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ANODIZATION OF COPPER IN CHLORIDE MEDIA

I. Abstract

The main objective of this phase was to lay the theoretical and experimental groundwork for the determination of standard potentials and complex ion formation constants for metal-metal ion-ligand systems. The metal of interest is copper and the ligands initially of interest chloride and ethylene glycol. The approach employs exact analysis of pulse voltammograms at copper microelectrodes.

II. Introduction

The corrosion of copper has been the subject of a great volume of research.[1-7] One of the points of interest is the role of cupric (Cu^{2+}) and cuprous (Cu^{+}) species in the anodization of Cu^0 in various media. In chloride-containing solution, seawater for example, the cuprous species CuCl and $CuCl_2^-$ are major products of copper anodization. In the absence of halides, however, concentrations of cuprous species are almost negligible in comparison to those of cupric species. Other factors of interest include temperature and oxygen concentration in solution, which have a marked effect on the rate of corrosion of copper.[1]

In 1990, May and coworkers[7] studied the anodization of a copper film electrode in a mixture of ethylene glycol and water (50 weight percent ethylene glycol), with various concentrations of chloride ion. Their interest was based on the role of copper corrosion in the failure of automotive cooling systems, where ethylene glycol is often present. The results of their cyclic voltammetric experiments led them to the conclusion that the presence of ethylene glycol will inhibit the corrosion of copper due to more facile formation of passivating films on copper. If the medium becomes too acidic, however, these films will be more soluble in the medium, and the copper surface may be less protected.

Our own efforts in this field have focused on the use of copper microelectrodes.[8-10] The advantages of using microelectrodes are that steady-state currents are achieved at short times, due to the enhanced diffusion to a microdisk, and that low ohmic drops are encountered even at high current densities. Wikiel, dos Santos and Osteryoung have used pulse voltammetry to study the anodization of copper in aqueous chloride solutions.[8] In a subsequent paper, Wikiel and Osteryoung extended this study to ethylene glycol-water mixtures.[9] In both of these works, overall formation constants of $CuCl_2^-$ (β_2) were determined, based on E-pCl diagrams. A simplifying assumption was used in these determinations, which rendered only the foot of the voltammetric wave useful for calculating β_2, and the formation of CuCl was ignored.

Our present aims in this research are to characterize the anodic reactions of copper which are important in the corrosion process. This will be achieved by subjecting our experimental data to a rigorous analysis which yields statistical information on formation constants, and does not rely upon simplifying assumptions. The analysis will be done on-line, as a new subroutine of the COOL algorithm, which has already proven to be quite valuable in other analyses.[11-13] This subroutine will not be limited to fixed conditions of temperature, chloride concentration or electrode area, nor will it be specific for the copper/chloride system. It will be general to the anodization of any metal in the presence of a complexing species. We anticipate that such an analysis will be beneficial in the evaluation of any ligands or materials which change corrosion rate.

III. Results

The first step in this work was the solution of the current-potential relationship for the M → MX_p system. The general form of the relevant equation is[14]

$$(1) \qquad E = E^o - (RT/nF)\ \{\ln\ [2^{1-p}p\beta_p[X_o]^{p-1}(D_{MX_p}/D_X)^{1/2}] + \ln\ [2^{p-1}(1-i/i_d)^p(i_d/i)]\},$$

where β_p is the overall formation constant of the product MX_p, $[X_o]$ is the bulk concentration of the ligand X, and i_d is the limiting current, given by

$$(2) \qquad i_d = 4nFD_X[X_o]r.$$

(Other terms in these equations have their usual electrochemical significance, such as D_X being the diffusion coefficient of species X and r being the electrode radius in cm.) This expression for current is time-independent, and refers to steady-state currents at given potentials. In the present case of the formation of CuCl and $CuCl_2^-$, we are interested in the values $p = 1$ and $p = 2$. Substituting unity for p in equation (1), for the production of CuCl, gives

$$(3) \qquad E = E^o - (RT/nF)\{\ln\ [\beta_1(D_{MX}/D_X)^{1/2}] + \ln\ [(1-i/i_d)(i_d/i)]\}.$$

It is common for this equation to be simplified by assuming that i/i_d is much less than unity. This assumption is best at the foot of the wave, where current is low. With this approximation, one can solve equation (3) for i as a function of E to obtain

$$(4) \qquad i_1[i \ll i_d] = i_dK_1(D_{MX}/D_X)^{1/2}\ \exp\ [(nF/RT)(E - E^o)],$$

where we have substituted K_1 for β_1 since they are the same. The full expression for i(E), for $|i/i_d| \leq 1$, is

(5) $i_1 = i_d K_1\{K_1 + (D_X/D_{MX})^{1/2} \exp[(-nF/RT)(E - E^o)]\}^{-1}$.

