

POLAROGRAPHIC STUDIES ON THE COMPOSITION OF NICKEL FERROCYANIDE COMPLEX

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INTRODUCTION

THE composition of nickel ferrocyanide complex has been the subject of many investigations. Werner^{1,2} studied for the first time the composition of nickel ferrocyanide complex and showed that Ni^{++} got precipitated with potassium ferrocyanide giving a stable complex of the composition $\text{Ni}_2 [\text{Fe} (\text{CN})_6]$. Gaspar³ and co-workers considered that the nickel ferrocyanide was a double complex or associated salt. Britton and Dodd⁴ observed that nickel reacted with $\text{K}_4\text{Fe} (\text{CN})_6$ to form normal salt which was converted by further precipitation into $\text{Ni}_2 [\text{Fe} (\text{CN})_6] \cdot x \text{K}_4 [\text{Fe} (\text{CN})_6]$, where x was less than one. Thermometric study⁵ of precipitation of nickel ferrocyanide was shown to have a composition either $\text{NiK}_2 [\text{Fe} (\text{CN})_6]$ or $\text{Ni}_4\text{K}_4 [\text{Fe} (\text{CN})_6]_3$, the composition varying with the conditions of precipitation. X-ray diffraction studies⁶ of nickel ferrocyanide revealed that as much as 0.3–0.4 mole $\text{K}_4\text{Fe} (\text{CN})_6$ existed with one molecule of $\text{Ni}_2 [\text{Fe} (\text{CN})_6]$. It was assumed that the ferrocyanide was adsorbed on the surface of highly dispersed crystals of $\text{Ni}_2 [\text{Fe} (\text{CN})_6]$ and not combined to form definite double salts. The present communication reports polarographic investigation of the nickel ferrocyanide complex. This method appeared desirable: Potassium ferrocyanide is not reduced⁷ at the d.m.e. and the method, therefore, is void of complications. Further, in a similar controversial circumstance, viz., investigation of the composition of the cadmium ferrocyanide polarographic method proved to be successful.⁸

EXPERIMENTAL

Nickel sulphate used was B.D.H. Analar sample. This was recrystallised in twice distilled water and dried at 50° C. for 48 hours. The exact concentration of the nickel solution prepared was estimated gravimetrically using dimethyl glyoxime.

Potassium ferrocyanide used was Merck sample. KCl employed was of B.D.H. Analar quality.

The polarograph used was assembled in our Laboratory; the electrical circuit employed was similar to the one described in an earlier communica-

tion.⁹ The diffusion current was obtained by measuring the potential difference developed across a known resistance introduced serially in the circuit; the accuracy of the measurement was adjusted to 0.1μ amp.

The capillary employed had the following characteristics:

$$m = 0.665 \text{ mgm./sec.}$$

$$t = 4.14 \text{ sec.}$$

These values were recorded in 0.1 M KCl solution in open circuit.

The method employed for investigating the nickel ferrocyanide complex involved the amperometric titration of a known volume of Ni^{++} solution of a fixed strength against standard potassium ferrocyanide. 1 M KCl solution was used as supporting electrolyte and 0.02 per cent. solution of gelatin was used as the maximum suppressor. The titrations were carried out at -1.9 volts where the diffusion current attained a limiting value; and in an inert atmosphere of nitrogen to avoid the possible oxidation of nickel ferrocyanide complex,¹⁰ leading to a change in colour of the precipitate from green to yellowish brown; it may be added that in the present studies no such change in the colour has been noticed.

