ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

DEPARTMENT OF CHEMISTRY

Graduate Project (Chem.774)

Study of CE mechanism by cyclic voltammetry: Cd(II) + Aspartic acid system

By

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Advisor: Prof. Theodros Solomon

In Partial Fulfillment of the Requirements for Master of Science Degree in Chemistry

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Declaration

I the undersigned confirm that the results reported in this work were obtained by research carried out by me under the supervision of my advisor in the Faculty of Science, Department of Chemistry, Addis Ababa University in the academic year 2009/2010.

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This project work has been submitted for examination with my approval as University advisor.

Prof. Theodros Solomon signature _____

Submitted to: School of Graduate Studies
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Abstract

The cyclic voltammetric study of cadmium(II) -aspartic acid system at pH 8 was undertaken. Through a series of diagnostic criteria, it was shown that the cadmium(II)-aspartic acid system at pH 8 underwent a CE (chemical reaction preceding an electron transfer) mechanism. Attempt was made to extract the kinetics of the homogeneous chemical reaction by using theoretical working curves drawn for such purpose and available in the literature.

Key words: cyclic voltammetry (CV), CE mechanism, aspartic acid.

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1. INTRODUCTION

The study of a CE mechanism, in which the charge transfer reaction follows a homogeneous chemical reaction, has been reported in the literature using several chronopotentiometric techniques such as constant current chronopotentiometry [1], chronopotentiometry with programmed current [2], and alternating current chronopotentiometry [3], and with planar and conventional sized spherical electrodes, square wave voltammetric (SWV) technique at a hanging mercury drop electrode. In SWV two cases have been analyzed:[4] cadmium(II) + nitrilotriacetic acid and the cadmium(II) + aspartic acid systems. In both situations the homogeneous reaction in buffered solutions and in the presence of an excess of ligand was considered to be first order. Two types of cadmium complex are formed with aspartic acid (ASP): the 1:1 and 1:2 species with formation constants β_1 and β_2 respectively. While the dissociation of the 1:2 species is very fast, a slow step with a rate constant k_d is associated with the dissociation of the 1:1 complex.

$$Cd(II) + ASP^{2-} \rightleftharpoons CdASP$$

$$CdASP + ASP^{2-} \rightleftharpoons CdASP_2^{2-}$$

$$CdASP_2^{2-} \rightleftharpoons CdASP$$

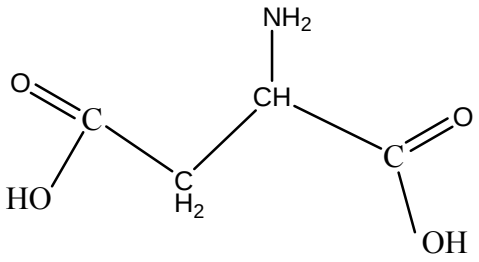
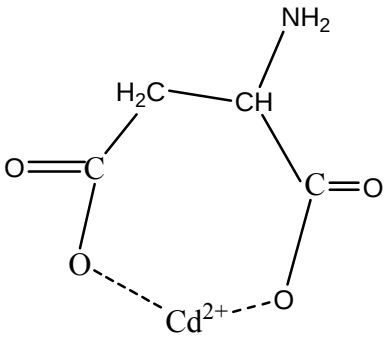
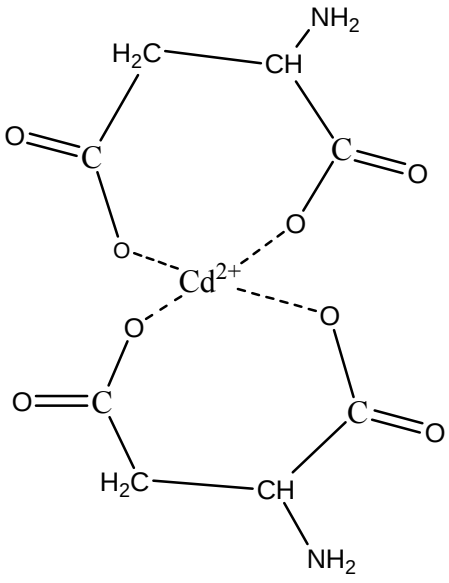
$$CdASP \underset{k_f}{\overset{k_d}{\rightleftharpoons}} Cd(II) + ASP^{2-}$$

the reduction $Cd(II) + 2e^- \longrightarrow Cd(Hg)$ being affected by the slow step (i.e. the dissociation of CdASP). The formula of aspartic acid and the possible structure of the complex are shown in scheme 1.

One of the major advantages of SWV when compared with other pulse techniques lies in its ability to achieve high effective sweep rates; this greatly reduces the time needed to measure voltammograms over a wide potential range. An additional advantage is that the shape of the reversible voltammetric response and its position on the potential scale are

almost independent of electrode geometry. This opens many important possibilities for new applications, such as the use of electrodes with ill-defined geometry and for diffusion perturbed by convection.[4] In these techniques, only one current signal is applied to the electrode. However, electrochemical techniques in which the electrical perturbation (potential or current) is applied more than once are of great interest both analytically and kinetically [5,6]

The study of this type of processes with kinetic complications can also be made by cyclic voltammetry, to characterize CE mechanism using mercury film electrode (MFE). Its use has been shown for the qualitative and quantitative study of electrode processes. From this general theory, analysis was made from the response obtained in cyclic voltammetry for a CE process and results discussed based on the influence of several variables, such as pH, the sweep rate, cathodic and anodic peak currents, peak potentials and half-peak potentials that can be used as a criterion to establish the presence of kinetic complications. The study also indicate how to obtain kinetic information of the process, and reach to conclude that cyclic voltammetry has real advantages as other techniques for the study of a CE mechanism.

Formula	Structure
$HO_2CCH_2CH(NH_2)CO_2H$ (ASP)	
CdASP (1:1 complex)	
$CdASP_2^{2-}$ (1:2 complex)	

Scheme 1 Structure and formula of aspartic acid and its complex with cadmium(II)

2. REVIEW OF RELATED LITERATURE AND OBJECTIVES

2.1 Review of related literature

Electrochemistry is the science of electron transfer across a solution-electrode interface. In electrochemical cells electron transfer occurs within the electrode-solution interface, with electron removal (oxidation) at the anode, and with electron introduction (reduction) at the cathode. The current through the solution is carried by the ions of the electrolyte, and the voltage limits are those for electron removal from an electron insertion into the solvent-electrolyte.[7]

The electrochemical reaction $Cd^{2+} + 2\ e- \rightleftarrows Cd(Hg)$ has been studied in dimethylsulfoxide containing tetraethylammonium perchlorate as a supporting electrolyte[8], using dc polarography, ac admittance measurements, cyclic voltammetry with convolution and chronoamperometry. It has been found that a chemical reaction, probably partial desolvation of the reactant, precedes the electron transfer and Cd^{2+} is reduced according to a CE mechanism.

A theoretical model of a surface electrode reaction coupled with a preceding chemical reaction (surface CE electrode mechanism) has been theoretically studied under conditions of square-wave voltammetry. The position and the shape of the theoretical voltammograms are function of the redox kinetic parameter. Theoretical methodologies for estimation of the kinetic and thermodynamic parameters of the electrode mechanism were proposed.[9]

The electrochemical behavior of catechol–boric acid complexes in aqueous solutions has been studied using cyclic voltammetry and steady-state voltammetry with a rotating disk electrode. Different patterns of reactivity and various kinetic pathways have been examined. Based on a CE mechanism, the dissociation constant and homogeneous rate constants of complex formation and dissociation were estimated for each pathway by comparing the experimental cyclic voltammograms with the digitally simulated results.[10]

The electrochemical behaviour of systems complicated by quasi-reversible electrode kinetic and preceding or following homogeneous chemical reactions under square-wave voltammetry (SWV) conditions were analysed theoretically. The results were discussed in detail, considering the influence of rate and equilibrium constants, together with experimentally controlled parameters such as f (frequency) and E_{sw} (square wave amplitude). Both kinetic stages act synergistically for the case of a CE mechanism, but the EC reaction scheme exhibits more complex behaviour, especially for reversible and quasi-reversible electrochemical reactions. These curves are characteristic for each system, providing not only the bases for their distinction but also for the extraction of kinetic and thermodynamic information.[11]

The use of square wave voltammetry (SWV) at a hanging mercury drop electrode to study a chemical reaction preceding a reversible electron transfer (CE mechanism) was reported. Two cases were analysed: cadmium(II) + nitrilotriacetic acid and the cadmium(II) + aspartic acid systems. In both situations the homogeneous reaction in buffered solutions and in the presence of an excess of ligand was considered to be first order.[4]

The cyclic voltammetric behavior for two electrochemical reaction mechanisms, the CEq (a quasi-reversible electron transfer following a preexisting chemical equilibrium) and CEqC2i, (a CEq reaction followed by an irreversible second-order reaction) were studied. To allow calculations at high homogeneous reaction rates, digital simulations with the heterogeneous equivalent (HE) approach were employed. Kinetic and diffusion control zone diagrams for both cases were presented, and the characteristic behavior in limiting regions was discussed. Working curves for analysis of the behavior in intermediate regions were also presented.[12]

The reduction of acids has been categorized according to the reaction mechanism and a variety of acids from pK_a 1.6 to 13.3 has been studied in dimethyl sulfoxide at platinum electrodes. Acids with pK_a up to ~ 5 are reduced by a CE mechanism involving prior dissociation to form the solvated proton which in turn is reduced to dihydrogen.[13]

A special CE (chemical reaction and electron transfer) process on the surface of MnO_2 nanowires modified GC electrode has been proposed and proved by cyclic voltammetry

and UV-Vis spectroscopy in the presence of p-phenylenediamine. p-Phenylenediamine can react with MnO_2 nanowires to produce diimine and the equilibrium of the two-electron and two-proton redox process of p-phenylenediamine on the electrode is changed, and consequently the reductive current is enhanced significantly[14].

