A NOTE ON POLAROGRAPHIC STUDIES ON FERROUS 5-NITRO, 1: 10 PHENANTHROLINE CHELATE (5-NITRO FERROIN)

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The present work deals with the determination of stability and composition of ferrous 5-nitro, 1 : 10 phenanthroline chelates by polarographic method to provide an additional experimental support in favour of earlier spectro-photometric results. The solution of the chelates were prepared in absolute alcohol. Polarograms were taken after bubbling nitrogen through solution for 15 minutes. The polarographic results agree with spectroscopic values.

Considerable amount of literature is available on O-phenanthroline and other substituted phenanthrolines[1,2] which are extensively used for colorimetric determination of iron (II). Stability and composition of iron (II) O-phenanthroline chelates has been determined by various workers[3]. Since the synthesis of 5-nitro, 1 : 10 phenanthroline by Walden *et al.*[4], it has been used as oxidation reduction indicator, in potentiometric titrations of iron (II) with cerimum (IV) in nitric acid or perchloric acid solutions. Its oxidised form has a pale blue colour whereas reduced form is red. Mehlig & Hullett[5] have compared, 5-nitro, 1 : 10 phenanthroline and O-phenanthroline as colorimetric reagent for iron (II). Though the study of ion (II) -5-nitro, 1 : 10 phenanthroline chelate and also the study of this ligand with other metal ions have already been reported in considerable detail[6,7], no polarographic studies on this chelate have been carried out. The present work was undertaken with a view to determine the stability and composition of the chelate by polarographic method, to provide additional experimental support in the favour of earlier spectrophotometric results.

AR grade ferrous ammonium sulphate (BDH) was used for preparing iron solutions. 5-nitro, 1 : 10 phenanthroline was also a BDH product, the solutions of which were prepared in absolute alcohol.

All polarograms were recorded by a Cambridge pen writing Polarograph. A 2 ml cell was used. Temperature was kept constant at $29 \pm 0 \cdot 1°C$. Ferrous concentration was 1 mM whereas ligand concentration varied from 0·1 to 0·6 mM. 0·1 mM potassium chloride was taken as supporting electrolyte in 80% alcohol as the solvent medium. Polarograms were recorded after bubbling nitrogen through the solutions for 15 minutes. A typical polarogram is reproduced in Fig. 1. Capillary characteristic and other observations are listed in Table I.

The stability constant of the chelate was obtained polarographically by utilizing equation (1).

$$(E_{1/2})_c - (E_{1/2})_s = \frac{0 \cdot 591}{n} \times K\text{instab.} - p. \frac{0 \cdot 0591}{n} \log (X^{b-}) \qquad (1)$$

TABLE 1

POLAROGRAPHIC CHARACTERISTICS OF 5-NITRO FERROIN AT DME

Temp. = 29 ± 0·1°C, Supporting electrolyte concentration = 0·1 M *KCl*, Medium = 80% alcohol, $m = 3{\cdot}99$ mg. sec.$^{-1}$, $t = 2{\cdot}85$ sec., $m^{2/3}\,t^{1/6} = 3{\cdot}012$ mg$^{2/3}$ sec.$^{-1/2}$, Ferrous ion concentration = 1 mM, Ionic strength = 0·1.

5-nitro-1 : 10 phenanthroline concentration (mM)	$E_{1/2}$ against mercury pool anode (volts)
0·0	1·290
0·1	1·457
0·2	1·483
0·3	1·498
0·4	1·508
0·5	1·517
0·6	1·523
0·7	1·530
0·8	1·534

where $(E_{1/2})_s$ = half wave potential of the simple metal ion.

$(E_{1/2})_c$ = half wave potential of the complex.

p = numbe of molecules of complexingr agent per atom of metal ion (co-ordination No.)

K_{instab} = Instability constant of the complex.

and

(X^{b-}) = Concentration of the complexing agent in the body of the solution.

