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# Cyclic Voltammetric studies of transition metal ion and other complexes with special reference of Cd (II) in different supporting electrolytes

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## Abstract

To determine the phases developed during metal depositing, cyclic Voltammetric analyses were performed on films of cadmium transition metal alloys. It was discovered that the deposition of cadmium involved the gradual decrease of divalent cadmium ions. It was discovered that the monovalent cadmium ion formed slowly. The film's cadmium concentration increased as a result of the anomalous cadmium alloy systems. Cadmium was seen to dissolve from the alloy. It was discovered that the dissolution took place in cadmium-rich intermediary phases.

**Keywords:** Transition metal Cyclic voltammetry, Cadmium ion, electrolytes, Concentration

## 1 Introduction

An electrochemical method for measuring the thickness of metallic coating was designed as early as 1928 and was based on the dissolving properties of plated samples. The thickness of the coating and the intermediate layer between the coating and the base metal, which often comprises of multiple phases, could be ascertained using this analytical technique. Additionally, information regarding the phase structure could be obtained. Electrons are moved via the already stated electronically conducting circuit rather than directly between atoms, ions, or molecules in electrochemical reactions. This phenomenon is what distinguishes an electrochemical reaction from a conventional chemical reaction [1]. The electrochemical process and its kinetics are most commonly estimated using cyclic voltammetry (CV), an electroanalytical technique. Generally speaking, CV studies include details on the kinetics of heterogeneous electron transfer reactions, the adsorption process, linked chemical and electrochemical events, and the redox behaviour of the electroactive materials. The deposition of metals on semiconductors encompasses a broad range of technologically important processes, with applications ranging from electronic devices to chemical sensors [2]. The Fe (II)/Fe (III) redox potentials of *N*, *N*-disubstituted *N*′-ferrocenoylthioureas and the respective ferrocene-1,1′-dicarbonic acid-di- *N*, *N*-dialkyl-thioureas are shifted cathodically by complexation of Ni (II), Cu (II), Co (III), Mn (II), Pt (II) and Pd (II) [3]. Cyclic voltammograms of iron (III) complexes indicate a reversible $Fe^{+3}/Fe^{+2}$ couple. X-ray data of [Fe $(MPz3Hex)_2$] $ClO_4 \cdot 2H_2O$ ($P_1$, triclinic) authenticate a $FeN_4S_2$ distorted octahedral coordination with the two azomethine nitrogen *trans* to each other; the pyrazolyl nitrogen and thiolate sulphur are in *cis*-positions, indicating an unusual rotation about the azomethine (C=N) double bond of the free HMPz3Hex during complexation with iron (III) [4]. The development of metal deposition processes based on electroless nickel, alloy and composite coatings on various surfaces has witnessed a surge in interest among researchers, with many recent applications made possible from many excellent properties [5].

It has been demonstrated that linear sweep voltammetry can be used as an*in situ* technique for characterization of electrodeposited thin layers of binary alloys. The anodic dissolution characteristics of linear sweep voltammograms are very sensitive to the type of electrodeposited alloy [6]. This is the first attempt by an electrochemical technique. Different electrochemical techniques such as galvanostatic [7] and potentiostatic [8–9] have been used. Cyclic Voltammetric studies were carried in mixtures of $SnSO_4$ and $ZnSO_4$ containing sodium gluconate in the *p*H range 6 to 8 at 30° and 60°C [10]. This is because surfactant can help to separate photoproducts through hydrophilic hydrophobic interaction of the micelle's interface [11]. The processes of interest may depend only on either monomer composition or on aggregate composition [12]. Cyclic voltammetry offers a convenient route towards the determination of ligand protonation/deprotonation constants and also for metal–ligand complex stability constants in aqueous media [13]. Cyclic voltammetry of iron-EDTA and iron-DETPA, in different supporting electrolytes showed electrochemical reversibility in ammonium citrate at pH 8.0, while quasi-reversible nature was noticed with iron-NTA [14]. Cyclic Voltammetric tests on Cadmium, Cadmium ion and Cadmium alloy systems that exhibit anomalous electrodeposition are described in this communication.

## 2 Experiment:

Elemental analyses, magnetic moment susceptibility, molar conductance, IR, electronic, and EPR spectral studies characterized the complexes. Electronic absorption and IR spectra of the complexes indicate octahedral geometry for chloro, nitrato, thiocyanato or acetato complexes[15]. 2,2′-((1E,1′E) -(ethane-1,2-diylbis(azanylylidiene)) bis(methanylylidene)diphenol (H2L) ligand and its Mn (II), Co (II), Pd (II) Zn (II) and Cd(II) chelates have been isolated and characterized by conventional and spectroscopic techniques including FTIR spectrum, 1HNMR , 13CNMR , powder X-ray diffraction [PXRD], UV–visible, mass spectroscopy besides elemental analyses, and magnetic susceptibility measurements [16]. The effect of nuclearity on electrochemical hydrogen generation using new heteroleptic Ni(II) complexes containing redox-active dipyrrin and dithiocarbamate ligands has been described [17].

