_o\sqrt{\tau-a} = \frac{nF\sqrt{\pi D_O}\,{}^*C_O}{2} + \frac{nF\Gamma}{a}\left[\sqrt{\tau} - \sqrt{\tau-a}\right] \tag{4}$$

where a is the length of time taken for desorption and τ is the time from the start of the experiment to the transition time. If we identify a with the time spent in the double layer charging region, then $a \ll \tau$ and Equation 4 becomes

$$i_o\tau = \tfrac{1}{2}nF\sqrt{\pi D_O}\,{}^*C\sqrt{\tau} + \tfrac{1}{2}nF\Gamma \tag{5}$$

This equation is the same, except for the factor of ½ in the second term on the right, as that derived by Lorenz[5] for the case in which a constant fraction of the applied current is consumed by reaction of the adsorbed species, the "constant current efficiency" model.

Sweep-Step Chronocoulometry. A potential sweep is applied from potential E_0 to E_1, followed by a step from E_1 to E_2. This routine was previously used to demonstrate the existence of the desorption effect.[2] We assume that the desorption takes place linearly with potential (or time) in the region E_0-E_1 and that the desorption is just complete at E_1 when the step to E_2 is applied. The Q-t behavior is then given by

$$Q(t>a) = \frac{2nF\sqrt{D_0}\,C_0^*}{\sqrt{\pi}}\sqrt{t-a} + nF\Gamma\left\{1 + \frac{2}{\pi}\left[\sqrt{\frac{t-a}{a}} - \frac{t}{a}\sin^{-1}\sqrt{\frac{a}{t}}\right]\right\} + \Delta q_{02} \qquad (6)$$

where a is the sweep time from E_0 to E_1. The E-t function and a Q-t response are shown in Figure 1b. If a is zero, Equation 6 becomes the chronocoulometric Equation 3.

Experimental

Potential step chronocoulometric measurements were carried out with the multi-channel analyzer data acquisition system previously described.[6] E_0 for these experiments was chosen as -300 mV, E_1 as -900 mV, and E_2 as -1400 mV vs. SCE.

The chronopotentiometric data were analyzed according to the "reacts first," the "constant current efficiency," the "reacts last" (Lorenz), and the "equilibrium-linear isotherm" models using the weighted least-squares procedure described by Lingane.[7] For the purpose of this analysis, we estimated the relative error in the transition time determination to be ± 5%. The analysis according to the "reacts last" model failed to converge.

The potential sweep-step experiments were carried out using an updated version of a multi-purpose electrochemical instrument.[8] The initial potential, E_0, was again chosen to be -300 mV. The instrument was adjusted so that the sweep was halted when a preset potential (-900 mV) was reached and a step to -1400 mV was then applied to the electrode. Sweep rates of 10 to 100 volts/second were used. The data were recorded on the multi-channel analyzer.

All solutions were prepared from reagent grade materials using triply distilled water.

A commercially available (Brinkman Instruments, Inc.) hanging mercury drop electrode was used. The electrode area was 0.032 cm^2. All potentials were measured, and are reported, with respect to the saturated calomel electrode (SCE).

Results

The values of $nF\Gamma$, D_0, and Δq_{02}, estimated by fitting the experimental chronocoulometric data to Equation 2, are shown in Table 1. The results seem to be little affected by variation in the delay time, a. The values of the diffusion coefficient are smaller than the infinite dilution value of 7.2 x 10^{-6} cm^2/sec, but they are the same as the diffusion coefficient of Cd(II) in one formal supporting electrolyte. The infinite dilution value for the diffusion coefficient of Cd(II) is also 7.2 x 10^{-6} cm^2/sec.

The values of $nF\Gamma$ shown in Table 1 are in good agreement with the value of 31 $\mu C/cm^2$ determined in the same solution by double potential step chronocoulometry.[1]

The values of Δq_{02} shown in Table 1 are in good agreement with the "blank" value of 33 $\mu C/cm^2$ measured in the absence of Zn(II) and with the value of 31 $\mu C/cm^2$ determined by double potential step chronocoulometry.[1] A further check on Δq_{02} may be made by using the relationship

$$\Delta q_{02} = \Delta q_{01} + \Delta q_{12} \qquad (7)$$

Since no faradaic current flows at E_1, Δq_{01} will be the step change in charge when the potential is stepped from E_0 to E_1; since Zn(II) is not adsorbed at E_1, a chronocoulometric plot (Q vs. $t^{1/2}$) for a potential step from E_1 to E_2 will have an intercept Δq_{12}. The sum of these two values (25.3 and 9.3 $\mu C/cm^2$, respectively) is in good agreement with the values of Δq_{02} shown in Table 1.

