

Electrodeposition of Cadmium from its Different Solution Complexes

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New electrolytes for the electrodeposition of highly pure cadmium on platinum and graphite electrodes have been investigated. The deposition was carried out from the metal salt solution in presence of a complexing agent at current density ranges from 0.02 to 1.0 A dm⁻² and controlled pH (1-11). Polarographic and X-ray diffraction analyses revealed the purity of cadmium to be 99.9%. The effect of different parameters on electrodeposition was studied. The quantity and quality of the deposit metal was found to depend on the type of the complexing agent used. The baths arrange themselves according to the quality of deposit metal in the following order: tartarate > dithizone > pyrogallol > ammonium chloride = ammonium hydroxide > citrate > cyanide = dimethylformamide > pyridine = o-phenanthroline > hydrazine sulphate > methyl violet > dimethylsulfoxide > iodide > 8-hydroxyquinoline > acetylacetone > thiocyanate > dipyriddy > chloride > thiosulphate > bromide > EDTA > oxalate. A mechanism for the cadmium deposition has been proposed and discussed.

INTRODUCTION

Recently, the removal of substances from an aqueous solution has drawn increasing attention in connection with the problem of water pollution.¹ Moreover cadmium is used in dry batteries², for electroplating steel, in alkaline Cd/Ni storage batteries in pigments³, and in easily fusible alloys.⁴ It is also used as control rods in nuclear reactors⁵ and in conjunction with cadmium sulphate in the Weston cadmium cell which is used as a standard E.M.F.⁶ Very few methods have been reported for the electrodeposition of cadmium. The effect of different surfactants on the cathodic deposition of cadmium was investigated in an effort to find additives which increase the polarization of cadmium⁷. Isakova⁸ obtained fine crystals of Cd from an electrolyte containing Cd sulfosalicylate, NH₄⁺ sulfosalicylate, wetting agent and pH 7.5-8.5 at 18-20°C and cathodic c.d. 0.5-2.0 A dm⁻². The electrolytic recovery of Zn and Cd from dilute, synthetic and technical solutions was investigated by Ronald et al.⁹ The dependence of potential on time in the electrodeposition of Cd by a pulsed current was studied¹⁰. The electrochemical nucleation of Cd vitreous carbon and onto SnO₂ electrodes and the influence of the supporting electrolyte were investigated¹¹.

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The present paper is intended to establish the possibility of electro-deposition of cadmium from new baths containing the cadmium salt and some complexing agents under optimum conditions and to elucidate the mechanism of deposition.

EXPERIMENTAL PROCEDURE

Standard solution of cadmium sulphate was prepared by dissolving the required quantity of BDH grade in twice distilled water. The metal ion concentration was determined by complexometric titration in alkaline solution with Solochrome Black T indicator as described by West¹². Other solutions used were prepared by dissolving or mixing the AR material in twice distilled water or in ethanol.

The electrodeposition of cadmium was carried out with an electrolytic cell with two compartments separated by a porous diaphragm as has been described in a previous paper.¹³ The cathodic compartment was provided with a platinum sheet (2 cm²) or graphite rod (2.4 cm length; 0.3 cm radius) spectral pure provided by GMBH, type RWO, W-Germany. The anodic compartment was provided with a platinum wire (2 cm long and 0.1 mm diameter). The current regulation was achieved by using a rheostat connected in a series with a 12 V battery. The bath temperature was adjusted at room temperature, about 25°C ($\pm 0.1^\circ\text{C}$).

During the preparation of different baths, the pH was adjusted with a Tacussel Électronique (France) digital pH meter combined with a glass electrode using HCl or NaOH solution. Each bath was prepared by mixing 5 cm³ of cadmium sulphate (0.6 M), few drops of concentrated HCl or NaOH to adjust the solution to the required pH value, the appropriate quantity of the complexing agent and the total volume is made up to 25 cm³ (Table 1). The structures of some cadmium complexes formed in some baths were determined conductometrically. A silvery white, smooth and compact deposit was obtained.