Equation (1) is also solved for the case $p = 2$, where the product is $CuCl_2^-$. The quantity $i_2[i \ll i_d]$ is isolated in the same manner in which $i_1[i \ll i_d]$ was isolated for $p = 1$; it is

(6) $i_2[i \ll i_d] = 2i_d\beta_2(D_{MX2}/D_X)^{1/2}[X_o] \exp[(nF/RT)(E - E^o)]$.

The complete expression for i_2 is considerably more cumbersome, as it involves the quadratic equation. The negative root is taken, since the positive root yields the physically impossible situation of infinitely large anodic current at very negative overpotentials. The resulting equation for i_2 is then

(7) $i_2 = (i_d/2)\{Z + 2 - (Z^2 + 4Z)^{1/2}\}$,

where Z is defined as

(8) $Z = (2\beta_2[X_o])^{-1}(D_X/D_{MX2})^{1/2} \exp[(-nF/RT)(E - E^o)]$.

The differences between the simplified and analytical expressions for i_1 and i_2 are shown graphically in Figures 1 and 2. For these plots, it was assumed that D_X, D_{MX} and D_{MX2} were all equal, but this is not a necessary assumption. It is clear that at any appreciable magnitude of current, the difference made by the simplifying assumption is great. Of course, the difference is expected to be large when (i/i_d) is not insignificant compared to 1, but this condition eliminates most of the voltammetric wave from accurate analysis. For example, in Figure 1, when (i_1/i_d) is equal to 0.1, the approximate expression for (i_1/i_d) is equal to 0.111, a difference of 11%. When (i_1/i_d) reaches 0.5, the approximate expression is equal to 1.0, a value which is in error by 100%. When p = 2 (Figure 2) the two expressions differ by 10% at $(E - E^o) = -76$ mV, or when $(i_2/i_d) = 0.05$; they differ by 20% at $(E - E^o) = -58$ mV, or when $(i_2/i_d) = 0.1$. These examples point out the extent to which use of the approximate expression of current limits analysis of the experimental results.

A family of curves generated for various bulk concentrations of X appears in Figure 3. In the figure the quantity (i_2/i_d) has been multiplied by $[X_o]$ to show the relative magnitudes of current in the different concentrations of X. The other terms in the normalizing factor i_d are not expected to vary significantly as $[X_o]$ varies. Values of K_1 (500 M^{-1}) and β_2 (10^6 M^{-2}) were taken from the literature.[15] These curves bear a strong resemblance to the experimental data shown in Figure 6 of reference 9. It is important to clarify here that the experimental work of Wikiel et al. was not carried out at steady state. Nevertheless those data are easily converted to steady-state currents by making use of an equation worked out by Aoki and Osteryoung which applies to current measured after a potential pulse.[16]

When copper is anodized in the presence of chloride, current is observed as a result of both reactions: p = 1 and p = 2. At the foot of the voltammetric wave, the concentration of Cu^+ produced is much less than the concentration of Cl^- near the electrode, and the product is $CuCl_2^-$. As the anodization progresses, Cl^- is depleted from the region near the electrode surface. The product of the Cu oxidation becomes CuCl. Thus the arrival of two Cl^- ions will result in the formation of two Cu(I) species, rather than one, and there is a second rise in current. As p changes from 2 to 1, n changes from ½ to 1. The result is a "pseudo-plateau," which was previously misinterpreted (in reference 9) as a limiting current. To interpret the current in terms of equations (5) and (7), the total anodization current was written as the sum of the (p = 1) and (p = 2) currents. The weighting factors for the two equations are (2 - p) and (p

