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POLAROGRAPHIC BEHAVIOUR OF METALLIC  
COMPLEXES WITH PYROPHOSPHATE

Part I. Iron

BY R. S. SUBRAHMANYA

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

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SUMMARY

Employing sodium pyrophosphate as the complexing agent a systematic study has been made on the polarographic behaviour of iron. It has been noticed that the polarograms consist of two waves both corresponding to the reduction of ferric to ferrous. With a decrease in pH, the height of the first wave increases, then remains constant, and again increases. These results are explained on the assumption of the formation of different species in sluggish equilibrium at different pH values. It has been noticed that the first wave is reversible while the second wave is irreversible. The addition of potassium nitrate suppresses the first wave. The formula of the ferric pyrophosphate is found to be  $(\text{FeP}_2\text{O}_7)^-$ . In presence of ammonia-ammonium chloride the formation of a new amino-pyrophosphate complex has been established. Solutions containing sodium carbonate and pyrophosphate are yellow in colour due to the formation of colloidal ferric oxide. It has been suggested that a combination of potassium nitrate with gelatin can be employed to estimate iron polarographically in presence of pyrophosphate.

INTRODUCTION

It is well known that a majority of multivalent cations form insoluble precipitates with aqueous pyrophosphate which, however, dissolve in excess of

pyrophosphate due to complex formation, the nature of which is not well understood.<sup>1, 2</sup> Rogers and Reynolds<sup>3</sup> have investigated the nature of complex formation of multivalent cations with sodium pyrophosphate using conductometric and polarographic methods. In the case of iron (III) they notice the formation of the complex ion  $(FeP_2O_7)$ . They have stated that iron gives one reversible polarographic wave corresponding to the reduction of iron (III) to iron (II) and no wave for the reduction of iron (III) to metallic iron, before the final rise of current. In the present work it has been noticed that the first wave is irreversible contrary to the observations made by Rogers and Reynolds.<sup>3</sup> In the present communication a detailed account is given of the polarographic behaviour of the ferric pyrophosphate complexes.

#### EXPERIMENTAL

The procedure employed in the present work has been essentially the same as that described previously.<sup>4, 5</sup> The 'm' values of the capillaries used are 1.370, 1.227 and 1.120 mg. per second and the droptime is 5 seconds a drop in 1 N potassium chloride solution.

Solutions of pyrophosphate are prepared from  $Na_4P_2O_7 \cdot 10H_2O$  (Baker's analysed). Acetic acid and sodium hydroxide are used to control the pH of the solution. The pH is determined using the Beckman pH meter. Potassium nitrate is used to keep the ionic strength at any desired value.

#### RESULTS

1. *Effect of pH.*—Some of the polarograms are given in Fig. 1. It is evident (Curves 3 to 6) that two waves are obtained in all the cases. In Curves 4 and 6, the first wave consists of a wavelet marked  $A_1$  and  $A_2$  respectively. In these experiments potassium nitrate is not added to maintain the ionic strength constant as this salt interferes with the nature of the polarograms. In presence of potassium nitrate at pH 4.3 (Curve 1) the first wave has been suppressed to a large extent while at pH 7.64 (Curve 2) the first wave is totally eliminated. The results of analysis of the waves showing the effect of pH are given in Table I. The results indicate that for the first wave (i) the height increases with decrease in pH and practically remains constant over a pH range 8.3 to 6.4 and then rapidly increases, (ii) the half-wave potential remains practically constant except at pH 5.41 and below, and (iii) the slope of the log plot is of the order of 0.054 V whilst the value for a reversible one electron step is 0.06014 V. In the case of the second wave, a lowering of the pH results (i) in a decrease in the wave-height, then a constancy over a pH range of 8.3 to 6.4 and finally a decrease to a value of 11.9 at pH 5.4, (ii) in a fall of the half-wave potential, rapid to begin with and more gradual afterwards. The slope of the log plot of the second wave is of the order of 0.17 V as compared to a value of 0.06014 V required by reversible one electron process. In Fig. 2 are presented the log plots of the various polarograms and it is clear that these plots are straight lines. The slopes of these lines are also given in