The electroreduction of bivalent metal cations may proceed by a CEE mechanism with a heterogenous chemical reaction on the electrode surface. The applications of the convolutive linear sweep voltammetry and chronoamperometry to study that mechanism were presented. The behaviour of the electrochemical reactions was simulated using an implicit finite difference technique for different values of kinetic parameters. The electroreduction of metal cations on mercury electrodes often involves a complex reaction mechanism. It was suggested that the electrodeposition proceeds through an anion intermediate which is partially desolvated and adsorbed on the electrode surface. The electrochemical reactions of bi- or polyvalent cations are usually more complicated than those of monovalent cations. Different mechanisms were proposed in the literature for the electrode reduction of metal cations, e.g., simple electron transfer process, stepwise electron transfer, disproportionation or dimerization of the intermediates, adsorption, CE or CEE mechanism [15-21], and slow transport across the double layer [22], etc. Some possible mechanisms were discussed by Bongenaar *et* al. [20]. CE mechanisms have been suggested for the electroreduction of cations for which the solvent exchange is slow [15-19]. It was also proposed for the electroreduction of alkali metals in HMPA[23] where kinetically limited waves were obtained. The another works of Bongenaar *et a/.*[20] and Strujis *et al.*[21] show that the electroreduction of Cd(II) in concentrated aqueous solutions of perchlorates and fluorides involves a CEE mechanism with a heterogenous chemical reaction, probably a partial desolvation of the depolarizer at the electrode surface.[24]

The complete theory corresponding to a CE mechanism when applying cyclic chronopotentiometry to a spherical electrode of any size was developed. The influence of several variables on the transition time ratios, such as the electrode radius, rate constants of the homogeneous chemical reaction and current density, were discussed. A simple and

practical criterion based on the variation of current density applied to the electrode were proposed for the detection of a CE mechanism.[25]

2.2 Objectives of the study

The main objective of this study is to characterize chemical-electrochemical reaction mechanism (CE mechanism) using cyclic voltammetry and attempt the determination of the kinetic parameters. The second point is to compare square wave voltammetric result (from literature)[4] and cyclic voltammetric technique(in this experiment) in the study of CE mechanism in general and reduction of cadmium with aspartic acid in particular.

3. THEORY

3.1 Cyclic Voltammetry, CV

Cyclic voltammetry is one of the most reliable electrochemical approaches to elucidate the nature of electrochemical processes, and to provide insights into the nature of processes beyond the electron-transfer reaction. Several investigations have extended this method to the study of the chemical kinetics for chemical processes that precede or follow the electron-transfer process, as well as for the study of various adsorption effects that occur at the electrode surface.

The basis of voltammetry is the current-voltage relationship exhibited by an indicator electrode immersed in a solution of an electroactive species. Cyclic voltammetry (CV) is a modification of linear scan voltammetry (LSV). The CV is an electroanalytical technique which has been effectively applied for analytical, mechanistic and kinetic studies of redox reactions in a variety of situations. Applications of CV have been extended to almost every aspect of chemistry. Examples of its versatile utility for the study of electroactive species include investigation of biosynthetic reaction pathways (organic chemistry), ligand effect on metal complex potential (inorganic chemistry), enzymatic catalysis (biochemistry), solar energy conversion (materials chemistry). The effectiveness of CV results from its capability for rapidly observing the redox behavior over a wide potential range. The resulting voltammogram is analogous to a conventional spectrum in that it conveys information as a function of an energy scan.

Voltammetry is an electroanalytical method in which information about the analyte is obtained from the measurement of current as a function of applied potential. The current – potential curve obtained is termed cyclic voltammogram. For the three-electrode configuration, the potential is applied to the working electrode with respect to a reference electrode, and an auxiliary electrode is used to complete the electrical circuit. A working electrode is typically made of noble metals (platinum or gold) or carbon (i.e., glassy carbon). The auxiliary electrode usually uses a platinum wire. Two commonly used reference electrodes are Ag/AgCl electrode (E^o = 0.20 V vs. SHE) and saturated calomel electrode (SCE, E^o = 0.25 V vs. SHE). The excitation wave in CV is a linear potential scan with a triangular waveform as shown in the figure 3.1.

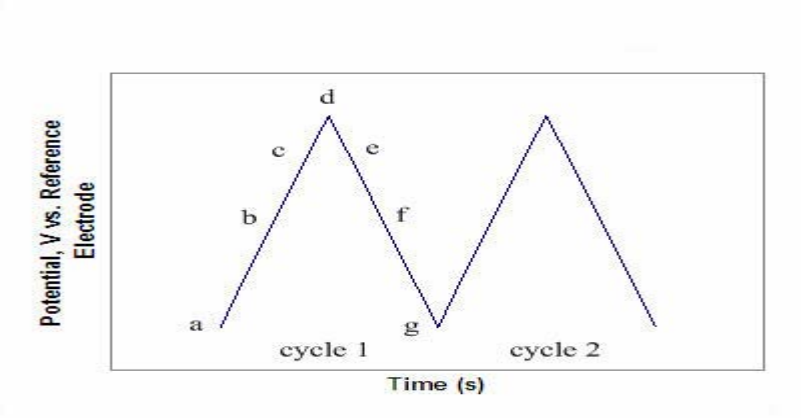


Figure 3.1 Cyclic voltammogram excitation signal

In this case the voltage is swept between two values at a fixed rate, however now when the voltage reaches "d" the scan is reversed and the voltage is swept back to "a". A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. A typical cyclic voltammogram recorded for a reversible single electrode transfer reaction is shown in figure below.

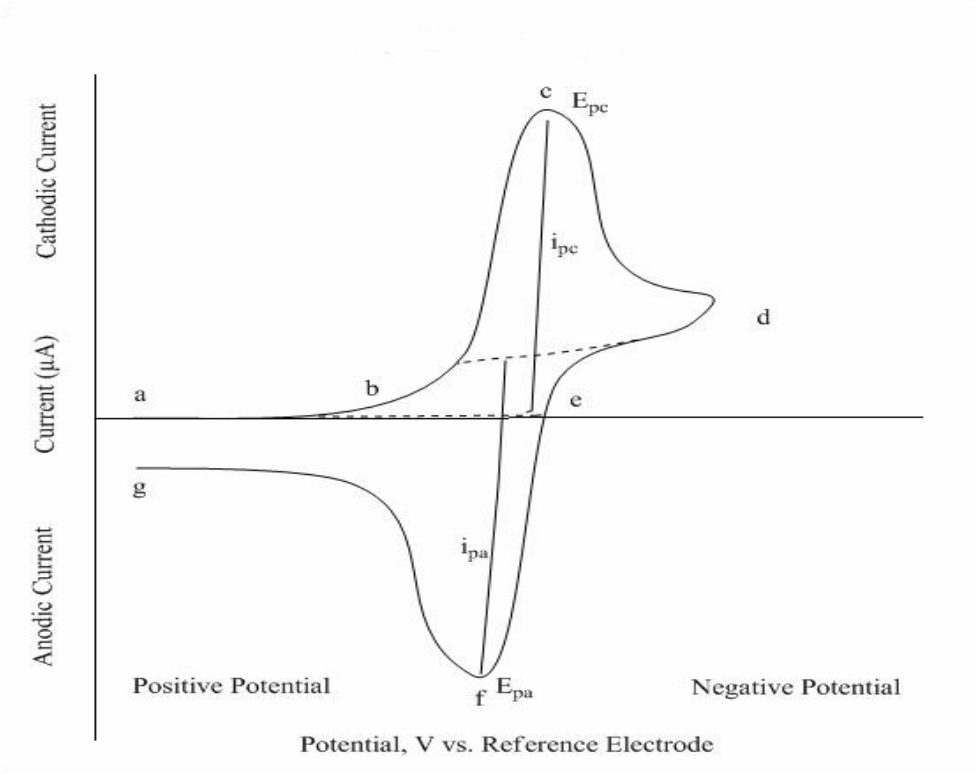


Figure 3.2 Voltammogram of a single electron oxidation-reduction

In Figure 3.2, the reduction process occurs from (a) the initial potential to (d) the switching potential. In this region the potential is scanned negatively to cause a reduction. The resulting current is called cathodic current (i_{pc}). The corresponding peak potential occurs at (c), and is called the cathodic peak potential (E_{pc}). The cathodic peak potential is reached when all of the substrate at the surface of the electrode has been reduced. After the switching potential has been reached (d), the potential scans positively from (d) to (g). This results in anodic current (I_{pa}) and oxidation to occur. The peak potential at (f) is called the anodic peak potential (E_{pa}), and is reached when all of the substrate at the surface of the electrode has been oxidized.

The forward sweep produces an identical response to that seen for the LSV experiment. When the scan is reversed we simply move back through the equilibrium positions gradually converting electrolysis product back to reactant. The current flow is now from the solution species back to the electrode and so occurs in the opposite sense to the forward sweep but otherwise the behavior can be explained in an identical manner.

The peak current for a reversible process is given by the Randles-Sevick equation:

$$i_p = (2.69 \times 10^5) n^{\frac{3}{2}} A D^{\frac{1}{2}} C v^{\frac{1}{2}}$$

Where A is the electrode surface area (cm^2)

D is the diffusion coefficient (cm^2/s),

C is the concentration of the electroactive species in the bulk solution (mol/cm^3)

ν is the scan rate (V/s).

Therefore, i_p is proportional to C and proportional to $\nu^{1/2}$. If A is known, then D can be calculated from the slopes of the linear plots described above. It is often instructive to consider the peak current ratio (peak current on the reverse scan/peak current on the forward scan) rather than the individual peak current values. For a reversible process, this ratio approaches unity; values significantly different from 1 are typically associated with chemical reactions coupled with the electron transfer.

For a reversible electrochemical reaction the CV recorded has certain well defined characteristics if the reaction is not coupled with chemical reaction.

I. The theoretical value for ΔEp for a reversible process is 0.059/n V, and it is independent of scan rate.

$$\Delta E = E_p^a - E_p^c = 59/n \text{ mV}$$

However, the measured value for a reversible process is generally higher due to uncompensated solution resistance and non-linear diffusion. Larger values of ΔEp, which increase with increasing scan rate, are characteristic of slow electron transfer kinetics.

II. The positions of peak voltage do not alter as a function of voltage scan rate. The formal redox potential ($E^{0'}$) for a reversible process is given by the mean of the peak potentials.

$$E^{o'} = (E_{pc} + E_{pa})/2$$

III. The ratio of the peak currents is equal to one

$$| i_p^a / i_p^c | = 1$$

IV. The peak currents are proportional to the square root of the scan rate

$$i_p^a \text{ and } i_p^c \quad \alpha \quad \nu^{1/2}$$

In an unstirred solution, mass transport of the analyte to the electrode surface occurs by diffusion alone.[26] Fick's Law for mass transfer diffusion relates the distance from the electrode, time, and the reactant concentration to the diffusion coefficient. During a reduction, current increases until it reaches a peak when all M^+ exposed to the surface of an electrode has been reduced to M. At this point additional M^+ to be reduced can travel by diffusion alone to the surface of the electrode, and as the concentration of M increases, the distance M^+ has to travel also increases. During this process the current which has peaked, begins to decline as smaller and smaller amounts of M^+ approach the electrode.