- 1), which vary linearly from 0 to 1 and from 1 to 0, respectively, as p goes from 2 to 1. Thus we write the total anodization current by

$$(9) \qquad i_t = (2 - p)\, i_1 + (p - 1)\, i_2.$$

The objective here is not simply the accurate description of experimental results, but the application of the analytical result in a data analysis routine which will give the best values of thermodynamic parameters based on the experimental data. We begin by writing the total current as a function of a dimensionless current function, ψ, which is defined as

$$(10) \qquad \psi = i_t/i_d.$$

ψ depends on all of the parameters which go into i_1, i_2 and i_t, namely, $[X_o]$, T, E, D_X, D_{MX}, D_{MX2}, r, K_1, β_2 and E^o. Of these, $[X_o]$, T and E are typically controlled or known in the experiment, and r can be measured in a separate experiment. Sufficiently accurate values for D_X, D_{MX} and D_{MX2} can be found in the literature. That leaves K_1, β_2 and E^o as the parameters of ψ. These too can be found in the literature, however reported values vary drastically with experimental conditions. Given the nature of the unusual experimental conditions to be explored in this project, we would like to determine these three parameters as products of a rigorous data analysis routine. The key to this routine is matching our dimensionless current function, ψ, which contains the shape of the voltammetric wave, to the experimental current, i.

We express the experimental current as

$$(11) \qquad i = a\psi + b,$$

that is, a linear function of ψ, with slope a and intercept b. Had we values for K_1, β_2 and E^o, we could compare i and ψ, and get a quantitative evaluation of their similarity (the correlation coefficient, R) by performing a linear regression analysis.

We can take this one step further by letting a program optimize the fit by finding values of K_1, β_2 and E^o which minimize (1 - R). This can be done with a three-dimensional simplex. Using initial estimates of the parameters to be determined, (1 - R) is calculated, then one parameter is changed at a time until values of the parameters are found which yield a minimum value of (1 - R). In this way, a multidimensional problem is reduced to a single linear regression analysis.

The simplex and the linear regression routine are already incorporated into the COOL algorithm. The analysis will only be meaningful if one has a good model of current (ψ). We are satisfied that our equation for total current (equations (5, 7-10)) accurately describes the experimental current without limiting our analysis to a small section of the voltammetric wave.

Unfortunately, what we would hope would be a three-dimensional simplex degenerates into a two-dimensional one. It is not possible to obtain a unique result which minimizes (1 - R) unless the parameters form an orthogonal basis set, i.e., the parameters must be truly independent. If we expand equation (10), we get

$$\begin{aligned}
\psi = {} & (2 - p)\, K_1\{K_1 + (D_X/D_{MX})^{1/2} \exp[(-nF/RT)(E - E^o)]\}^{-1} \\
& + (p - 1)\,(1/2)[(2\beta_2[X_o])^{-1}(D_X/D_{MX2})^{1/2} \exp[(-nF/RT)(E - E^o)] \\
& + 2 - \{(2\beta_2[X_o])^{-2}(D_X/D_{MX2}) \exp[(-2nF/RT)(E - E^o)] \\
& + 4(2\beta_2[X_o])^{-1}(D_X/D_{MX2})^{1/2} \exp[(-nF/RT)(E - E^o)]\}^{1/2}].
\end{aligned} \tag{12}$$

Examination of all four terms involving E^o reveals that it appears each time as either $K_1^{-1}\exp[(-nF/RT)(E - E^o)]$ or $\beta_2^{-1}\exp[(-nF/RT)(E - E^o)]$. Recalling that the second overall formation constant is equal to the product of the first and second stepwise formation constants (that is, $\beta_2 = K_1K_2$), the second expression above can be rewritten as $(K_1K_2)^{-1}\exp[(-nF/RT)(E - E^o)]$. Thus, K_1 and E^o are degenerate, since they never appear separately. This means that E^o will have to be determined experimentally. This will be discussed in depth below.

Based on the explicit description of ψ above, two new data analysis programs were written, one which requires a single diffusion coefficient value and another which requires the user to supply three separate diffusion coefficient values: D_X, D_{MX} and D_{MX2}. When analyzing data from copper anodization in ethylene glycol-water mixtures containing chloride, the programs gave back formation constants for CuCl and $CuCl_2^-$, which were independent of the initial estimates and step sizes for all values tried. The value of E^o in the ethylene glycol-water mixture is unknown. A brief example of the results of this program are given in Table 1. These results, based on the value of E^o in aqueous solution in one case and a hypothetical value of 0.3 V vs. SCE in the other, are given as evidence of the uniqueness of the results despite different initial estimates.

