

Biamperometric Titration of Cd(II) with Potassium Hexacyanoferrate(II) in Presence of Hg(II)

J. P. RAWAT & D. K. SINGH

Department of Chemistry, Aligarh Muslim University
Aligarh 202001

Received 1 October 1975; accepted 1 March 1976

Cd(II) (2.75-110 mg) can be determined accurately by biamperometric titration against potassium hexacyanoferrate(II) in the presence of various foreign ions. The interference of Hg(II) is removed by masking it with 2% KI solution. The equivalence point corresponds to the mole ratio 8:7 between Cd(II) and $\text{Fe}(\text{CN})_6^{4-}$ for the direct and reverse titrations thereby indicating the formation of a complex $\text{K}_{12}\text{Cd}_8[\text{Fe}(\text{CN})_6]_7$.

VARIOUS methods such as electrolytic deposition¹, gravimetric², titrimetric³⁻⁶ and potentiometric⁷ are reported in literature for the determination of Cd(II). However, the gravimetric methods are not accurate since in most of the cases either Cd(II) is not quantitatively precipitated or the thiocomplex formed cannot be dried to a constant weight². Cd(II) in amounts ranging from 1 to 25 mg can also be determined by amperometric titration using β -naphthoquinoline⁸. Amperometric titrations with two polarized electrodes are rapid and the end point detection is sharp. These titrations require simple instrumentation and can be performed at low voltage and are also known as "dead stop end point titrations".⁹ This technique has now been applied for the determination of Cd(II) by potassium hexacyanoferrate(II) and the results are presented in this note.

All the reagents used were of E. Merck (Darmstadt) or Analar BDH grades. Cadmium nitrate solution was prepared in 0.1M HNO_3 , and standardized with EDTA¹⁰. Potassium hexacyanoferrate(II) solution was prepared in conductivity water, and standardized with zinc¹¹. Potassium iodide solution (2%) was prepared in conductivity water.

The titration assembly was similar to that of Foulk and Bawden⁹. A conductivity cell (cell constant 1.29) was used for two identical Pt-electrodes and the voltage was supplied by a 2 V battery using a rheostat as a potential divider.

Procedure — An aliquot (50 ml) of Cd(II) solution containing 2.75-110 mg of Cd(II) taken in a 100 ml beaker was titrated against potassium hexacyanoferrate(II) solution under efficient stirring. The current was noted after each addition of titrant from a microburette. The equivalence point as indicated by the break in the curve was found to be sharp when the titration was carried out at 100-500 mV. The results are given in Table 1.

The mole ratios between Cd(II) and $\text{Fe}(\text{CN})_6^{4-}$ as calculated from the equivalence point were 1:143:1, 1:148:1, 1:143:1, 1:43:1, 1:153:1, 1:143:1 at 25, 50, 100, 300, 400 and 500 mV respectively. The composition of the complex was determined by carrying out direct and reverse titrations at 100 mV.

TABLE 1 — DETERMINATION OF Cd(II) BIAMPEROMETRICALLY

Cd(II)		Error (%)
Taken (mg)	Found (mg)	
2.754	2.754	0.00
5.508	5.508	0.00
11.015	10.872	-1.30
27.538	27.676	0.42
55.076	55.076	0.00
110.152	109.050	-0.99

TABLE 2 — TITRATIONS OF DIFFERENT AMOUNTS OF Cd(II) AGAINST POTASSIUM HEXACYANOFERRATE(II) AT 100 mV

Cd(II) taken (μmoles)	$\text{Fe}(\text{CN})_6^{4-}$ used (μmoles)	$[\text{K}_4\text{Fe}(\text{CN})_6]$ M	Mole ratio $\text{Fe}(\text{CN})_6^{4-}:\text{Cd(II)}$
1.96	1.72	0.020	1:1.139
19.52	17	0.010	1:1.148
19.52	17	0.052	1:1.148
24.50	21.32	0.052	1:1.148
97.60	86	0.020	1:1.135
976	852.72	0.102	1:1.144
1952	1728.48	0.052	1:1.129