### 2.1 INSTRUMENT

The cyclic voltammograph CV-1 made by Bioanalytical Systems Inc., West Lafayette, USA. In combination with a series 2000 digi-graphic xy/t recorder made by Digital Electronics Limited, Mumbai was used for recording all the cyclic voltammogram. The xy/t recorder had a 1/3 second pen response. The initial and final potentials were fixed with the CV-1 module. The potentials were adjusted to the desired value with the help of a digital multimeter, ZE-1501 (Zenith Electro Systems Limited). The temperature was maintained at the desired value by immersing the whole set up in a cryostat type MK-70, East Germany.

### 2.2 TYPE OF ELECTRODES

#### 2.2.1 Working Electrodes:

Hanging Mercury Drop Electrode (HMDE) was used as the working electrode.

Hanging Mercury Drop Electrode (HMDE): This electrode was obtained as a gift from Prof. Wictor Kemula, polish academy of science, Warsaw (Poland). The top most part of the electrode was made up of a round metallic cap, which could be rotated backward and forward on a circular scale. With the help of a circular scale the size of the mercury drop was maintained constant. Below it there was a mercury reservoir connected with a glass capillary. In the middle part of the electrode there was a small hole for the connecting wire. (Fig. **1).** Triply distilled mercury was used in all the experiments and a fresh drop of mercury was taken for every set of experiments.

### 2.2.2 Reference Electrode

A saturated calomel electrode (SCE) was used as a reference electrode throughout the work and all the potentials reported in this study were measured with respect to this electrode. The SCE was connected to the test solution through a potassium chloride (KCI) salt bridge.

### 2.2.3 Auxiliary Electrode

The auxiliary electrode was constructed by a pure platinum wire 11.0 cm length and 0.74 mm diameter at the low end of a soft glass tube in a spiral form. The electrode was cleaned once every day before fixing in the test solution and starting the experiments. The cleaning was done by boiling the electrode in nitric acid (for 5-10 minutes in approximately 5 M nitric acid), followed by washing and boiling with double distilled water. The spiral auxiliary electrode was always fixed in the test solution in such a manner that its position with respect to the working electrode remained the same. The electrode connections were secured by filing the electrode glass with mercury. When the electrode was not in use it was stored in triple distilled water.

## 2.3 VOLTAMMETRIC CELL

A special type of voltammetric cell, made up of corning glass was fabricated and used throughout the investigations. The cell contained the three electrodes assembly, the middle one of which was the working electrode (HMDE). The cell had two side tubes one at the upper end and the other at the lower end (Fig. 1). The lower side tube, near the bottom, was used for bubbling nitrogen into the test solution for deaeration. The upper side tube was used to maintain an inert atmosphere over the solution surface when actual current-potential curves were recorded.

## 2.4 DEOXYGENATION

Pure nitrogen gas was employed for removing dissolved oxygen from the experimental test solutions. Nitrogen is further purified by passing it through Vanadous chloride solution (Fig. 2.3). Finally, it was passed through double distilled water. Pure nitrogen was bubbled through the solution for nearly 25-30 minutes before recording the current voltage curves (underlined line).

Oxygen does not interfere when the investigations are carried out at positive potentials but regardless of this, all electrolytic solutions were deareated with nitrogen whether the studies were conducted at anodic or cathodic potentials. During the actual recording the gas stream was passed over the surface of the test solution.

## 2.5 TEMPERATURE CONTROL

All experiments were carried out at 28 ±0.5 °C by immersing the cell in a cryostat type MK-70, WEB MLW PRUF GERATE - WERK (GDR).

## 2.6 REAGENTS

All the reagents used in the present investigation of analytically pure grade solutions were prepared with double distilled water second distillation being done by alkaline permanganate. Solutions were standardized wherever necessary. The solution of Cadmium Nitrate and Zinc sulphate were prepared in double distilled water.

Mercury was purified for Voltammetric studies by treating it with dilute Nitric acid in which vigorous air bubbling was done. It was then washed thoroughly with distilled water. Finally, it was distilled three times under reduced pressure.

Various supporting electrolytes used during investigations were also of analytically pure grade and their solutions were prepared in double distilled water.

## Ligands

Ligands used during complex studies were of analytically pure grade. Glycine, N, N-dihydroxiethylglycine (Bicine) and N- [Tris(hydroxymethyl) methyl] glycine (Tricine) was obtained from Sigma Chemical Company, USA and were used without further purification.