Our next undertaking was the determination of E^o for the $Cu^{0/+}$ couple in the presence of ethylene glycol. The first attempt employed a Pt-Pt rotating ring-disk electrode in $CuSO_4/H_2SO_4$ solutions of various concentration. Copper was first plated onto the platinum disk. Then the ring was scanned in the positive direction while the disk was maintained at open circuit. In this scheme, Cu^+ is produced by the reproportionation reaction between Cu^{2+} in solution and Cu^0 on the disk:

$$(13) \quad Cu^0 + Cu^{2+} = 2Cu^+.$$

The product Cu^+ is detected when it is oxidized at the ring to Cu^{2+}. This technique has been used successfully by others to determine the equilibrium constant of the reproportionation reaction in aqueous $HClO_4$.[17]

The experiment was first carried out at a Pt-Pt RRDE in H_2SO_4 solutions. In that medium it works well. However ethylene glycol is oxidized at the ring to form a partially passivating surface layer. A representative voltammogram, scanning in the positive direction, appears in Figure 4. In the voltammogram there is a rise in anodic current beginning around 0.4 V (vs. Cu wire) due to the oxidation of ethylene glycol. Beyond 0.65 V, anodic current decreases. This decrease is the result of the formation of a passivating layer on the platinum surface. At 0.9 V there is a second increase in anodic current. The origin of this current is not known, but it is only observed when ethylene glycol is present in solution. The current due to the oxidation of ethylene glycol completely obscured, or prohibited, the oxidation of Cu^+ at the ring when a Cu film was on the disk and Cu^{2+} was in solution. The oxidation of ethylene glycol at a Pt surface has been documented in the literature, and is also known to occur on Au.[18,19]

We are currently performing the same type of experiment on glassy carbon (GC-GC) electrodes. One of the important aspects in successfully performing this experiment is the formation of a good copper film on the glassy carbon disk. By using low overpotentials for copper deposition for a long time in a well-deaerated solution, we have produced apparently smooth, clean copper surfaces.

IV. Future plans

The next step of the project is to determine E^o for $Cu^{0/+}$ in the presence of ethylene glycol. Equipped with the value of E^o in the presence of ethylene glycol, electrochemical data can be evaluated for the anodization of copper in aqueous solution and in the ethylene glycol-water mixture. The data analysis program successfully produces values of formation constants of CuCl and $CuCl_2^-$ when values of E^o are assumed. Such analyses are performed very quickly (about 10 seconds per voltammogram), and a large volume of suitable data already exists.

In general, this program can be used to determine the effect of other corrosion prohibitors, such as benzotriazole, on the formation of various products of copper corrosion. Formation constants given in the literature frequently vary significantly, and sometimes are not available under the proper conditions. The program is also applicable to the study of corrosion of other metals, not simply those which form 1+ ions, in various complexing media, with no modifications in the code necessary.

Our primary interest is in the characterization of biologically-influenced corrosion of copper in natural waters, or biocorrosion. We propose to characterize this process by investigating the initial reactions of copper with species present in the natural water and in the "biofilm," the film on the metal surface which results from bacteria and their products. Biocorrosion is a complex physical process, but the key to understanding it is obtaining a quantitative description of the specific reactions involved and their dependence on the local environment.

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VI. Figures

Figure 1. Normalized steady-state current for copper anodization, analytical expression when p = 1, equation (5) (solid line) compared with the approximate expression, equation (6) (dashed line). Calculation for $(D_X/D_{MX})^{1/2}/K_1 = 1$.