The influence of the voltage scan rate on the current for a reversible electron transfer can be seen below

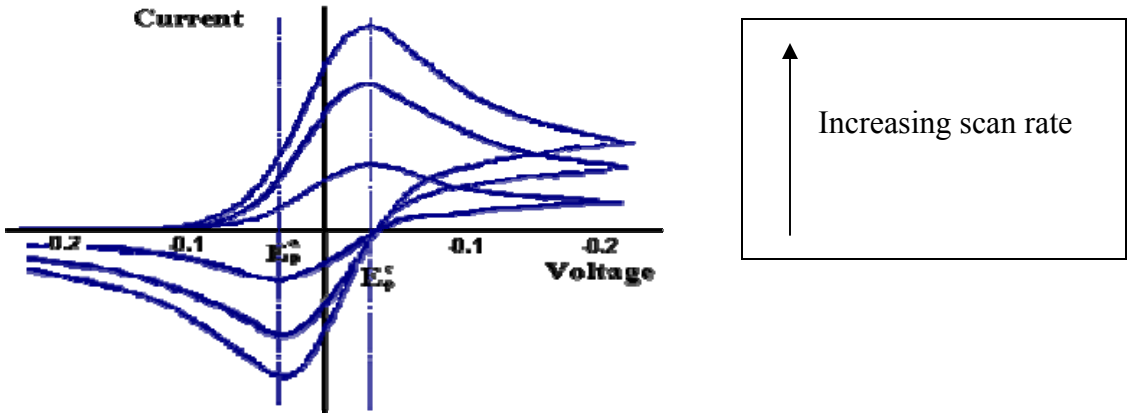


Figure 3.3 Cyclic voltammogram of a reversible electron transfer at different scan rate

The CV for cases where the electron transfer is irreversible shows considerably different behavior from their reversible counterparts. The figure below shows the voltammogram for a quasi-reversible reaction for different values of the reduction and oxidation rate constants.

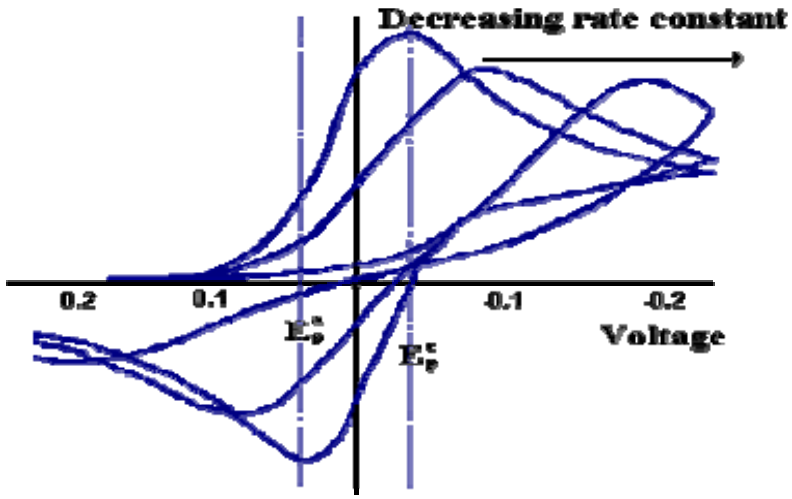


Figure 3.4 Cyclic voltammogram of quasi-reversible electron transfer at different oxidation and reduction rate constants

The first curve shows the case where both the oxidation and reduction rate constants are still fast. However, as the rate constants are lowered the curves shift to more reductive potentials. This is because equilibrium at the surface is no longer establishing rapidly. In these cases the peak separation is no longer fixed but varies as a function of the scan rate. Similarly the peak current no longer varies as a function of the square root of the scan rate. In general, cyclic voltammetry can be used to study qualitative information about electrochemical processes under various conditions, such as the presence of intermediates in oxidation-reduction reactions, the reversibility of a reaction. CV can also be used to determine the electron stoichiometry of a system, the diffusion coefficient of an analyte, and the formal reduction potential, which can be used as an identification tool. In addition, because concentration is proportional to current in a reversible, nernstian system, concentration of an unknown solution can be determined by generating a calibration curve of current vs. concentration[27, 28].

Based on the nature of CV, the following diagnostic criteria have been developed for coupled chemical reaction in general and CE mechanism in particular. Different situations are considered in which electron transfer is reversible, quasi-reversible or irreversible for the analysis of a given cyclic voltammogram[29].

Diagnostic test for electron transfer reaction process.

Reversible systems

1. $\Delta E_p = E_{pa} - E_{pc} = 59/n$ mV
2. $|E_p - E_{p/2}| = 59/n$ mV
3. $|i_{pa}/ i_{pc}| = 1$
4. $i_p \alpha \quad \nu^{1/2}$
5. E_p is independent of ν
6. at potentials beyond E_p, $i^{-2} \alpha \ t$

Quasi-reversible systems

1. $|i_p|$ increases with $\nu^{1/2}$ but is not proportional to it
2. $|i_{pa}/ i_{pc}| = 1$ provided $\alpha_C = \alpha_A = 0.5$

3. ΔE_p is greater than 59/n mV and increases with increasing ν
4. E_{pc} shifts negatively with increasing ν

Totally irreversible systems

1. No reverse peak. However, such a feature on its own does not necessarily imply an irreversible electron transfer process, but could be due to a fast following chemical reaction. Other tests must therefore be made.
2. $i_{pc} \alpha \nu^{1/2}$
3. E_{pc} shifts $-30/\alpha_C n_\alpha$ mV for each decade increase in ν
4. $|E_p - E_{p/2}| = 48/\alpha_C n_\alpha$ mV

Diagnostic test for CE mechanism

1. $i_{pc}/\nu^{1/2}$ decreases as ν increases
2. $|i_{pa}/i_{pc}|$ increases with ν

3.2 Coupled Chemical Reactions

A heterogeneous electron transfer reaction may be accompanied by a homogeneous chemical reaction. Particularly a reactive intermediate of a redox reaction is more susceptible to coupled reactions. An electrode reaction which is coupled to a homogeneous chemical reaction induces different mechanism than a simple electron transfer reaction. Cyclic voltammetry (CV) may be used to diagnose such a 'complex' reaction. For a complex reaction a variety of possibilities exist including chemical reactions preceding or following a reversible or irreversible electron transfer. Sometimes a substance is intentionally added to a solution of the electroactive substance in order to study the rate of homogeneous reaction and the nature of interaction of the original substrate. The results of CV studies are helpful in interpreting the sequence of electron transfer and chemical reactions at the interface. Mechanistic studies require a knowledge of the nature of intermediate(s) produced, effect of additive on the substrate and the speed of the reaction(s) involved. The interest in mechanism elucidation has accelerated the development of various electrochemical techniques. Moreover coupling of spectroscopic

techniques with electrochemical techniques has enabled precise monitoring of several coupled reactions.

Basically, cyclic voltammetry (CV) is widely used for the initial characterization of electrochemically active systems. In addition to indicating the number of different oxidation states, and their relative energies, CV can also be used for mechanistic studies of systems in which the electron transfer reactions are coupled to chemical reactions, due to the characteristic appearance of cyclic voltammograms associated with different mechanisms.

The theory of stationary electrode polarography for both single scan and cyclic triangular wave experiments has been extended to systems in which preceding, following, or catalytic (cyclic) chemical reactions are coupled with reversible or irreversible charge transfers. A numerical method was developed for solving the integral equations obtained from the boundary value problems, and extensive data were calculated which permit construction of stationary electrode polarograms from theory. Correlations of kinetic and experimental parameters made it possible to develop diagnostic criteria so that unknown systems can be characterized by studying the variation of peak current, half-peak potential or ratio of anodic to cathodic peak currents as a function of rate of voltage scan.

Diagnosis of coupled chemical reactions is often based on the relative heights of the anodic and cathodic peak currents. Nicholson and Shain [30] have given tables of current functions from which the peak currents can be calculated for coupled chemical reactions. With the advancement in computer technology, digital simulation has proved a very useful tool to characterize the voltammograms for selected electrochemical reactions alone or coupled to homogeneous chemical reactions.

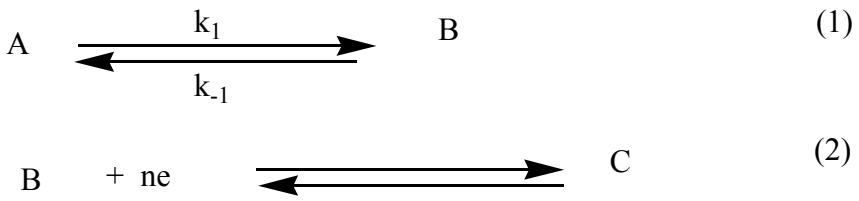
Electrochemical mechanisms are important to all redox chemistry including corrosion, redox active photochemistry including photosynthesis, other biological systems often involving electron transport chain and other forms of homogeneous and heterogeneous electron transfer. Such reactions are most often studied with standard three electrode techniques such as cyclic voltammetry (CV), chronoamperometry, and bulk electrolysis as well as more complex experiments involving rotating disk electrodes and rotating ring-

disk. In the case of photoinduced electron transfer the use of time-resolved spectroscopy is common.

3.3 CE mechanism

The nomenclature used to describe the mechanisms is based on C for a chemical reaction and E for an electron transfer reaction; for example, a CE mechanism consists of a chemical reaction (C) followed by an electron transfer reaction (E). CE reaction mechanism also could be expressed as C_rE_r, C_iE_i, C_rE_i and C_iE_r, in which "r" stands for reversible and "i" stands for irreversible process. Kinetics of some homogeneous chemical reactions can be measured by electrochemical methods because the chemical disbalance can be maintained at the electrode surface by the electro-consumption of one of the components of the system [31]. This is called a CE mechanism [6]. Some examples of the preceding reactions are the dissociation of metal complexes [32, 33], the dehydration of carbonyl compounds [34], or the deprotonation of acids [35]. The theory of CE mechanism was developed for various electrochemical methods, such as chronoamperometry,[32,35] polarography,[36] pulse polarography,[37] cyclic voltammetry,[31,38] rotating disk and square-wave voltammetry,[39,40] using a stationary planar,[40] a stationary spherical, [32,35,39] expanding plane, [41] expanding sphere [37] and cylindrical [38] diffusion models under the steady-state,[32,35] or transient conditions.[37-41] The steady-state models are based on the assumption that the difference between the equilibrium concentrations and the actual concentrations of electroinactive and electroactive forms of the reactant is independent of time. This condition is satisfied if the ratio of concentrations of electroinactive and electroactive forms is very high at equilibrium. In that case, the current depends entirely on the rate of the preceding reaction. If this rate tends to zero, the current vanishes. However, if the equilibrium ratio of concentrations of two forms of the reactant is rather small, the diffusion of electroactive form from the bulk of the solution towards the electrode surface contributes significantly to the current. Thus, the current does not vanish even if the rate of the preceding reaction is reduced to zero. This observation can be explained only by general models, in which no steady-state approximations are applied [34].