## Characterization:

Since metal-based complexes show weak absorption bands, electrochemical methods are considered more feasible and preferable over spectroscopic methods for easy characterization [18]. Many workers studied the reduction of Cd (II) using mercury electrode. Researchers have made a kinetic study of the Cd (II)/Cd (Hg) couple in dimethyl sulphoxide. they had studied the reduction of Cadmium ion at the dropping mercury electrode in ammonical medium by potentiometric triangular pulse method. Nicholson and Perone have studied the quasi-reversible nature of Cd (II) at very fast scan rates, in 1.0 M sodium sulphate.

## 3 Result and Discussion

### 3.1 CYCLIC VOLTAMMETRY OF Cd (II) IN 0.1M $Na_2SO_4$

The concentration of Cadmium Nitrate used during the study was 1 x 103 M, 1 x 104 M and 4 x 104 M in 0.1 M Sodium Sulphate solutions. Three cyclic voltammograms of 4 x 104 M Cd (II) at scan rates 40, 80 and 120 mV/sec. have been shown in figure - 3.1 The value of Cathodic and anodic peak potentials and currents of cyclic voltammograms obtained with Cd (II) in sodium sulphate at different scan rates are given in Tables 3.1, and 3.2

**Table 3.1**
**Cyclic voltammetry of 1 x 10-3 M Cd (II) in 0.1 M sodium sulphate solution**

| Scan rate (mV/sec.) | Epe (Volts) | Epa (Volts) | ΔE (mV) | Ipe (٣٨) | Ipa (µA) | Ipa/Ipc | E (Volts) |
|---|---|---|---|---|---|---|---|
| 40 | -0.655 | -0.615 | 40 | 4.1 | 8.0 | 1.95 | -0.635 |
| 50 | -0.660 | -0.615 | 45 | 4.9 | 8.1 | 1.65 | -0.637 |
| 60 | -0.670 | -0.623 | 47 | 5.4 | 8.5 | 1.57 | -0.646 |
| 70 | -0.660 | -0.610 | 50 | 5.8 | 8.7 | 1.50 | -0.635 |
| 80 | -0.665 | -0.605 | 60 | 6.3 | 8.7 | 1.38 | -0.635 |
| 90 | -0.655 | -0.610 | 45 | 7.1 | 8.9 | 1.25 | -0.632 |
| 100 | -0.665 | -0.610 | 55 | 7.7 | 9.0 | 1.16 | -0.630 |
| 110 | -0.660 | -0.600 | 60 | 8.2 | 9.2 | 1.12 | -0.630 |
| 120 | -0.665 | -0.595 | 60 | 8.3 | 9.3 | 1.12 | -0.630 |

### Table 3.2
### Cyclic voltammetry of 1 x 104 M Cd (II) in 0.1 M sodium sulphate solution

| Scan rate (mV/sec.) | Epc (Volts) | Epa (Volts) | ΔE (mV) | Ipc (μA) | Ipa (μA | Ipa/Ipc | Er (Volts |
|---|---|---|---|---|---|---|---|
| 40 | -0.650 | -0.610 | 40 | 0.635 | 1.092 | 1.71 | -0.630 |
| 50 | -0.655 | -0.613 | 42 | 0.715 | 1.120 | 1.56 | -0.634 |
| 60 | 0.650 | -0.615 | 35 | 0.805 | 1.135 | 1.55 | -0.632 |
| 70 | 0.660 | -0.617 | 43 | 0.835 | 1.160 | 1.40 | -0.638 |
| 80 | 0.655 | -0.620 | 35 | 0.865 | 1.165 | 1.34 | -0.637 |
| 90 | 0.660 | -0.623 | 42 | 0.900 | 1.175 | 1.30 | -0.644 |
| 100 | 0.655 | -0.613 | 47 | 0.935 | 1.190 | 1.27 | -0.636 |
| 110 | 0.652 | -0.610 | 45 | 0.010 | 1.220 | 1.20 | -0.632 |
| 120 | 0.655 | -0.605 | 50 | 0.070 | 1.255 | 1.17 | -0.630 |

## Conclusion

During recent years a number of methods have been developed for the evaluation of heterogeneous rate constant (Ka), and transfer coefficient a, for an electrode reduction. Numerous studies on the reduction of Cd (II) present in different supporting electrolytes by various methods and different investigations have yielded a range of values for a and K 20-28 Bouer29 has presented an explanation for the range of values of a and Ks reported for aqueous Cd (II).

The author has made a exhaustive study of the reduction process of Cd (II) in various sodium salts as supporting electrolytes using cyclic Voltammetric techniques. The observed values of peak potentials and peak currents were used to establish the nature of the reduction process. The dependence of AE on scan rates has been noted and variation in peak height by changing the concentration of Cd (II) ions has been studied.