Figure 2* shows plots of Q vs. $(t-a)^{1/2}$ for various delay times at -900 mV. (The double layer charging contribution has been removed by subtracting the appropriate value of Δq_{jk} from the data for all experiments. Since, for a given value of (t-a), less of the desorbed material is recovered the longer it had to diffuse away from the electrode, there is a downward trend as the delay time, a, is increased.

A similar comparison of the experimental sweep-step chronocoulometric data with the predictions of Equation 6 was made. In order to show the comparison as clearly as possible, the quantity plotted was the value of the term in Equation 6 due to the desorbed material, $nF\Gamma\{1 + (2/\pi)[\sqrt{(t-a)/a} - (t/a)\sin^{-1}\sqrt{a/t}]\}$. The curves were calculated using $nF\Gamma = 33\ \mu C/cm^2$ and the various values of a. The points were calculated from the experimental data by subtracting Δq_{01} and the value of Q(t) (at t = t-a) for a direct step from -900 to -1400 mV from the corresponding value of Q(t > a) for the sweep-step combination.

$$nF\Gamma\left\{1 + \frac{2}{\pi}\left[\sqrt{\frac{t-a}{a}} - \frac{t}{a}\sin^{-1}\sqrt{\frac{a}{t}}\right]\right\} = Q(t > a)_{\text{sweep-step}} - Q(t=t-a)_{\text{step: -900 → -1400}} - \Delta q_{01}$$

Less of the desorbed material is recovered, for a given value of (t-a), the larger the value of a. Agreement between theory and experiment was good.

The chronopotentiometric results are given in Table 2 which presents the results of the analysis of the data according to the various chronopotentiometric models.

Discussion

The good fit of the chronocoulometric data to Equation 2 (cf. Table 1) indicates that the desorption is rapid and is complete when the potential is stepped to -900 mV. This was expected since adsorption equilibrium is generally attained at the diffusion limited rate and no Zn(II) is adsorbed at equilibrium at -900 mV.

The assumption of a linear desorption between -300 and -900 mV in the sweep-step experiments was less well obeyed. Nevertheless, the fact that the experimental data is predicted semi-quantitatively by Equation 6 indicates that the desorption is approximately linear in time.

The chronopotentiometric results in Table 2 show that the "constant current efficiency" model gives one-half of the chronocoulometric value for $nF\Gamma$, but the data are not sufficiently precise to allow us to say that the data fits this model better than any of the others.

This work is further evidence for the unreliability of chronopotentiometry for the quantitative study of adsorption, since it both illustrates the need for large amounts of precise data, as pointed out by Lingane,[7] and it demonstrates that there is yet another possible bias, i.e., desorption, which needs to be considered.

Even though the Zn(II)-thiocyanate system is unusual, in that complete desorption is obtained before the faradaic reaction starts, any desorption, or adsorption, in the double layer charging region must affect, to a greater or lesser extent, the value on $nF\Gamma$ determined by fitting the data to any chronopotentiometric model and must invalidate any conclusion about the mechanism of the reaction of the adsorbed material. We are in accord with Lingane's conclusion that chronopotentiometry is of very limited value for the quantitative study of adsorption.[7]

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* Symbols on Fig. 2 and the delay times are: Δ, O (a single step from -300 to -1400 mV); o, 0.4125 msec; o, 6.600 msec; , 52.8 msec; , ▪, i.e., a single step from -900 to -1400 mV.

