ABSTRACT

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A study of the electroreduction of cis-dichlorotetraaquochromium (III) chloride was made in the presence of (ethylenedinitrilo)-tetraacetic acid. It was found that the reduction product reacts with the complex forming agent to form a complex which is electrochemically oxidized at the same potential. The chronoamperometric method was used to study the kinetics of such electrode processes. The finite difference approximation method has been applied to solve the partial differential equations obtained by Fick's laws under second order conditions. The working curves have been prepared and the second order rate constants have been measured for the reaction of Cr(II) with EDTA. The activation parameters have been calculated for the reaction under study. A mechanism for this reaction is suggested.

ELECTROCHEMICAL STUDIES OF FAST REACTIONS.
THE EC(-E)MECHANISM

by

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APPROVAL SHEET

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July 20 1971

Date of Examination

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INTRODUCTION

The ECE mechanism, which can be represented as:

$$A + n_1e = B$$

$$B + Z \xrightarrow{k} C$$

$$C + n_2e = D$$

is an important type of mechanism in which a chemical reaction is coupled between two electron transfer processes. The effect of the coupled chemical reaction depends on the reduction potential of A and C. If C is more easily reducible than A, which is true in many cases, then the polarographic current at the reduction potential of A will be increased because of simultaneous reduction of C produced by the chemical reaction. The rate constants for the intermediate chemical reaction can be calculated from the enhanced polarographic current. The reduction of o-nitrophenol[1, 2] and the reduction of p-nitrophenol[3-6] are examples of reactions which follow the ECE mechanism and have been studied extensively. Chronopotentiometric and chronoamperometric methods have been used to calculate rate constants for the coupled chemical reaction.

Recently, a report by Fisherova and coworkers[7] was published in which they studied two systems:

a. the reduction of dichlorotetraaquochromium(III) chloride,

$[Cr(H_2O)_4Cl_2]Cl$, in the presence of (ethylenedinitrilo)-tetraacetic acid (commonly called ethylenediaminetetraacetic acid, EDTA).

b. the reduction of bis-(ethylenediamine)dichlorocobalt(III) ion in the presence of ethylenediamine.

In their study, these authors presented evidence that the electrode process follows a different mechanism. This new mechanism which will be referred to as EC(-E) can be represented as follows:

$$A + n_1e = B$$

$$B + Z \xrightarrow{k} C$$

$$C - n_2e = D$$

which for the case of the dichlorotetraaquochromium(III) ion and trianion of EDTA (HY^{-3}) can be written as,

$$CrCl_2^{+} + e^{-} = CrCl_2$$

$$CrCl_2 + HY^{-3} \xrightarrow{k} CrHY^{-} + 2Cl^{-}$$

$$CrHY^{-} - e^{-} = CrY^{-} + H^{+}$$

The substance C(the chromium(II)-EDTA complex) is oxidized at the potential where A(dichlorotetraaquochromium(III) ion) is reduced. Tanaka and Ebata[8] also suggested earlier that the reaction of EDTA with hexaaquochromium(III) and hexaaminechromium(III) behaves according to the EC(-E) mechanism. Pecsok, Shields and Schaefer[9] reported a study of complexes of chromium(II) and chromium(III) with EDTA. Hamm[10] reported EDTA complexes with chromium(III). Pathak, Bhat and Shanker[11] have reported catalytic effects observed during the reaction of chromium-

(II) with EDTA. The common theme of these studies is that chromium(II) and chromium(III) slowly form complexes with EDTA and that chromium(II)-EDTA complexes can be oxidized at the potentials where chromium(III) is reduced.

Since polarography is useful only for reactions where the half life is of the order of the drop time, Fisher and coworkers[12] developed a chronopotentiometric method to study the reduction of dichlorotetraaquochromium(III) ion in the presence of EDTA. The chronopotentiometric method is an electro-analytical technique by which the effect of coupled chemical reactions can be observed. The transition time would be longer or shorter because of intermediate chemical reaction than that expected on the basis of concentration of A alone. The rate constants can be calculated from this shift in transition times. They measured the pseudo first order and second order rate constants of the intermediate chemical reaction. They have suggested in their mechanistic scheme that the trianion of EDTA (HY^{-3}) reacts with the chromium(II) ion. Tanaka and Yamada[13] also studied the reaction of chromium(II)hexaamine complex with EDTA and postulated that the reaction proceeds simultaneously with both the di- and trianion of EDTA. The fact that the two reports are in conflict suggests that the mechanism is not completely understood.

The purposes of the present study are:

1. To extend the theory of chronoamperometry to EC(-E) mechanism.

2. To investigate the suitability of the chronoamperometric method for the study of the EC(-E) mechanism.
3. To resolve the controversy about the mechanism of the reaction of chromium(II) complexes with EDTA.

In the present work, the reduction of dichlorotetraaquochromium(III) ion in the presence of EDTA has been investigated. Octahedral dichlorotetraaquochromium(III) ion can exist in cis and trans isomeric forms[14]. A detail study on the reaction of cis-isomer with EDTA has been undertaken in this work. The trans isomer was also investigated briefly. Chronoamperometry and polarography were used to investigate the mechanism of the coupled chemical reaction. The chronoamperometric method has been used successfully by various workers[15] to study coupled chemical reactions. The suitability and applicability of this technique, when applied to the EC(-E) mechanism, was investigated in the present work. The rate constants for the chemical reaction involved in the reduction of dichlorotetraaquochromium(III) ion in the presence of EDTA are calculated using this technique.

The Laplace transformation method has been used to solve the partial differential equations describing the chronoamperometric method. The solution of Fick's laws was used to generate working curves whereby pseudo first order rate constants for the EC(-E) mechanism can be calculated. It is impossible to solve these partial differential equations using Laplace transformations under second order conditions without drastic approximations. In the present work, finite difference approximation of Fick's laws has been used to solve the partial differential equations when the concentration of substance Z (C_Z) is not much greater than the concentration of substance A (C_A). The working curves calculated by both methods agree when C_Z becomes greater than C_A.

The question, "What species of EDTA reacts with chromium(II)?" was an important part of this study. If the equilibrium between the different species of EDTA (H_4Y, H_3Y^{-1}, H_2Y^{-2}, HY^{-3}, Y^{-4}) in solution is slow, then the concentration of H_2Y^{-2}, HY^{-3} and other highly charged species of EDTA will be so much smaller than Cr(III) that it will be difficult to see the effect of the chemical reaction since no more will be formed in the time scale of the experiment. On the other hand, if the equilibrium is fast and the second order rate constants are independent of the concentration of one particular species of EDTA, then we may be able to infer details about the reaction mechanism.

EXPERIMENTAL

Determination of the Dissociation Constants of EDTA.

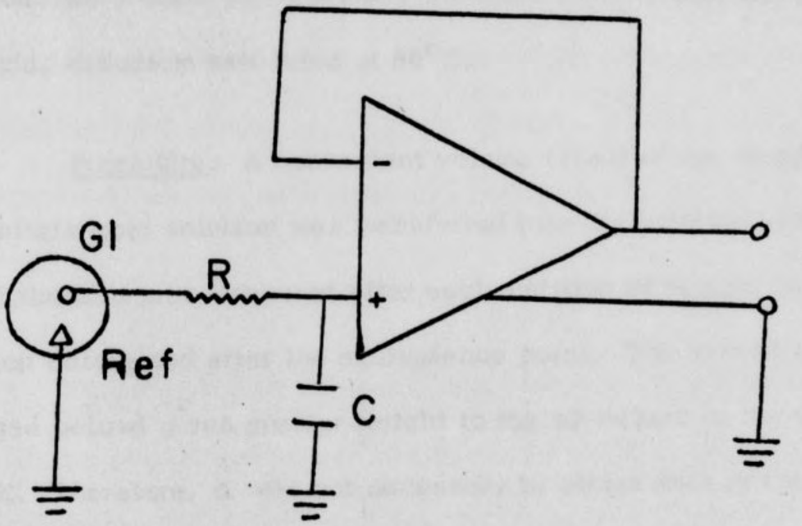
pH Measurements. All pH measurements were made with a pH meter constructed using an operational amplifier (Figure 1). The operational amplifier, Philbrick SP2AU, had a 10 picoamperes maximum input current. The glass electrode was connected to the positive input of the amplifier through a RC filter in order to minimize noise. The reference electrode was connected to ground. Corning combination electrode (476050) were used. The guard input was connected to the negative input as suggested in the instruction manual for the amplifier. Millivolts readings were taken with a Heath Universal Digital instrument (EU-805) used as the digital voltmeter mode. The pH electrode is usable in the 0-14 pH range. The titrations and standardization of the solutions were carried out at 25.0°C. The pH electrode was found to have a linear response of 58.7 mV/pH unit using buffers suggested by The National Bureau of Standards[16]. Measurements were reproducible to ± 0.2mV.

Solutions. The basic titrant was a mixture approximately 0.1 M in sodium hydroxide and 2.4 M in sodium chloride. The sodium chloride was used in all cases to control the ionic strength. The technique used

FIGURE 1

Schematic of pH meter constructed with operational amplifier.

Gl, Glass electrode; Ref, reference electrode; R, 10M resistor; C, .01µF capacitor; DVM, digital voltmeter; OA, Philbrick SP2AU operational amplifier.


GI
R
Ref
C
+
-
TO DVM

to prepare the solution is reported to keep CO_2 concentration to less than 0.1%[17]. This solution was standardized to 0.1% using potassium hydrogen phthalate[17]. The acid solution was approximately 0.1M hydrochloric acid and 2.5 M sodium chloride. This solution was standardized to 0.1% with Tris-(hydroxymethyl)aminomethane(THAM)[17]. EDTA solutions were made using primary standard (ethylenedinitrilo)-tetraacetic acid, disodium salt dried at 80°C.

Procedure. A convenient volume (25ml) of the standard hydrochloric acid solution was transferred into the titrating vessel and the emf of the cell was measured after each addition of sodium hydroxide solution before and after the equivalence point. The method of calculation (see below) gives greater weight to the pH values in the vicinity of each pK. Therefore, it was not necessary to obtain data in the vicinity of the equivalence point[18]. Nitrogen was passed over the top of the titrating vessel to exclude atmospheric carbon dioxide. Stirring and temperature control were necessary for accurate results. Similar titrations were carried out with a 1mM solution of EDTA and a 1mM solution of sodium hydroxide. A computer program[19] was used to calculate the successive dissociation constants of EDTA. A listing of the program employed is given in Appendix B.

Polarography.

All polarographic measurements were made with a commercially available three electrode dropping mercury electrode assembly (Heath EAU-19-6). The polarographic module (EAU-19-2) was modified to work with transistorized operational amplifiers. Polarograms were recorded on a Heath recorder (EUW-20A) with damping switch set in the normal position. All solutions were deaerated 15 minutes with high purity nitrogen before taking any polarograms. The extrapolated background current was approximately 0.2 μA. The mercury height (H) was 55.6 cm and the capillary had a drop time of 6.64 seconds. Polarographic measurements were made at room temperature (23°C).

Chronoamperometric Measurements.

Reagents. The solutions containing only *trans*-dichlorochromium(III) ion were prepared by dissolving commercially available green chromium(III)chloride[20]. Solutions containing essentially pure *cis*-dichlorochromium(III) ion were prepared using an ion exchange method[21]. A solution of chromium(III)chloride in acetone-ether mixture contains relatively large amounts of *cis*-dichlorochromium(III) ion. The *cis*-isomer appears to be more soluble in this mixture. The mixture is extracted with 0.2 *M* perchloric acid and further purified with an anion exchange resin. A Dowex 50W x8(50-100 mesh) ion exchange resin was used and elution was carried out at low temperature (5°C) by 0.2 *M* perchloric acid.

Spectrophotometric Measurements.

A Beckman DK-2A spectrophotometer was used to measure the absorption spectra. The pure cis-dichlorochromium(III) species separated by the ion exchange procedure was frozen and stored. Fresh solutions were prepared every day from the frozen stock solution. The concentration of cis-dichlorochromium(III) was determined by the spectra taken at wavelengths from 700 to 350 nm. The concentration of cis-dichlorochromium (III) was determined by the spectra taken at wavelengths from 700 to 350 nm. The concentration of cis-dichlorotetraaquochromium was calculated from the absorbance at 450 and 635 nm, using the molar absorptivity reported by King, Woods and Gates[14].

Apparatus.

Cell and Electrodes.

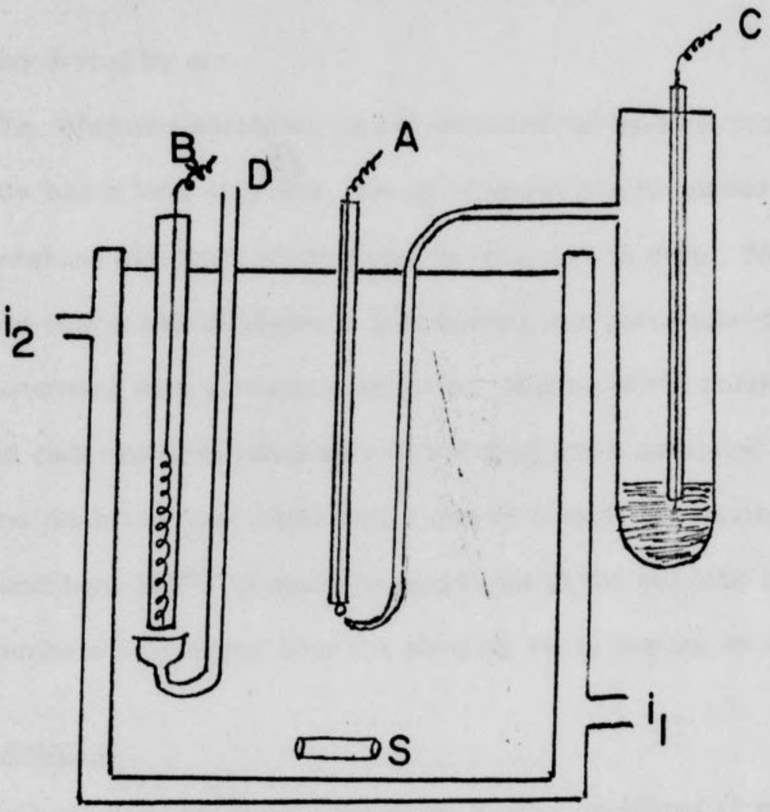
Cell (Figure 2) was used for all electrochemical experiments. Water at a constant temperature was circulated through the cell. A teflon lid was machined to fit the cell. Holes of various sizes were drilled to allow insertion of the various electrodes and a nitrogen inlet.