Quantitative analysis of the deposited cadmium metal was done by dissolving it in 5 cm³ concentrated HCl, made up with water to 25 cm³, followed by polarographic analysis. The instrument used was a Polarecord 506 Metrohm with a dropping mercury electrode, Switzerland. The optimum parameters were: drop time, 0.4 sec; d.c. current sensitivity, 2×10^{-8} A mm⁻¹; Hg flow rate, 0.384 mg sec⁻¹ and the nitrogen gas was passed 20 min in the determined solution before each run. The Cd wave appears at -0.6 V. The solid cadmium deposit was subjected to X-ray diffraction measurements, using the method described in the literature¹⁴ (Geiger Flex D/MAX-IA, Regaku with Co K _{α} nickel filter, $\lambda = 1.790 \text{ \AA}$).

Further, the absence or presence of cadmium oxides during the deposition was confirmed by titrimetry using standard ferrous and permanganate solutions in the presence of sulphuric acid. The deposit

TABLE I
OPTIMUM CONDITIONS OF DEPOSITION OF CADMIUM FROM DIFFERENT BATHS

[Each bath was prepared by mixing 5 cm³ (0.6M) cadmium sulphate with water, the appropriate amount of the complexing agent and few drops of concentrated HCl or NaOH to adjust the pH giving a total volume of 25 cm³. The current density 0.1 A dm⁻² and the duration of cathodic deposition 10 min.]

No.	Bath	Complexing agent	pH	Complex species	Ref.
1.	Tartrate (tart)	1.0 g tartaric acid	2.5	[Cd ₂ tart] ²⁺	15,*
2.	Dithizone (DTH)	0.05 g dithizone + 5 cm ³ ethyl alc.	3.5	[CdDTH] ⁺	16
3.	Pyrogallol (Pg)	0.5 g pyrogallol	5.1	[CdPg] ²⁺	15,*
4.	Ammonium chloride	1.0 g NH ₄ Cl	5	[Cd(NH ₃) ₄] ²⁺ , [CdCl] ⁺	2,9,*
5.	Ammonium hydroxide	5 cm ³ conc. ammonia	12.5	[Cd(NH ₃) ₄] ²⁺ , [Cd ₂ (OH)] ³⁺	17
6.	Citrate (cit)	1.0 g citric acid	2.52	[Cd ₂ Cit] ⁺	15,*
7.	Cyanide	1.0 g KCN	12.3	[CdCN] ⁺	18,21,*
8.	Dimethylformide (DMF)	5 cm ³ DMF	6.4	[Cd(DMF) ₂] ²⁺	15,*
9.	Pyridine (P _y)	5 cm ³ pyridine	9.3	[Cd(P _y) ₄] ²⁺	19
10.	o-phenanthroline (o-phen)	0.01 o-phen + 2 cm ³ ethyl alc.	8	[Cd(o-phen) ₂] ²⁺	19
11.	Hydrazine sulphate (hyd)	0.5 g hydrazine sulphate	2	[Cd(hyd) ₂] ²⁺	15,*
12.	Methyl violet (MV)	0.1 g methyl violet	4.3	[Cd(MV) ₂] ⁴⁺	18
13.	Dimethylsulfoxide (DMSO)	5 cm ³ DMSO	7.5	[Cd(DMSO) ₂] ²⁺	15,*
14.	Iodide	1.0 g KI	7.7	[Cd] ⁺	17,19,21
15.	8-hydroxy quinoline (8-HQ)	0.1 g 8-HQ + 10 cm ³ ethyl alc.	4	[Cd(8-HQ)] ⁺	20,*
16.	Acetylacetone (acac)	5 cm ³ acac + 5 cm ³ ethyl alc.	4.4	[Cd(acac)] ⁺	2,15,*
17.	Thioacetate	1.0 g KCNS	5.2	[Cd(SCN)] ⁺	18,*
18.	2,2'-dipyridyl (dipy)	0.02 g dipyridyl + 5 cm ³ ethyl alc.	9.5	[Cd(dipy) ₂] ²⁺	2,19
19.	Chloride	1.0 g KCl	6.7	[CdCl] ⁺	2,19,21,*
20.	Thiosulphate	1.0 g Na ₂ S ₂ O ₃	8.2	[CdS ₂ O ₃] ²⁺	19,*
21.	Bromide	1.0 g KBr	6.2	[CdBr] ⁺	17,19
22.	EDTA	0.2 g EDTA	2.4	[Cd ₂ EDTA] ²⁺	15,*
23.	Oxalate (Ox)	0.5 g oxalic acid	2	[Cd ₂ Ox] ⁴⁺	15,*

*confirmed by the conductance measurements

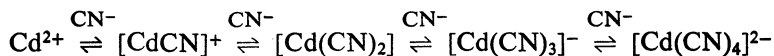
metal was dissolved in concentrated sulphuric acid and excess standard ferrous solution was added. The latter solution was titrated with standard potassium permanganate. The same volume of titrant was consumed if no cadmium oxide was deposited, while less volume of titrant was found in the presence of oxide. The results obtained was consistent with those obtained by polarographic analysis.

