Polarography of Cadmium and Palladium Using Allyl Amine as a Complexing Agent

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The polarographic behaviour of Cd(II) and Pd(II) in allyl amine has been studied. In both the cases the reductions were found to be diffusion controlled, but the reduction was reversible in the case of cadmium while it was irreversible with Palladium. The composition and formation constant of the cadmium complexes were calculated by Deford and Hume method. The forward rate constant $k^{\circ}_{f,h}$ and the nα transfer coefficient were calculated in the case of palladium. The diffusion current constants were calculated to be 3 20 for cadmium and 4.19 for palladium. Based on the constancy of these values over a wide range of concentrations, methods have been given for the determination of these metal ions in pure solutions, synthetic samples and certain alloys.

Bjerrum, Schwarzenbach and Sillen (1) compiled the stability constants of metal ion complexes of amines. The ligands containing nitrogen as the coordinating atom are of particular interest since they provide more stable bonds than the oxygen containing ligands and some of them are specific and selective. The most important organic reagents are Pyridine (2); monoethanolamine (3); glycine (4) and ethylenediamine (5). Recently a systematic study of various metal ions was undertaken by Kumar (6) with polyethylene polyamines. Rao and Gupta (7) have reported the use of pentaethylene hexamine as a supporting electrolyte for the polarographic determination of metal ions. The present paper describes the polarographic behaviour of Cd (II) and Pd (II) using allyl amine as the complexing agent.

EXPERIMENTAL

SOLUTIONS

All the chemicals used were of analytical grade and the stock solution were prepared in double distilled water. Ionic strength was maintained constant using KNO_3.

APPARATUS AND PROCEDURE

A Toshniwal digital polarograph was used for obtaining the current voltage curves. The capillary parameters were m = 3.5 mg/sec., and t = 2.6 sec. in distilled water and in open circuit. A saturated calomel electrode connected to the cell through agar-KCl bridge was used as a reference electrode. All pH measurements were made on a Phillips pH meter and experiments were conducted at 25 ± 0.1°C. Triton-X 100 was used as maximum suppressor. Purified nitrogen was used for deaeration. The number of electrons (n) involved in the reduction process was determined by the method of De Vries and Kroon(8) which gave the value of n equal to 2 with both the metals.

RESULTS AND DISCUSSION

EFFECT OF pH

The effect of pH on the polarograms of Cd II and Pd II in solution containing 0.4 M allyl amine was studied and it was observed that better results are obtained in the pH ranges of 8.0 - 8.5 for Cd (II) and 8.5 - 9.2 for Pd (II).

EFFECT OF MERCURY PRESSURE

Polarograms for the metal amine solution at various heights of the mercury column were recorded with both the metal ions. The linear dependency of the limiting current on the square root of the height of the mercury column indicates that the reductions are diffusion controlled.

EFFECT OF ALLYL AMINE CONCENTRATION

The variation of allyl amine concentration from 0.1 to 1.0 M has no effect on the shape of the cadmium polarograms. But the $E_{1/2}$ shifts to more potentials showing the complex formation of the metal ion with the amine The plot of log [i/(i -i)] vs.E in the case of cadmium results in a straight line with a slope of the order of 30 + 2 mV indicating that the electrode process is reversible. The plot of $E_{1/2}$(vs) log [amine] is a smooth curve showing the formation of more than one complex. The composition and the formation constant of the different complexes are calculated by Deford and Hume's method(9). The values of the stability constants of Cd (allylamine) and Cd $(allylamine)_2$ are found to be 9.2 and 12.5. The percentage distribution of Cd (II) and its complexes has been calculated and given in Fig.1

The plot in the case of Palladium showed that the reduction is irreversible. Hence the kinetic parameters $k_{f,h}$ and αn_a have been calculated using Kouteckv's treatment as extended by Meites and Israel (10). The results are given in Table 1. The values of the rate constants indicate that the cathodic depolarization of the Pd-allyl amine system proceeds in an irreversible manner.

EFFECT OF THE METAL ION CONCENTRATION

The metal ions gave well defined waves in 0.1 M allyl amine. The diffusion current constant (I) calculated under these conditions using the Ilkovic equation were 3.2 for cadmium and 4.19 for Palladium and were constant over a range of concentration (1.0 to 2.8 mM for Cd and 1.0 to 3.0 mM for Pd). Therefore the polarographic results can be used for the quantitative determination of these ions.