A commercially available Brinkman (E410) hanging mercury drop electrode was used as a working electrode. A drop of reproducible area could be obtained by turning a given number of turns on the micrometer. The capillary of the microburet type electrode becomes contaminated after use for some time. For thorough cleaning of the electrode, a procedure outlined by Perone, Jones and Gutknecht[22] was used. For quick cleaning a short procedure was adopted which required first sucking 10ml of

FIGURE 2

Diagram of the electrochemical cell showing arrangement of various electrodes.

A, hanging mercury drop electrode; B, auxiliary electrode; C, saturated calomel electrode; D, deaerator; S, stirrer bar; i_1 and i_2, inlet and outlet for water respectively.


C
B
D
A
i2
i1
S

ether and drying by air.

The reference electrode was a saturated calomel electrode. This electrode has a long side arm, the tip of which can be placed very close to the working electrode to minimize the effect of IR drop. The auxiliary electrode was a coil of platinum wire placed in a glass tube containing water saturated with potassium chloride. Mixing of the solutions in the tube and cell was minimized by a fritted disk and a saturated KCl-agar gel. The deaerator was made from a coarse fritted disk sealed to glass tubing and bent 180°. It could be raised out of the solution to maintain an atmosphere of nitrogen over the solution while running an experiment.

Instrumentation.

A block diagram of a chronoamperometric apparatus is shown in Figure 3. A potential step is applied between auxiliary and working electrode in such a manner that the desired potential is achieved between the reference and working electrodes. The electrochemical reaction takes place at the working electrode and current passing through the cell is monitored by a current follower and oscilloscope (or similar device).

All chronoamperograms were taken using the circuit illustrated in Figures 4 and 5. The potentiostat (Figure 4) is of conventional operational amplifier design[23]. Amplifier (1) is a voltage follower and is used as a high impedance buffer between the calomel reference electrode and the potentiostat. Amplifier (2) is a control amplifier of the potentiostat and is used in an adder configuration. Amplifier (4) is a current

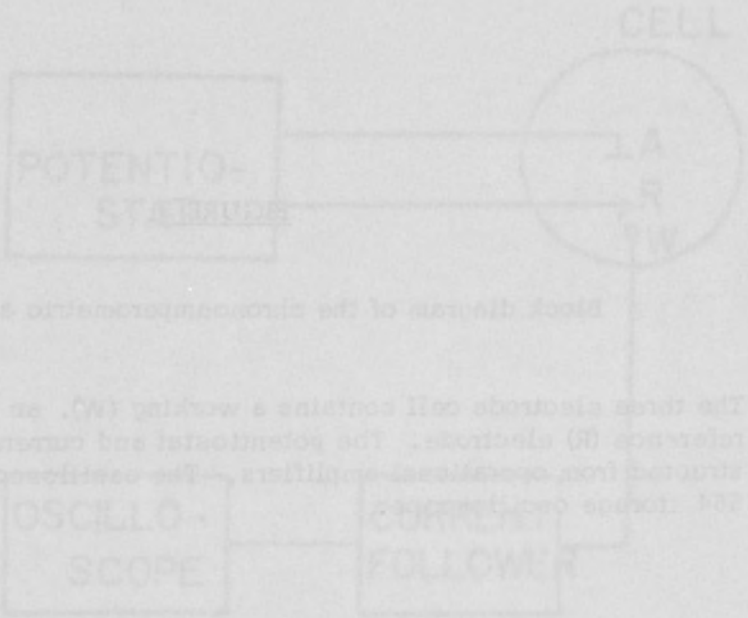
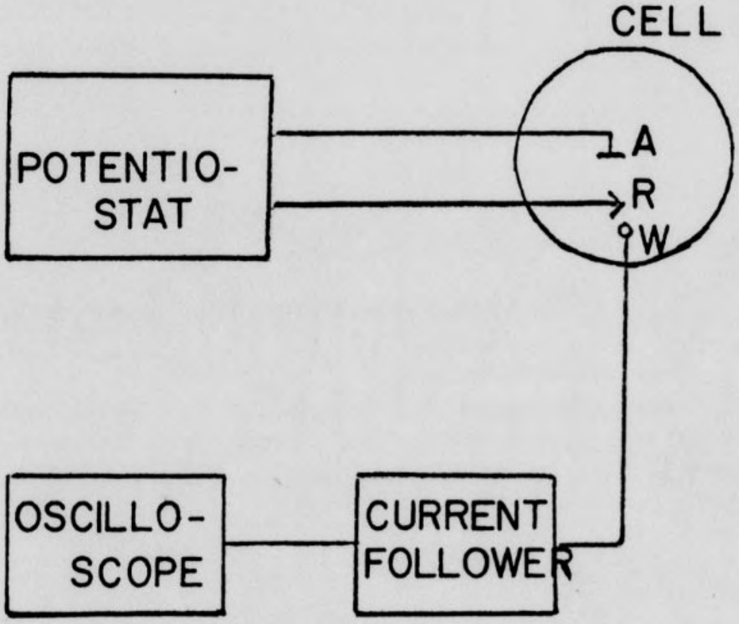

CELL
A
R
W
POTENTIO-
STAT
OSCILLO-
SCOPE
CURRENT
FOLLOWER

FIGURE 3

Block diagram of the chronoamperometric apparatus.

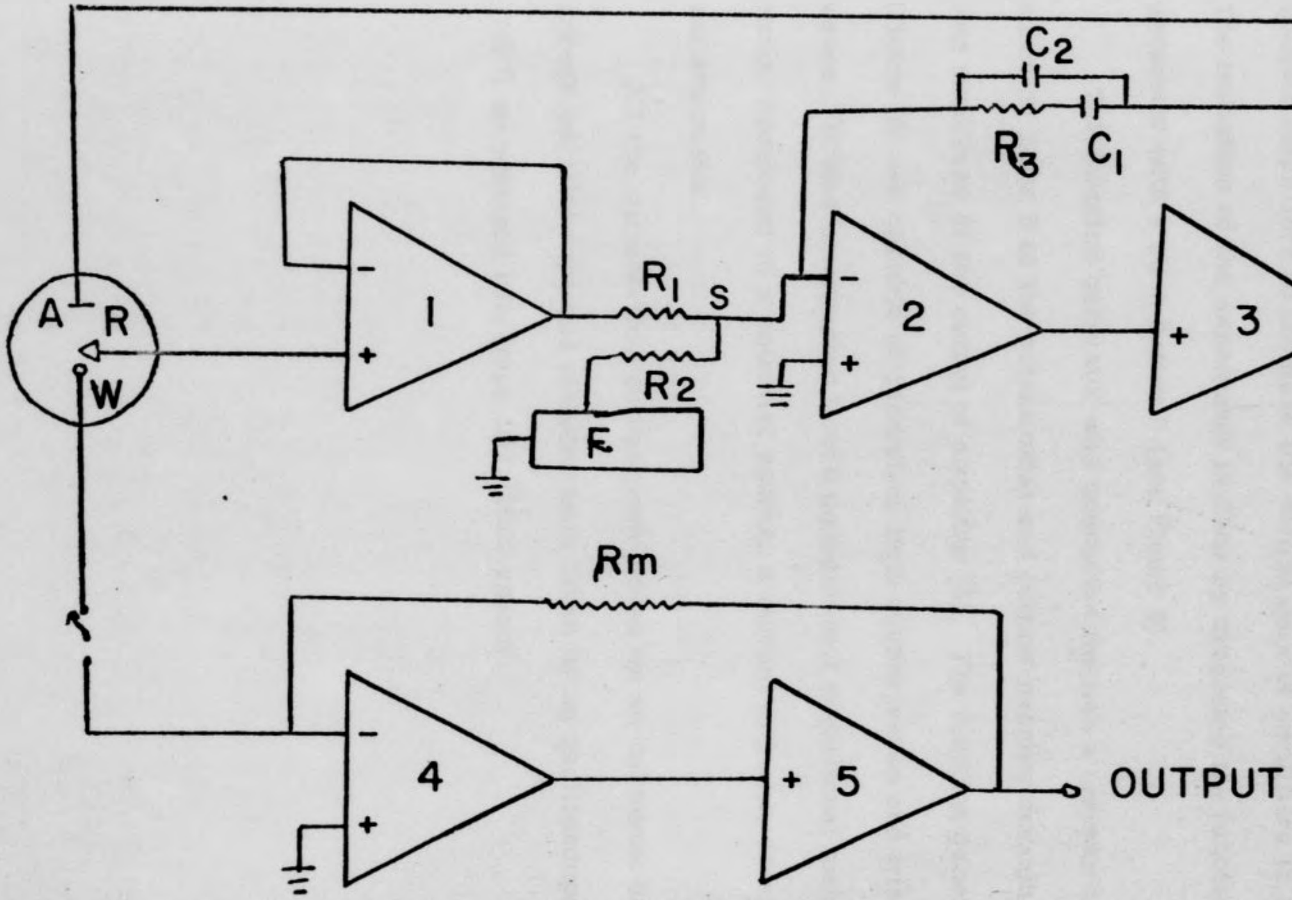
The three electrode cell contains a working (W), an auxiliary (A) and a reference (R) electrode. The potentiostat and current follower are constructed from operational amplifiers. The oscilloscope is a Tektronic 564 storage oscilloscope.


CELL
POTENTIO-
STAT
A
R
W
OSCILLO-
SCOPE
CURRENT
FOLLOWER

<u>FIGURE 4</u>

Circuit of potentiostat with boosted output.

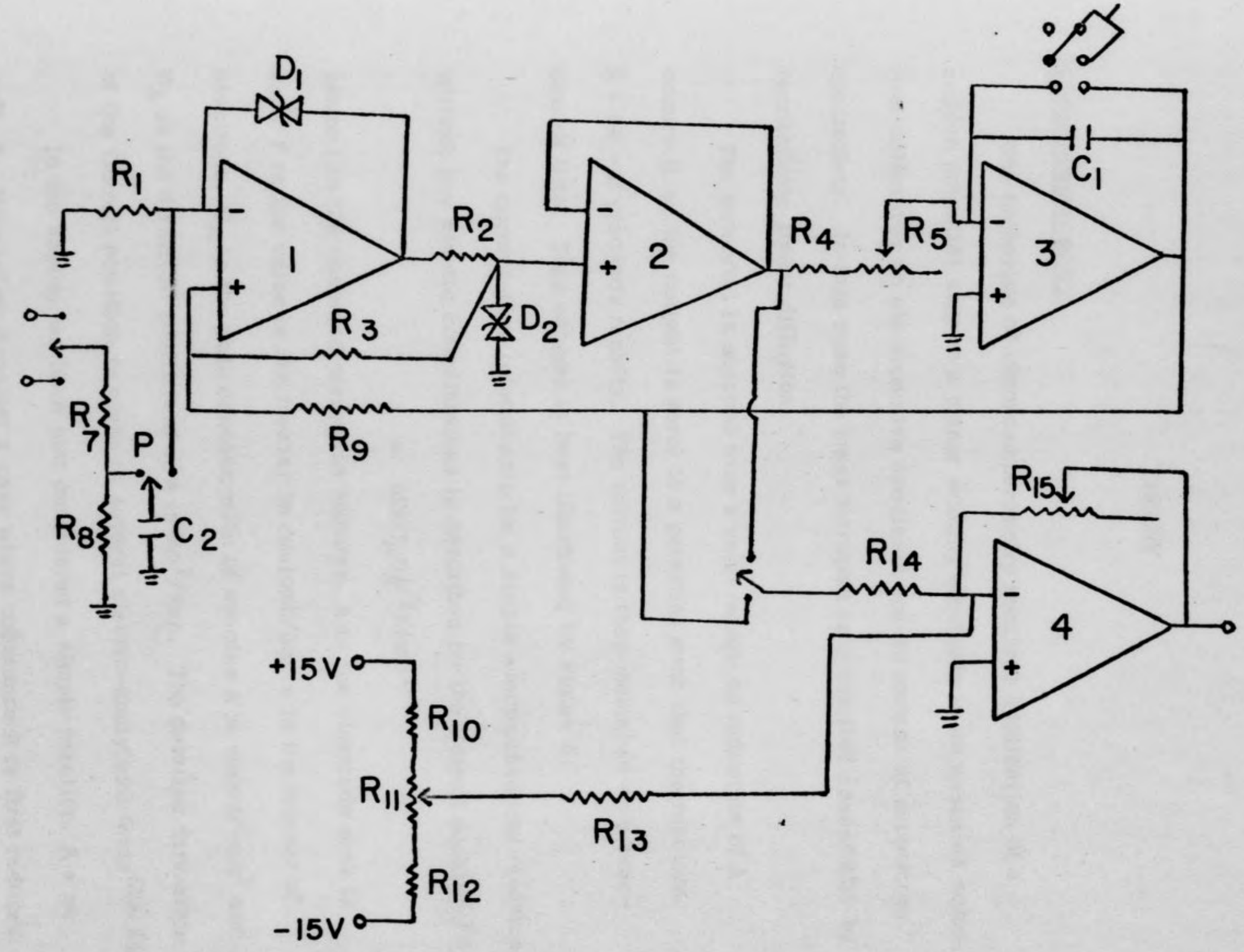
R_m, measuring resistor (1 to 20k); R_1, 10k resistor; R_2 variable (10K or 100K); R_3, 499K resistor; C_1, 0.002μF; C_2, 100μF. Operational amplifiers 1, 2, 4 are Analog Devices (118) and 3 and 5 are Analog Devices (B100).


C_2
R_3
C_1
A
R
W
1
2
3
4
5
R_1
S
R_2
F
Rm
OUTPUT
+
−

follower and uses current measuring resistor R. Amplifiers (3 and 5) are booster amplifiers to increase the current gain of amplifiers (2 and 4). The initiation of the experiment is done by triggering the function generator with a push button P (see Figure 5).