RESULTS AND DISCUSSION

Cathodic Deposition of Cadmium

Many experiments were carried out to determine the optimum conditions for electrodeposition of cadmium using various complexing agents and at different values of pH, current densities, ligand concentrations, metal ion concentration and temperature. The convenient parameters and baths are shown in Table 1. The results of X-ray analysis of the cadmium deposit revealed that its purity was 99.9%. Further, the chemical analysis confirmed that no oxide was deposited at the cathode.

The structure of some cadmium complexes formed have been confirmed by plotting the conductance against the amount of the complexing agent. The plots exhibited breaks corresponding to the formation of the 1 : 1 cadmium: cyanide, thiocyanate, thiosulphate, acetylacetone and chloride. Cotton and Wilkinson¹⁷ have also proved the stepwise formation of cadmium cyano-complexes as follows:



Similarly it is possible for cadmium chloride, bromide, iodide, thiocyanate and ammonium complexes to be formed.

Moreover, breaks corresponding to the formation of the 2 : 1 cadmium tartarate, citrate, EDTA and oxalate complexes were formed. The structure of other cadmium ion complexes in Table 1, have been studied earlier^{2, 15-21}.

The effect of complexing agent/metal ion ratio

The effect of complexing agent/metal ion ratio on the deposition of cadmium has been investigated. It was observed that in the absence of the complexing agent cadmium is deposited in very thin layer and noncoherent form. Small quantities of cadmium metal were deposited at a very low concentration (<4 g/litre) of the complexing agent (e.g. tartarate). The amount of the metal deposited increases at a certain concentration limit of the ligand (4-14 g/litre). Maximum deposition was obtained at 8-14 g/litre of the ligand. When the ligand concentration was increased beyond 14 g/litre up to 160 g/litre, the quantity of cadmium deposited decreased. This effect of ligand concentration may be attributed to the change of the positive

charge of complex to negative value at a high concentration of the ligand. The yield of the element deposited increased very slowly with increase in cadmium concentration from 0.02 to 0.3M, after which a noncoherent deposit was formed. The optimum concentration for the deposition of cadmium was 0.12M.

Effect of pH

Cadmium deposition was studied in the pH range (1–10.8). Figure 1 shows the yield of deposited cadmium (mg) as a function of pH for the baths tartarate, ammonium chloride and DMSO. As may be seen, the amount of Cd deposited increases with pH reaches a maximum in the pH range 2.5–4 for taratarate, 5–7 for ammonium chloride and 6–7.5 for DMSO and again decreases. No deposition of cadmium occurred below pH 1. This may be attributed to the attack of the element by hydrogen ions and the resulting dissolution of cadmium at this pH. Although, the deposition of cadmium decreases sharply at pH above 8, which may be attributed to the formation of cadmium hydroxide²⁰, some baths give maximum deposition at higher pH's. This may due to the stability of the metal complexes formed than the metal hydroxide.

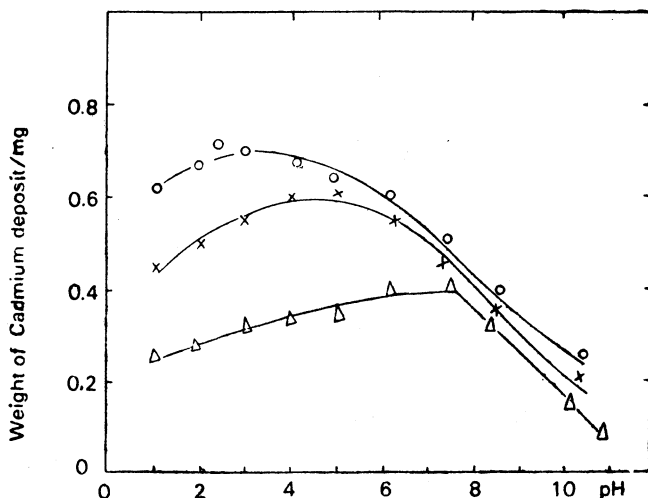


Fig. 1 Effect of pH on the yield of Cd deposit using tartrate (O), ammonium chloride (x) and DMSO (Δ) baths.

