

# POLAROGRAPHIC BEHAVIOUR OF METALLIC COMPLEXES WITH PYROPHOSPHATE

## Part II. Lead and Cadmium

BY R. S. SUBRAHMANYA

(Department of General Chemistry, Indian Institute of Science, Bangalore-3)

Received April 30, 1956

### SUMMARY

1. The polarographic behaviour of lead and cadmium pyrophosphate complexes has been studied at various pH values.
2. The phenomenon of split-wave is quite marked in the case of cadmium and totally absent in lead.
3. The reduction process is irreversible with lead complexes above pH 7 and below pH 7 the process becomes progressively more reversible. The reduction of cadmium complexes follows a similar behaviour.
4. Polarographic measurements have indicated that the formula of the lead complex is  $\text{Pb}(\text{P}_2\text{O}_7)^-$ . In the case of cadmium it has not been possible to arrive at any formula due to the complicated nature of the waves.

### INTRODUCTION

A few polarographic measurements in pyrophosphate solutions employing lead and cadmium as the cations have been made by Rogers and Reynolds.<sup>1</sup> They have obtained, with lead, reversible polarographic waves which could be employed to estimate the element. In the case of cadmium, however, no diffusion current plateau has been noticed before hydrogen discharge. Their studies have been limited to a narrow pH range. Preliminary investigations in this laboratory at various pH values have indicated that lead and cadmium give an irreversible reduction step in pyrophosphate solutions at high pH values while the reduction process becomes reversible as the pH is lowered. In the present work, a detailed study of the behaviour of pyrophosphate complexes with lead and cadmium has been made at various pH values to elucidate the nature of the electrode process and complex formation.

### EXPERIMENTAL

The procedure used in this work has been essentially the same as that described previously.<sup>3</sup> The droptime ' $t$ ' has been maintained at 5 seconds in normal potassium chloride and the values of ' $m$ ' of the two capillaries employed are

1.370 and 1.227 mg. per second respectively. As there is no maxima on the C-V curves no maximum suppressor is added.

## RESULTS

1. *Effect of pH*

Some polarograms of lead and cadmium at different pH values are given in Figs. 1 and 2. From the figures it is clear that lead gives a very good polarographic wave at all pH values, while in the case of cadmium, long drawn-out split-waves give place to single wave polarograms as the pH is lowered. The results of analysis of the waves are given in Table I.

TABLE I

*Effect of pH on the polarographic behaviour of lead and cadmium in pyrophosphate*

Concentration of pyrophosphate 0.138 Molar    Concentration of lead 1.024 Millimolar ;  
Concentration of cadmium 1.127 Millimolar.

Cation used	pH	$E_{1/2}$ vs. S.C.E. (Volt)	$E_{1/2}$ $E_{1/4}$ (Volt)
Lead	10.40	-- 0.666	0.055
	7.64	- 0.598	0.047
	6.44	- 0.543	0.032
	5.41	-- 0.501	0.031
Cadmium	10.40	-- 0.845 I Wave	..
		-- 1.191 II Wave	..
		-- 1.329 III Wave	Irreversible waves
	8.30	-- 0.843 I Wave	Irreversible waves
		- 1.194 II Wave	..
		-- 1.209 III Wave	..
	7.64	-- 0.798	
	Highly extended bend before the diffusion current plateau over a range of - 0.5 V.		
6.44	-- 0.700	0.034	
5.41	-- 0.658	0.033	

2. *Effect of concentration of pyrophosphate at pH 10.4*

In these experiments the ionic strength at various concentrations of pyrophosphate has been maintained constant by the addition of potassium nitrate. Table II shows the analysis of the waves.

TABLE II

*Polarographic behaviour of lead and cadmium in presence of pyrophosphate at pH 10.4*

Concentration of lead = 0.840 Millimolar ; Concentration of cadmium = 1.127 Millimolar

Cation used	Concentration of pyrophosphate (Molar)	$E_{\frac{1}{2}}$ vs. S.C.E. (Volt)	$E_{\frac{3}{2}} - E_{\frac{1}{2}}$ (Volt)	
Lead .. ..	0.138	- 0.666	0.055	
	0.069	- 0.640	0.051	
	0.0345	- 0.620	0.050	
	0.01725	- 0.606	0.058	
	0.00862	- 0.594	0.060	
Cadmium ..	0.138	- 0.845 I Wave		
		- 1.191 II Wave		
		- 1.329 III Wave		
	0.059	- 0.764 I Wave		
		- 0.842 II Wave		
		- 1.130 III Wave		
	0.0345	- 0.741		
		- 0.817		
		Third wave not distinctly visible		
	0.0175	- 0.697		
- 0.803				
	Third wave not distinctly visible			

It is clear from the table that lead gives an irreversible wave in pyrophosphate solutions. In the case of cadmium, the third wave is not prominent at lower concentrations of pyrophosphate.