The function generator was connected through a resistor to the summing point S of the potentiostat and current passing through the cell was monitored at the output of amplifier (5). The function generator (Figure 5) was capable of generating both square waves and triangular waves. It was constructed from a conventional operational amplifier circuit composed of a potential switch, a current follower, integrator and attenuator.

All the current-time curves were stored on the tektronix 564 B storage oscilloscope and pictures were taken by an oscilloscope camera (C-27) on polaroid film (type 107, 3000 speed).

D1
R1
1
R2
2
R4
R5
3
C1
R3
D2
R9
R7
P
R8
C2
R15
R14
4
+15V
R10
R11
R13
R12
-15V
-
+

THEORY

Chronoamperometry.

The technique of chronoamperometry involves application of a sudden potential step to a planar working electrode in an unstirred solution containing an electroactive species A and an excess of supporting electrolyte. In this case the mass transport is controlled essentially by semiinfinite linear diffusion.

The potential is stepped from a value where no reduction of A occurs (i.e. the current is zero) to a potential such that the reaction, A + ne = B proceeds rapidly. The current is then measured as a function of time. This scheme is best illustrated by Figure 6.

The current-time relationship for a simple electrochemical reaction without any kinetic complications is described by the Cotrell equation[24].

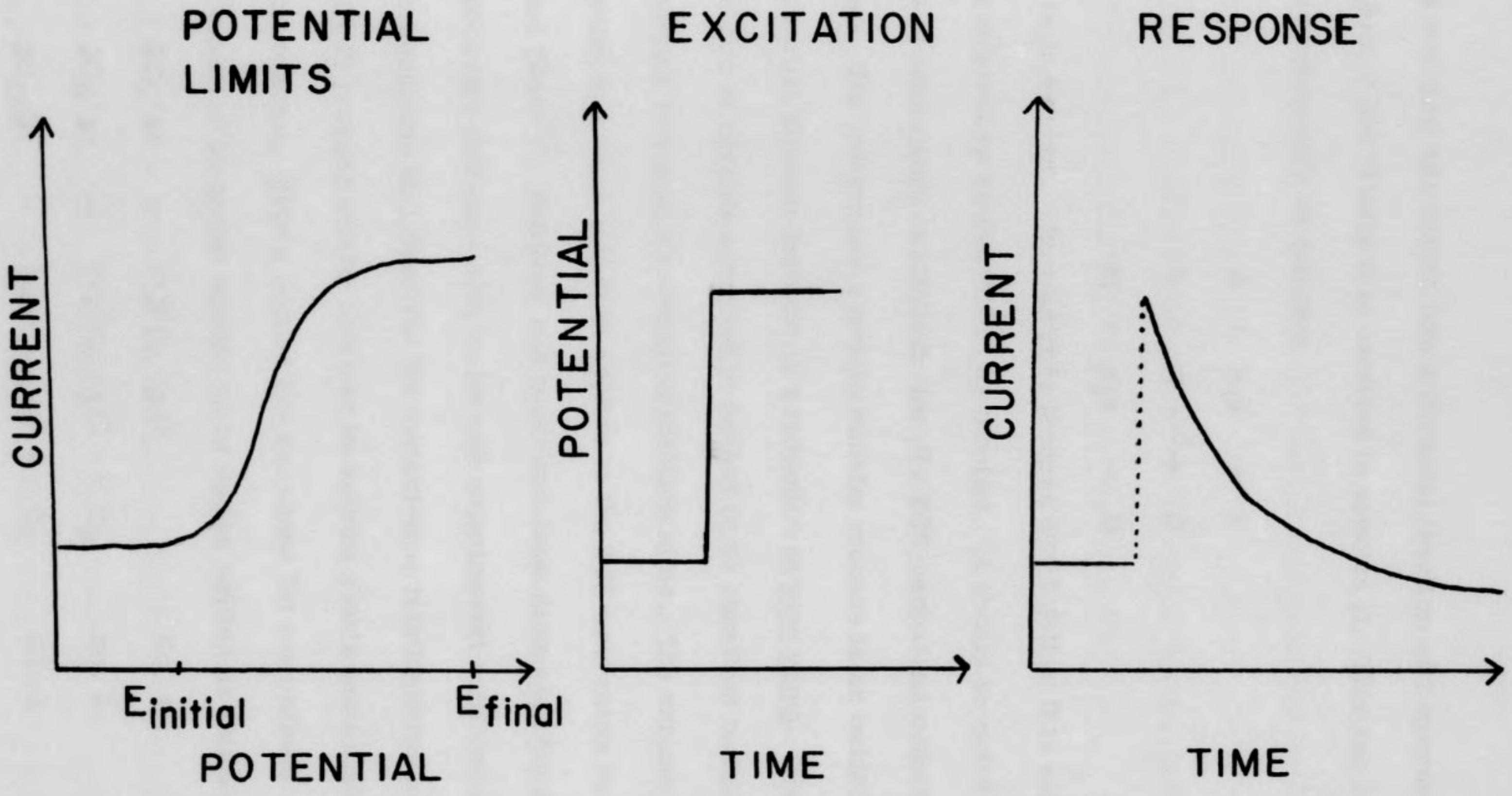
$$i = nFAC_A D_A^{1/2}/(\pi t)^{1/2}$$

where i is the observed current in amperes, A is the electrode area in cm^2, F is the value of the faraday in coulomb/eq, n is the number of electrons, C_A is the bulk concentration of species A in moles/-cm^3 and D_A is the diffusion coefficient of A in cm^2/sec. The detailed derivation of the Cotrell equation is given in several electro-analytical texts(25, 26).

In the above, we have just considered a simple reaction, A + ne $\dashrightarrow$ B. Now let us consider a case where substance A is first reduced

FIGURE 6

Experimental steps in a chronoamperometric experiment.


POTENTIAL LIMITS
CURRENT
$E_{initial}$
E_{final}
POTENTIAL
EXCITATION
POTENTIAL
TIME
RESPONSE
CURRENT
TIME

to give B and B in turn enters into a chemical reaction with species Z to give product C and finally C is oxidized to species D. This can be written schematically as follows:

$$A + n_1e = B$$

$$B + Z \xrightarrow{k} C$$

$$C - n_2e = D$$

where Z is in excess. The electrode process which follow this scheme would be referred to as the EC(-E) mechanism. It should be noted that this type of mechanism is different than the ECE mechanism commonly referenced. The subsequent electron transfer process is an oxidation when the initial electron transfer is a reduction or vice versa. The potentiostatic or chronoamperometric method is an excellent technique for determining intermediate chemical reaction rates. The chronoamperometric technique was first applied to the ECE mechanism by Alberts and Shain[15]. Feldberg and coworkers have discussed the nuances of ECE processes and were able to present experimental verifications[27, 28].

The equations that describe the current-time relationships for an ECE or EC(-E) process can be obtained by solving Fick's laws using Laplace transforms. Fick's second law equations for semiinfinite linear diffusion modified by proper kinetic terms can be written as follows:

$$\partial C_A/\partial t = D\partial^2 C_A/\partial x^2 \qquad \text{Eq. 1}$$

$$\partial C_B/\partial t = D\partial^2 C_B/\partial x^2 - k.C_B \qquad \text{Eq. 2}$$

$$\partial C_C/\partial t = D\partial^2 C_C/\partial x^2 + k.C_B \qquad \text{Eq. 3}$$

where the C's refer to the concentration of various species, x is the distance from the electrode surface, t is the time and k is the pseudo first order rate constant. It is assumed that the diffusion coefficients (D) for species A, B and C are all equal.

The initial and boundary conditions for the above problem are:

1. when $t=0$ and $x=0$ then, $C_A = C_A^o$ and $C_B = C_C = 0$

   where the superscript o refers to the bulk concentration.

2. when $t \geq 0$ and $x \dashrightarrow \infty$ then, $C_A \dashrightarrow C_A^o$, C_B, $C_C \dashrightarrow 0$

   and when $t > 0$ and $x = 0$ then $C_A = C_C = 0$ and

   $D\,(\partial C_A/\partial x) = -D\,(\partial C_C/\partial x)\ x=0$

The net current is given by the following expression:

$$i\ /\ FAD = n_1\ (\partial C_A/\partial x)\ x = 0\quad -n_2(\partial C_C/\partial x)\ x=0 \qquad \text{Eq. 4}$$

The negative sign in Equation 4 indicates the second electron transfer is of the opposite sign. EC(-E).

An extremely powerful tool for solving partial differential equations is the method of Laplace transforms[29]. The set of equations above, is first simplified by substitution ($C = C_B + C_C$) before application of the method. A similar approach was used by Alberts and Shain[15] for the ECE system. The final solution is as follows:

$$it^{1/2} = AFD^{1/2}C/\pi^{1/2}\ \ (n_1 - n_2(1 - e^{-kt}))\ /(\pi t)^{1/2} \qquad \text{Eq. 5}$$

The subscripts 1 and 2 on n refer to the first and second electron transfer, respectively. k is the pseudo first order rate constant for intermediate chemical reaction. When the product of kt is zero, Equation 5 can be simplified,

$$i_o t^{1/2} = n_1 F A D^{1/2} C / \pi^{1/2} \qquad \text{Eq. 6}$$

The subscript o on i refers to the limiting value of current when the chemical reaction is unimportant.

Dividing Equation 5 by Equation 6, we have

$$i t^{1/2} / i_o t^{1/2} = 1 - n_2/n_1 (1 - e^{-kt}) \qquad \text{Eq. 7}$$

when $n_1 = n_2$ (as in our case) this equation further simplifies to:

$$i t^{1/2} / i_o t^{1/2} = e^{-kt} \qquad \text{Eq. 8}$$

This expression is valid only for the EC(-E) mechanism. The results for the ECE mechanism[15] are:

$$i t^{1/2} / i_o t^{1/2} = 2 - e^{-kt} \qquad \text{Eq. 9}$$

Equation 5 can be linearized for small values of kt by expansion of exponential term and substitution. Thus,

$$e^{-kt} = 1 - kt$$

and $$i t^{1/2} = A F D^{1/2} C / \pi^{1/2} . (n_1 - n_2 kt) \qquad \text{Eq. 10}$$

The length of time in which experiment is performed is the main factor in seeing the effect of the chemical reaction. At short times, current will be dependent only on the reduction of A to B. At longer times, the net current will be close to zero and it will not be possible to see the effect of the intermediate chemical reaction. At intermediate times, when the chemical reaction is significant, the current can be related to the rate constant of the chemical reaction.

The above equations are not useful when the assumption, the ratio C_Z/C_A is large, is no longer valid. A completely different mathematical technique must be used. This technique, the finite difference method[31], allows calculation of the concentration, distance and time relationships for any system. The equations that follow for the chronoamperometric method and the EC(-E) mechanism are used to calculate the current at various times. The product $it^{1/2}$ or any other important number can be calculated easily.

Modified Fick's laws can be written for a true second order EC(-E) reaction as:

$$\partial C_A/\partial t = D\partial^2 C_A/\partial x^2 \qquad \text{Eq. 11}$$

$$\partial C_B/\partial t = D\partial^2 C_A/\partial x^2 - k.C_B.C_Z \qquad \text{Eq. 12}$$

$$\partial C_C/\partial t = D\partial^2 C_C/\partial x^2 + k.C_B.C_Z \qquad \text{Eq. 13}$$

$$\partial C_Z/\partial t = D\partial^2 C_Z/\partial x^2 - k.C_B.C_Z \qquad \text{Eq. 14}$$

where k is the second order rate constant. The initial and boundary conditions are same for chronoamperometry and current can be calculated by Equation 4. The above partial differential equations involving second order rate constants can be written in finite difference form. Thus, for species x,

$$\partial C_A/\partial t = C_A(x, t+\Delta t) - C_A(x, \Delta t) \;/\Delta t \qquad \text{Eq. 15}$$

$$\partial C_A/\partial x = C_A(x+\Delta x, t) - C_A/(x, \Delta t) \;/\Delta x \qquad \text{Eq. 16}$$

and

$$\partial^2 C_A/\partial x^2 = \frac{C_A(x+\Delta x, t) - {}^2C_A(x, t) + C_A(x-\Delta x, t)}{(\Delta x)^2} \qquad \text{Eq. 17}$$

A grid[32] such as that illustrated in Figure 7 (a) is helpful in understanding the finite difference method. The x-axis and the y-axis represents distance and time respectively. The points represent concentration at various times and distances from the electrode surface. The concentration at point 4 is calculated by using the concentration at points 1, 2 and 3. Figure 7 (b) illustrates the concentration profile. After the application of the potential step the concentration is zero at the electrode surface. The curve becomes less steep as we get further from the electrode and finally levels off.

The finite difference representation of the partial derivatives are substituted in Equation 11. Thus we have,

$$C_A(x, t+\Delta t) - C_A(x, t) = D\Delta t/(\Delta x)^2 \left[C_A(x+\Delta x, t) - 2C_A(x, t) + C_A(x-\Delta x, t)\right]$$

Rearranging and letting $D\,\Delta t/(\Delta x)^2 = D'$ gives,

$$C_A(x, t+\Delta t) = (1 - 2D')\,C_A(x, t) + D' \left[C_A(x+\Delta x, t) + C_A(x-\Delta x, t)\right] \quad \text{Eq. 18}$$

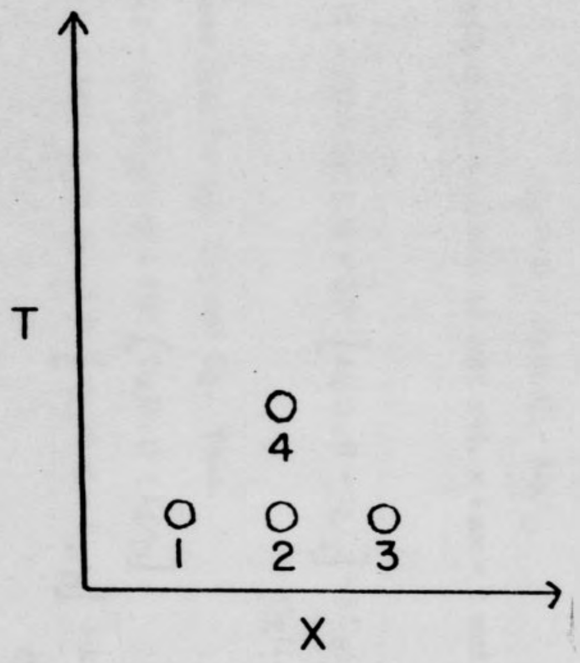
The terms on the left side correspond to point 4 and terms on right correspond to points 2, 3 and 1 respectively. Similar expressions can be derived in same manner for Equations 12, 13 and 14. The following are the final equations for other species.