Titrations of Cd(II) using different concentrations of cadmium and hexacyanoferrate(II) (Table 2) revealed that Cd(II) formed a complex with potassium hexacyanoferrate(II) of the formula $\text{K}_{12}\text{Cd}_8[\text{Fe}(\text{CN})_6]_7$ which is in agreement with the results of Bellamo and coworkers⁷. The same stoichiometry was also revealed when the reverse titration was performed. The shape of the curve for direct titration followed the trend of the titration of an irreversible couple with a reversible couple. In the reverse titration, initial current was very low. However, the current increased with the addition of the titrant and reached to a maximum around the midpoint and then decreased to nearly zero at the equivalence point, further addition of the titrant showed no appreciable change in the current. These results are in agreement with the titration of a reversible couple with an irreversible titrant. The results of varying pH and temperature revealed that the titration can be performed at pH 1 to 6 and at temperature between 15° and 80°. For the convenience the titration was performed at the room temperature. Determination of Cd(II) (5.508 mg) was also performed in the presence of several cations and anions. It was found that NH_4^+ (40 mg), K^+ (280 mg), Ba^{2+} (170 mg), Sr^{2+} (80 mg), Ca^{2+} (20 mg), La^{3+} (40.28 mg), Y^{3+} (35.56 mg) and Mg^{2+} (10.5 mg) did not interfere while Zn^{2+} , Hg^{2+} , Al^{3+} , Cu^{2+} , Mn^{2+} and Fe^{3+} showed interference. Cl^- , SO_3^{2-} , SO_4^{2-} , NO_3^- , I^- , CO_3^{2-} and CrO_4^{2-} did not interfere while PO_4^{3-} and HCOO^- interfered. The interference of Hg(II) was removed by adding KI solution (2%) till HgI_2 precipitated was dissolved completely forming $(\text{HgI}_4)^{2-}$. Determination of Cd(II) in the presence of Hg(II) was carried out and the results (Table 3) were quite accurate (error = -0.183 to 0.00%).

TABLE 3 — DETERMINATION OF Cd(II) IN THE PRESENCE OF Hg(II)

Hg(II) added (mg)	Cd(II)		Error (%)
	Taken (mg)	Found (mg)	
10.030	2.754	2.751	-0.072
10.030	4.406	4.406	0.000
30.088	5.508	5.508	0.000
50.148	5.508	5.498	-0.183
50.148	8.262	8.262	0.000

The authors are grateful to Prof. W. Rahman for facilities, and to the CSIR, New Delhi, for financial assistance to one of them (D.K.S.).

References

- BETLSTEIN, F. & JAWEIN, L., *Berichte der Busengesellschaft für Kalische Chemie*, **12** (1879), 759.
- DUVAL, C., *Inorganic thermogravimetric analysis* (Elsevier, Amsterdam), 1953.
- TANANAEV, I. V. & KOZLOV, A. S., *Zhur. anal. Khim.*, **6** (1951), 149.
- DESHMUKH, G. S. & VENUGOPALAN, M., *J. Indian chem. Soc.*, **33** (1956), 222.
- BELCHER, R. A., NUTTIN, J. & STEPHEN, W. I., *J. chem. Soc.*, (1951), 3444.
- THOMSON, T. L., *Ind. engng Chem. analyt. edn.*, **13** (1941), 164.
- BELLOMO, A., DEMARCO, D. & CASTLE, A., *Talanta*, **19** (1972), 1236.
- SAUDBERG, B., *Svensk Chem. Tidskr.*, **58** (1946), 197.
- FOULK, C. W. & BOWDEN, A. T., *J. Am. chem. Soc.*, **48** (1926), 2045.
- REILLEY, C. N., SCHMID, R. W. & SADEK, FAWZYS, J., *chem. Educ.*, **36** (1959), 555.
- KOLTHOFF, I. M., SANDELL, E. B., MEEHAN, E. J. & BRUCKENSTEIN, S., *Quantitative chemical analysis* (The Macmillan Co., London), IV edn, 1969, 800, 824.

Potentiometric Study of Complex Formation between Thiovanol & Th(IV), Zr(IV) & UO₂(VI)

K. M. KANTH*, K. B. PANDEYA† & H. L. NIGAM
Department of Chemistry, University of Allahabad
Allahabad

Received 13 May 1975; revised 5 March 1976;
accepted 22 May 1976

Complex formation between thiovanol (1-thioglycerol) and Zr(IV), Th(IV) and UO₂(VI) has been studied potentiometrically. Formation of 1:2 (metal-ligand) complex has been observed in each case. The log K₁^H for thiovanol comes out to be 8.75. Stability constants of the metal complexes follow the order Th⁴⁺ > Zr⁴⁺ > UO₂²⁺.