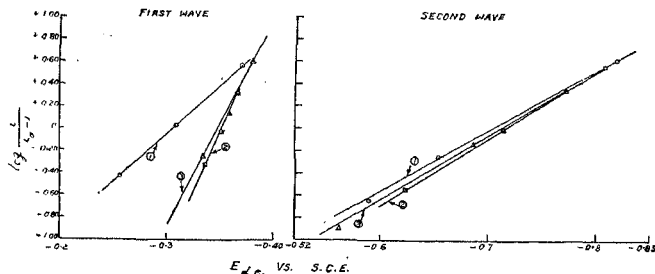


FIG. 2. Curves 1, 2 and 3 were obtained in base solutions containing 0.138 M Pyrophosphate at pH 5.41, 7.64, and 8.30 respectively.

Table I. Polarograms have been taken up to pH 3.9 below which the pyrophosphate is unstable. It is interesting to note that as the pH is decreased the total height remains almost the same. In all the cases the height of the first wave increases at the expense of the second one and at pH 3.95 the second wave is hardly noticeable.

TABLE I

*Effect of pH on the half-wave potential, reversibility, and wave-height of the polarographic waves of iron (III) in pyrophosphate media*

Concentration of pyrophosphate 0.138 Molar ; Concentration of iron 1.182 millimolar

pH	First wave			Second wave				Total Height I+II waves $s/30$	
	$(E_{1/2})_1$ vs. S.C.E. (Volt)	Slope of log plot (Volt)	Height at $s/30$	$(E_{1/2})_2$ vs. S.C.E. (Volt)	$(E_{1/2})_2$ (rev.) vs. S.C.E. (Calculated reversible value) (Volt)	Over-voltage (Volt)	Slope of the log plot (Volt)		Height at $s/30$
10.40	-0.363	*	1.08	-0.838	-0.710	0.128	0.159	24.85	25.93
8.30	-0.352	0.048	6.10	-0.714	-0.617	0.088	0.169	19.54	25.64
7.64	-0.349	0.054	4.97	-0.712	-0.604	0.108	0.178	20.95	25.92
6.44	-0.350	†	5.67	-0.709	-0.600	0.108	0.166	20.17	25.84
5.41	-0.306	0.057	13.77	-0.705	-0.612	0.093	0.182	11.94	25.71
3.95	-0.190	0.059	22.00	Wave hardly noticeable					25.98

\* Too small for measurements.

† Interference due to wavelet.

2. *Effect of concentration of pyrophosphate at pH 10.4.* In solutions of pH 10.4 the first wave is very small, as noticed previously. Potassium nitrate is therefore employed to equalise the ionic concentration in the base solution at different concentrations of the pyrophosphate and the properties of the second wave are studied in detail. The results are given in Table II. From the table it is clear that (i) the half-wave potential decreases with a decrease in the concentration of the pyrophosphate, (ii) the slopes of the log plots are about 0.17 V as compared with a value of 0.06014 V required by a reversible one electron process, and (iii) the total height of the wave shows a slight increase.

TABLE II

*Effect of concentration of pyrophosphate on the half-wave potential, reversibility and wave-height of the polarographic waves of iron (III)*

Concentration of iron 1.182 millimolar

Concentration of pyrophosphate (Molar)	Half-wave potential $E_{1/2}$ vs. S.C.E. (Volt)	Slope of the log plot (Volt)	$\alpha$ (fraction of the total applied potential that favours the forward reaction)	Height of the wave $\times 10^3$
0.138	-0.838	0.159	0.371	25.96
0.069	-0.733	0.180	0.328	(1.08) 27.28
0.0175	-0.685	0.166	0.356	28.44

3. *Effect of concentration of pyrophosphate at pH 7.6 and below.* In these experiments potassium nitrate has been added to maintain the ionic strength constant. Some of the polarograms are given in Fig. 3 and the results obtained under various conditions are included in Table III.

The results indicate that the half-wave potential diminishes with pH and the heights of the waves are practically the same at different pH values. At low concentrations of pyrophosphate, there is a tendency for the formation of a small pre-wave at  $-0.20$  V when the pH is less than 7. The slope of the log plot indicates that the reduction process is irreversible in character.