"CE" (chemical-electrochemical) mechanisms involve a chemical step preceding the electron transfer:



They are of very common occurrence in coordination electrochemistry, the preceding chemical step being a ligand exchange reaction.[42] It indeed very often happens that two forms of the electroactive complex coexist in the solution and that the minor form (B) is easier to reduce (or to oxidize) than the major form (A). Then reaction (1) will control the magnitude of the reduction (or oxidation) current at the potential where B is reduced (or oxidized). The reduction (or oxidation) wave of B is thus a function of the standard potentioal, E^o, of the B/C couple and of the equilibrium and rate constants of reaction (1). Therefore the current height, potential location and shape of the B/C reduction (or oxidation) wave contain information which can be treated to extract these rate constants. Cyclic voltammetry is a convenient technique for extracting this information from chemical-electrochemical experiments provided that the rate of the electrode electron transfer(2) does not interfere significantly in the overall electrode kinetics. This is the case when its standard rate constant is large and/or when the sweep rate is low.

For a process in reaction (1) and (2), [CE (chemical-electron-transfer) mechanism] the shape of the resulting peak depends on the chemical reaction rate. If the chemical reaction is very slow, the current is kinetically controlled, and therefore a wave instead of a peak is observed. If however, the chemical reaction is very fast, the voltammogram is that for a diffusion-controlled electron-transfer. For an intermediate condition, the concentration of the electroactive species (and the current) is partially controlled by the chemical reaction and its maximum value is lower than that for the diffusion-controlled process. Hence, for a reduction process an increase of ν causes $i_{pc}/ \nu^{1/2}$ to decrease. This

mechanism requires a system in which two species are in equilibrium, with only one species being electroactive. The appearance of the voltammograms will therefore depend upon the equilibrium constant (K) for these two species, as well as k/ν, where k is rate constant and ν is scan rate.

The behavior of this system depends on the magnitudes of both first-order rate constants, k_1 and k_{-1} (s^{-1}), and the equilibrium constant, K. It is convenient to describe the reactions in terms of dimensionless parameters related to the rate constants of the reactions (or the characteristic reaction lifetimes) and the duration of the experiment.

If first of all we consider the case where the electron transfer is reversible and where the chemical step is very slow, the current will be purely kinetically controlled (i.e. there is no component of diffusion control) and therefore no peaks will be observed on the cyclic voltammogram. Instead a simple steady state type wave will be obtained and the chemical rate constants can be obtained directly from the limiting current using the equation [29]

$$i_l = -nFC_\infty D^{1/2} K (k_1 + k_{-1})^{1/2}$$

provided the value of the equilibrium constant, K is known. At the other extreme, if the chemical reaction is very fast the cyclic voltammogram will be that for a simple diffusion controlled electron transfer. Under intermediate conditions the surface concentration of the reducible species B and hence the current, will be partially controlled by the kinetics of reaction (1) and the shape of the cyclic voltammogram, particularly that of the forward peak, will be slightly different from that for reversible behavior. The change over from purely kinetic to purely mass transport control is a complex function of the relative values of K, k_1 and k_{-1} and ν.

Theoretical cyclic voltammograms for the CE system under various conditions were obtained by Nicholson and Shain[30] who also describe how real voltammograms may be analyzed to determine rate constants. Their data are presented as a normalized current plotted as a function of potential for various values of $(K\lambda^{1/2})^{-1}$ where λ is defined by

$$\lambda = \left(\frac{k_1 + k_{-1}}{\nu}\right)\frac{RT}{nF}.$$

Thus increasing values of $(K\lambda^{1/2})^{-1}$ correspond to increasing sweep rates for any given system.

The typical cyclic voltammogram of C_rE_r is shown in figure 3.5 below for different scan rates.

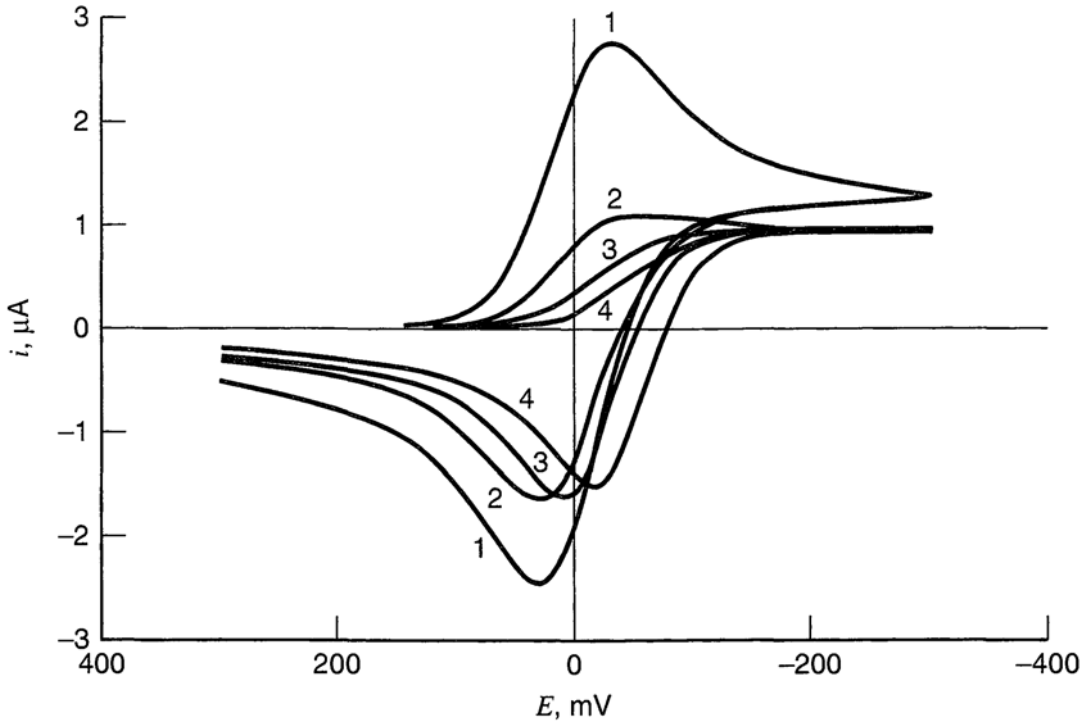


Figure 3.5 Cyclic voltammograms for the CrEr case. A ⇆ B; B + e ⇆ C, where $E^{o'}_{B/C}$ = 0.0 V C^* = 1 mM, A = 1 cm^2, $D_A = D_B = D_C = 10^{-5}cm^2/s$, $K = 10^{-3}$, $k_f = 10^{-2}$, $k_b = 10\ s^{-1}$, T = 25°C, and scan rates, v of (1) 10; (2) 1; (3) 0.1; (4) 0.01 V/s[6].

They show empirically that the ratio of the kinetic peak current, i_p^k, to the value that the current would have been, in the absence of kinetic effects, i_p^d (determined from slow sweep data), is given by[6, 29]

$$\frac{i_p^{\ k}}{i_p^{\ d}} = \frac{1}{1.02 + 0.471/K\lambda^{1/2}}$$

and figure 3.6 shows a working curve obtained from this equation. By determining i_p^k/i_p^d values for a range of sweep rates and fitting this to the working curve, $K\lambda^{1/2}$ values may be obtained from which the kinetic parameters may be determined.

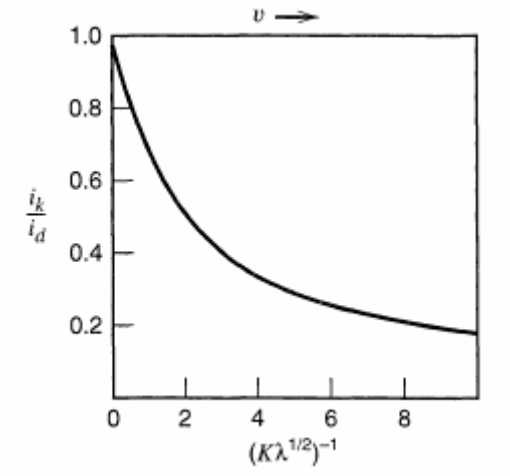


Figure 3.6 Theoretical working curve of i_k / i_d vs. $(K\lambda^{1/2})^{-1}$ for the CE reaction scheme.

The working curve applied in this experiment is the ratio of anodic to cathodic peak current versus kinetic parameter $(K\lambda^{1/2})^{-1}$ as shown in figure 3.7.

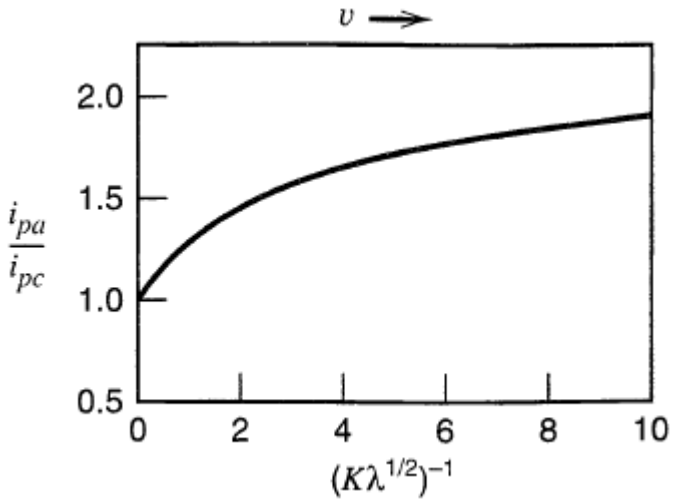


Figure 3.7 Ratio of anodic to cathodic peak currents as a function of the kinetic parameters for the CE reaction scheme [6, 30].

An alternative theoretical working curve is a plot of $E_{p/2}$ versus log ($K\lambda^{1/2}$) [6, 30], and this is shown below.

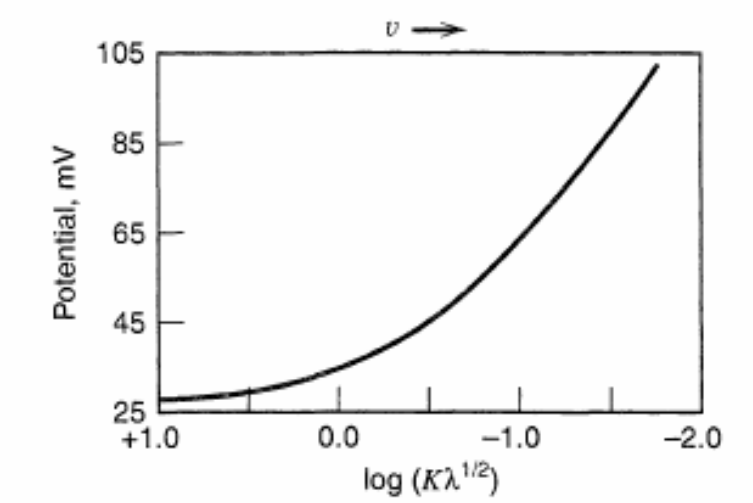


Figure 3.8 Variation of $E_{p/2}$ with $K\lambda^{1/2}$ for the C_rE_r reaction scheme. Potential axis is $n(Ep/2 - E_{1/2}) -(RT/F) ln[K/(l + K)]$. ν ⟶ shows direction of increasing scan rate.