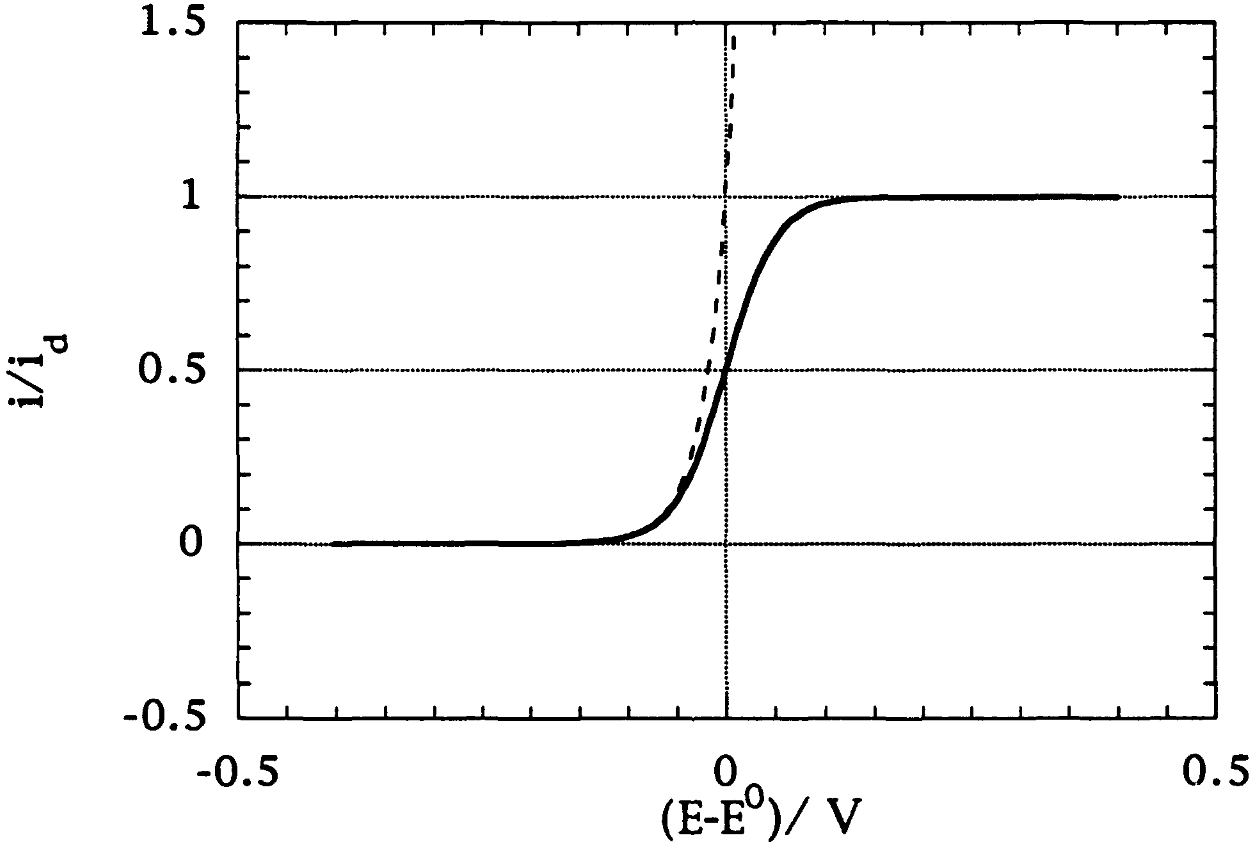
1.5
1
0.5
0
-0.5
i/i_d
-0.5
0
0.5
$(E-E^0)/\ V$

Figure 2. Normalized steady-state current for copper anodization, analytical expression when $p = 2$, equation (7) (solid line) compared with the approximate expression, equation (8) (dashed line). Calculation for $(2\beta_2[X_o])^{-1}(D_X/D_{MX2})^{1/2} = 1$.