3. *Effect of concentration of pyrophosphate at pH 7.6 and below*

The pH of the solutions has been lowered by the addition of acetic acid while potassium nitrate has been added to keep the ionic strength constant. Table III gives the analysis of the waves.

TABLE III

*Effect of pH on the polarographic behaviour of lead and cadmium at pH 7.6 and below in base solutions containing potassium nitrate*

Cation used	pH	Concentration of pyrophosphate (Molar)	$E_{\frac{1}{2}}$ vs. S.C.E. (Volt)	$E_{\frac{1}{2}}$ $E_1$ (Volt)	Remarks
Lead	6.44	0.069	-- 0.531	0.035	
	5.41	0.069	-- 0.487	0.028	
	7.64	0.0345	-- 0.563	0.049	
	6.44	0.0345	-- 0.511	0.037	
	5.41	0.0345	-- 0.479	0.030	Some precipitation
	7.64	0.01725	-- 0.548	0.053	
	6.44	0.01725	-- 0.502	0.034	Some precipitation
	5.41	0.01725	-- 0.460	0.028	Some precipitation
	7.64	0.00863	-- 0.532	0.058	
	6.44	0.00863	-- 0.482	0.029	Some precipitation
	5.41	0.00863	-- 0.448	0.028	Some precipitation
Cadmium	7.64	0.069	-- 0.725 I Wave -- 0.813 II Wave	Elongated	bend before the final current rise
	6.44	0.069	-- 0.684	0.038	
	5.41	0.069	-- 0.641	0.031	Some precipitation
	7.64	0.0345	-- 0.697 I Wave -- 0.804 II Wave	Elongated	bend before the final current rise
	6.44	0.0345	-- 0.661	0.039	
	5.41	0.0345	-- 0.623	0.029	Some precipitation

4. *Effect of concentration of the cation on the diffusion current constant*

It has already been stated that Rogers and Reynolds<sup>1</sup> have developed a method for the estimation of lead employing the reduction of pyrophosphate complexes. Sartori<sup>2</sup> has stated that cadmium ion can be estimated polarographically in pyrophosphate solutions. He has not, however, given the pH of the solutions. The present studies have indicated that the polarograms (Fig. 2) obtained with cadmium are too complicated to be made use of in the estimation of the metal. When the pH is lowered the split-waves give place to one single reversible polarographic

wave, the half-wave potential of which is quite close to that of aquo-cadmium ion. The solubility, however, is far too small for polarographic purposes. It therefore appears that the use of pyrophosphate media for the estimation of cadmium is not of much practical importance.

## DISCUSSION

### 1. *Splitting of the polarographic wave in cadmium-pyrophosphate system*

The splitting of the polarographic wave is prominent in cadmium-pyrophosphate system in contrast to the behaviour of lead-pyrophosphate system where the splitting is totally absent. In this respect, cadmium resembles iron<sup>2</sup> which also shows splitting in pyrophosphate solutions. However, the addition of potassium nitrate prevents the formation of the first wave in the case of iron while with cadmium it has no influence on wave formation. As in the case of iron, split-waves are due to sluggish equilibrium<sup>2</sup> between different species of pyrophosphate complexes of cadmium.

The half-wave potential of the first wave (Table I) of the pyrophosphate complex does not change as the pH is reduced from 10.4 to 8.3, although the height increases from 10 to 16. The half-wave potential of the second wave also does not alter when the pH is reduced to 8.3, in spite of the fact that at this pH, the percentage of  $\text{HP}_2\text{O}_7^{\text{m}}$  and  $\text{P}_2\text{O}_7^{\text{m}}$  has changed from 10 to 90% and from 90 to 4% respectively.<sup>2</sup> Similar anomalies have also been noticed by Meites<sup>3</sup> with copper-citrate complexes. It looks as if there is some other factor, influencing the shift in the half-wave potential with a decrease in pH, besides the mere alteration of the properties of different ionic species. Decrease in pH below 8.3, lowers the half-wave potential of the first wave, with a diminution in the concentration of  $\text{HP}_2\text{O}_7^{\text{m}}$  while the second wave gradually disappears (Fig. 2). It is therefore reasonable to expect the first wave to be due to the reduction of  $\text{HP}_2\text{O}_7^{\text{m}}$  complex while the second is due to  $\text{P}_2\text{O}_7^{\text{m}}$  complex.

### 2. *Effect of pH*

The results of Table I indicate that in lead-pyrophosphate system there is a steady fall in the half-wave potential when the pH is lowered. The fall in the half-wave potential for pH change from 10.4 to 7.64 suggests that in presence of  $\text{P}_2\text{O}_7^{\text{m}}$  ion, the lead- $\text{P}_2\text{O}_7^{\text{m}}$  complex is preferentially formed. When the pH is decreased below 7.64, there is a greater fall in the half-wave potential showing the formation of a new complex, presumably having lead- $\text{HP}_2\text{O}_7^{\text{m}}$ .