4. EXPERIMENTAL PART

4.1 Reagents and Chemicals

The reagents and chemicals used were cadmium nitrate (Wagtech International Ltd., UK) (1.0×10^{-4} M), aspartic acid (ALDRICH, USA) (in the range of 5.0×10^{-3} to 3.0×10^{-2} M), sodium perchlorate (BDH chemicals Ltd., England) (0.7 M), mercurous nitrate (dihydrate) (BDH Laboratory Supplies, England), potassium nitrate (Fluka Chemie AG, CH-9470 Buchs, Switzerland), conc. nitric acid and borate buffer (5.0×10^{-2} M H_3BO_3 (BDH Laboratory chemical division, England) + 5.0×10^{-3} M NaOH (BDH Laboratory Supplies, England)). All solutions were prepared using deionized water.

4.2 Instrumentation

The electrochemical experiments were carried out with BAS 100A (Bioanalytical systems, USA) electroanalyzer, which was connected to a Dell computer of Pentium 4 model. This was used together with mercury film working electrode, a Ag/AgCl (3M KCl) reference electrode and a platinum wire auxiliary electrode. All cyclic voltammograms were recorded at room temperature and the solutions were deaerated with pure nitrogen for 10 min before the voltammetric runs and which was kept over the surface during the measurements. The pH of the buffer solution was measured with a Hanna digital pH 301 meter model.

4.3 Procedures

In the experiment (Cd(II) + ASP system) the medium was 0.7 M of $NaClO_4$ and the pH was adjusted as 5, 6, 7, 8, 9 and 10 with a borate buffer (5.0×10^{-2} M H_3BO_3 + 5.0×10^{-3} M NaOH). Both cadmium and aspartic acid were prepared in this medium (0.7 M of $NaClO_4$) after measuring the required mass using LA204 digital balance for the stated concentration.

A deoxygenated solution of 1.0 M KNO_3 containing 5.7 mM mercurous ion and 0.5% concentrated nitric acid was used for mercury film electrode preparation. Mercury deposition on platinum electrode was carried out by the application of a potential of 0.51 V versus Ag/AgCl (3M KCl) reference electrode. Following deposition the electrode was washed with doubly distilled water before further use [43].

5. RESULT AND DISCUSSION

5.1 The effect of pH

The pH dependence of cadmium(II)-aspartic acid complex were recorded from cyclic voltammograms of the solutions prepared in 0.7M $NaClO_4$ buffered with borate, at pH values of 5, 6, 7, 8, 9 and 10. It was noticed that pH 8 provide maximum anodic and cathodic peak currents as shown in Figure 5.1. This pH was used in subsequent studies.

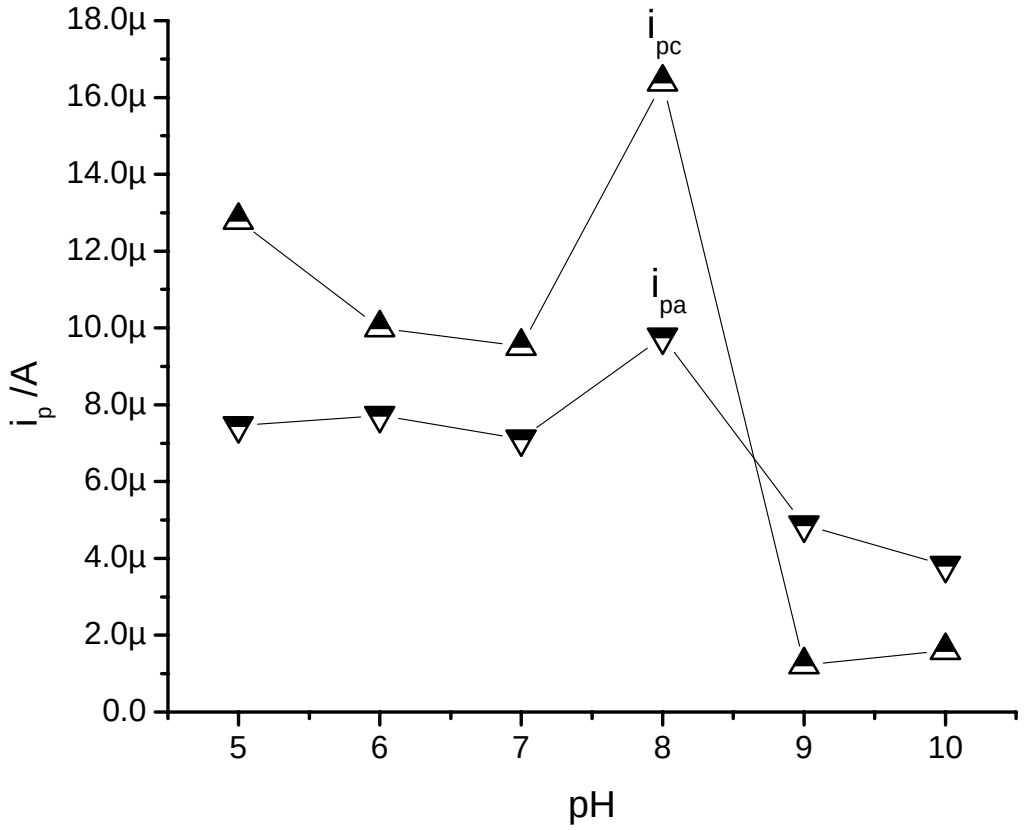


Figure 5.1 a plot of peak current versus pH of the solution at a scan rate of 1.0 Vs^{-1} for cadmium(II)-aspartic acid complex.

5.2 The effect of ligand and its concentation

When cyclic voltammogram of cadmium(II), aspartic acid and cadmium(II)-aspartic acid complex were recorded from solutions prepared in 0.7M $NaClO_4$ buffered with borate, it was noticed that, (Figure 5.2) free cadmium ion gives highest reduction peak current (a) and no wave is observed in case of aspartic acid (c). But in the complex (b) the cathodic peak current is much less than that of (a) because of the coupled chemical reaction (i.e. dissociation of the complex followed by reduction of cadmium(II)). The negative shift reduction potential is consistent with the literature result by square wave voltammetry[4].

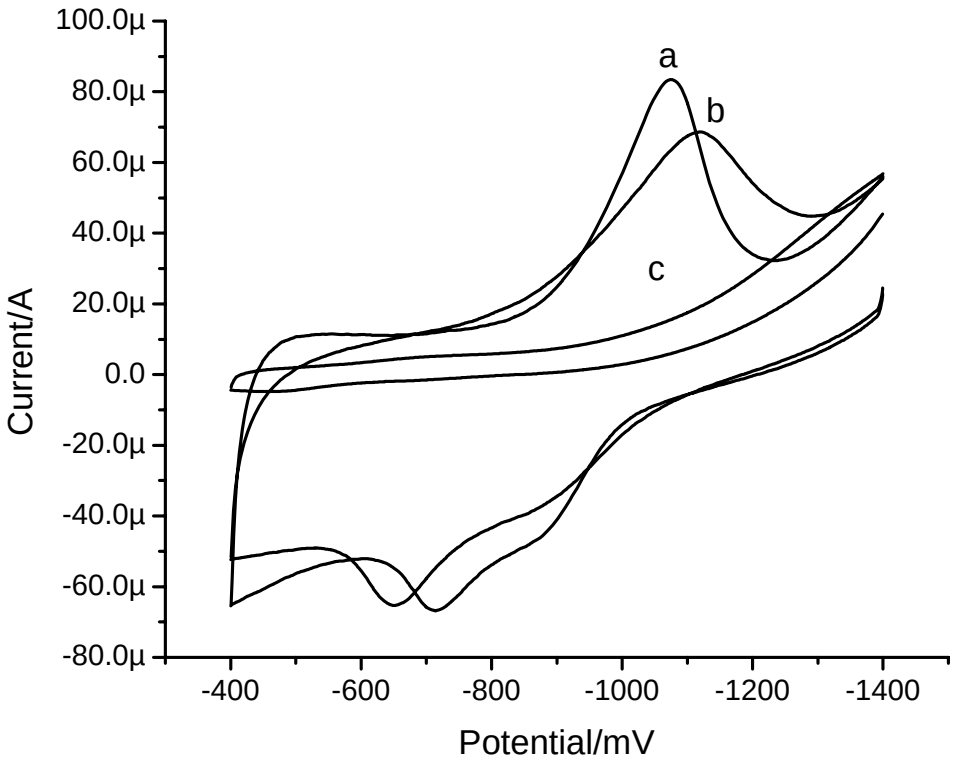


Figure 5.2 Cd(II) + ASP system: experimental cyclic voltammogram for Cd(II) reduction in 0.7M $NaClO_4$, pH=8 (borate buffer), $\nu = 1.0\ Vs^{-1}$, (a) $[Cd(II)] = 1.0x10^{-4}$ M; (b) $[Cd(II)]=1x10^{-4}$ M and $[ASP] = 1.0x10^{-2}$ M and (c) $[ASP] = 1.0x10^{-2}$ M

As can be seen in Figure 5.3, the cyclic voltammogram of $1.0x10^{-4}$ M Cd(II) reduction in 0.7M $NaClO_4$, pH = 8 (borate buffer), with different concentration of aspartic acid (5.0×10^{-3} through 3.0×10^{-2} M) at a scan rate of 100 mVs^{-1} provide the concentration effect on current peaks. As the concentration of ligand increases the peak current also increases.