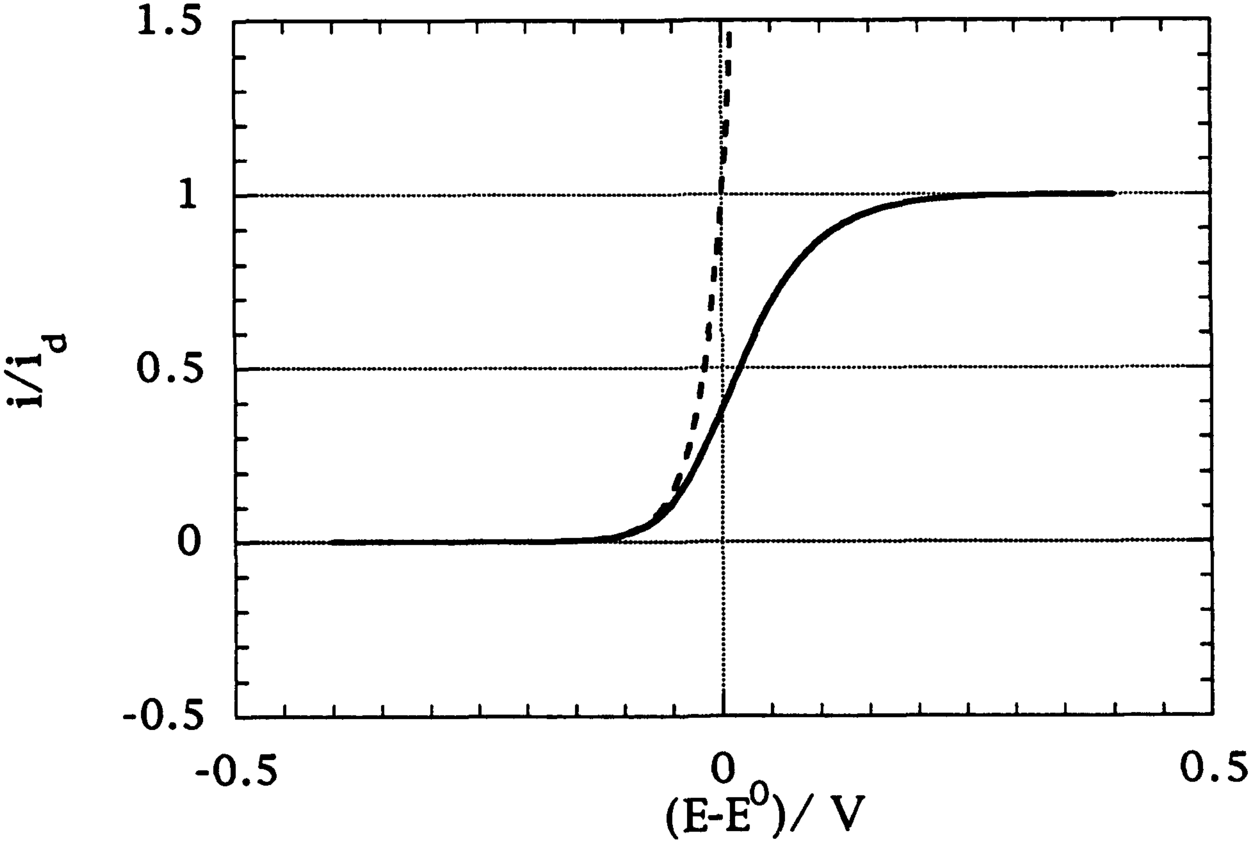
1.5
1
0.5
0
-0.5
i/i_d
-0.5
0
0.5
(E-E^0)/ V

Figure 3. Steady-state current for copper anodization in aqueous chloride solutions computed from equation (9); $[X_0]/M$ = (a) 1, (b) 0.7, (c) 0.5, (d) 0.3, (e) 0.2, (f) 0.1, and (g) 0.05.