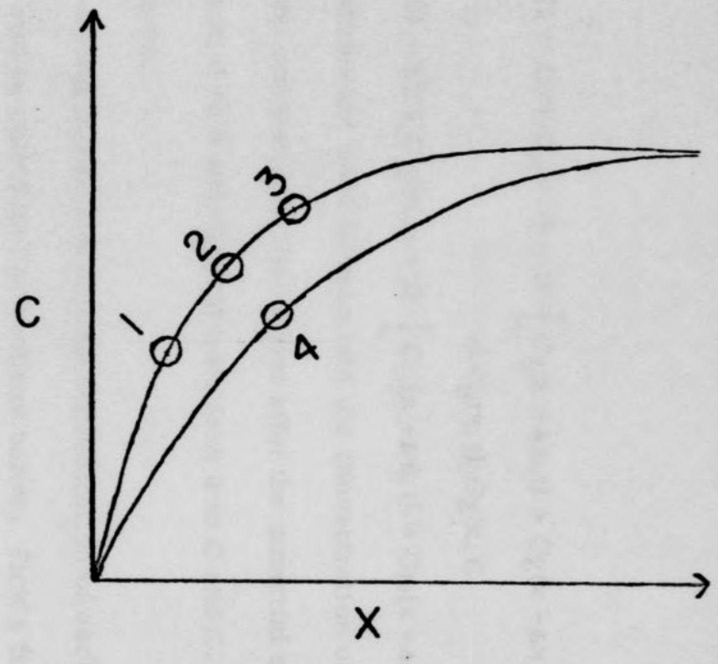
$$C_B(x, t+\Delta t) = (1 - 2D')\,C_B(x, t) + D' \left[C_B(x+\Delta x, t) + C_B(x-\Delta x, t)\right] - kC_B(x, t)\,C_Z(x, t) \quad \text{Eq. 19}$$

$$C_C(x, t+\Delta t) = (1 - 2D')\,C_C(x, t) + D' \left[C_C(x+\Delta x, t) + C_C(x-\Delta x, t)\right] + kC_B(x, t)\,C_Z(x, t) \quad \text{Eq. 20}$$

FIGURES 7 (a) AND 7 (b)

Grid and concentration profile for the finite difference approximation of Fick's law.


T
X
1
2
3
4


C
X
1
2
3
4

$$C_Z(x, t+\Delta t) = (1 - 2D')\, C_Z(x, t) + D' \left[C_Z(x+\Delta x, t) + C_Z(x-\Delta x, t)\right] - kC_B(x, t)\, C_Z(x, t) \qquad \text{Eq. 21}$$

$$C_D(x, t+\Delta t) = (1 - 2D')\, C_D(x, t) + D' \left[C_D(x+\Delta x, t) + C_D(x-\Delta x, t)\right] \qquad \text{Eq. 22}$$

The above equations are used to calculate the concentration of species in the bulk of the solution. At the instant after the potential step, $C_A(0, 1)$ goes from C to 0 and $C_B(0, 1)$ goes from 0 to C and C, Z and D remains unchanged.

After the initial instant the surface concentration of each electroactive species can be calculated as outlined below. Fick's first law for B can be written as:

$$D \, \frac{C_B(2, t) - C_B(0, t)}{2} = i_B$$

or

$$C_B(0, t) = C_B(2, t) - 2i_B/_D \qquad \text{Eq. 23}$$

substituting $C_B(0, t)$ into Equation 19 with $x=1$, $x+\Delta x = 2$ and $x-\Delta x = 0$ gives,

$$C_B(1, t+\Delta t) = (1 - 2D')\, C_B(1, t) + 2D' \left[C_B(2, t) - i_B/_D\right] - kC_B(1, t).\, C_Z(1, t)$$

Similar equations hold for C_A, C_C and C_Z. Thus,

$$C_A(1, t+\Delta t) = (1 - 2D')\, C_A(1, t) + 2D' \left[C_A(2, t) - i_A/_D\right]$$

$$C_C(1, t+\Delta t) = (1 - 2D')\, C_C(1, t) + 2\,D' \left[C_C(2, t) - i_C/_D\right] + kC_B(1, t).\, C_Z(1, t)$$

$$C_Z(1, t+\Delta t) = (1 - 2D')\, C_Z(1, t) + 2D' \left[C_Z(2, t) - i_Z/_D\right] - kC_B(1, t)\, C_Z(1, t)$$

Since, $C_A(1, t+\Delta t)$ and $C_C(1, t+\Delta t)$ are zero in chronoamperometric simulation, i_A and i_C can be calculated. Therefore,

$$i_A = D(\partial C_A/\partial x)_{x=0} = DC_A(2,t)$$

and $$i_C = D(\partial C_C/\partial x)_{x=0} = D.C_C(2,t) + k.C_B.(1,t) .C_Z.(1,t)$$

The total current can be calculated by

$$i_T = i_A - i_C$$

the surface concentration of B and Z needed in the computer program are derived by noting that $i_B = i_A$ and $i_Z = 0$. Thus

$$C_B(1,t+t) = (1-2D')\,C_B(1,t) + 2D'\left[C_B(2,t) + i_A/_D\right] - kC_B(1,t).\,C_Z(1,t)$$

and $$C_Z(1,t+t) = (1-2D')\,C_Z(1,t) + 2D'\left[C_Z(2,t) + i_C/_D\right] - kC_B(1,t).\,C_Z(1,t)$$

These equations in slightly modified form are incorporated in the FORTRAN computer program shown in Appendix A. Once the total current is known, the product $it^{1/2}$ can be calculated and compared with the $i_ot^{1/2}$ value computed from the Cotrell equation.

Polarography.

Polarography, invented by Jaroslav Heyrovsky[33], is a technique in which a linearly varying potential is applied to a dropping mercury electrode. A series of current measurements at each potential is then made. A plot of i vs. Eapplied is called a polarogram (Figure 8). An appropriate excess of supporting electrolyte is added to the solution to eliminate other contributions to the limiting current. The mass transport is said to be controlled only by diffusion under these conditions.

Ilkovic[34] derived the following equation for the diffusion current from the equations describing diffusion at a dropping mercury electrode(DME):

$$i_d = 607\, n\, D^{1/2}\, C\, m^{2/3}\, \tau^{1/6} \qquad \text{Eq. 24}$$

where i_d is the average current in microamperes (A) during the life of the drop, n is the number of electrons, D is the diffusion coefficient (cm/sec), C is the concentration (millimoles/liter), m is the rate of flow of mercury (mg/sec), and τ is the drop time in seconds. The proportionality of diffusion current to concentration is clearly shown by this equation. The electroactive substance is characterized by its polarographic half wave potential. This is the potential at the point of inflection on the current-voltage curve, one half the distance between the residual current and final limiting current plateau.

So far we have discussed only electrode processes which are controlled by the rate of diffusion. There is a possibility of electrode

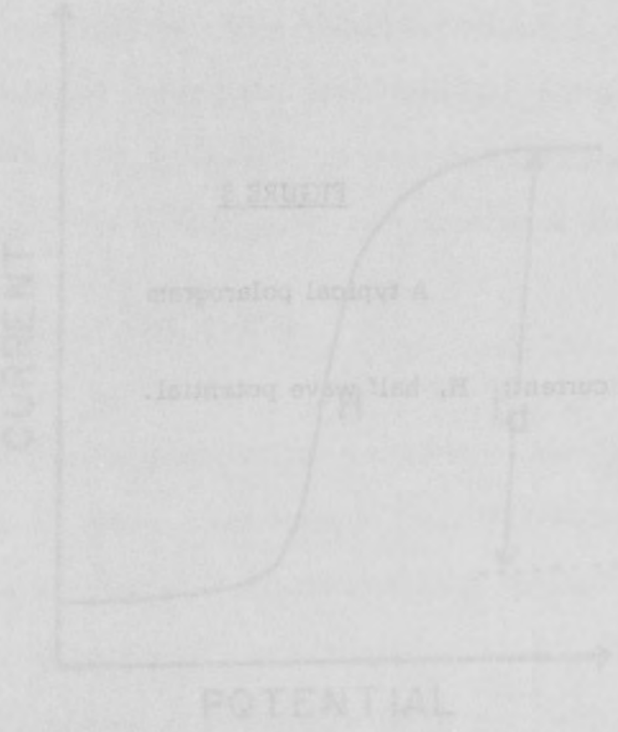
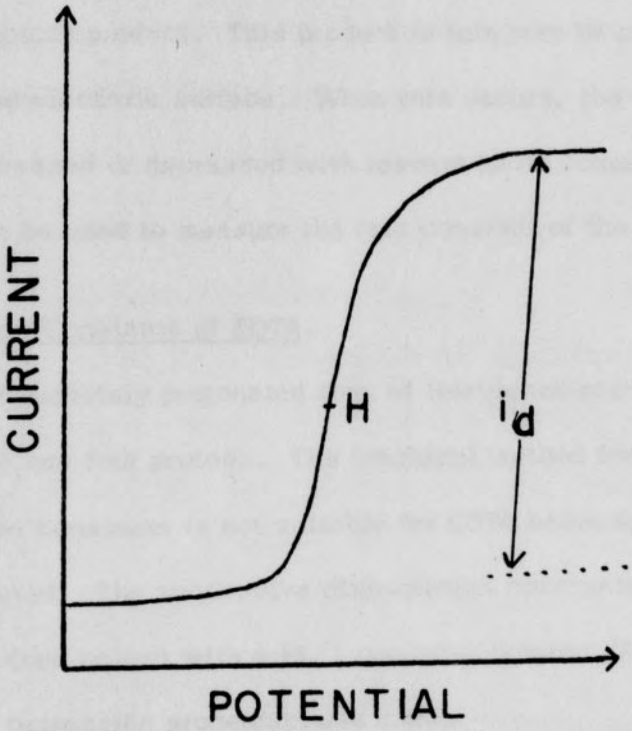

CURRENT
POTENTIAL

FIGURE 8

A typical polarogram

i_d, diffusion current; H, half wave potential.


CURRENT
H
i_d
POTENTIAL

processes where the diffusion current is controlled by a chemical reaction taking place in the vicinity of the electrode. For instance, there are cases where the product from the electroreduction process may enter into a chemical reaction with some other substance in the solution to give a chemical product. This product in turn may be reduced or oxidized at the electrode surface. When this occurs, the diffusion current will be increased or decreased with respect to its former value. The change can be used to measure the rate constant of the chemical reaction.

Dissociation Constants of EDTA.

The completely protonated form of (ethylenedinitrilo)-tetraacetic acid (EDTA) has four protons. The graphical method for determining dissociation constants is not suitable for EDTA because its pK's are not well separated. The successive dissociation constants of EDTA were calculated (see below) with a PL/1 computer program (Appendix B). A non-linear regression procedure was used.

The autoprotolysis constant of water, used in the PL/1 computer program, was evaluated by a strong acid-strong base titration. Elimination of the junction potential is done by extrapolation of equations below to zero hydrogen and hydroxyl ion concentration.

$$pH_c - pH_a = b - m.(H) \qquad \text{Eq. 25}$$

and $$pH_a - p^{OH}{}_c - b = p.(K_w)_c - m'.(OH^-) \qquad \text{Eq. 26}$$

The subscripts a and c refer to activity and concentration respectively. b is the intercept of the straight line, m and m' are the slopes of

Equations 25 and 26 respectively. The method of least squares[35] is used to calculate the slopes and intercepts. The intercept of Equation 25 is used in Equation 21. The autoprotolysis constant of water is the intercept of Equation 26.

A titration of EDTA with base is necessary to calculate its dissociation constants. Data form the titration are input to the computer program. The non-linear regression program uses derivatives approximated with the formula.

$$\partial f/\partial_x = \left[f(x+\Delta x) - f(x-\Delta x)\right] / _{2\Delta x}$$

The following function, f, is minimized in the procedure.

$$f = N_a^+ + (H^+) - (H_3 Y^-) - 2(H_2 Y^{-2}) - 3(HY^{-3}) - 4(Y^{-4}) - (OH^-)$$

or

$$f = \frac{C_bV_b}{V_bV_a} + 10^{-pH_c} \frac{-C_aV_a}{V_bV_a} \Big[(H^+)^3 K_1 + 2(H^+)^2 K_1K_2 + 3(H^+)$$

$$K_1 K_2 K_3 + 4 K_1 K_2 K_3 K_4\Big] /_D - (KW)_c{}^{10pH_c}$$

where $D = (H^+)^4 + (H^+)^3 K_1 + (H^+)^2 K_1 K_2 + (H^+) K_1 K_2 K_3 + K_1 K_2 K_3 K_4$

Approximate values for K_1, K_2, K_3 and K_4 are required by the program. The output consists of the dissociation constants and their respective standard deviation.

RESULT AND DISCUSSION

The absorption spectra of trans- and cis-dichlorochromium(III) is shown in Figure 9. Maxima are observed at wavelengths 450 and 635nm. The absorption ratio at A_{450}/A_{635} for both cis and trans isomers is reported by King, Gates and Wood[14]. Our results for this ratio in freshly prepared solutions agree very well with the results of those workers. The data are shown in Table I. The cis isomer prepared by the ion exchange procedure was frozen and used as a stock solution. Under these conditions, the isomerization and / or euqation was very slow and a given solution could be used for more than a week until the ratio of absorbance A_{450}/A_{635} decreased to 1.43 whereupon fresh solution had to be prepared.