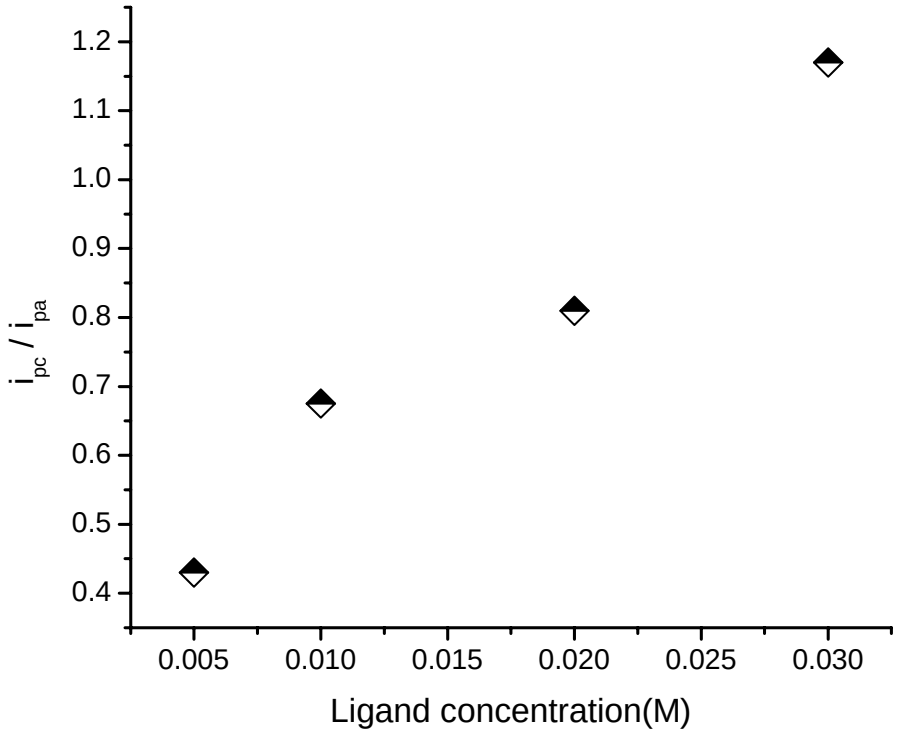


Figure 5.3 A plot of peak current ratio versus ligand concentration at scan rate of 100 mVs^{-1} with a total concentration of metal ion 1.0×10^{-4} M and aspartic acid in the range of 5.0×10^{-3} to $3.0 \times {}^{10\text{-}2}$ M.

5.3 The effect of scan rate

Figure 5.4 shows the cyclic voltammogram of $1.0x10^{-4}$ M Cd(II) reduction in 0.7M $NaClO_4$, pH = 8 (borate buffer), with different scan rate (0.1-3 Vs^{-1}) at room temperature

in the absence of ligand. Note that there is an increase of peak current with increasing scan rate.

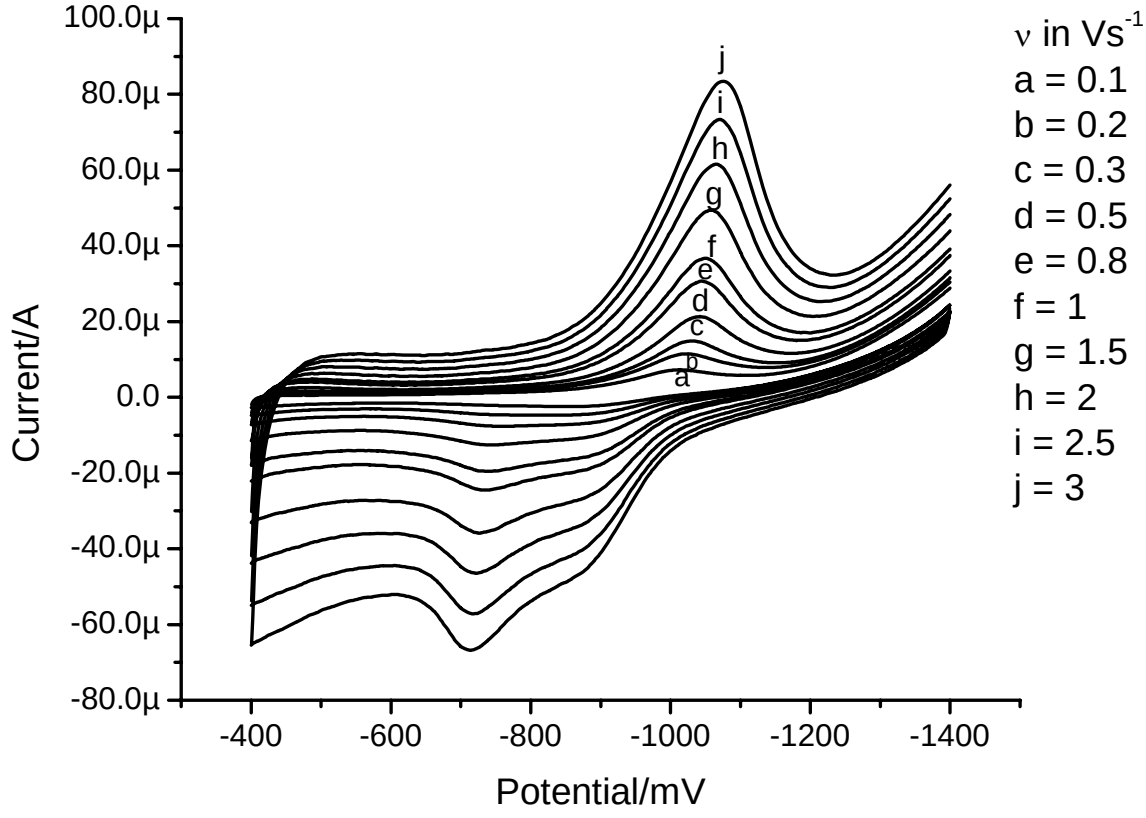


Figure 5.4 Cyclic voltammogram for 1.0×10^{-4} M Cd(II) reduction in 0.7M $NaClO_4$, pH = 8 (borate buffer), with different scan rate (0.1-3 Vs^{-1}) at room temperature in the absence of ligand.

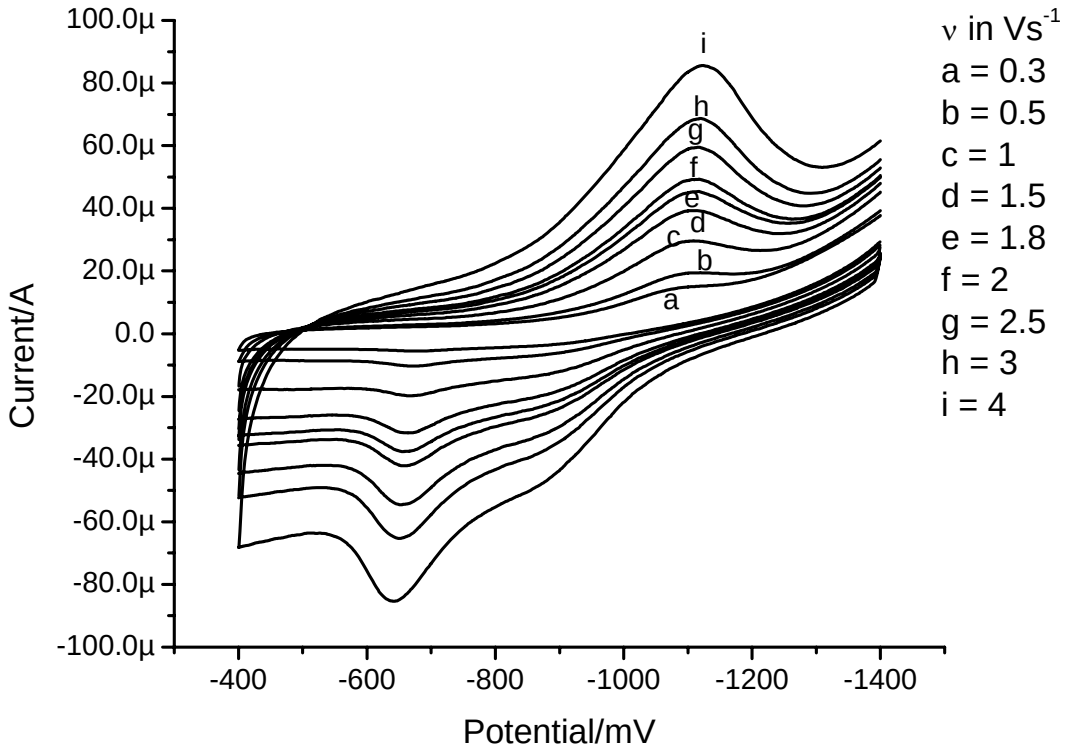


Figure 5.5 Cd(II) + ASP system: experimental cyclic voltammogram for Cd(II) reduction in 0.7M $NaClO_4$, pH=8 (borate buffer), with different scan rate (0.3-4 Vs^{-1}), Cd(II)] = $1.0x10^{-4}$ M and [ASP] = $1.0x10^{-2}$ M.

In the case of cadmium(II)-aspartic acid complex, the reduction peak is relatively less than free cadmium(see also figure 5.2) even at higher scan rate and it is observed that peak currents increase as the scan rate increases (figure 5.5).

Based on the diagnostic test for CE mechanism stated in the cyclic voltammetric technique $i_{pc}/ \nu^{1/2}$ should decrease as ν increases. This diagnostic criteria has been satisfied as shown in figure 5.6, $i_{pc}/\nu^{1/2}$ decreases significantly with an increase of the scan rate as is supposed to happen in slow preceding reactions. [30]

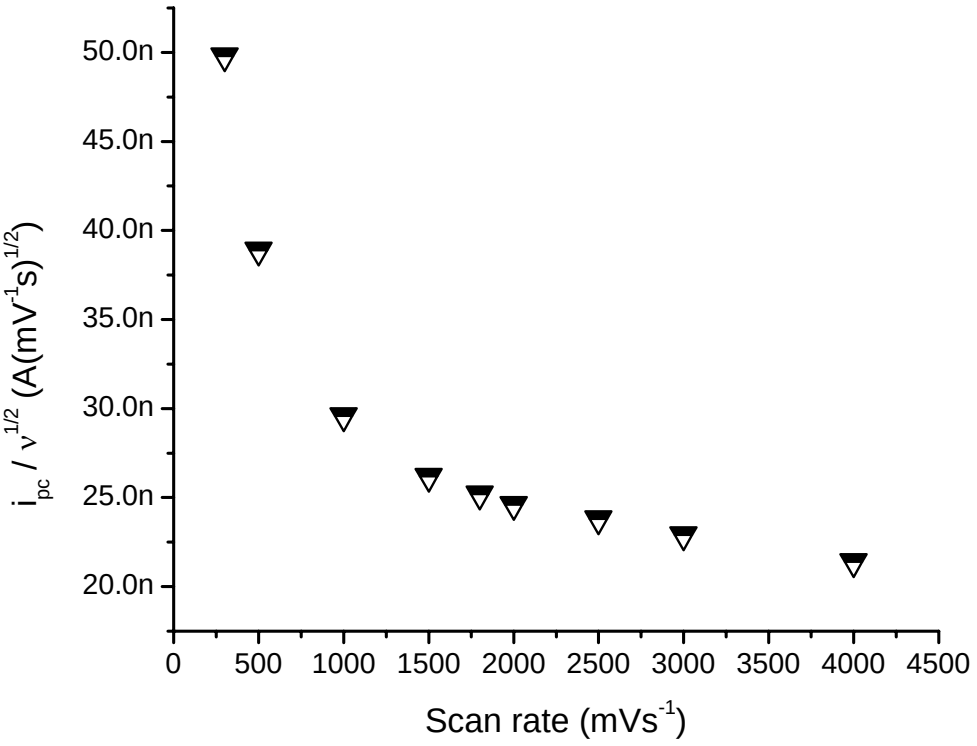


Figure 5.6 A plot of ($i_{pc}/ \nu^{1/2}$) vs. scan rate for the cadmium(II)-aspartic acid complex.