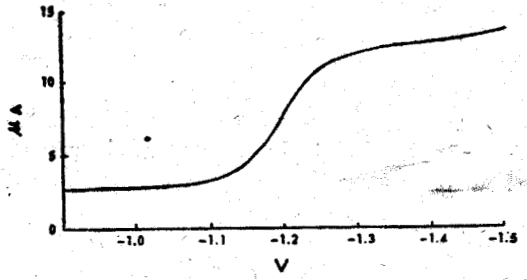

Fig. 1—Potential in *V* against mercury pool anode $Fe^{++} = 10^{-3}$ M.

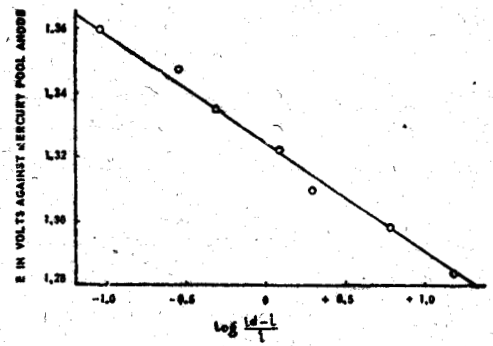

Fig. 2—Variation of $\log \frac{i_d - i}{i}$ against E [slope = 0·03].

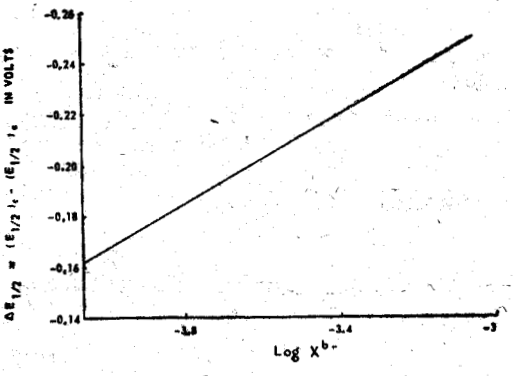

Fig. 3—Variation of $\log \left[\frac{b-}{X} \right]$ against $[(E_{1/2})_c - (E_{1/2})_s]$ [Slope = 0·086].

A plot of log $\frac{id - i}{i}$ against E for complex is reproduced in Fig. 2. A straight line thus obtained reveals the reversible nature of the polarographic wave. The slope of the plot gives a value of n equal to 2.

The shifts in half wave potential $\triangle E_{1/2} = [(E_{1/2})_c - (E_{1/2})_s]$ were plotted against log (X^{b-}) [See equation (1)]. A straight line with a slope equal to 0·086 (Fig. 3) was obtained. Since the slope of the curve is given by $p.\ \frac{0{\cdot}059}{n}$ the value of p will be equal to 3 (taking $n = 2$). The value of p thus evaluated was put into equation (1) to get K_{instab} which is found to be $5{\cdot}129 \times 10^{-18}$. $pK_{\text{instab}} = -17{\cdot}2899$.

Brandt *et al.*[6] from spectrophotometric measurements have reported the values of pK for 5-nitro, 1 : 10 phenanthroline-iron (II) complex as −16·7. The value obtained polarographically, in the present work agrees reasonably well with this value.

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REFERENCES

1. VOGEL, A. I., "A Text Book of Quantitative Inorganic Analysis" (Longmans Green & Co. Ltd.) ELBS Edition (1964), 101.
2. BRANDT, W. W. & SMITH, G. F., *Anal. Chem.*, **21** (1949), 1313.
3. LEE, T. S., KOLTHOFF, I. M. & LEUSSING, D. L., *J. Amer. Chem. Soc.*, **70** (1948), 2348.
4. WALDEN, HAMETT & CHAPMAN, *J. Amer. Chem. Soc.*, **56** (1934), 1092.
5. MEHLIG, J. P. & HULLETT, H. R., *Ind. Eng. Chem. Anal.*, **14** (1942), 869.
6. BRANDT, WARREN, W. & GULLSTROM, DELORA, K., *J. Amer. Chem. Soc.*, **74** (1952), 3532.
7. BANKS, CHARLES, K. V. & BYSTROFF, R. I., *J. Amer. Chem. Soc.*, **81** (1959), 6153.
8. VOGEL, A. I., "A Text Book of Quantitative Inorganic Analysis" (Longmans Green & Co. Ltd.) ELBS Edition (1964), 1010.