Voltammetric Investigations on Ferric-Triethanolamine System for Trace Analysist

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The complexing ability of triethanolamine has been utilised to investigate Fe(III)/Fe(II) redox system at the DME. The DC polarogram of ferric iron in presence of triethanolamine displays a reversible reduction wave which has further been confirmed by cyclic-voltammetric study at a hanging mercury drop electrode.

The ferric-triethanolamine complex is estimable in sub-micro levels by employing differential pulse polarography. The technique has yielded the iron contents in drinking, ground and industrial waste waters.

KEY WORDS: Cyclic voltammetry, Ferric-Triethanol system, trace analysis iron, water samples.

INTRODUCTION

The standard potential of the reduction of ferric ion ($+0.77$ V) is near the reduction potential of mercurous ion ($+0.79$ V).[1] Thus the reduction of simple ferric ion cannot be studied at the dropping mercury electrode (DME) since, at this electrode, it gives a wave which is mixed with the oxidation wave of mercury. To obtain a polarographic wave whose half wave potential ($E_{\frac{1}{2}}$) is characteristic of the ferric-ferrous system, it becomes necessary to employ a supporting electrolyte that should form a sufficiently stable complex

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with ferric ion. The $E_{\frac{1}{2}}$ of the complexed ion would thus be shifted to a sufficiently negative value so as to be observable at the DME.

Although polarographically active complexes of Fe(III) are known with oxalate, citrate, and tartrate,[2] these are not suitable for simultaneous estimation of iron along with other common ions like copper, lead, cadmium, zinc etc. Wolfson[3] had employed triethanolamine (TEA) in ammonical medium to complex iron(III); subsequently Jessop[4] used this ligand in strongly alkaline medium and reported its characteristics in presence of other ions. The authors have made a detailed study of triethanolamine as a complexing ligand in alkaline medium to obtain a reversible reduction wave of Fe(III). Differential pulse polarographic (DPP) behaviour of the complex has been used for estimating total iron content in drinking, ground and industrial waste waters in presence of other common ions.

EXPERIMENTAL

i) Chemicals

All chemicals used were of reagent grade purity. Solution of ferric iron was prepared by dissolving pure iron wire in a small amount of nitric acid which was finally diluted to the requisite volume in 0.01 M hydrochloric acid. The exact concentration of ferric iron was determined by treatment with $SnCl_2$ and titration with standard potassium permanganate solution.[5] The estimation was also made colorimetrically employing 1:10 phenenthroline.[6] Both methods gave identical results.

ii) Instrumentation

A 174-A polarographic analyzer was used along with a drop timer (Model 174/70). A micro saturated calomel electrode (SCE) was used as the reference electrode. Natural drop time was employed for DC polarography while one second drop time was chosen for DPP. The modulation amplitude was kept at 50 mv. Cyclic voltammograms were taken on a hanging mercury drop electrode. A series 2000-digigraphic Xy/t recorder (Digital Electronic Ltd., Bombay) along with cyclic voltammetric instrument CV-1 (Bioanalytical System, USA) was used for recording the cyclic voltammograms.

iii) Sample treatment

The water samples were digested with nitric acid to ensure that all the iron remained in the trivalent state and free ionic form. For estimations 25 ml of water samples were taken and digested with 5 drops of concentrated nitric acid. The contents were transferred to a 25 ml volumetric flask and made up to the requisite volume. All experiments were performed at room temperature (25–27°C).

RESULTS AND DISCUSSION

A DC polarogram of Fe(III) in presence of TEA (0.05 M) and sodium hydroxide (0.05 M) is shown in Figure 1. The polarogram shows two distinct reduction waves. The first wave represents the reduction of Fe(III) to Fe(II) and the second one shows the reduction of Fe(II) to the metallic form. The $E_{\frac{1}{2}}$ of the waves are -1.1 and -1.7 V vs SCE respectively.

On varying the concentration of TEA from 0.01 M to 0.38 M in presence of 0.05 M sodium hydroxide, it was observed that there was no notable shift in the $E_{\frac{1}{2}}$ of the first wave. The logarithmic analysis of the first wave indicated a slope value of 0.066 V.