Figure 5.7 confirms the second diagnostic test for CE mechanism which explains the relationship between the ratio of anodic peak current to cathodic peak and sweep rate, i.e. $|i_{pa}/ i_{pc}|$ increases with ν.

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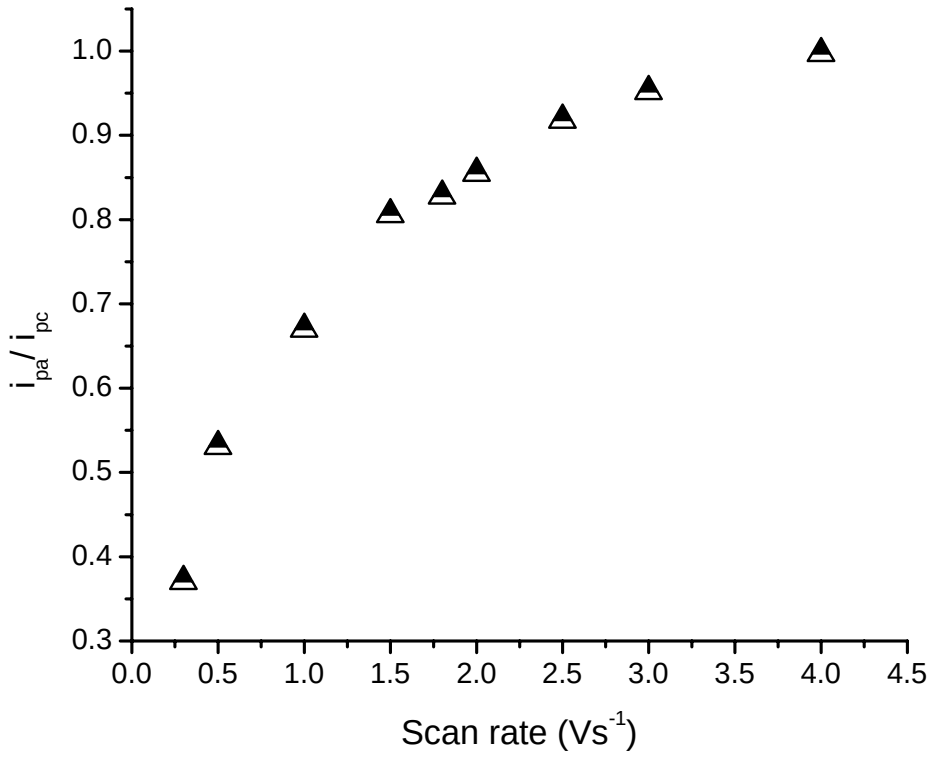

Figure 5.7 A plot of $|i_{pa}/ i_{pc}|$ vs. scan rate for the cadmium(II)-aspartic acid complex.

After once conformation of CE mechanism approved, reversibility also tested according to the criteria formulated for results obtained from cyclic voltammetry experiment. Most of the diagnostic tests for reversible charge transfer are not consistent with the result obtained in this experiment. Thus it is possible to conclude that the charge transfer of the reaction mechanism is not reversible. The other test was carried out for quasi-reversibility and figure 5.8 indicates $| i_p |$ increases with $\nu^{1/2}$ but is not proportional to it.

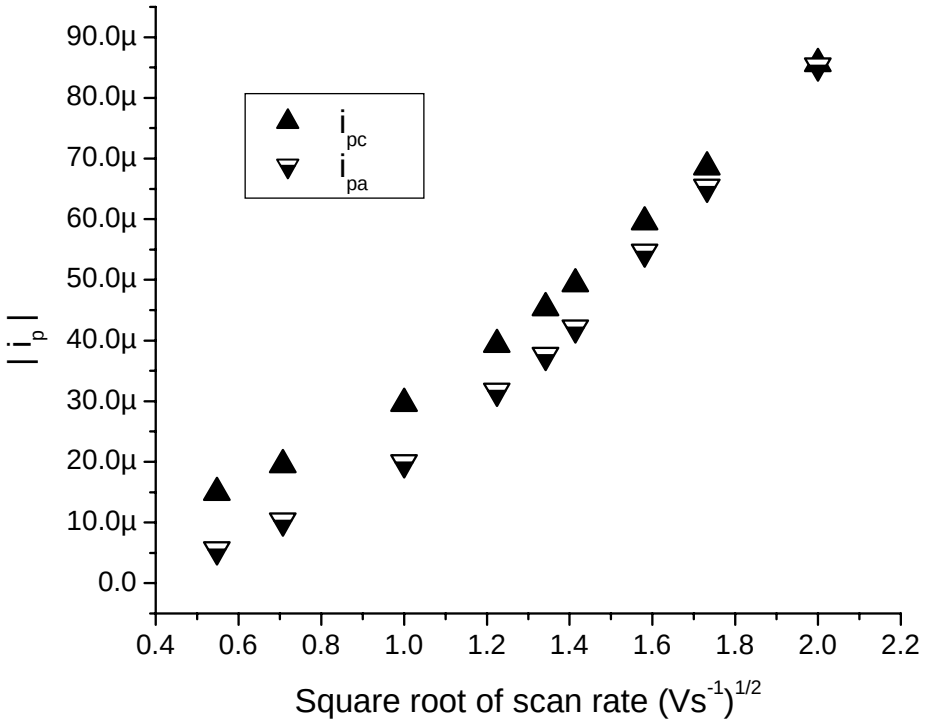

Figure 5.8 A plot of peak current vs. square root of scan rate in case of cadmium(II)-aspartic acid system.

Another tests for quasi-reversibility are the dependency of change of peak potential on scan rate, ΔE_p is greater than 59/n mV and increases with increasing ν (figure 5.9) and the negative shift of cathodic peak potential, i.e. E_{pc} shifts negatively with increasing ν (figure 5.10) are in agreement with experimental results.

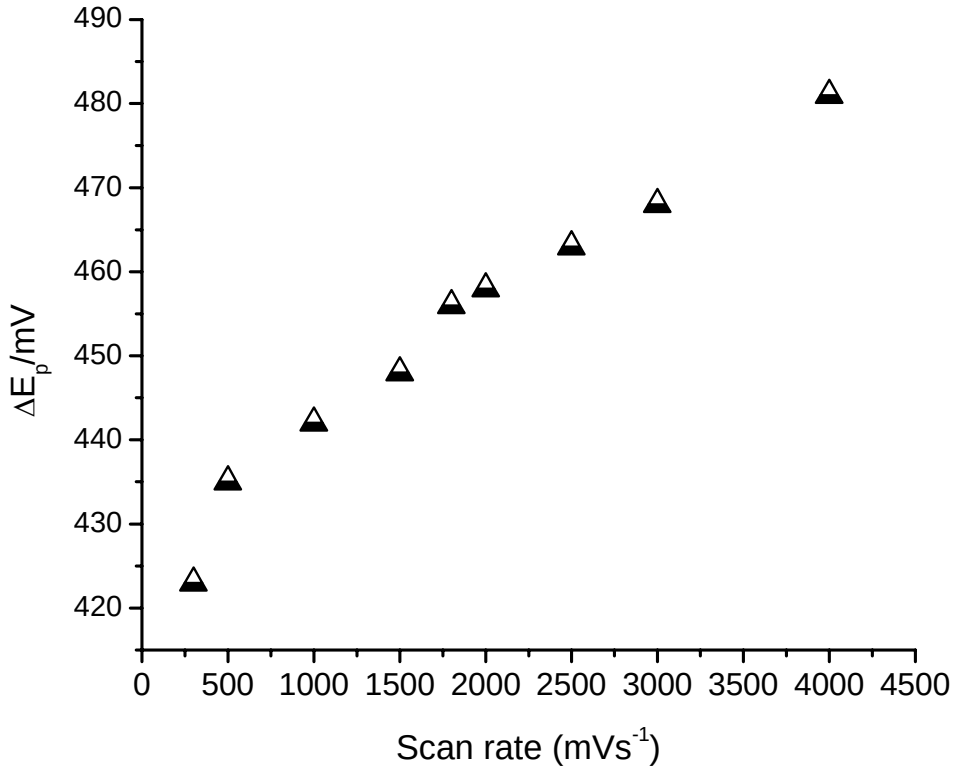

Figure 5.9 A plot of change of peak potential as a function of scan rate for the cadmium(II)-aspartic acid complex.

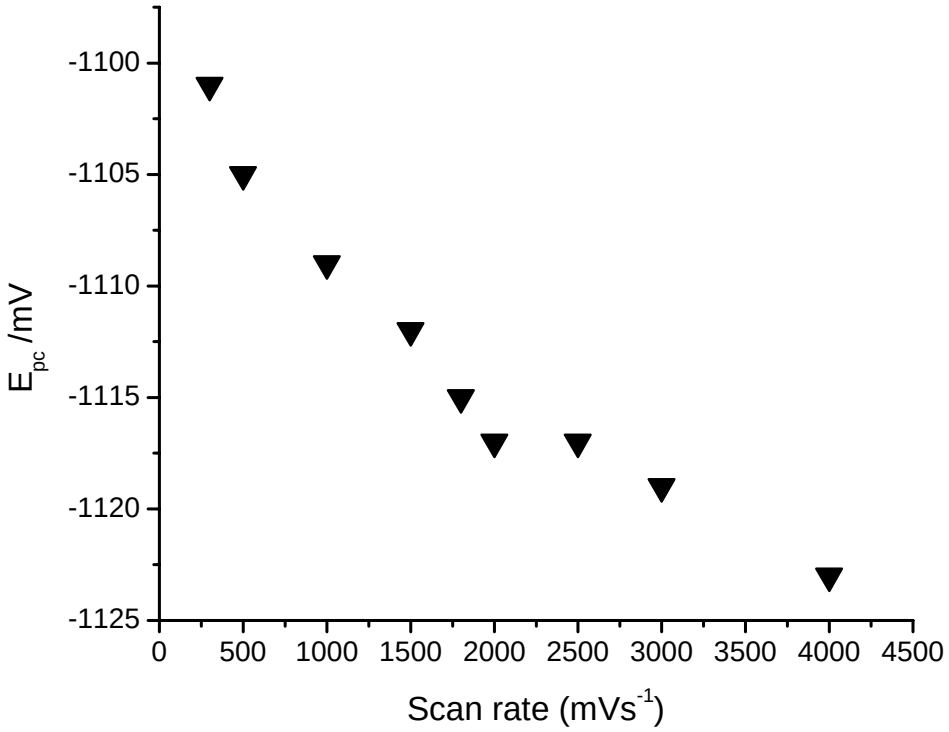

Figure 5.10 A plot of cathodic peak potential as a function of scan rate for the cadmium(II)-aspartic acid complex.

