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Effect of ammonia on the redox reaction of cobalt(II) with potassium ferricyanide in alkaline medium

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ABSTRACT

The effect of ammonia on the redox reaction of cobalt(II) with potassium ferricyanide was studied potentiometrically as a function of pH, the concentration of ammonia and concentration of cobalt using as platinum as an indicator electrode and saturated calomel electrode as a reference electrode. In the presence of ammonia the formal potential of the Co(III)/Co(II) system is lower than the $[Fe(CN)_6]^{3-}$/ $[Fe(CN)_6]^{4-}$ coupled at a pH of 9.0 – 11.0, and hence it is possible to oxidize it quantitatively with potassium ferricyanide which is not possible otherwise. Thus, the addition of complexing agent increases the sharpness of the endpoint of titration with ferricyanide. The precision and accuracy of the method have been assessed by the application of lack-of-fit test and other statistical methods. Overall mean recovery and the mean standard analytical errors obtained were 99.81% and 0.0084 respectively. An interference study was carried out to check the possible interference of other metal ions.

Keywords— *Redox reactions, Potentiometry, Cobalt determinations, Ammonia, Ligand effect, Potassium ferricyanide*

1. INTRODUCTION

Cobalt ores are generally used for the manufacture of cobalt salts and not for the extraction of metals. It is used in the manufacture of special steels such as satellite which contains 55% cobalt. This steel is used for cutlery, surgical instruments lathe tools and for permanent magnets. Cochrome containing 60% cobalt is used for making resistance wires. Cobalt is also used for electroplating iron and other base metals. The estimation of trace amounts of cobalt has become of increasing importance, it was therefore considered desirable to develop simpler and sensitive titrimetric procedures for the purpose.

According to Serjeant [1], reactions used for potentiometric titration should have a large equilibrium constant to obtain a large potential near the equivalence point. This is possible only in the presence of suitable complexing agents forming stable complexes with the metal ions. The redox potential of the cobalt(III)-cobalt(II) couple varies in a wide range of values (from 1.8 to -0.6V) depending on the degree of complexation of cobalt(II) and cobalt(III), which is controlled by ligands selection, their concentration, and the solution pH. Many cobalt(II) complexes with amines are rather strong reducing agents capable of reducing some metal ions to the metallic state [2] and therefore used in electroless plating systems for the deposition of metallic coatings.

The oxidimetric determination of cobalt(II) in ammoniacal solution with hexacyanoferrate(III), was developed by Dickens and Massen [3] and Tomicek and Freiberger [4]. Lingane [5] thoroughly reinvestigated the qualities of the determination in the absence of other metals. Poppe and Den Boef [6] observed that the determination of smaller amounts of cobalt by this method proves to be impossible, because of poor response of the electrode employed. Lee [7] substituted polarised bimetallic electrodes for the platinum and calomel electrodes and observed excellent response at the endpoint for the titration of microgram quantities of cobalt. The use of amino acids instead of ammonia in the determination of cobalt with ferricyanide has been proposed by Kopanica and Dolezal [8] who used glycine as a complexing agent. Agasyan and Khakimova [9] used a mixture of alanine or phenylalanine and ammonia. The determination of cobalt includes determination by complexing it with malonate [10], colorimetrically [11], photometrically [12], by oxidation with chloramine-T [13], by acridine method [14], polarographically [15], by complexometric titrations [16], with periodate or thiocyanate [17] and iodometrically [18]

Cobalt(II) ion is more stable, as it cannot be oxidized easily to cobalt(III) state, which is far less stable. All cobalt(II) salts are therefore stable, however, in basic solutions oxidation of cobalt(II) to cobalt(III) takes place relatively easily. The present work deals with the determination of cobalt in alkaline solutions in the presence of ammonia as a chelating agent. The effect of ammonia on the redox reactions was studied potentiometrically as a function of pH, the concentration of ligand and concentration of cobalt using platinum as an indicator electrode and saturated calomel electrode as a reference electrode.

2.REAGENTS

All solutions were prepared using analytical grade reagents. Double distilled water was used throughout the present investigation. Standard solutions of 0.1M cobalt(II) sulphate solution and 0.1M ferricyanide were prepared from reagent grade chemicals.0.01M and 0.001M solutions were prepared from 0.1M solution by suitable dilution. Ammonium citrate solution was prepared by dissolving 50.0 mL of pure citric acid in 100.0 mL of water with 67.5 mL of concentrated ammonia solution. Aqueous ammonia was prepared by dissolving 30.0 mL of concentrated ammonia in 100.0 mL of distilled water.