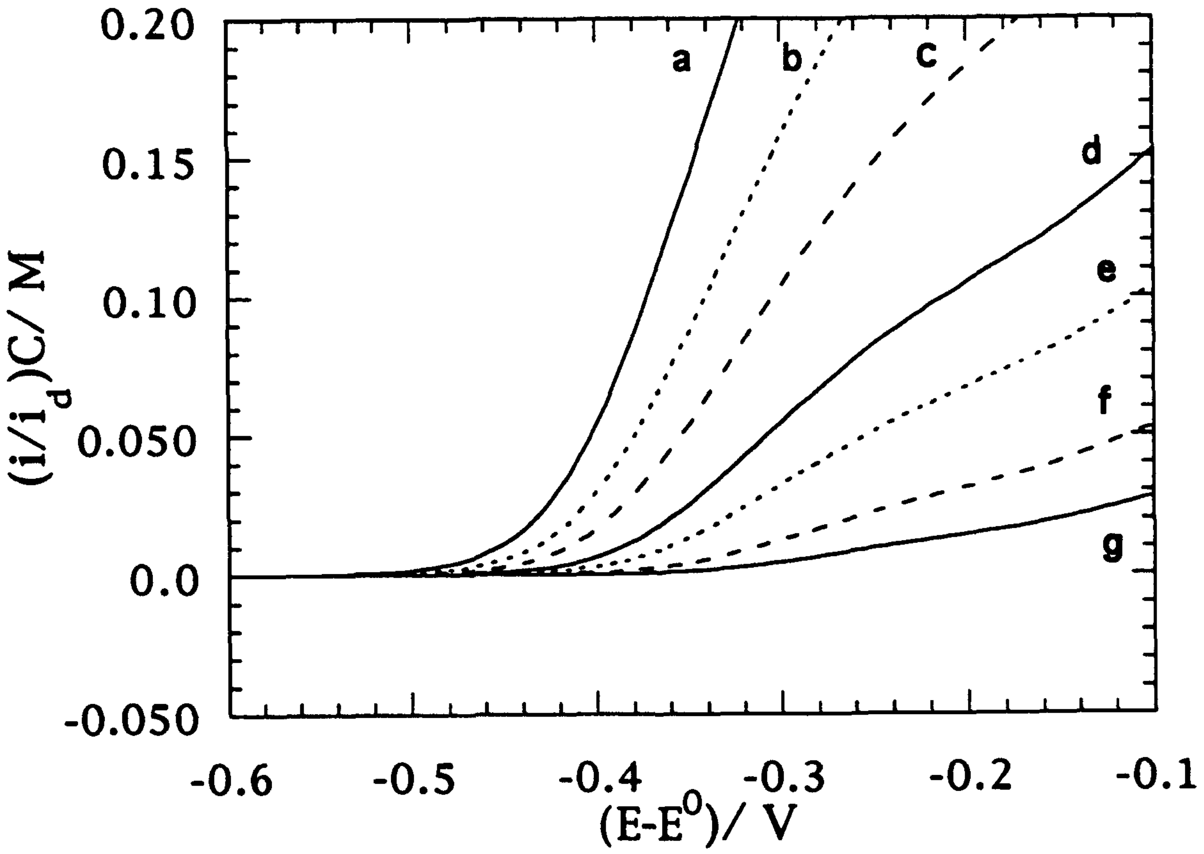
0.20
0.15
0.10
0.050
0.0
-0.050
$(i/i_d)C/\ M$
a
b
c
d
e
f
g
-0.6
-0.5
-0.4
-0.3
-0.2
-0.1
$(E-E^0)/\ V$

Figure 4. Staircase voltammogram of a Pt rotating disk electrode (area = 1.2 cm^2) in 1 M H_2SO_4, in an ethylene glycol-water mixture (50 volume percent). The frequency is 1 Hz, the step height is 4 mV and the rotation rate is 1000 rpm. E_i = 0 V, E_f = 1.5 V vs. Cu wire.