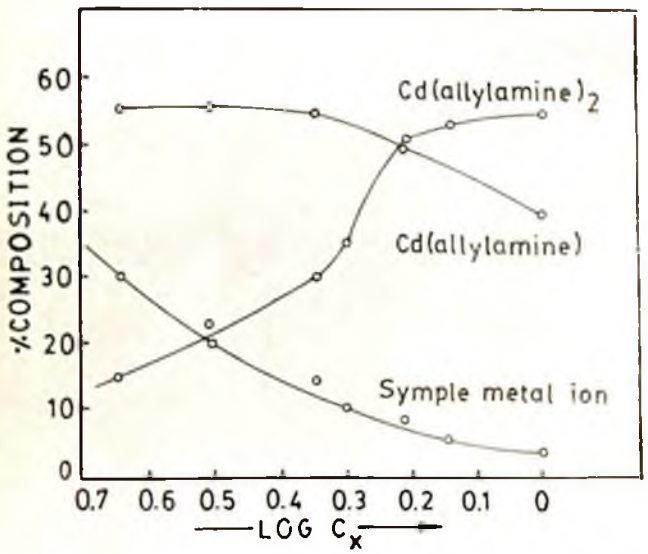


Fig.1 Distribution of Complexes in Cd (11) allylamine system

TABLE 1

POLAROGRAPHIC DATA FOR PALLADIUM-AMINE SYSTEM

Palladium = 0.8 mM ; μ = 0.1 m KNO_3 ; pH = 9.0

amine (M)	i_d (μa)	$E_{1/2}$ mV	$D_0^{1/2} \times 10^3$ (cm.sec$^{-1/2}$)	slope (mV)	αn	$k^\circ_{f,h} \times 10^{-6}$ (cm.sec)
0.1	8.74	850	2.873	125	0.434	4.0
0.2	8.20	855	2.695	117	0.463	2.4
0.4	7.65	880	2.514	150	0.361	8.1
0.5	7.60	886	2.498	160	0.339	10.9
0.6	7.44	890	2.445	148	0.366	6.6
1.0	7.13	900	2.343	165	0.340	8.9

GENERAL PROCEDURE FOR THE DETERMINATION OF CADMIUM/PALLADIUM

Different concentrations of the metal solution was taken to which allyl amine (0.1 M) and Triton-X (0.005%) were added. The pH was adjusted to 8.5 and the polarograms were drawn. The calibration plots were prepared. The amount of the metal in the unknown solution was determined by recording the polarogram under similar conditions and referring the i_d obtained to the calibration curve. Some typical results are given in Tables 2 The method may be extended for the analysis of various synthetic samples and alloys The results of the analysis of some Pd alloys are given in Table 3.

EFFECT OF DIVERSE IONS

The effect of various ions at fixed concentration of the metal ion (Cd or Pd) were ascertained. Anions like nitrate, acetate, sulphate, salicylate have no effect on the $E_{1/2}$. Co,Ni,Pb and Zn did not interfere with these ions. Alkaline earth metal ions and Mg also did not interfere.

TABLE 2

DETERMINATION OF CADMIUM AND PALLADIUM
ALLYLAMINE 0.1M; pH 8.5; SENSITIVITY 1/20

S.No.	Amount of metal taken (mg)	Found (mg)	Error %
Cadmium			
1.	1.124	1.120	- 0.35
2.	2.248	2.240	- 0.36
3.	3.372	3.384	0.36
4.	4.496	4.490	- 0.15
5.	5.620	5.630	0.02
Palladium			
1.	0.968	0.970	0.20
2.	1.452	1.450	- 0.14
3.	1.936	1.940	0.20
4.	2.420	2.415	- 0.21
5.	2.904	2.900	- 0.14

TABLE 3

DETERMINATION OF PALLADIUM IN ALLOYS

Alloy	Certificate composition	Amount of Palladium taken (mg)	found (mg)	Avarage (mg)	Error %
Oakay	Pd-10.5; Pt-20.0. Ni-60.0; V -9.5.	2.625	2.621 2.620 2.625 2.615 2.622	2.621	-0.15

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