For a reversible process, $|i_{pa}/ i_{pc}| = 1$ or approaches unity; this is also true for quasi-reversible charge transfer, provided $\alpha_C = \alpha_A = 0.5$. But, values significantly different from 1 are typically associated with chemical reactions coupled with the electron transfer. Therefore, unable to fit with this test is probably the effect of preceding homogeneous reaction rate or the deviation of α value from 0.5 or the contribution of both effects.

The value of n (number of electrons) was estimated using two methods as shown in figure 5.11 and 5.12. As a result the n value was taken as approximately 2. The area of electrode used was 0.02 cm^2 and diffusion coefficient of 7.0 x 10^{-6} cm^2s^{-1} also taken from literature [44].

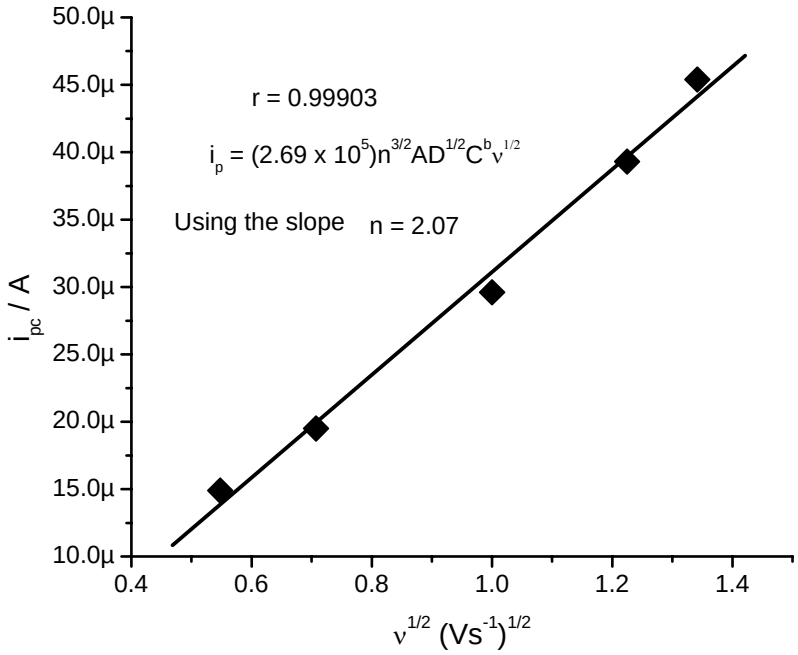

Figure 5.11 A plot of cathodic peak current as a function of square root of scan rate at relatively slow scan rate (0.1 – 0.5 Vs^{-1}).

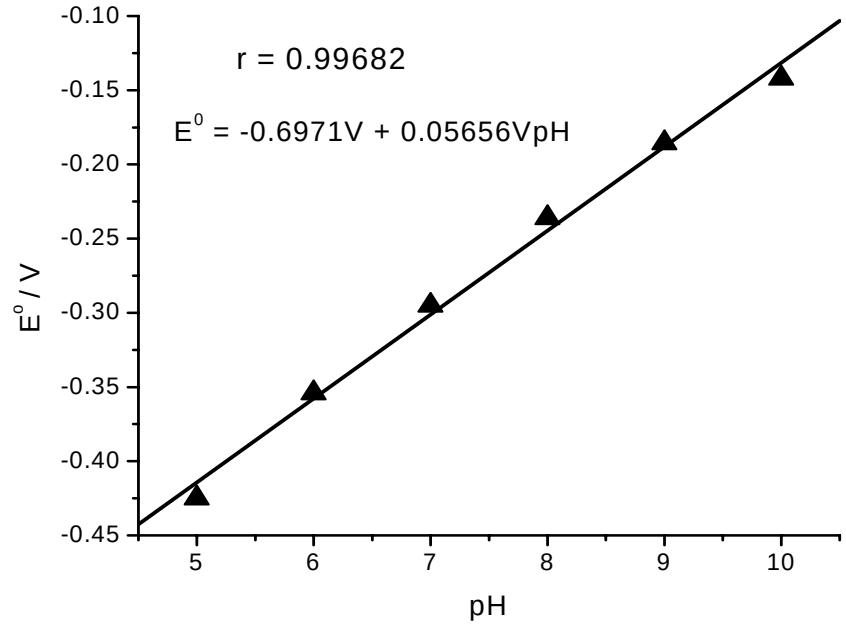

Figure 5.12 A plot of formal potential (E^o) vs. pH of cadmium(II)-aspartic acid complex.

$E^0 = -0.6971V + 0.05656VpH$

$E^0 = E^0_{pH=0} - (2.303mRT/2F)pH$ where m is number of protons = number of electron.
n = 1.913 (n ≅ 2) [45].

5. 4 Kinetics determination

According to Nicholson and Shain[30] the equilibrium constant, rate constants of dissociation and formation of the chemical reaction can be determined for the C_rE_r reaction scheme from either Figure 3.7 which is the ratio of anodic to cathodic peak currents as a function of the kinetic parameters $(K\lambda^{1/2})^{-1}$, or Figure 3.8 which is potential as a function of the kinetic parameters log $(K\lambda^{1/2})$, where potential is defined as

$$n(Ep/2 - E_{1/2}) - (RT/F)\ ln[K/(l + K)].$$

The experimental i_{pa} / i_{pc} values were however found to be lower (were all less than 1.0) than the theoretical values given in Figure 3.7, and therefore it was not possible to use it in the working curve to investigate kinetics. Nevertheless, since $(K\lambda^{1/2})^{-1}$ is equal to

$$\frac{\nu^{1/2}}{K}\left[\frac{nF}{RT(k_1 + k_{-1})}\right]^{1/2}$$

$\frac{i_{pa}}{i_{pc}}$ was plotted as a function of $\frac{\nu^{1/2}}{K}$. Figure 5.13 shows such a plot and it is seen that it has the same dependence as figure 3.7.

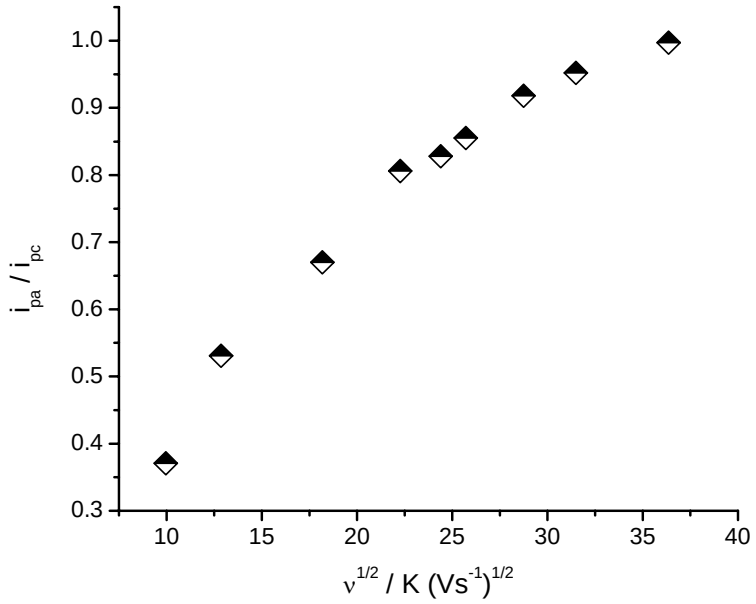

Figure 5.13 The experimental peak current ratio (i_{pa} / i_{pc}) as a function of $\frac{\nu^{1/2}}{K}$.

Similarly, it was found that the experimental potential, where potential is equal to *n(Ep/2 - $E_{1/2}$) -(RT/F) ln[K/(l + K)]* was higher (greater than 1.7V) than the potential in the working curve of Figure 3.8. Hence it was also not possible to use Figure 3.8 to determine the kinetic parameter. Nevertheless, since log ($K\lambda^{1/2}$) is equal to

$$\log\left(\frac{K}{\nu^{1/2}}\right) + \log\left[\frac{(k_1 + k_{-1})RT}{nF}\right]^{1/2}$$

the experimental potential was plotted as a function of $\log\left(\frac{K}{\nu^{1/2}}\right)$. Figure 5.14 shows such a plot, and it is seen that it has the same dependence as Figure 3.8.

Therefore, even though the trend is the same in both working curves the values are significantly different and therefore it was difficult to determine the kinetics of the reaction.

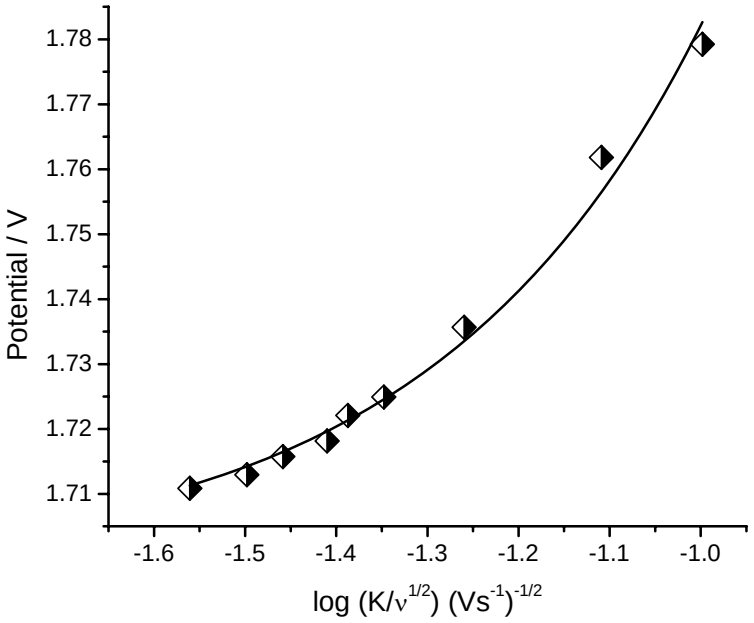

Figure 5.14 Experimental values of the variation of potential with log $(K/\nu^{1/2})$ for the C_rE_r reaction scheme. Potential axis is $n(Ep/2 - E_{1/2}) - (RT/F)\ ln[K/(l + K)]$.

6. CONCLUSION

According to the experimental results, the reduction of the cadmium(II) complex with aspartic acid has been shown to follow a CE mechanism. Various diagnostic criteria were used to arrive at this conclusion. The reduction of free cadmium exhibited higher currents than that of the corresponding complex. The complex dissociates in a slow process in a preceding reaction. In the attempt to extract kinetic parameters of the preceding homogeneous chemical reaction, the literature method [30] of using theoretical working curves was applied.

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