RESULTS AND DISCUSSION

Figure 1 gives a typical series of results on the variation of diffusion current during the progress of the amperometric titration of Ni^{++} with $\text{K}_4\text{Fe}(\text{CN})_6$ in presence of 1 M KCl used as supporting electrolyte. The data in Fig. 1 show that sharp end points could be obtained during the

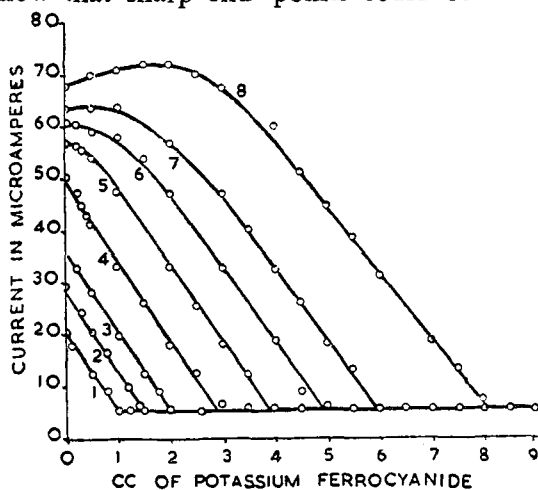


FIG. 1. Amperometric titration of Ni against potassium ferrocynide.

Concentration of ferrocynide 100 mM. Curves 1 to 8 refer respectively to 5, 7.5, 10.0, 15.0, 20.0, 25.0, 30.0, 40.0 millimolar of Ni^{++} , applied voltage -1.9 volts.

titration of Ni⁺⁺ with ferrocyanide polarographically. The observed quantities of potassium ferrocyanide for different concentrations of Ni⁺⁺ are given in Table I. It is interesting to note from the data in columns 3 and 4 (Table I) that the composition of nickel ferrocyanide complex corresponded to Ni₅K₆ [Fe (CN)₆]₄; this appears to follow the stoichiometric relationship according to the equation



TABLE I

Polarographic investigation of nickel ferrocyanide complex

Volume of Ni⁺⁺ solution in the cell 25.00 ml.

Concentration of Ni ⁺⁺ solution in mM (1)	Concentration of K ₄ Fe (CN) ₆ in mM (2)	Observed titre value in ml. (3)	Volume required on the basis of the formula Ni ₅ K ₆ [Fe(CN) ₆] ₄ (4)
1.25	50	0.5	0.5
2.5	50	1.0	1.0
5.0	50	2.05	2.0
7.5	50	3.0	3.0
10.0	50	4.0	4.0
12.5	50	5.0	5.0
15.0	50	6.05	6.0
17.5	50	7.0	7.0
20.0	50	8.0	8.0
25.0	50	10.05	10.0
30.0	50	12.0	12.0
40.0	50	16.05	16.0
5.0	100	1.0	1.0
7.5	100	1.45	1.5
10.0	100	2.0	2.0
15.0	100	3.0	3.0
20.0	100	4.0	4.0
25.0	100	5.0	5.0
30.0	100	6.05	6.0
40.0	100	8.0	8.0

The results showed conclusively that over a wide range of concentration of Ni⁺⁺ and K₄Fe (CN)₆, the composition of the complex, as derived from the end points of amperometric titration curves, appeared to be Ni₅K₆ [Fe (CN)₆]₄ or 3 NiK₂ [Fe (CN)₆], Ni₂ [Fe (CN)₆].

The data further show that the method could be employed with ease for quantitative estimation of Ni^{++} . The experimental error involved is less than 1 per cent.

A detailed examination of the titration curves shows a significant feature in the variation of the diffusion current at the initial stages of the titration. While the diffusion current was expected to decrease continuously with the addition of the titrant leading to the familiar *L*-shaped curves, in the present investigation the current values did not decrease in the initial stages and remained almost unaffected; this feature was more apparent at higher concentrations of nickel; in fact the current values increased (see curves 6-8, Fig. 1). Extrapolation of the straight line portion of the curves to Y-axis indicated that initial values of the limiting current should be much greater than the observed values.