The reversibility of the system was further confirmed from the cyclic voltammogram of the system, recorded at a hanging mercury drop electrode. Both the cathodic and anodic peaks were observed. The difference in peak potential ΔE was found to be 0.06 V, which corresponded to a reversible redox system. A typical cyclic voltammogram of Fe(III) recorded at a scan rate of 40 mv/sec is shown in Figure 2.

The DPP of Fe(III) in presence of 0.05 M TEA and 0.05 M NaOH showed a peak which was distinguishable from those of copper(II), lead(II), cadmium(II) and zinc(II). A DPP of a mixture of the above ions is shown in Figure 3. The peak potentials are given below.

Metal ions	Peak potentials vs SCE
Copper	>0 V
Lead	-0.42 V
Cadmium	-0.76 V
Iron(III)	-1.00 V
Zinc	-1.46 V
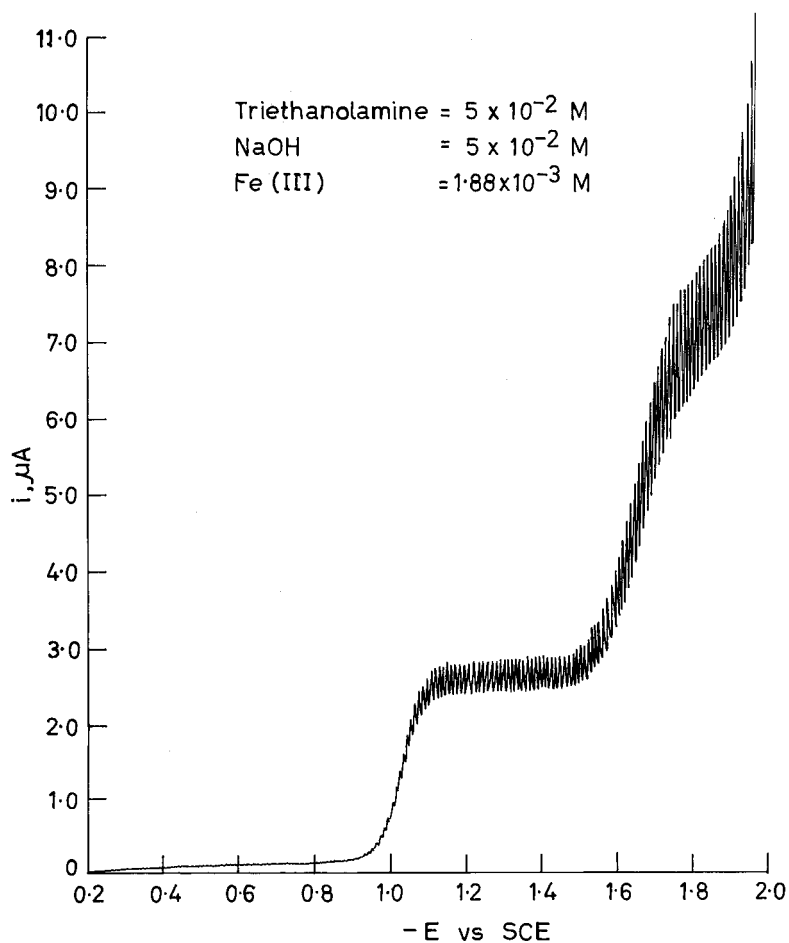
FIGURE 1   A DC polarogram of Fe(III) containing 1.8 m M, 0.05 M TEA, and 0.05 M NaOH.

Anodic
portion

Cathodic
portion

0·7   1·4
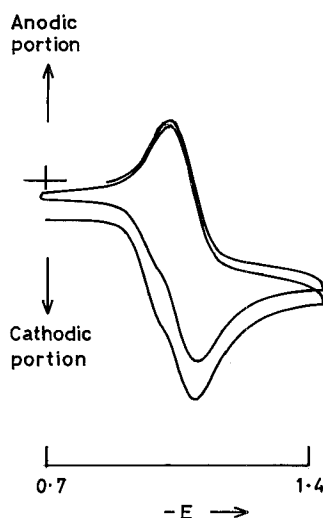
−E ⟶

FIGURE 2   Cyclic voltammogram of Fe(III) containing 1.8 mM Fe(III), 0.05 M TEA and 0.05 M NaOH.
           Scan rate = 40 mv/sec.

Thus copper, lead, cadmium and zinc do not interfere during the estimation of iron by DPP technique.