WE have recently reported¹⁻⁶ preparation and characterization of some transition metal complexes of thiovanol. The present note describes the results of pH-metric studies on complex formation of UO₂(VI), Zr(IV) and Th(IV) with thiovanol in solution.

*Present address: Department of Chemistry, R.D. & D.J. College, Monghyr, Bhagalpur University, Bihar.

†Present address: Department of Chemistry, University of Delhi, Delhi 110007.

TABLE 1 — METAL-LIGAND STABILITY CONSTANTS OF THE COMPLEXES

Metal ion	log K ₁	log K ₂	β ₂	ΔF° (kcal/mole)
Zr ⁴⁺	6.60	2.25	8.85	-12.10
Th ⁴⁺	6.25	2.85	9.10	-12.49
UO ₂ ²⁺	5.95	2.20	8.15	-7.12

Thiovanol (Evans Chemetics, New York) was used as such. Its fresh solutions were prepared in doubly distilled water and estimated iodometrically. Stock solutions of metal ions were prepared from analytical grade reagents and standardized by usual methods (Th was precipitated as [Th(C₂O₄)₂] and weighed as ThO₂; Zr, as [ZrH₂(PO₄)₂] and weighed as ZrP₂O and UO₂ as [UO₂(C₉H₆ON)₂-C₉H₇ON] and weighed as U₃O₈). A Leeds Northrup pH-meter fitted with a general purpose glass electrode was used for pH-measurements. All measurements were carried out at 25° in a nitrogen atmosphere. The following solutions were titrated against 0.1M NaOH solution: (i) 5 ml of 0.01M HClO₄+2.5 ml of 0.04M NaClO₄+42.5 ml water, (ii) 5 ml of 0.01M HClO₄+2.5 ml of 0.04M NaClO₄+2.5 ml of 0.009M thiovanol+17.5 ml water, (iii) 5 ml of 0.01M HClO₄+2.5 ml of 0.04M NaClO₄+25 ml of 0.009M thiovanol+2.5 ml of 0.01M metal ion (UO₂²⁺, Th⁴⁺ or Zr⁴⁺)+15 ml water.

The plots of pH versus the volume of alkali added gave S-shaped curves. Values of \bar{n}_H , \bar{n} and ρL at different pH values were calculated using standard relationships⁸⁻¹⁰. All calculations were made below pH 5.0. Absence of hydrolytic side reactions was also confirmed. A \bar{n}_H versus pH curve was obtained, which yielded the ρK_{1H} value for thiovanol as 8.75. The values of log K₁ were directly read from the \bar{n} - ρL formation curves and those of log K₂ were calculated using the method of Bjerrum¹¹ as modified by Irving and Rossotti¹² and Rossotti and Rossotti¹⁰. The results are presented in Table 1. The stabilities of thorium(IV) and zirconium(IV) complexes obey the Mellor and Maley order¹¹ (Th⁴⁺ > Zr⁴⁺).

Thanks are due to Messrs Evans Chemetics Inc., New York, for supplying thiovanol as a gift sample.

References

- NIGAM, H. L. & PANDEYA, K. B., *Indian J. Chem.*, **8** (1970), 454.
- NIGAM, H. L., MATHUR, V. K. & PANDEYA, K. B., *Indian J. Chem.*, **9** (1971), 1292.
- NIGAM, H. L. & PANDEYA, K. B., *Curr. Sci.*, **41** (1972), 449.
- NIGAM, H. L. & PANDEYA, K. B., *Proceedings, chemistry symposium, Chandigarh*, Part 2, 1961, 147.
- KANTH, K. M., PANDEYA, K. B. & NIGAM, H. L., *Indian J. Chem.*, **11** (1973), 103.
- KANTH, K. M., PANDEYA, K. B. & NIGAM, H. L., *Indian J. Chem.*, **11** (1973), 1034.
- VOGEL, A. I., *Quantitative inorganic analysis* (Longmans, Green, London), 1968, 539.
- BJERRUM, J., *Metal-ammine formation in aqueous solutions* (Haase, Copenhagen), 1941, 152.
- IRVING, H. M. & ROSSOTTI, H. S., *J. chem. Soc.*, (1954), 2904.
- ROSSOTTI, H. S. & ROSSOTTI, F. J. C., *Determination of stability constants* (McGraw-Hill, New York), 1961, 107.
- MELLOR, J. W. & MALEY, G. F., *Nature, Lond.*, **159** (1947), 370; **161** (1948), 436.