References

1. R. L. Myers and R. A. Osteryoung, unpublished experiments, 1966.
2. J. H. Christie and R. A. Osteryoung, Anal. Chem., 38, 1620 (1966).
3. J. H. Christie, G. Lauer, and R. A. Osteryoung, J. Electroanal. Chem., 7, 60 (1964).
4. J. H. Christie, G. Lauer, R. A. Osteryoung, and F. C. Anson, Anal. Chem., 35, 1979 (1963).
5. W. Lorenz, Z. Elektrochem., 59, 730 (1955).
6. G. Lauer and R. A. Osteryoung, Anal. Chem., 38, 1137 (1966).
7. P. J. Lingane, Anal. Chem., in press.
8. G. Lauer, H. Schlein, and R. A. Osteryoung, Anal. Chem., 35, 1789 (1963).

Table 1: Results of Analysis of Chronocoulometric Data According to Equation 2.

1.0 mF $Zn(NO_3)_2$ in 0.5 F NaSCN + 0.5 F $NaNO_3$

Delay Time m sec	$D \times 10^6$ cm^2/sec	$nF\Gamma$ $\mu C/cm^2$	Δq_{O_2} $\mu C/cm^2$
0.4125	6.2	32.3	37.5
	6.2	33.4	37.5
1.6500	6.4	34.3	37.1
	6.6	35.5	37.2
3.3000	6.1	32.6	35.3
	6.4	36.2	35.1
6.6000	6.2	34.2	35.9
	6.1	33.0	35.2
13.2000	6.3	33.6	35.9
	6.0	33.3	35.0
26.4000	6.5	30.9	36.0
	6.5	31.9	35.5
52.8000	6.4	27.7	34.9
	6.3	27.1	34.2

Table 2: Results of Analysis of Chronopotentiometric Data According to Various Models

1.0 mF $Zn(NO_3)_2$ in 0.5 F NaSCN • 0.5 F $NaNO_3$

Model	$nF\Gamma$ $\mu C/cm^2$	$D \times 10^6$ cm^2/sec	$\chi^2/N-3$
"reacts first"	28.8	7.6	0.86
"reacts last"	failed to converge		
"constant current efficiency"[a]	17.0	7.4	0.76
"reacts last" (Lorenz)	8.2	5.6	0.63
"equilibrium-linear isotherm"	19.8	7.4	0.80

(a) Equation 5 predicts fit to "constant current efficiency" model with $nF\Gamma$ equal to one-half the true value.

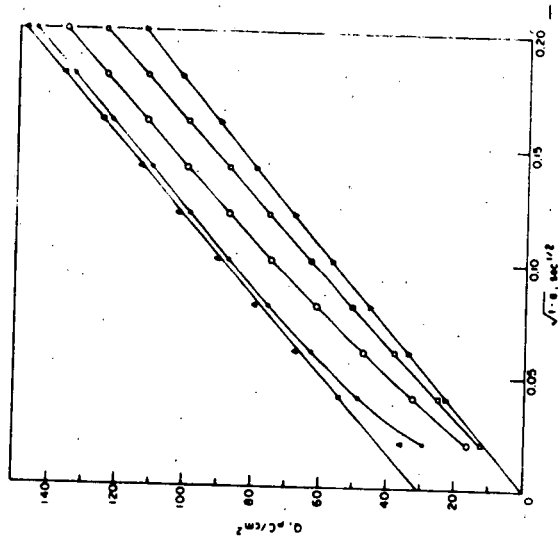
Q, μC/cm²
0
20
40
60
80
100
120
140
0.05
0.10
0.15
0.20
√t-a, sec^1/2

Fig 2

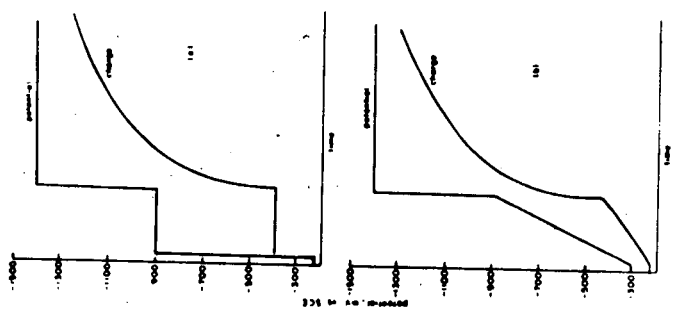
potential
charge
time
-900
-700
-500
-300
-1100
-900
-700
-500
-300
-1100
-900
-700
-500
-300
potential
charge
time

Fig 1