ESTIMATION OF TOTAL IRON IN WATER SAMPLES

The ferric to ferrous DPP wave has been made the basis for micro estimation of total iron in aqueous matrices. Experiments were made to check the interference by other common metal ions during the estimation of iron. DP polarogram of test solution containing copper, cadmium, lead, iron and zinc ions in the presence of 0.05 M triethanolamine and 0.05 M sodium hydroxide were taken. The polarograms indicated that the peak potential of iron did not overlap with peak of any other ion.

Analyses were made from samples of drinking, ground and industrial waste waters for their total iron content. The concentrations of total iron thus found are given in Table I.
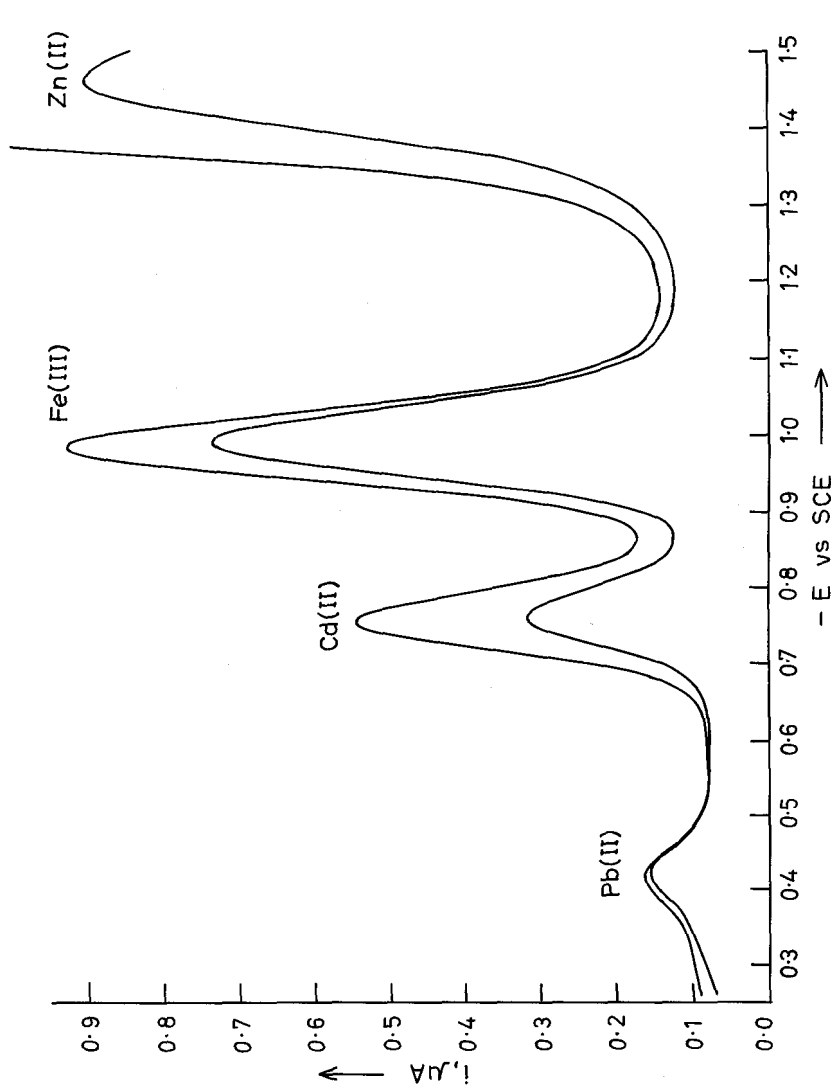
FIGURE 3 DPP of a solution containing; 1.8×10^{-5} M Fe(III), 1.2×10^{-6} Pb(II), 2.0×10^{-6} M Cd(II), 0.6×10^{-5} M Zn(II) ions in the presence of 0.05 M TEA and 0.05 M NaOH.

Scan rate = 2 mv/sec
Modulation amplitude = 50 mv
Pulse duration = 57 ms
Clock time of pulse = 1 sec

TABLE I

S. No.	Sample	Concentration of total iron in ppm		
		Minimum	Maximum	Average
1.	Drinking water	0.07	0.34	0.13
2.	Ground water	0.08	0.78	0.34
3.	Industrial wastewater	0.33	2.0	0.95

Determination limit = 0.05 ppm.
Precision   = ± 4%.

Acknowledgement

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