4. *Effect of sodium carbonate in the base solutions.*—In base solutions containing sodium carbonate the solubility is quite low. Even in 0.138 M pyrophosphate the solution is clear to begin with but it develops a yellow colour at the end of electrolysis, evidently due to the formation of colloidal ferric hydroxide. On keeping, the depth of colour increases. The wave-height is 21 in contrast to a value of 27 in absence of sodium carbonate indicating that iron in the form of colloidal ferric hydroxide has escaped the polarographic reduction. In solutions

TABLE III

Effect of pH on the half-wave potential, reversibility and the height of the polarographic waves in base solutions containing potassium nitrate

Concentration of iron 1.182 millimolar

pH	Concentration of pyrophosphate (Molar)	Half-wave potential $E_{\frac{1}{2}}$ vs. S.C.E. (Volt)	Slope of the log plot (Volt)	Height of the wave $s/30$
7.64	0.069	-0.708	0.179	27.50
"	0.0345	-0.684	0.180	27.32
"	0.01725	-0.610	0.170	27.41
6.44	0.069	-0.688	0.185	27.32
"	0.0345	-0.672	0.190	27.77
"	0.01725	-0.200 Two -0.500 waves	0.050 Two 0.180 waves	5.00 Two 23.40 waves
5.34	0.069	-0.650	0.310	27.96
"	0.0345	-0.638	0.240	27.77
"	0.01725	-0.220 Two -0.520 waves	..	4.00 Two 24.00 waves

containing less of pyrophosphate the height is nearly halved. The half-wave potentials increase with a decrease in the pyrophosphate concentration (-0.87 V in 0.138 M pyrophosphate and -0.99 V in 0.0345 M pyrophosphate). The values of  $E_{\frac{1}{2}} - E_{\frac{1}{2}}$  in these solutions are 0.18 V and 0.24 V respectively indicating that the irreversibility increases with a decrease in the concentration of pyrophosphate.

5. *Effect of ammonia-ammonium chloride.*—In ammonium chloride (1 M)-ammonium hydroxide (1 M), the half-wave potentials in presence of 0.118, 0.059 and 0.0197 molar pyrophosphate are -0.553, -0.547 and -0.532 V vs. S.C.E. respectively. The values of  $E_{\frac{1}{2}} - E_{\frac{1}{2}}$  are 0.121, 0.122 and 0.126 V respectively. The concentration of iron has been 1.182 millimolar. The half-wave potential corresponding to the reduction of ferric to ferrous is about 0.2 V more positive than with solutions containing only pyrophosphate, pH remaining constant, indicating the formation of a new amino-pyrophosphate complex.

6. *Effect of concentration of iron on the diffusion current.*—Results obtained above indicate that in solutions of pH > 7, the current-voltage curves show only

a single wave in presence of potassium nitrate. Proportionality of the diffusion current with concentration of iron has been tested in solutions of 0.069 M pyrophosphate containing different amounts of potassium nitrate. The results are presented in Table IV. It is clear that when the concentration of potassium nitrate

TABLE IV

*Effect of concentration of iron (III) on the diffusion current constant and half-wave potential at 0.069 M pyrophosphate*

Concentration of potassium nitrate (Molar)	Gelatin (%)	$m^{3/2}t^{3/2}$ at -1.1 V vs. S.C.E. mg. <sup>3/2</sup> sec. <sup>3/2</sup>	Concn. of iron (Millimolar)	Diffusion current constant $i_d$ C.m. <sup>3/2</sup> t <sup>3/2</sup>	Half-wave potential $E_{1/2}$ vs. S.C.E.
A. 0.4	..	1.388	1.182	1.59	0.72
	..	..	2.364	1.55	0.71
	..	..	5.910	1.52	0.70
	..	..	11.82	1.49	0.68
B. 0.4	0.005	..	1.182	1.51	0.75
	..	..	11.82	1.42	0.76
C. 1.0	0.005	1.381	1.182	1.49	0.75
	..	..	2.364	1.49	..
	..	..	5.910	1.49	..
	..	..	11.82	1.47	0.75

is 0.4 M the value of the diffusion current constant slightly falls off at higher concentrations of iron. Even the addition of gelatin does not in any way improve the constancy of the values (Table IV, Column B). When the concentration of potassium nitrate is increased to 1 M the wave has a poor shape. Addition of gelatin gives very good waves and greatly improves the constancy of the diffusion current constant (Table IV, Column C). It has been noticed that further increase in the concentration of potassium nitrate does not offer any decided advantage. It can therefore be concluded that 1 M potassium nitrate containing 0.005% gelatin is a good base solution for analytical purposes.