Dichlorotetraaquochromium(III) ion on standing undergoes aquation and isomerization. It has been reported[20] that cis-isomer is slightly more stable than the trans-isomer. The three aquated species are $[Cr(H_20)_4Cl_2](Cl$ (I), $[Cr(H_20)_5Cl]Cl_2$ (II) and $[Cr(H_20)_6]Cl_3$ (III). The conversion of species I to II is relatively faster than the conversion to III. The rate constant for the aquation of trans-dichlorotetraaquochromium(III) ion was determined by us spectrophotometrically. The absorbances were measured on a solution of the trans-isomer in .01M HCl at different time intervals. The data are given in the Table II. A

FIGURE 9

Spectra of trans and cis dichlorotetraaquochromium(III) ion.

(a) spectrum of cis-dichlorotetraaquochromium(III) ion in 0.2M $HClO_4$ prepared by ion exchange.

(b) spectrum of freshly prepared trans-dichlorotetraaquochromium(III) ion in water.

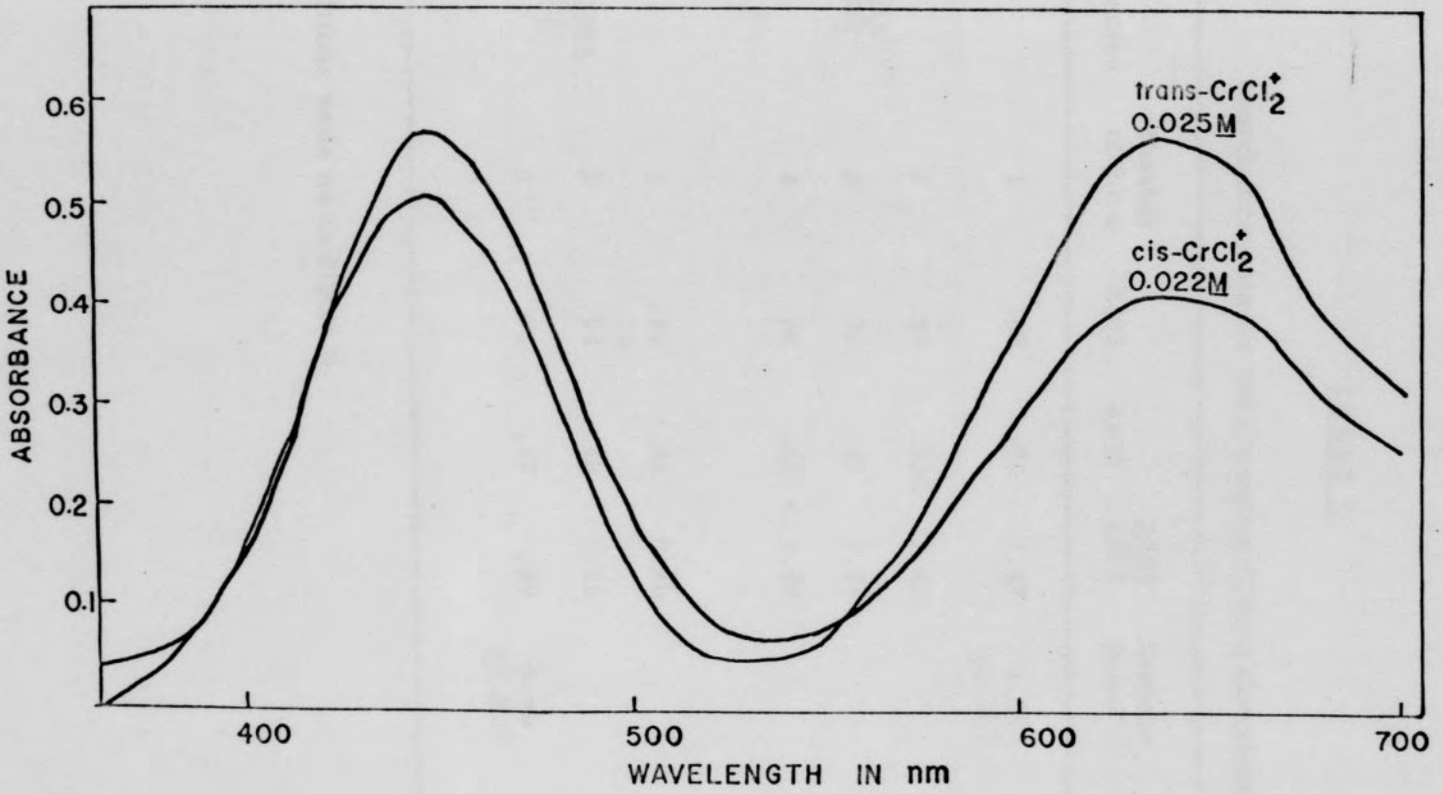

trans-$CrCl_2^+$
0.025M
cis-$CrCl_2^+$
0.022M
ABSORBANCE
0.1
0.2
0.3
0.4
0.5
0.6
400
500
600
700
WAVELENGTH IN nm

TABLE I

Absorbance data for the Chromium Chloro Complexes

Species	Number of Runs	A635	A450	$\frac{A450}{A635}$	Average Value	Reported Value
Cis- $CrCl_2^+$	1	.62	.91	1.47	1.46 ±0.007	1.46
	2	.57	.835	1.46		
	3	.33	.48	1.45		
	4	.38	.55	1.45		
Trans $CrCl_2^+$	1	.59	.53	0.90		.90
	2	.54	.48	0.89		
	3	.63	.57	.90	0.90 ±0.003	

Conditions same as in Figure 9.

TABLE II

Absorbance Data for Equation of Trans-dichlorochromium(III)

Time (sec)	$A - A_\infty$	$\log (A - A_\infty)$
0	.24	-.62
600	0.223	-0.65
1200	0.210	-0.68
1800	0.199	-0.70
2400	0.184	-0.73
3000	0.170	-0.77
3600	0.158	-0.80
10812	0.058	-1.20

Solution of trans $CrCl_2^+$ 0.03 M in 10^{-2} M
Temp 23°C.

plot was made of log absorbance vs. time and the pseudo first order rate constants were calculated from the least square fit of the straight line,

$$\log(A) = -kt/2.303 + \log(A_o) \qquad E_q.\ 27$$

where A is the absorbance, k is the pseudo first order rate constant, t is the time and A_o is the extrapolated absorbance at zero time. k, calculated from the slope, is 13.20×10^{-5} sec^{-1} and is in agreement with the value of 8.23×10^{-5} sec^{-1} found by Johnson and Reynolds[20]. Calculation with our measured rate constant indicates that a 10% concentration change takes about 12 minutes. It was necessary to keep the substance in dichloro form for a longer time in order to make the chronoamperometric measurements. This was accomplished by adding an excess of chloride ions in the solution. It was qualitatively determined that no appreciable change in concentration occurred for about 3 hours after the addition of chloride ions. The cis-isomer is expected to be even more stable in the presence of high chloride concentration.

Dissociation Constants of EDTA.

Since the experimental measurements are made in a medium of 2.5 M ionic strength, it is necessary to determine the dissociation constants of EDTA in the medium used. The measured values of 2.5 for the autoprotolysis constant of water $(K_w)_c$ and the dissociation constants (K_2, K_3) of EDTA are given in Table III, along with the literature values (0.1) for these quantities. Since our values for K_2 and K_3 are close to the literature values and we were not able to evaluate K_1 and K_4, we

TABLE III

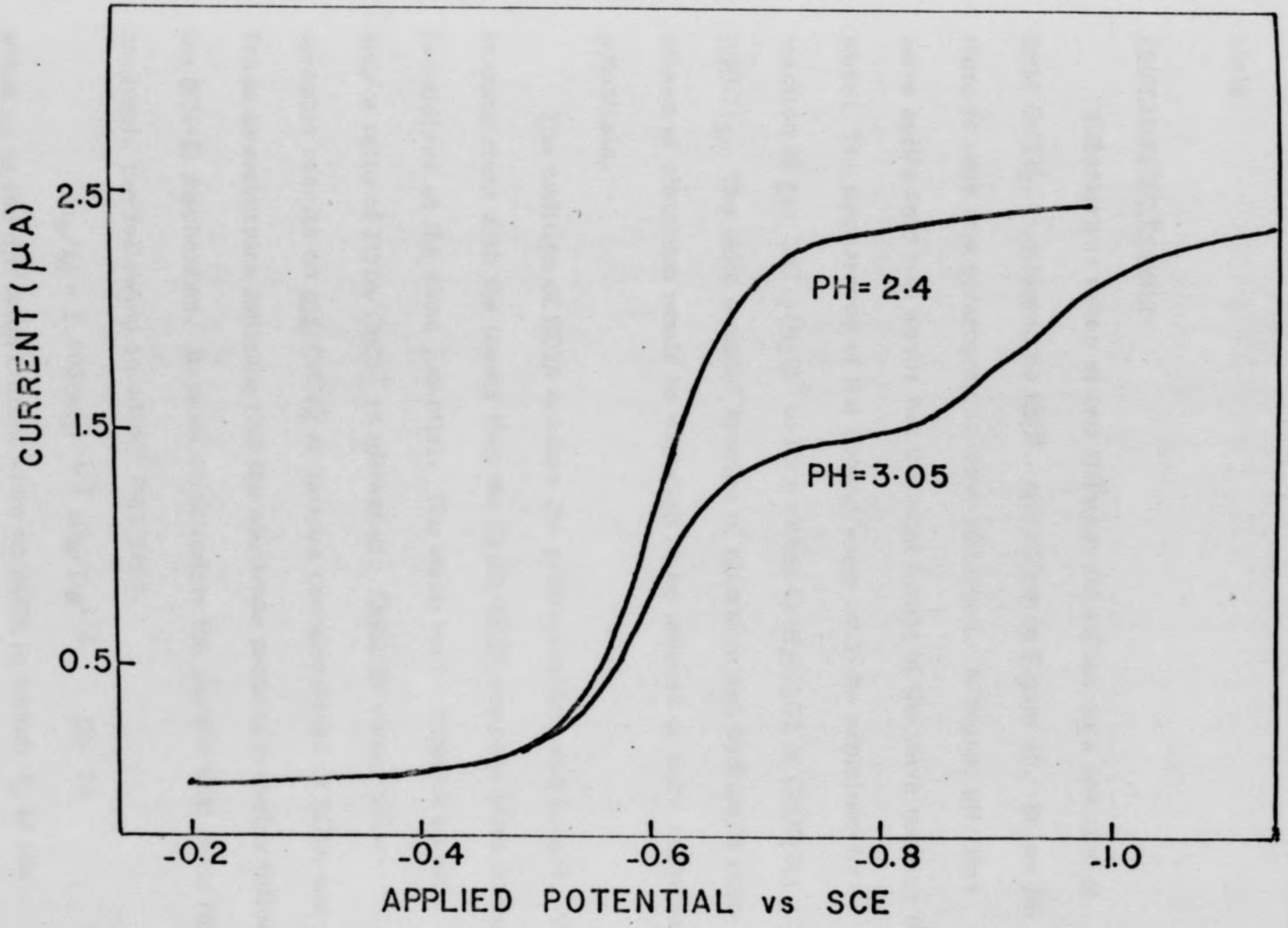
Dissociation Constants Data of EDTA

	Run (2.5M) 1	2	lit. value (0.1M)
$(KW)_C$	14.020	14.027	13.78
K_1	——	——	1.009×10^{-2}
K_2	3.78×10^{-3}	2.81×10^{-3}	2.218×10^{-3}
K_3	1.94×10^{-6}	6.80×10^{-7}	6.902×10^{-7}
K_4	——	——	5.47×10^{-11}

FIGURE 10

Polarograms of cis-dichlorotetraaquochromium(III) ion at two pH values.

1 mM cis-dichlorotetraaquochromium(III) ion in 2.5M NaCl; drop time, 6.64 sec.; temperature, 23°C; m, 0.93 mg/sec.


CURRENT (μA)
2.5
1.5
0.5
PH = 2.4
PH = 3.05
-0.2
-0.4
-0.6
-0.8
-1.0
APPLIED POTENTIAL vs SCE

decided to use only the literature values in our calculations. However, further experiments are planned to measure these constants more accurately.

Polarographic Results.

Polarograms taken at two different pH values on a solution of 1mM $CrCl_2^+$, containing no EDTA, are shown in Figure 10. Below pH 3 there is only one polarographic wave observed. At higher pH, this wave splits into two waves but the total height of the wave remains the same. The appearance of the second wave could be explained by a reaction of cis $CrCl_2(H_2O)_4$ to form either $Cr(H_2O)_5Cl$ or $Cr(H_2O)_3(OH)Cl_2$. The more aquated species of chromium and hydroxide complexes of chromium would be expected to be reduced at more negative potentials.

The addition of EDTA reduces the polarographic wave height. This is consistent with the theory that the Cr(II)-EDTA complex when formed, is oxidized at the same potential. The wave height reduces as pH and/or ratio of EDTA/$CrCl_2^+$ is increased. Table IV shows polarographic results on cis-$CrCl_2^+$ at various concentrations of EDTA and pH. These observations indicate that the electrode process probably follows the EC(-E) mechanism. In order to calculate the pseudo first order rate constant, the following equation[7] was used,

$$i_z/i_d = 1.003(kt_1)^{-1/2}\,(D_A/D_B)^{1/2} \qquad \text{Eq. 28}$$

where i_d is the diffusion current when no EDTA is added, i_z is the

TABLE IV

Polarographic Results for Cis-dichlorotetraaquochromium(III) ion

Conc. of EDTA x 10^3 (M)	Conc. of $CrCl_2^+$ x 10^3 (M)	pH	i_d*(μA)	Wave Height (μA) i_z	i_d/i_z	k	k/EDTA x 10^{-3} l/(mole.sec$^{-1/2}$)
1.09	1.02	1.626	2.45	1.80	1.36	0.28	0.26
1.07	1.02	1.988	2.45	1.25	1.96	0.58	0.55
2.21	0.82	1.971	1.99	0.74	2.69	1.10	0.50
3.02	0.84	1.993	2.02	0.68	2.98	1.35	0.44
4.02	0.84	1.982	2.02	0.54	3.74	1.46	0.36

*Diffusion currents were calculated from the Ilkovic equation using the diffusion current constant measured at pH 1.626.

diffusion current after addition of EDTA, k is the pseudo first order rate constant, t_1 is drop time, D_A and D_B are diffusion coefficients of species $CrCl_2$(A) and Cr(II)-EDTA complex(B). This equation is an approximate expression which Fishrova et al[7] claim has an inherent error of approximately 12%. With the assumption that the diffusion coefficients for species A and B are equal, it is possible to calculate the pseudo first order rate constant from polarographic results. This data are given in Table IV. The agreement of these results with the chronoamperometric data discussed later, is not very good. For this reason, the polarographic method, in our opinion, does not appear to be the best technique to study this system.