The reduction of Cd (II) has been studied at a hanging mercury drop electrode in different supporting electrolytes namely sodium sulphate, sodium chloride, sodium nitrate, sodium thiocyanate, sodium acetate. The scan rates were varied from 40 mV/sec. to 120 mV/sec. in all the cases the starting and returning potential were kept at - 0.2 Volts to 1.0 Volts.

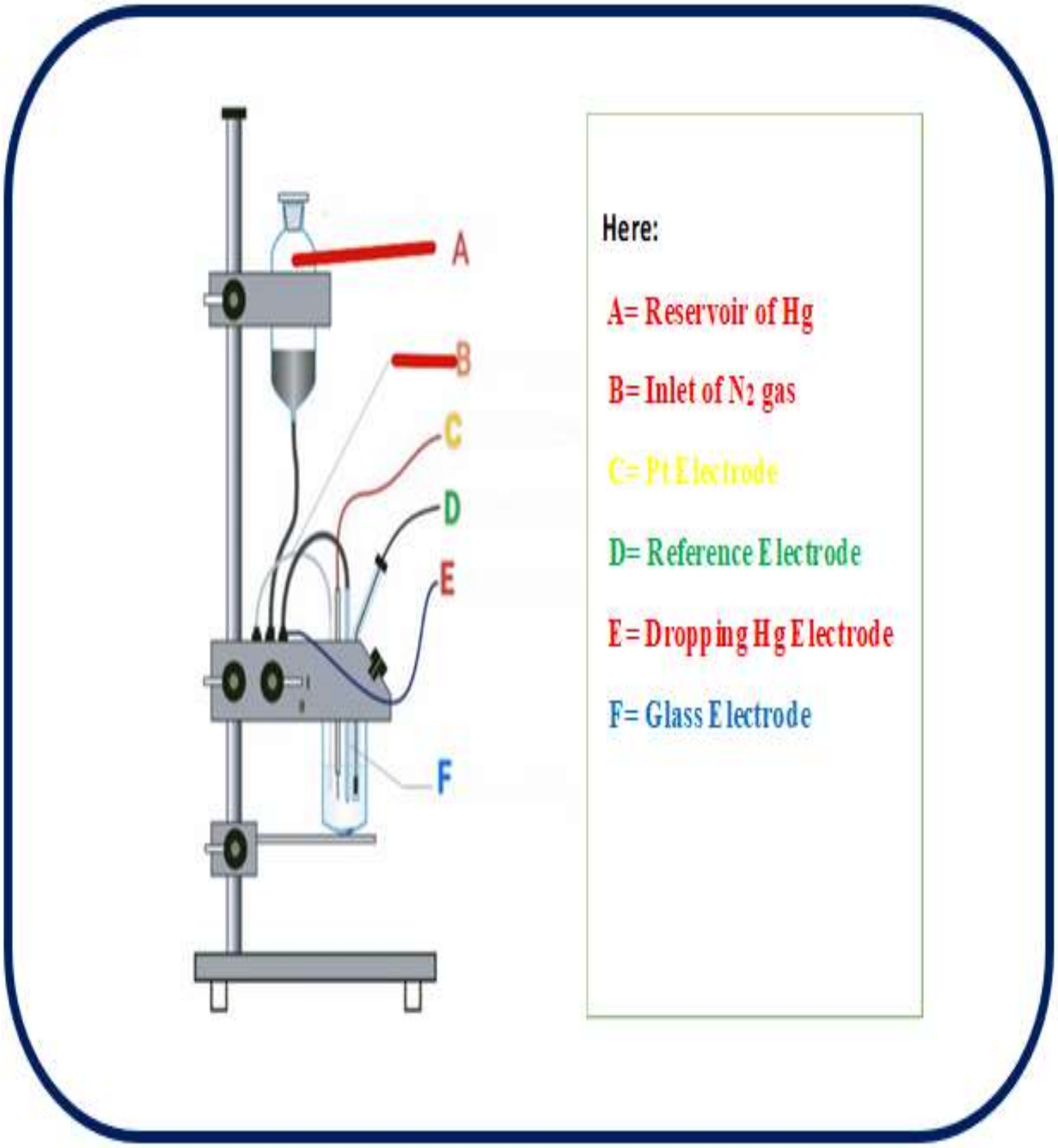

**Fig 1. Methodology set up**

**A Statement of Competing Interests:** The authors affirm that no known competing financial interests or personal ties could have influenced any of the material presented in this study.

**Data accessibility:** Both the addendum and the manuscript contain all of the material.

**Declaration of generative AI and AI-assisted technologies in the writing process**: During the preparation phase, the authors used GPT 4 to improve the language and readability of the document. The authors accepted full responsibility for the publication's content after using this tool/service, and they reviewed and made any necessary changes.

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