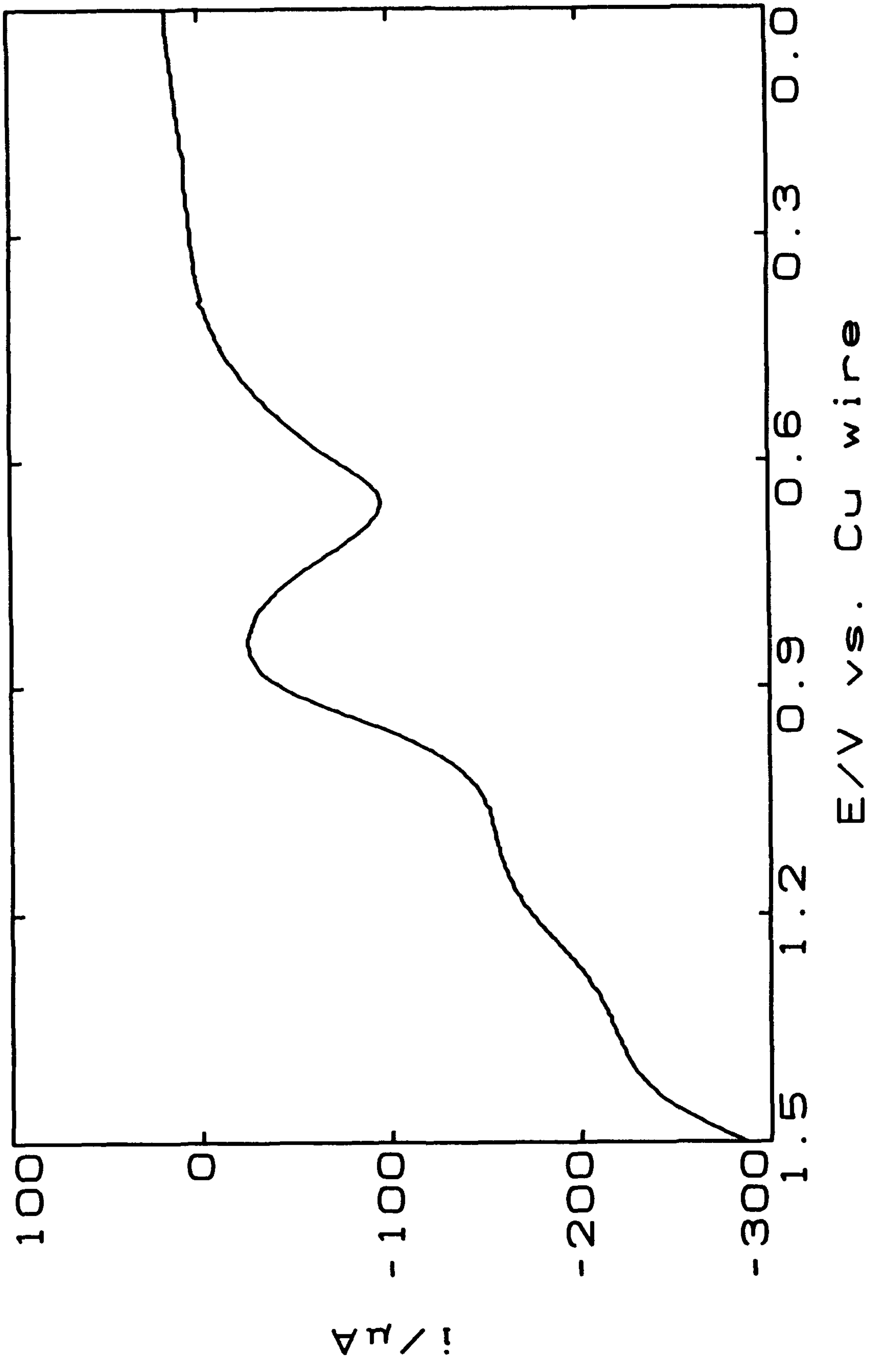
100
0
-100
-200
-300
i / μA
0.0
0.3
0.6
0.9
1.2
1.5
E/V vs. Cu wire

Table 1. Extraction of equilibrium constant values from experimental voltammograms.[a]

E^o/V vs. SCE	**Initial estimates**		**Results**	
	log K_1	**log β_2**	**log K_1**	**log β_2**
0.2805	1.00	3.00	1.35	4.94
0.2805	3.00	6.00	1.35	4.94
0.3000	1.00	3.00	1.68	5.27
0.3000	3.00	6.00	1.68	5.27

[a] 50 mM Cl^-, 50 % (v/v) ethylene glycol, $D = 4.0 \times 10^{-6}$ cm^2/s for all species.

The following presentations presented aspects of the work described above.

Applications of Pulse Voltammetry, UNC, Charlotte, February, 1993.

Analytical and Mechanistic Applications of Pulse Voltammetry, Duke University, February, 1993.

Analytical and Mechanistic Applications of Pulse Voltammetry, UNC Greensboro, March, 1993.

Modern Voltammetry, National ACS Meeting, Denver, March 1993.

Examination of Chemical Processes by Pulse 'Voltammetry, Department of Materials Science and Engineering, NCSU, May, 1993.

Modern Voltammetry, Seventh Annual Symposium on Analytical Chemistry, Hercules, Wilmington, DE, May, 1993.

Pulse Voltammetry, Seventh National Conference on Analytical Chemistry, Rio de Janeiro, September, 1993.