2.1 Equipment

The potential and pH measurements were carried out with a digital pH/mV meter (Elico, Model L1-120) at ambient temperature (25ºC) with a precision of ±1 mV. The conventional potentiometric assembly consists of 100.0 mL titration cell, 10.0 mL burette and a mini magnetic stirrer. The pH meter was calibrated with 0.05 M phthalate (pH 4.02) and 0.05 M borax (pH 9.0) standard buffers prepared according to specification.

2.2 Procedure for the titration of Cobalt(II) with potassium ferricyanide.

An aliquot of 0.001 M cobalt (II) sulphate solution was transferred to the titration cell followed by 10.0 mL of ammonium citrate solution and 40.0 mL of aqueous ammonia the resulting solution was diluted to 100.0 mL. An aliquot of this solution was then titrated with an appropriately diluted potassium ferricyanide solution. Potential measurements were recorded with platinum as an indicator electrode and a saturated calomel electrode as a reference electrode. The precision of the proposed method was assessed by performing repeated titrations on each concentration of cobalt. An interference study was performed to check the possible interference.

3.RESULTS AND DISCUSSIONS

The direct titration of cobalt with potassium ferricyanide can be represented as,

$$\mathrm{Co^{2+} + [Fe(CN)_6]^{3-} \rightleftharpoons Co^{3+} + [Fe(CN)_6]^{4-}}$$

The equilibrium constant of the redox reaction of cobalt(II) with potassium ferricyanide can be written as

$$\log K = \log \frac{[\mathrm{Co^{3+}}][\mathrm{Fe(CN)_6}]^{4-}}{[\mathrm{Co^{2+}}][\mathrm{Fe(CN)_6}]^{3-}} = \frac{E^0_{\text{(ferri-ferrocyanide)}} - E^0_{\text{(cobalt)}}}{0.059}$$

where $E^0_{\text{(ferri/ferrocyanide)}}$ (0.36V vs. NHE) and E^0_{Co} (1.81V vs. NHE) are the standard redox potentials of the $[\mathrm{Fe(CN)_6}]^{3-}$/ $[\mathrm{Fe(CN)_6}]^{4-}$ and Co(III)/Co(II) systems, respectively, the equilibrium constant is calculated to be $10^{-24.75}$; the direct titration of cobalt(II) with potassium ferricyanide is impossible.

If ammonia forms complexes with cobalt(III) and cobalt(II), the redox potential of the Co(III)/Co(II) system can be written as,

$$E'_{\mathrm{Co}} = E^0_{\mathrm{Co}} + 0.059 \log \frac{\alpha_{\mathrm{Co(II)(ammonia)}}}{\alpha_{\mathrm{Co(III)(ammonia)}}} + 0.059 \log \frac{C_{\mathrm{Co(III)}}}{C_{\mathrm{Co(II)}}}$$

where α denotes the side reaction coefficient taking in to account the complex formation of cobalt(III) and cobalt(II) with ammonia $C_{\mathrm{Co(III)}}$ and $C_{\mathrm{Co(II)}}$ are the total concentration of cobalt(III) and cobalt(II) respectively.

In the presence of aqueous ammonia, the ammine complex of cobalt predominates. The formation constants for the cobalt(III) hexamine and cobalt(II) hexamine are,

$$\frac{[\mathrm{Co(NH_3)_6^{3+}}]}{[\mathrm{Co^{3+}}][\mathrm{NH_3}]^6} = 10^{34}, \frac{[\mathrm{Co(NH_3)_6^{2+}}]}{[\mathrm{Co^{2+}}][\mathrm{NH_3}]^6} = 10^5$$

In presence of ammonia, the conditional redox potential of the Co(III)/Co(II) system reported was,

$$\mathrm{Co(NH_3)_6^{3+} + e^- \rightleftharpoons Co(NH_3)_6^{2+}}, E' = +0.1\mathrm{V}$$

and the equilibrium constant of the reaction under the most favorable conditions of pH about 10.0 and concentration of ammonia not less than 1.0 M is 10^6, thus making the direct titration of cobalt(II) with ferricyanide possible in their presence, which is not feasible otherwise.