Effect of current density

At a current density of 0.02 A dm^{-2} , a very thin film of cadmium was deposited, due to the low rate of the cathodic reduction occurring at the cathode. The optimum current density was found to be $0.05\text{--}0.20 \text{ A dm}^{-2}$. At higher current densities, more than 1 A dm^{-2} , a nonadherent silvery

white randomly-oriented deposit of cadmium was obtained over platinum and graphite surfaces.

The mass of deposited cadmium was varied from 0.05 to 5.8 mg according to the current density 0.05-0.20 A dm⁻². The maximum current efficiency was found to be 98.67, 89.6 and 82.50% with tartarate, ammonia solution, and DMSO respectively using Pt electrode, while it was found to be 44.92% with tartarate bath using graphite electrode (Table 2). Using

TABLE 2
EFFECT OF CURRENT DENSITY ON THE ELECTRODEPOSITION OF
CADMIUM FROM CADMIUM SULPHATE USING DIFFERENT BATHS
[Duration time 10 min. and the deposit mass ranges from 0.05 to 5.8 mg]

Current density, A dm ⁻²	Current efficiency, %, *			
	Pt electrode		Graphite electrode	
	Tartarate	Ammonia solution	DMSO	Tartarate
0.02	98.67†	89.60†	—	—
0.03	89.80	87.50	82.50†	44.92†
0.05	75.14	68.80	68.60	—
0.10	71.55	63.20	35.55	24.92
0.20	63.54	48.90	26.70	19.26
0.25	59.40	40.90	20.85	14.60
0.50	53.55	30.60	18.20	9.90
0.75	41.64	28.20	14.50	2.90
1.00	—	25.10	—	—

*Calculated from the weight of the metal in g using Faraday's equation²² and the mass of deposited cadmium (experimentally) in g.

†Maximum current efficiency.

the Pt electrode, the minimum value (14.50%) was attained at a current density of 0.75 A dm⁻². Two factors are probably responsible for the lower value of the current efficiency: (i) the use of a platinum plate substrate possibility leads to a lower current efficiency than that obtained using the ring disc electrode or platinum gauze for analytical purposes²³. Using the graphite electrode, the minimum value 2.90% obtained at a current density of 0.75 A dm⁻². In addition to the two factors mentioned above the metallic properties of the cathode plays an important role in the deposition process.

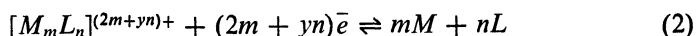
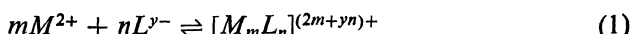
Effect of temperature

Increasing the temperature of the bath from 25°C to 70°C favours the deposition of the metal and its yield. This due to the acceleration of both

the ionic migration of complex species and assisting deposition due to the non-evolution of the H_2 gas, i.e. it increases the hydrogen overvoltage and protects the metal from oxidation²⁴.

Mechanism of cadmium deposition

It is concluded that the deposition of cadmium proceeds at first by the formation of the corresponding positive complex species (from the complexing agent and cadmium ions) followed by migration to the cathode. This is followed by the discharge of these species and dissociation to yield the metal on the surface of the cathode. The suggested mechanism for the deposition of cadmium can be summarized as follows:



where M^{2+} is cadmium ion; m , the number of moles of metal ion; n , the number of moles of ligand; and y , charge of the ligand (0, -1, -2 and -3). Adsorption of the ligand at the cathode surface prevents cadmium oxidation giving smooth coherent film of deposited metal.

The baths arrange themselves according to the greater yield of cadmium deposited as follows: tartarate > dithizone > pyrogallol > ammonium chloride = ammonium hydroxide > citrate > cyanide = DMF > pyridine = o-phenanthroline > hydrazine sulphate > methyl violet > DMSO > iodide > 8-hydroxyquinoline > acetylacetone > thiocyanate > dipyridyl > chloride > thiosulphate > bromide > EDTA > oxalate.

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JAVED HUSAIN PRIZE

Dr. D. D. Sarma working in the Solid State and Structural Chemistry Unit of the Indian Institute of Science, Bangalore, has won the 1989 Javed Husain Prize for Young Scientists awarded by UNESCO. He shares the prize with Dr. Gaumo-Avarez of Spain.