The following Ilkovic's equation gives the theoretical values of limiting current i_d for different concentration of an electro-active substance:

$$i_d = 605 nCD^{\frac{1}{2}} mt^{\frac{1}{2}}$$

where C is the concentration of the substance in millimolars; n , the number of electrons involved in the electrode reaction; D , the diffusion coefficient of the ion in $\text{cm}^2 \text{sec}^{-1}$; m , the rate of flow of mercury in mgm./sec. ; and t , the time in secs. for 1 drop of mercury flowing through the capillary. Table II gives the observed values and the values of i_d calculated from the above equation for different concentrations of Ni^{++} ; in these,

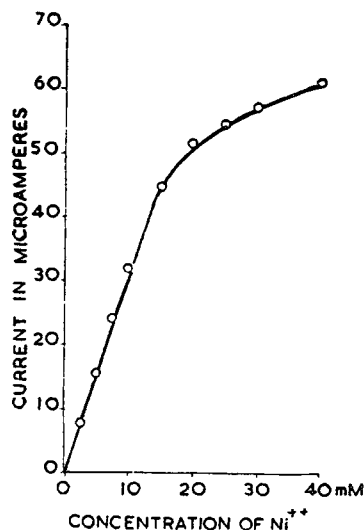


FIG. 2. Variation of the limiting current with the concentration of Ni^{++} .

D has been taken as 0.69×10^{-5} cm.²/sec.¹¹ The data in Table II show clearly that the i_d values do not follow Ilkovic's equation above 15 mM. concentration (see also Fig. 2). It is interesting to note from these data that

TABLE II
Applicability of Ilkovic's equation to the limiting current of Ni⁺⁺

Concentration of Ni ⁺⁺ in mM.	i_d calculated from Ilkovic's equation in μ amps.	i_d observed in μ amps.	Deviation per cent.
(1)	(2)	(3)	(4)
2.5	7.67	7.7	1.0
5.0	15.35	15.3	0.3
7.5	20.02	24.1	4.6
10.0	30.7	31.8	3.5
15.0	46.05	44.3	3.8
20.0	61.4	51.5 (61.0)	16.1
25.0	76.75	54.9 (75.0)	29.8
30.0	92.1	57.4 (90.0)	37.6
40.0	122.8	61.1 (117.0)	50.2

The values of i_d given in the paranthesis refer to those obtained by extrapolation of straight line portion of amperometric curves to the Y-axis (see Fig. 1).

the peculiar behaviour of the amperometric titration curves, viz., the non-linear variation of the current in initial stages of the titration, is closely associated with the non-applicability of Ilkovic's equation at higher concentrations. Since, however, the end points even at these high concentrations were very sharp, Ni⁺⁺ could be estimated polarographically upto 40 mM. concentration using K₄Fe(CN)₆ as the titrant,

SUMMARY

The composition of nickel ferrocyanide was investigated following the amperometric titration of Ni^{++} up to 40 mM. concentration against potassium ferrocyanide; it appeared to be $3 \text{NiK}_2 [\text{Fe}(\text{CN})_6]$, $\text{Ni}_2 [\text{Fe}(\text{CN})_6]$ or $\text{Ni}_5\text{K}_6 [\text{Fe}(\text{CN})_6]_4$. The data showed the possibility of estimating Ni^{++} polarographically within an experimental error of 1 per cent.

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REFERENCES

1. Werner .. *Pharm. Zty.*, 1918, **55**, 211-12.
2. ————— .. *Z. anal. Chem.*, 1919, **58**, 23-24.
3. Gaspar, Arnal and Alberto .. *Anales Soc. espan. fis. quim.*, 1926, **24**, 323-35.
Castro, Girona
Y. Pozurama
4. Britton and Eric N. Dodd .. *J. Chem. Soc.*, 1933, 1543-46.
5. Rene Paris .. *Compt. rend.*, 1934, **199**, 863-65.
6. Harry, Weiser, Milligan and .. *J. Phys. Chem.*, 1938, **42**, 945-54.
Bates
7. Sanigar, G. .. *Trav. Chim. Pays. Bas.*, 1925, **44**, 59.
8. Ramaiah and Agarwal .. *Proc. Ind. Acad. Sci.*, 1956, **44 A**, 134.
9. ————— .. *Ibid.*, 1956, **44 A**, 26.
10. Nilsson .. *Chem. Zentr.*, 1942, **1**, 2972.
11. Kolthoff and Lingane .. *Polarography*, Interscience Publication, Inc., New York, 1952, **1**.