The discrepancy in the polarographic and chronoamperometric results could however be explained by the following reasons:

a. Our polarographic measurements were made at room temperature.

b. It is assumed that the diffusion coefficients of species A and B are equal.

c. Inherent error in the approximate equation used to calculate the rate constants.

d. Diffusion currents (i_d) of <u>cis</u>- $CrCl_2$ without added EDTA, were not measured at each pH value.

Even if more exact equations are used, measurement of rate constants by the polarographic method requires much more experimental effort. Due to these reasons, the polarographic method was used only for preliminary experiments. The chronoamperometric method appears to be a convenient and simple technique and was used to measure rate constants more accurately (see below).

Chronoamperometric Results.

A typical current-time curve is shown in Figure 11. Current-time data taken from this picture are shown in Table V. If there are no chemical kinetic complications, then the product $it^{1/2}$ would be a constant. The data in the table clearly show that the product $it^{1/2}$ decreases linearly with time. The correlation coefficient, obtained from a least square fit (linear regression), can be compared with the values given in the table in reference(35). In all experimental measurements made on the Cr(III)-EDTA system, it was observed that a regression of $it^{1/2}$ vs t was indeed a straight line with a confidence level of 99%. These observations strongly indicate that the system does indeed follow the EC(-E) mechanism. This is in agreement with the results of previous studies[24, 27]. This behaviour can be contrasted with the more common ECE mechanism where the product $it^{1/2}$ would have increased linearly with time.

The finite difference method was employed to calculate working curves for the second order EC(-E) mechanism. This method was checked carefully with the equations derived using Laplace transforms. The ratio of $it^{1/2}/(it^{1/2})_o$ calculated by the finite difference method was compared with the ratio calculated by an exact solution. It is seen from Table VI

TABLE V

Chronoamperometric Data on Cis-dichlorotetraaquochromium(III) ion

Time (t) (sec)	Current (i) μA	$it^{1/2}$ (μA-sec$^{1/2}$)	$it^{1/2}/(it^{1/2})_o$	K x 10^{-8} l/(mole-sec$^{-1/2}$)
0.10	17.60	5.56	0.95	1.89
0.15	14.00	5.42	0.929	1.87
0.20	12.00	5.36	0.919	1.80
0.30	9.00	4.92	0.843	2.15
0.35	8.20	4.85	0.831	1.95
0.40	7.40	4.68	0.800	1.91
0.45	7.00	4.69	0.804	1.98

Concentration of EDTA, 1.09 x 10^{-3} M;
Concentration of $CrCl_2^+$, 1.015 x 10^{-3} M;
pH, 1.96;
$(it^{1/2})_o$, 5.83 amp sec$^{1/2}$;
Area of electrode, 0.054 Cm$^{1/2}$.

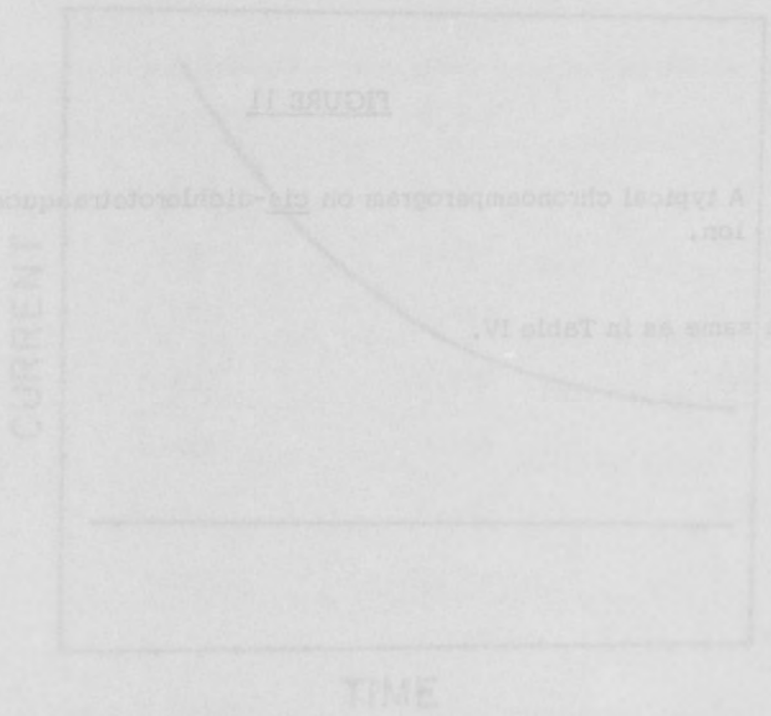

CURRENT
TIME

FIGURE 11

A typical chronoamperogram on cis-dichlorotetraaquochromium(III) ion.

Data same as in Table IV.

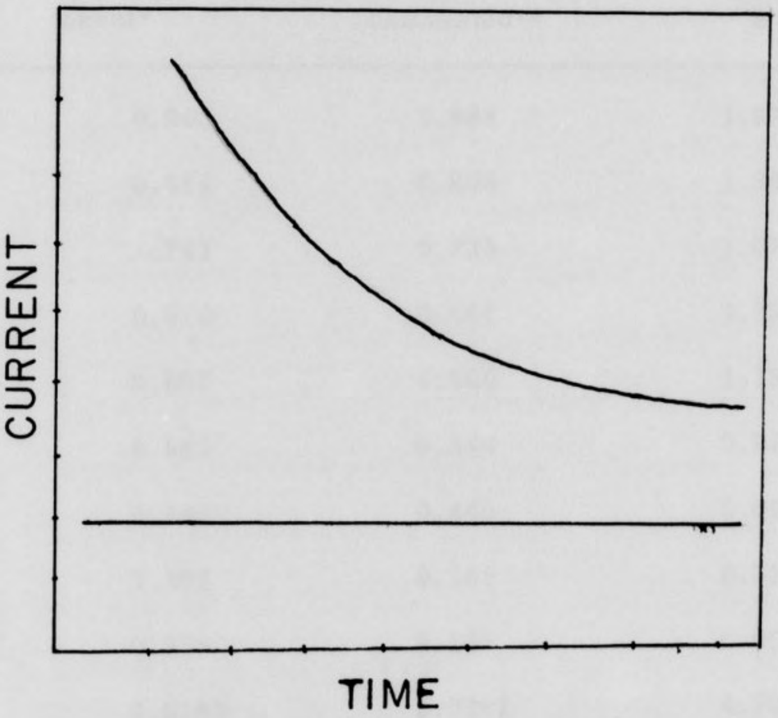

CURRENT
TIME

TABLE VI

Comparison of Working Curves for the EC(-E) Mechanism
Calculated by Two Different Methods

kt	$it^{1/2}/(it^{1/2})_o$ exact*	$it^{1/2}/(it^{1/2})_o$ calculated**	error %
0.1	0.905	0.888	1.87
0.2	0.819	0.808	1.34
0.3	.741	0.733	1.07
0.4	0.670	0.664	0.89
0.5	0.607	0.600	1.15
0.6	0.549	0.544	0.91
0.8	0.449	0.445	0.89
1.0	0.368	0.365	0.81
2.0	0.135	0.135	0.00
4.0	0.0183	0.0192	4.90
5.0	0.00674	0.00702	13.05

*Calculated with the use of Equation 5 in text.
**Calculated by the finite difference method.

$C_Z / C_A = 100$
Assumed k = .01
Diffusion Co-ef = 0.245 (Cm/sec)
$(it^{1/2})_o = 0.279 \times 10^6$ amp $sec^{1/2}$
Values tabulated at every 10 time units

that at a ratio of $C_Z/C_A = 100$ and kt less than 4, the agreement is very good. At higher values of kt, the error appears to increase. The finite difference method gives good results even at a ratio of $C_Z/C_A = 5$. Table VII shows the agreement to be still good at small values of ^{c}kt.

The linearized form of the exact solution for the EC(-E) mechanism,

$$it^{1/2} = (it^{1/2})_o(1-kt)$$

appeared useful to calculate the rate constant. The intercept, $(it^{1/2})_o$, divided into the slope, $k(it^{1/2})_o$, gives k. In order to determine whether this procedure would work, we plotted theoretical $it^{1/2}$ vs to for various values of C_Z/C_A, taking values of kt in the range of 0.1 to 0.4. From Table VIII it is seen that this procedure gives k good values for the intercept $(it)_o$. The error is approximately 2 for higher ratios of C_Z/C_A. Table IX illustrates that this is not a good way to determine rate constants. The error here is greater than 20%. A polynomial regression method gave improved values for the intercept but there was no substantial improvement in the values for the rate constant. It is believed that a non-linear regression procedure might give better values of rate constants. In the calculation of second order rate constants, the slope/intercept method was not employed but only the values of intercept $(it^{1/2})_o$ were determined by plotting $it^{1/2}$ vs t.

The above considerations led us to adopt the following procedure for data analysis. A series of values of $it^{1/2}$ and t are collected. The intercept of the plot of $it^{1/2}$ vs t is obtained by a least squares

TABLE VII

Comparison of Working Curves for the EC(-E) Mechanism by Two Different Methods

kt	$it^{1/2}/(it^{1/2})_o$ exact*	$it^{1/2}/(it^{1/2})_o$ calculated**	error %
0.1	.905	0.888	1.87
0.2	0.819	0.811	0.97
0.3	0.741	0.737	0.40
0.4	0.670	0.671	0.15
0.5	0.606	0.611	0.82
0.6	0.549	0.556	1.27
0.8	0.449	0.463	3.11
1.0	0.368	0.388	5.43
2.0	0.135	0.168	24.44
4.0	0.0183	0.0445	143.1
5.0	0.0067	0.0281	316.91

*Calculated with the use of Equation 5 in text.
**Calculated by the finite difference method.

$C_Z/C_A = 5$;
Other conditions being same as in Table V.

TABLE VIII

Evaluation of the Feasibility of Extrapolation to Determine $(it^{1/2})_o$

C_Z/C_A	$(it^{1/2})_o$ Calculated $\times 10^{-6}$	error %
100	0.272	2.5
10	0.272	2.5
5	0.272	2.5
2	0.271	2.9
1	0.270	3.2
1.5	0.271	2.9
0.5	0.268	3.9

Assumed $(it^{1/2})_o$, 0.279×10^{-6}; kt, 0.1 to 0.4 range;
Other conditions are same as in Table V.

TABLE IX

Evaluation of the Feasibility of the Slope-intercept Method to Determine k for the EC(-E) Mechanism

C_Z/C_A	Calculated x 10^3	error %
100	0.795	20
10	0.786	21
5	0.770	23
2	0.740	26
1.5	0.720	28
1.0	0.690	31
.5	0.600	40

Assumed, 1.0 x 10^{-3};
Other conditions are same as in Table VIII.

procedure. Only data which satisfied the conditions kt 0.5 was used to calculate the intercept. This value of $(it^{1/2})_o$ allows us to calculate the ratio, $it^{1/2}$ $(it^{1/2})_o$. Second order working curves (Figure 12) were then utilized to calculate the values of kCt. The second order rate constant is calculated by dividing kCt by the time and concentration of EDTA. Rate constants at varying concentrations of EDTA and pH are given in Table X.

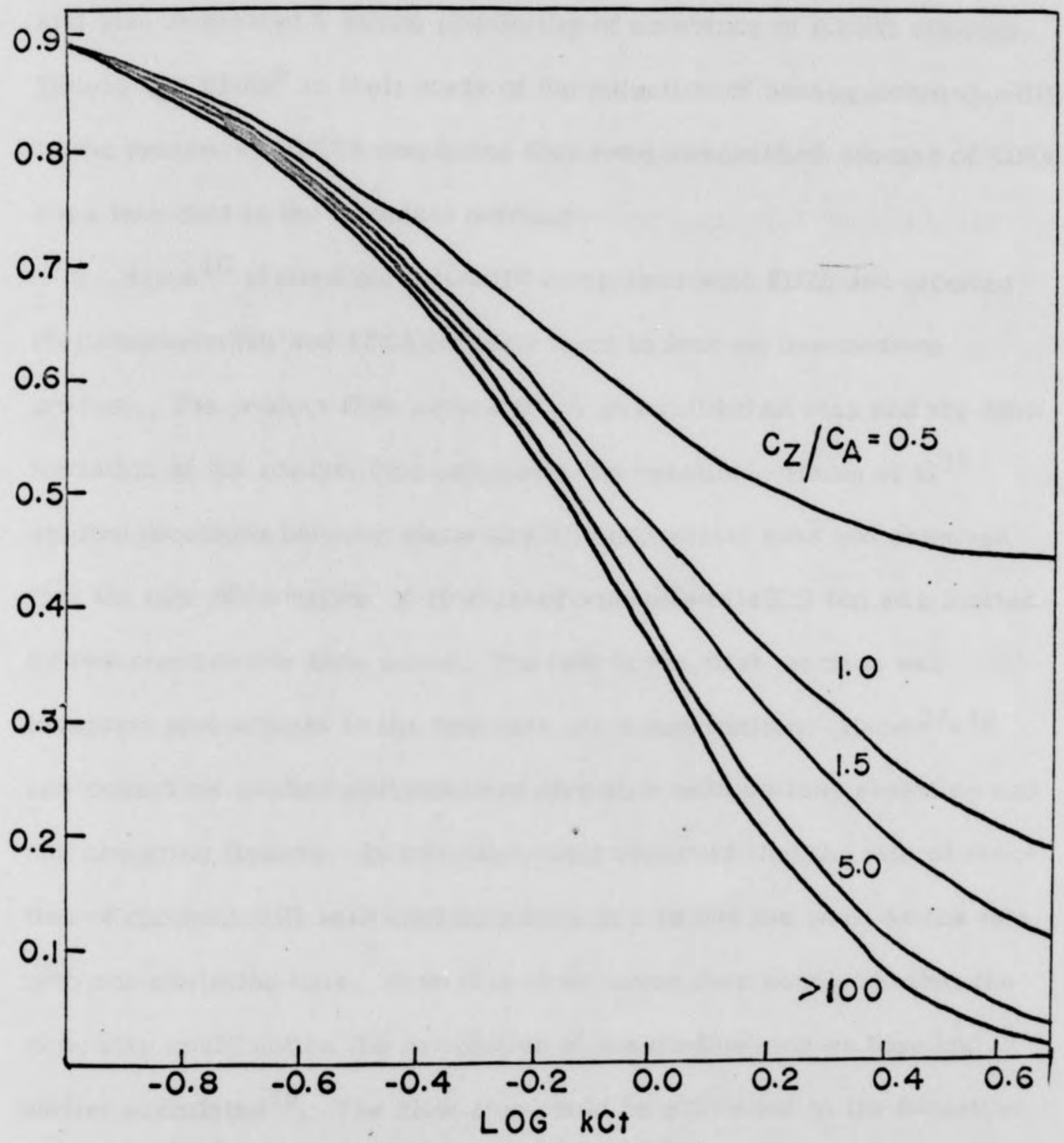
Before postulating a mechanism for the chemical reaction between Cr(II) and EDTA, it would be of interest to discuss the results of studies made by other workers with the same or similar systems.