The effect of pH on the proportion of different ions in pyrophosphates are given in Table V. These values are calculated from the acid dissociation constants.<sup>4</sup>

TABLE V

*Effect of pH on the proportion of different ions in pyrophosphate*

pH	% of $\text{H}_2\text{P}_2\text{O}_7^{2-}$	% of $\text{HP}_2\text{O}_7^{3-}$	% of $\text{P}_2\text{O}_7^{4-}$
	ca.	ca.	ca.
10.4	0.02	10	90
8.0	5.00	90	4
6.4	63.0	37 ]	..
5.4	94.9	5.1	..
4.3	98.8	0.2	..

## DISCUSSION

1. *Split waves.*—It has been noticed in pyrophosphate solutions that the height of the polarographic wave remains almost the same at different pH values. There is a slight tendency for the splitting of the wave into two at pH 10.4. As the pH is diminished, the first wave grows in height at the expense of the second. Similar results have been noticed by Laitinen and Onstott<sup>7</sup> in copper-pyrophosphate systems. These results are to be ascribed to the sluggish equilibrium between different species of the pyrophosphate complexes of iron (III) getting reduced to iron (II). The first wave can be expected to be due to  $(\text{H}_2\text{P}_2\text{O}_7)^{2-}$ . At pH 10.4 the height is small as the concentration of  $(\text{H}_2\text{P}_2\text{O}_7)^{2-}$  is negligibly small (Table V). At pH 8, the concentration of  $(\text{H}_2\text{P}_2\text{O}_7)^{2-}$  increases 250 times resulting in a large increase in wave-height. With further pH fall the relative ratio of  $(\text{H}_2\text{P}_2\text{O}_7)^{2-}$  to other pyrophosphate ions does not alter to any great extent and hence the height of this wave does not alter much. When the pH is diminished from 6.44 to 5.41, there is not only an enhancement of the concentration of  $(\text{H}_2\text{P}_2\text{O}_7)^{2-}$  but a rapid diminution in the concentration of  $(\text{HP}_2\text{O}_7)^{3-}$  resulting in a great enhancement of the height of the first wave. With a further increase in acidity, the concentration of  $(\text{H}_2\text{P}_2\text{O}_7)^{2-}$  is only slightly enhanced resulting in a limiting value for the height of the first wave. The presence of only two waves for the first reduction indicates that there is rapid equilibrium between complexes containing  $(\text{HP}_2\text{O}_7)^{3-}$  and  $(\text{P}_2\text{O}_7)^{4-}$ . This is further confirmed by the fact that an increase of either  $(\text{HP}_2\text{O}_7)^{3-}$  or  $(\text{P}_2\text{O}_7)^{4-}$  does not result in a marked increase in the wave-height as long as the sum of  $(\text{HP}_2\text{O}_7)^{3-}$  and  $(\text{P}_2\text{O}_7)^{4-}$  does not alter considerably. The theoretical aspect of complex formation is not sufficiently well developed to give a quantitative idea of the process.

2. *Effect of pH on the half-wave potential.* The slope of the log plot of the first wave (Table I) indicates that the reduction of this species occurs reversibly. The constancy of the half-wave potential up to pH 6.44 indicates that the co-ordination numbers of the ferrous and the ferric remain the same. However, in the pH range 6.44 to 5.41, the half-wave potential falls from  $-0.350$  V to  $-0.306$  V though the concentration of  $(\text{H}_2\text{P}_2\text{O}_7)^{2-}$  increases from 60 to 98%. Such peculiar shifts have also been noticed by Meites<sup>8</sup> but in the present state of our knowledge it is not possible to explain such exceptions.