### 3. *Irreversibility of the Polarographic Waves*

(i) *Lead-pyrophosphate system*: It is clear that above pH 7, the reduction process is irreversible while below this pH the opposite effect is noticed. It is surprising that the reduction of lead- $\text{P}_2\text{O}_7^{\text{m}}$  complex is activation controlled in contrast to the behaviour of lead- $\text{HP}_2\text{O}_7^{\text{m}}$  complex.

(ii) *Cadmium-pyrophosphate complex*: The irreversibility of cadmium- $P_2O_7$  complex is very high, the wave extending over a range of about 0.6 volt in contrast to cadmium- $HP_2O_7$  complex, the reduction of which occurs reversibly at the dropping mercury electrode. Explanation similar to the one given for lead-pyrophosphate system can be given in this case also.

#### 4. Nature of complex formation in pyrophosphate solutions

(i) *At pH 10.4*.—Application of the equation for irreversible waves<sup>3</sup> at pH 10.4 to the data presented in Table II for lead-pyrophosphate system indicates that one pyrophosphate group enters the complex so that the formula can be written as  $Pb(P_2O_7)$ . In the case of cadmium, however, it has not been possible to give the composition of the complex at this pH on the basis of the polarographic data, due to the complicated nature of the waves.

(ii) *At pH 6.44 and 5.41*.—At these pH values there is precipitation due to a low concentration of the complexing ion  $HP_2O_7$ , when the concentration of pyrophosphate is below 0.0345 M (Table I). At the same time the reduction process becomes more reversible. Hence it has not been possible to draw definite conclusions regarding the formula of the complex.

#### ACKNOWLEDGEMENT

The author expresses his sincere thanks to Prof. K. R. Krishnaswami and Dr. M. R. A. Rao for helpful discussions.

#### REFERENCES

1. Rogers, L. B. and Reynolds, J. *Amer. Chem. Soc.*, 1949, **71**, 2081. C. A.
2. Subrahmanya, R. S. .. *J. Indian Inst. Sci.*, 1956, **38 A**, 87.
3. Sartori, G. .. *Gazz. Chim. ital.*, 1934, **64**, 3.
4. Subrahmanya, R. S. .. *Proc. Indian Acad. Sci.*, 1956, **43 A**, 133.
5. Meites, L. .. *J. Amer. Chem. Soc.*, 1950, **72**, 180.

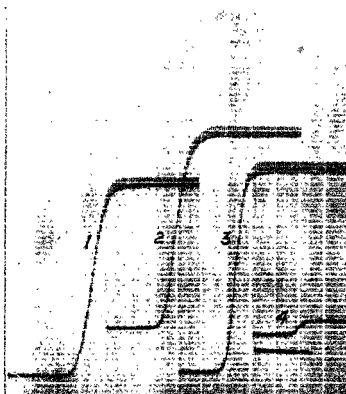


FIG. 1. Effect of pH on the polarographic behaviour of lead (0.840 millimolar) in pyrophosphate.

Curves 1, 2, 3 and 4 have been obtained at pH 10.4, 7.64, 6.44 and 5.41 respectively. The base solution contains 0.0345 M pyrophosphate to which potassium nitrate is added to keep the ionic strength constant. There is some precipitation at pH 5.41. Sensitivity:  $s/30$ .

The voltage line just before the beginning of the polarogram corresponds to  $-0.273$  V. vs. S.C.E.

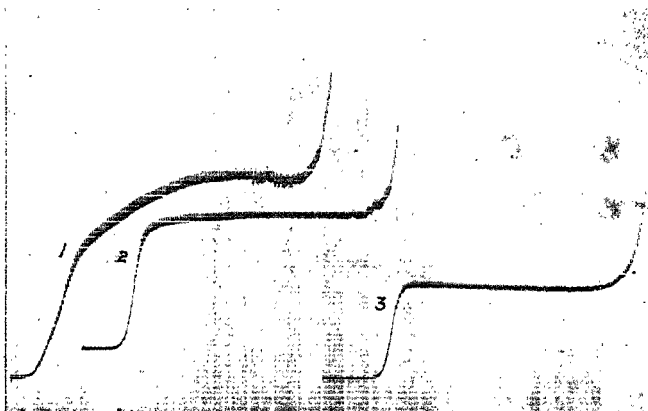


FIG. 2. Effect of pH on the polarographic behaviour of cadmium (1.127 millimolar) in pyrophosphate.

Curves 1, 2 and 3 have been taken in base solutions containing 0.138 M pyrophosphate at pH 7.64, 6.44 and 5.41 respectively. There is some precipitation at pH 6.44 and 5.41. Sensitivity:  $s/30$ .

The voltage line just before the beginning of the various polarograms correspond to  $-0.573$ ,  $-0.473$  and  $-0.373$  V. vs. S.C.E. respectively.