Fisher and coworkers[12] have studied the reduction of dichlorotetraaquochromium(III) ion in the presence of EDTA. They were able to calculate pseudo first order rate constants from chronopotentiometric first transition time data. Second order rate constants calculated from these numbers were independent of the concentration of the trianion of EDTA. From these observations they concluded the trianion is the only species of EDTA involved in the kinetic scheme.

Tanaka and Yamada[13] took into consideration the reaction of chromium(II) complexes with various ions of EDTA and concluded that the reaction proceeds simultaneously with the di- and trianion of EDTA. The values of second order rate constants for the reaction of Cr(II) with EDTA (HY^{-3}), as reported by Tanaka and Yamada, are 2.20×10^8 liter/mole sec.

FIGURE 12

Working curves to calculate second order rate constants for coupled chemical reaction.


0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
$it^{1/2}/(it^{1/2})_0$
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
LOG kCt
$C_Z/C_A = 0.5$
1.0
1.5
5.0
>100

Pecsok and Shield[9] studied the complexes of chromium(II) and chromium(III) with EDTA and suggested that CrY is a dominant complex and also suggested a strong possibility of existence of (CrHY) complex. Tanaka and Ebata[8] in their study of the reduction of hexaaquochromium(III) in the presence of EDTA concluded that some unspecified species of EDTA does take part in the chemical reaction.

Hamm[10] studied chromium(III) complexes with EDTA and reported that chromium(III) and EDTA initially react to form an intermediate product. The product then looses H^+ in an equilibrium step and the slow formation of the chelate ring completes the reaction. Hamm et al[36] studied reactions between chromium(III) and oxalate ions and observed that the rate of formation of dioxalatediaquochromate(III) ion was limited by two consecutive slow steps. The rate of the first reaction was inversely proportional to the hydrogen ion concentration. Hamm[37, 38] and coworkers studied complexes of chromium with various chelating and non chelating ligands. In this study they observed that the rate of reaction of chromium(III) with chelating ions was nearly the same as the rate with non chelating ions. From this observation they concluded that the slow step could not be the completion of the chelate ring as they had earlier postulated[36]. The slow step could be attributed to the formation of the first covalent bond to the chromium. Subsequent steps leading to the chelated structure are relatively rapid. The rate expressions derived for these reactions shows an inverse correlation of rate constant with hydrogen ion concentration.

In view of these studies, there seems to be two possible mechanisms suggested for the reaction of Cr(II) with EDTA. One suggested by Fisher and coworkers would give rate constants proportional to the concentration of HY. The other possible mechanism similar to the one suggested by Hamm et al for the reaction of hexaaquochromium with organic acids, would give rate constants inversely proportional to the hydrogen ion concentration. The two different mechanisms are discussed below in more detail to determine if our data are consistent with either of the reaction schemes.

The mechanism for the chemical reaction suggested by Fisher et al can be represented by the following equation:

$$CrCl_2 \quad + \quad HY^{-3} \quad \dashrightarrow \quad CrHY^- \quad + \quad 2Cl^- \qquad \text{Eq. 29}$$

The rate of this bimolecular process would be simply proportional to the concentration of HY^{-3}. Experimental values of pseudo first order rate constants can be divided by the concentration of HY^{-3} to test this proportionality. Alternatively, a plot of pseudo first order rate constant versus HY^{-3} should be a straight line with a good correlation coefficient. The concentration of HY^{-3} can be calculated by the following equation, if it is assumed that the equilibrium between each species of EDTA is maintained.

$$HY^{-3} = \frac{Ka_4\ Ka_3\ Ka_2\ HC}{(H^+)^4 + Ka_4\ (H^+)^3 + Ka_4\ Ka_3\ (H^+)^2 + Ka_4\ Ka_3\ Ka_2\ (H^+) + Ka_4\ Ka_3\ Ka_2\ K_1} \qquad \text{Eq. 30}$$

TABLE X

Chronoamperometric Results for Dichlorotetraaquochromium(III) ion

Conc. of EDTA x 10^3 (M)	Conc. of $CrCl_2$ x 10^3 (M)	Hydrogen ion conc. H^+ (M)	Conc. of HY^{-3} x 10^8 (M)	k	k/HY^{-3} x 10^8 1/(mole.sec$^{-1/2}$	k/EDTA x 10^{-3} 1/(mole. sec$^{-1/2}$)
1.452	0.99	1.63 x 10^{-2}	.292	.307	1.05	.211
2.207	0.825	1.07 x 10^{-2}	1.253	.758	.605	.343
3.018	0.840	1.01 x 10^{-2}	1.965	1.457	.741	.482
1.07	1.015	1.05 x 10^{-2}	.635	.509	.801	.475
1.09	1.015	2.40 x 10^{-2}	.802	.0989	.123	.0907
1.32	0.945	3.63 x 10^{-3}	7.56	3.25	.430	2.462
1.08	0.980	1.05 x 10^{-3}	45.90	3.88	.084	3.592
1.138	0.980	8.88 x 10^{-3}	1.00	1.82	1.820	3.918

where Ka_1, Ka_2, Ka_3, Ka_4 are successive dissociation constants of EDTA. H^+ is the hydrogen ion concentration and C is the concentration of EDTA.

A plot of the pseudo first order rate constant k versus HY^{-3} gave a poor correlation coefficient (0.22). We concluded from this that the rate constants are probably not simply proportional to the concentration of HY^{-3}.

The other mechanism for the chemical reaction similar to one suggested by Hamm and coworkers can be represented by the following reactions:

$$B + Z \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B' \qquad \text{Eq. 31}$$

$$B' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B'' + H^+ \qquad \text{Eq. 32}$$

$$B'' \xrightarrow[k_3]{slow} C \qquad \text{Eq. 33}$$

The rate equation for the slow step is

$$\frac{d\,[Crt]}{dt} = -k_3 \ B'' \qquad \text{Eq. 34}$$

Where Crt represents the total concentration of chromium affecting the chemical step of the EC(-E) mechanism

$$[Crt] = B + B' + B'' \qquad \text{Eq. 35}$$

The equilibrium steps indicated in Equation 31 and 32 are

$$\frac{[B']}{[B]\,[Z]} = \frac{k_1}{k_{-1}} = K_1 \quad \text{and} \quad \frac{[B'']\,[H^+]}{[B']} = \frac{k_2}{k_{-2}} = K_2$$

or

$$[B] = \frac{[B''][H^+]}{K_1\,K_2\,[Z]} \qquad [B'] = \frac{[B'']\,[H^+]}{K_2}$$

Substituting values of B and B' in Equation 35 we have

$$[\mathrm{Crt}] = \frac{[\mathrm{B''}]\,[\mathrm{H^+}]}{\mathrm{K_1\,K_2\ \ Z}} + \frac{[\mathrm{B''}]\,[\mathrm{H^+}]}{\mathrm{K_2}} + \mathrm{B''}$$

or $$\mathrm{B'} = \frac{\mathrm{K_1\,K_2}\,[\mathrm{Z}]\,[\mathrm{Crt}]}{[\mathrm{H^+}] + \mathrm{K_1}\,[\mathrm{Z}]\,[\mathrm{H^+}] + \mathrm{K_1\,K_2}\,[\mathrm{Z}]}$$

Substituting value of $[\mathrm{B''}]$ in Equation 34 we have

$$\frac{d\,[\mathrm{Crt}]}{dt} = \frac{-\mathrm{K_1\,K_2\,k_3}\,[\mathrm{Z}]\,[\mathrm{Crt}]}{[\mathrm{H^+}] + \mathrm{K_1}\,[\mathrm{Z}]\,[\mathrm{H^+}] + \mathrm{K_1}\,[\mathrm{Z}]\,\mathrm{K_2}}$$

$$= \frac{-\mathrm{K_1\,K_2\,k_3}\,[\mathrm{Z}]\,[\mathrm{Crt}]}{[\mathrm{H^+}] + \mathrm{K_1}\,[\mathrm{Z}]\,(\mathrm{H^+} + \mathrm{K_2})}$$

which under the condition $\mathrm{K_1}\,[\mathrm{Z}] \gg 1$ reduces to

$$\frac{d\,[\mathrm{Crt}]}{dt} = \frac{-\mathrm{k_3\,K_2}\,[\mathrm{Crt}]}{\mathrm{H^+} + \mathrm{K_2}} \qquad \text{Eq. 36}$$

This expression can be rewritten as,

$$\mathrm{Rm} = \frac{-\mathrm{k_3\,K_2}}{[\mathrm{H^+}] + \mathrm{K_2}} \qquad (\mathrm{Rm} = \text{measured rate constant})$$

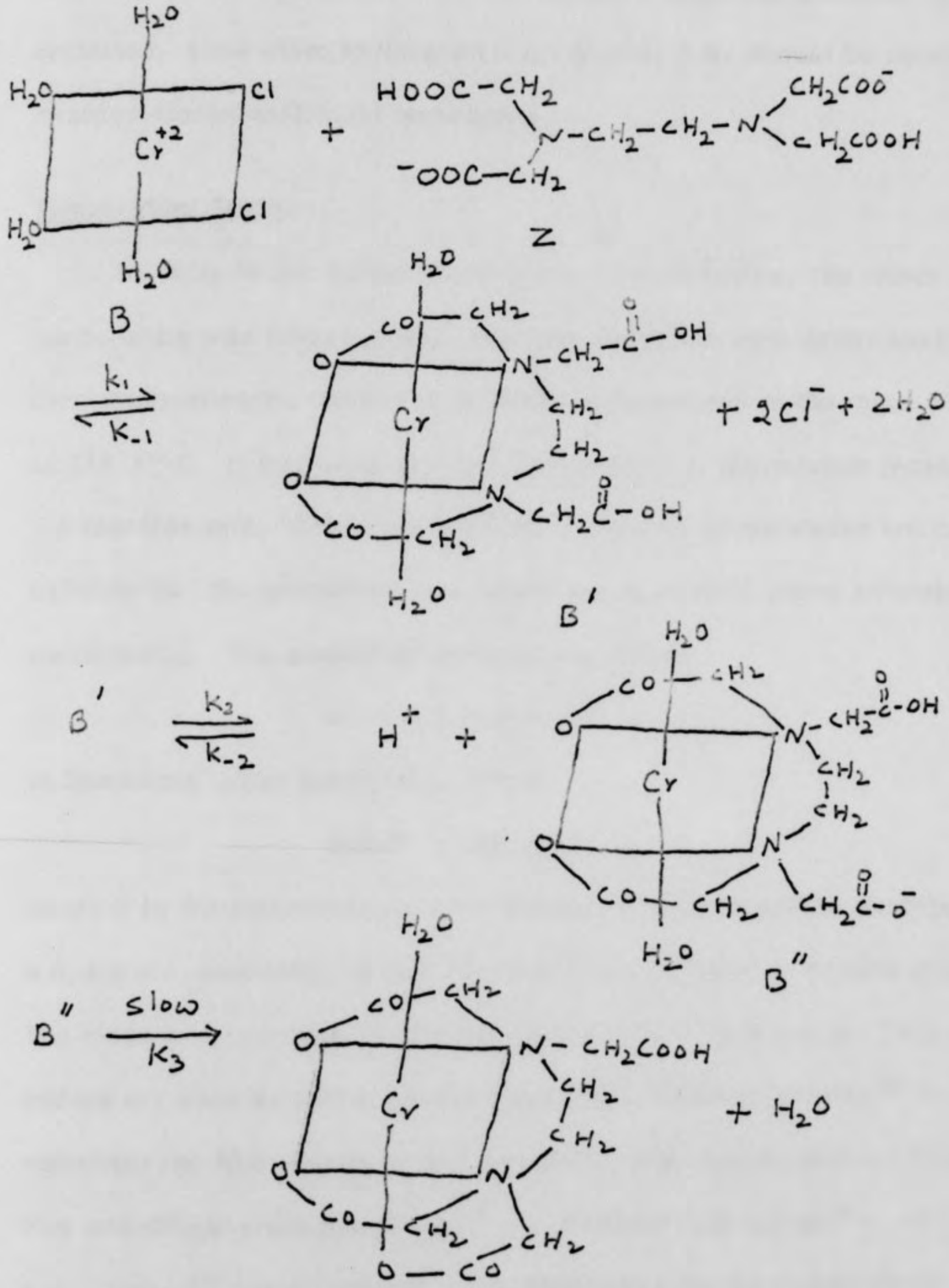
or $$\mathrm{Rm}\,(\mathrm{H^+} + \mathrm{K_2}) = \mathrm{k_3\,K_2}$$

Dividing by Rm and rearranging, we have

$$[\mathrm{H^+}] = \frac{-\mathrm{k_3\,K_2}}{\mathrm{Rm}} - \mathrm{K_2} \qquad \text{Eq. 37}$$

This mechanism can be tested by plotting $[\mathrm{H^+}]$ ion concentration versus the reciprocal of the measured rate constant. In this case the least square procedure gave a correlation coefficient of 0.93. This value is clearly better than the one calculated for the mechanism discussed earlier. We have concluded from this that our data are more consistent with the mechanism suggested by Hamm.