The slope of the log plot of the second wave indicates that the reduction of this species occurs irreversibly. The calculated values for reversible half-wave potentials<sup>9</sup> (Table I) indicate similar variations in pH. The initial rapid fall of the half-wave potential is due to a rapid fall in the concentration of  $(\text{P}_2\text{O}_7)^{4-}$  from 90% at pH 10.4 to 4% at pH 8.0. The variation of half-wave potential with pH is complicated on account of the dissociation of the complexing substance into three types of ions, the proportions of which alter with pH.

It has to be pointed out that the addition of potassium nitrate to the base solution results in suppressing the first wave. It looks probable that a high concentration of potassium nitrate diminishes the concentration of  $(\text{H}_2\text{P}_2\text{O}_7)^{2-}$  which is responsible for the production of the complex giving the first wave. When the pH is lowered below 7, the first wave reappears at low concentrations of the pyrophosphate.

3. *Effect of concentration of pyrophosphate.* Rogers and Reynolds<sup>7</sup> have stated that the pyrophosphate complex of iron is reduced reversibly at the dropping mercury electrode. But the present work does not confirm this view. The slope of the log plot is of the order of 0.18 V while that required for a reversible wave is 0.06014 V indicating that an activation controlled process is the rate-determining step in the reduction process. Applying equations for irreversible waves<sup>10</sup> (Table II) one gets that one pyrophosphate ion is attached to the ferric iron. The formula can therefore be written  $[\text{Fe}(\text{III})\text{P}_2\text{O}_7]^-$ . It is interesting to note that the potentiometric studies of Rogers and Reynolds<sup>8</sup> also indicate that one pyrophosphate group co-ordinates to the ferric iron.

4. *Effect of concentration of iron on the diffusion current constant.* Reynolds and Rogers<sup>11</sup> have stated that the optimum pH for estimating iron in pyrophosphate media is between 9 and 11. The present work shows that when pure pyrophosphate is employed below pH 10.4, two waves appear due to the reduction of two species of complexes. When 0.01% gelatin is added the first wave is eliminated but a long drawn-out wave is obtained, the first wave reappearing in a shortened form at higher concentrations of iron ( $> 5$  millimolar). Further it has been noticed that when the polarograms contain the first wave the constancy of the diffusion current constant is not quite good. However, by incorporating potassium nitrate (1 M) and gelatin (0.005%) good constancy is obtained (Table IV). It is



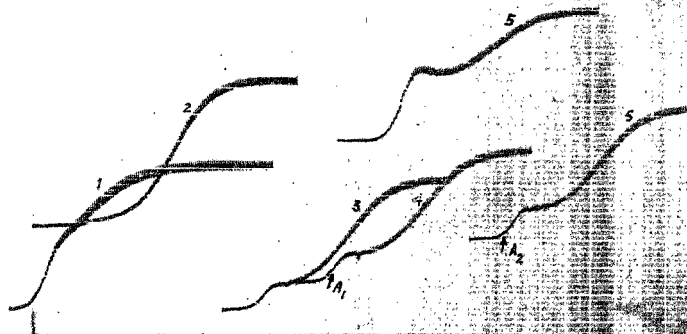


FIG. 1

Effect of pH on the polarographic behaviour of iron (1.182 millimolar) in base solutions containing pyrophosphate.

Curves 1 and 2 are obtained in solutions containing potassium nitrate and 0.0175 M and 0.00875 M pyrophosphate at pH 4.30 and 7.64 respectively. Curves 3, 4, 5 and 6 are obtained with 0.138 M pyrophosphate at pH 7.64, 6.44, 5.41 and 8.30 respectively. Sensitivity:  $s/30$ .

The voltage line just before the beginning of the various polarograms corresponds to: 0.027 V., 0.027 V., -0.173 V., -0.173 V., -0.027 V., -0.173 V., vs. S.C.E.



FIG. 3

Effect of pH on the polarographic behaviour of iron (1.182 millimolar) in 0.0345 M pyrophosphate.

Curves 1, 2 and 3 have been obtained at pH 7.64, 6.44 and 5.34 respectively. Sensitivity:  $s/30$ .

The voltage line just before the beginning of the polarogram corresponds to -0.173 V, vs. S.C.E.

therefore suggested that the combination of potassium nitrate with gelatin can be employed to estimate iron polarographically in presence of sodium pyrophosphate.

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