Considering all the above information, we propose one possible path for the reaction of cis-$CrCl_2$ with EDTA;



The kinetic steps indicated in the above scheme are written without any experimental evidence, but are put forward as a working hypothesis for future work. However, to study the detailed steps and possible intermediates, some other techniques e.g. N M R, I.R. should be employed besides electroanalytical techniques.

Temperature Study.

In order to get further insight into the mechanism, the effect of temperature was investigated. The rate constants were determined by the chronoamperometric method at different temperatures in the range 274° K to 314.5° K. It was observed that an increase in temperature increased the reaction rate. Rate constant data at various temperatures are given in Table XI. The activation parametere are calculated using Arrhenius relationship. The simplified Arrhenius equation,

$$k = a.T.\exp(-b/T)$$

is linearized using logarithms. Thus,

$$\ln k/T = \ln a - b/T$$

where k is the measured rate constant and T is the absolute temperature. a and b are constants. A plot of ln(k/T) vs. 1/T gave a straight line. The slope and intercept of this line gives values for a and b. These values are used as initial guesses in a PL/1 computer program[19] to calculate the best values of $\Delta S^{\#}$ and $\Delta H^{\#}$. The values obtained from this non-linear procedure are $\Delta H^{\#} = 8.85$ Kcal/mole and $\Delta S^{\#} = -19.1$ e.u. Hamm[10] has calculated these parameters for the Cr(III)-EDTA

TABLE XI

Rate constants data on Cis-dichlorotetraaquochromium (III) ion at different temperatures.

k	Temp. (absolute)	$\Delta H^{\#}$ koal/mole	$\Delta S^{\#}$ (e.u.)
0.515×10^{2}	274.0	8.55	-19.1
0.721×10^{2}	281.0		
0.182×10^{3}	291.0		
0.264×10^{3}	298.0		
0.355×10^{3}	307.0		
0.418×10^{3}	314.5		

Solution contains 0.992×10^{-3} M Cis-$CrCl_2^{+}$ and 2.5 M NaCl as supporting electrolyte. pH = 1.72.

reaction and reported the values, $\Delta H^{\#}$ = 21.3 Kcal/mole and $\Delta S^{\#}$ = - 8.7 e.u. A high enthalpy of activation for Cr(III) is expected, especially when the entropy contribution to the rate is small, in light of the observation of its very slow substitution behaviour. Substitution reaction of Cr(III) have been accelerated by the addition of Zn dust which reportedly[39] forms a small amount of the faster reacting Cr(II). From these observations we would expect Cr(II) to have lower values for $\Delta H^{\#}$ than Cr(III). Faster substitution reactions of Cr(II) could also be explained from the crystal field theory. The lability of Cr(II), a d^4 system, and inertness of Cr(III), a d^3 system, are predicted by crystal field theory[40]. The negative values of $\Delta S^{\#}$ for the reaction of Cr(II) with EDTA molecule will be somewhat more restricted in the activated state as supported by Hamm et al[41]. The observed large negative values of $\Delta S^{\#}$ can be explained on the basis that at higher values of ionic strength (2.5M), sodium ions will solvate the water molecule and also restrict the free carboxylic group. In this way, the EDTA and water molecule will be relatively more restricted in the activated state at higher ionic strength. Hence, $\Delta S^{\#}$ becomes more negative. A similar observation is reported by Hamm and coworkers[42] for the reaction of Cr(III) with EDTA.

SUMMARY

In conclusion, we find that the chronoamperometric method is suitable and convenient for the study of the EC(-E) mechanism. The finite difference approximation method has been used to solve the partial differential equations obtained by Fick's laws under second order conditions (where C_Z is not much greater than C_A). The working curves have been prepared and tested. The second order rate constants have been measured for the reaction of Cr(II) and EDTA using chronoamperometric technique. Chronoamperometric and polarographic results have shown that the system under study follows the EC(-E) path, and the reaction of Cr(II) and EDTA takes place by the mechanism suggested by Hamm et al[38]. The activation parameters ($\Delta H^{\#}$, $\Delta S^{\#}$) have been calculated for the reaction of Cr(II) and EDTA.

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APPENDIX A

PROGRAM TO CALCULATE WORKING CURVES FOR EVALUATION OF SECOND ORDER RATE CONSTANTS

```
C     THIS PROGRAM SIMULATES THE SOLUTION OF FICK'S LAW.
C     THE EQUATION IS PERTURBED BY AN ECE NUANCE UNDER
C     CHRONOAMPEROMETRIC BOUNDARY CONDITIONS   SECOND ORDER
      DIMENSION X(1000),Y(1000),XX(1000),YY(1000),Z(1000),ZZ(1000),W(100
     10),WW(1000),ZI(3),VV(1000),V(1000)
      READ (1,903) L
903   FORMAT (I10)
      DO 4 M=1,L
      READ (1,900) D,C,RK, RATIO
900   FORMAT (5E10.4)
      XITHFO=SQRT(D)*C/1.77245
      WRITE (3,901) D,C,XITHFO,RK,RATIO
901   FORMAT( 1H1,7E15.5)
      B=(1.-2.0*D)
      CV = RATIO*C
      RK = RK/CV
      DO 101 I=2,999
      X(I)=C
      V(I) = CV
      Z(I)=0.
      W(I)=0.
101   Y(I)=0.0
      V(1) = CV
      X(1)=0.
      Y(1)=C
      Z(1)=0.
      W(1)=0.
      DO 4 J=1,500
      XM=J
      IK=5.*SQRT(D*XM)+3.
      DO 3 I=2,IK
      XX(I)=B*X(I)+D*(X(I+1)+X(I-1))
      ZZ(I)=B*Z(I)+D*(Z(I+1)+Z(I-1))+RK*Y(I)*V(I)
      WW(I)=B*W(I)+D*(W(I+1)+W(I-1))
      VV(I)=B*V(I)+D*(V(I+1)+V(I-1))-RK*Y(I)*V(I)
3     YY(I)=B*Y(I)+D*(Y(I+1)+Y(I-1))-RK*Y(I)*V(I)
      ZI(1)=X(2)*D
      ZI(2)=Z(2)*D+ RK*Y(1)*V(1)/2.
      ZI(3)=ZI(1)-ZI(2)
      IF (MOD(J,5 ))  6,5,6
5     XITHF=ZI(3)*SQRT(XM)
      XITHF=XITHF/XITHFO
      RKT = RK*XM*CV
      EXACT = EXP(-RKT)
      WRITE (3,902) ZI(3),XM,XITHF,Y(1),EXACT,RKT
902   FORMAT(7E15.5)
6     YY(1)=B*Y(1)+2.*D*(Y(2)+ZI(1)/D)-RK*Y(1)*V(1)
      WW(1)=B*W(1)+2.*D*(W(2)+ZI(2)/D)
      VV(1) = B*V(1) -RK*Y(1)*V(1) +2.*D*V(2)
```

```
      DO 61 K=2,IK
      X(K)=XX(K)
      Z(K)=ZZ(K)
      W(K)=WW(K)
      V(K) = VV(K)
   61 Y(K)=YY(K)
      V(1) = VV(1)
      Y(1)=YY(1)
      W(1)=WW(1)
    4 CONTINUE
      STOP
      END
//G.SYSIN DD *
```

APPENDIX B

PROGRAM TO CALCULATE SUCCESSIVE DISSOCIATION CONSTANTS OF EDTA

```
 MAIN: PROCEDURE OPTIONS(MAIN);
      DECLARE (DELV(6),V(15),SV(15),PH(75),VB(75),A(4,4) ,B(4),
D(15),RELV(15),MV(75),SLOPE1,SLOPE2) FLOAT DEC(14);
      DECLARE (#SETS,L,M,O,P,I,CNTR,J,II,K) FIXED;
      DECLARE (DELX,RSDL,FF,W,T,K1,K2,K3,K4,CS,CB,VS,KW,PHC,VOLB,H,
OH,NA,DENOM,DF,H3Y,H2Y,HY,Y,AA,BB,LOGX) FLOAT DEC(14);
      GET LIST (#SETS);
      PUT LIST (#SETS);
       /* # OF TITRATION CURVES TREATED WITH ONE XEQ */
      D=0;
      DELV=0;
      DO L=1 TO #SETS;
      GET LIST (M,O,N);
      PUT LIST (M,O,N);
       /* M IS # OF UNKNOWNS, K1 K2 ETC.; O IS # OF OTHER KNOWN*/
       /*  VARIABLES; N IS # OF DATA PAIRS IN TITRATION CURVE*/
      DELX=.001;
      P=M+O;
       /* P IS SUM OF KNOWN AND UNKNOWN VARIABLES */
      DO I=1 TO P-2;
      GET LIST (V(I),SV(I));
      PUT LIST (V(I),SV(I));
       /* V(1) TO V(M) ARE FIRST GUESSES AT UNKNOWN VARIABLES*/
       /*V(M+1) TO V(M+O-2) ARE VALUES OF KNOWN OTHER VARIABLES*/
       /* EXCEPT PHC AND VB WHICH ARE READ IN IN DO LOOP BELOW*/
       /* IT IS CONVENIENT TO DEFINE THEIR MEANINGS IN THE */
       /* F PROCEDURE BELOW */
       /* SV'S ARE STANDARD DEVIATION OF VARIABLES */
      END ;
      Q=1;
GET LIST(AA,BB,LOGX,SLOPE1,SLOPE2);
PUT LIST(AA,BB,LOGX,SLOPE1,SLOPE2);
      DO I=1 TO N;
      GET LIST (VB(I),MV(I));
      PUT LIST (VB(I),MV(I));
PHA=(MV(I)-BB)/AA;
PH(I)
  =LOGX+PHA+SLOPE1*10.**(-PHA)-SLOPE2*V(8)/10.**(-PHA);
       /* SV(P-1) AND SV(P) ARE STANDARD DEVIATION OF PHC AND VB */
PUT LIST (VB(I),PH(I));
      END ;
      GET LIST (SV(P-1),SV(P));
      PUT LIST (SV(P-1),SV(P));
 LOOP: A=0;
      B=0;
      RSDL=0;
      DO J=1 TO N;
      V(P-1)=PH(J);
      V(P)=VB(J);
```

```
          FF=F;
          DO I=1 TO P;
          CALL DERIV;
          END ;
          W=0;
          DO I=M+1 TO P;
          W=W+(SV(I)*D(I))**2;
          END ;
          W=1/W;
          RSDL=RSDL+FF**2*W;
          DO I=1 TO M;
          DO II=1 TO M;
          A(I,II)=A(I,II)+D(I)*D(II)*W;
          END ;
          B(I)=B(I)+D(I)*F*W;
          END ;
          END ;
          PUT SKIP;
          PUT LIST (' SUM OF WEIGHTED SQUARES OF RESIDUALS IS',RSDL);
          CALL SMLEQ;
          DO I=1 TO M;
          V(I)=V(I)-DELV(I);
          RELV(I)=DELV(I)/V(I);
          PUT SKIP;
          PUT LIST('V(',I,') = ',V(I));
          END ;
          DO I=1 TO M;
          IF ABS(RELV(I))>.0001
     THEN GO TO LOOP;
          END ;
     OUT: DO I=1 TO M;
          PUT SKIP;
          SV(I)=SQRT(A(I,I));
          PUT LIST('STD DEV SV(',I,') = ',SV(I));
          END ;
 NEWDATA: END;
          STOP ;
   DERIV: PROCEDURE ;
          V(I)=(1-DELX)*V(I);
          D(I)=-F;
          V(I)=(1+DELX)*V(I)/(1-DELX);
          D(I)=F+D(I);
          V(I)=V(I)/(1+DELX);
          D(I)=D(I)/(DELX*V(I)*2);
          RETURN ;
          END DERIV;
   SMLEQ: PROCEDURE ;
          DO I=1 TO M;
          T=A(I,I);
          A(I,I)=1;
          DO J=1 TO M;
          A(I,J)=A(I,J)/T;
          END ;
          DO K=1 TO M;
```

```
       IF K=I
THEN   GO TO ELP3;
       T=A(K,I);
       A(K,I)=0;
       DO J=1 TO M;
       A(K,J)=A(K,J)-T*A(I,J);
       END ;
ELP3:  END ;
       END ;
       DELV=0;
       DO J=1 TO M;
       DO I=1 TO M;
       DELV(J)=DELV(J)+A(J,I)*B(I);
       END ;
       END ;
       RETURN ;
       END SMLEQ;
F:     PROCEDURE ;
        /* THE DEFINITIONS FOLLOW OF ALL VARIABLES */
        /* THE CHARGE BALANCE IS USUALLY  IN THE RETURN STATEMENT */
       K2=V(1);
       K3=V(2);
       K4=V(3);
       K1=V(4);
       CS=V(5);
       CB=V(6);
       VS=V(7);
       KW=V(8);
       PHC=V(9);
       VOLB=V(10);
       H=10**-PHC;
       OH=KW/H;
       NA=CB*VOLB/(VOLB+VS);
       DENOM=H**4+K1*H**3+K1*K2*H**2+K1*K2*K3*H+K1*K2*K3*K4;
       DF=VS/(VS+VOLB);
       H3Y=CS*DF*K1*H**3/DENOM;
       H2Y=CS*DF*K1*K2*H**2/DENOM;
       HY=CS*DF*K1*K2*K3*H/DENOM;
       Y=CS*DF*K1*K2*K3*K4/DENOM;
 RETURN(OH+H3Y+2*H2Y+3*HY+4*Y-H-NA);
       END F;
       /**/END;
```