3.1 Effect of pH and concentration of ammonia

A large concentration of free ammonia is necessary for a sufficiently large equilibrium constant of the titration reaction. Because of the protonation of ammonia, the concentration of free ammonia is dependent upon the pH and the total (analytical) concentration of ammonia. The presence of a large concentration of ammonium ion is essential. With 3.0 M ammonia much of the Co(II) cobalt precipitates, if the concentration of ammonium ion is only 0.10 M, presumably because of relatively high pH. This is prevented by increasing the ammonium ion concentration to about 1.0 M, which decreases the pH from about 10.7 to 9.7.

For a given concentration of ammonia, enough ammonium ions must be present to keep the pH about 10.0. In the following precise titrations, the effect of ammonia was monitored by titrating cobalt(II) with potassium ferricyanide in the presence of 1.0 M ammonium citrate and three different concentrations of ammonia were prepared [1.0-3.0 M], and the typical titration curves are shown in figure 1. The stability constants of the complexes of cobalt(II) and cobalt(III) with ammonia can be used to show that an analytical concentration of ammonia of 1.0 M at pH 10.0 results in a maximum value of the equilibrium constant further increase in pH or analytical concentration of ammonia does not result in a larger value of the equilibrium constant.

To ascertain whether removal of dissolved air (oxygen) from the analyte solution was necessary, the trial with 2.0 mg of cobalt were run after the others and the air was not removed from the analyte solution or from the titrant solution used. Since the error is just as small (and positive) as in other cases it is evident that removal of air from the analyte and titrant solution is unnecessary.

The sensitivity of the potentiometric determination with a volume of about 100.0 mL, the concentration of ammonia was 1.0 M and that of ammonium citrate was 1.0 M. The lowest cobalt concentration studied was 29 µg. In a concentration range down to 10^{-5} M, as expected the rate of change of potential at the equivalence point with 2.9 µg of cobalt is very small and an error of about greater than 3% occurred at the end point. Below a concentration of 10^{-4} M an accurate determination of the equivalence point is impossible. Moreover, the reproducibility becomes very bad. When assumed 50.0 mL to be the lower limit of the titration volume, and conclude that 0.2 to 1.0 mg of cobalt can be determined potentiometrically with reasonable accuracy (within 1%) in the presence of other interfering elements. This is an agreement with the previously published results.

The titrations were also carried out by taking potassium ferricyanide solution in the beaker, and the cobaltous salt in the burette, the results are shown in figure 2. From many trials, the potential at the equivalence point was found to be large and it is reproducible within ± 3 mV, as we done in the previous case where cobalt solution was taken in the beaker, and a waiting period of about 2 min was allowed after each increment of titrant solution were added.

3.2 Interference studies

The determinations were carried out using the same procedure as for the determination of the various amount of cobalt. The direct titration was the more convenient and is recommended except for cases in which cobalt is determined in the presence of silver or in the presence of chromate, vanadate and molybdate together. The back-titration must be used in these cases. With the conditions pH about 10, a citrate medium and ammonia as a complexing agent, the most common elements do not interfere except for manganese(II) and chromium(III).

In the direct titration, chromium(III) interferes only when it is present in an amount more than 100 times that of cobalt because the oxidation of chromium(III) to chromate by hexacyanoferrate(III) is slow. In the case of the back titration, small amounts of chromium(III) interfere because the chromium(III) is in contact with an excess of hexacyanoferrate(III) for some time and oxidation to chromate is appreciable. Hence prior oxidation is preferable but the reproducibility of the determination is then worse. Manganese(II) interferes seriously, in the potentiometric determination of cobalt, because it is oxidized by hexacyanoferrate(III). In presence of citrate, the oxidation product is a manganese(III) citrate complex and no precipitate appears. The reaction took place in the pH region 7.0-11.0, in which the oxidation of cobalt(II) with hexacyanoferrate(III) was investigated.

In the absence of citrate, manganese(II) is oxidized to manganese dioxide, according to the reaction.

$$2\mathrm{Fe(CN)}_6^{3-} + \mathrm{Mn}^{2+} + 4\mathrm{OH}^- \longrightarrow 2\mathrm{Fe(CN)}_6^{4-} + \mathrm{MnO}_2 + 2\mathrm{H}_2\mathrm{O}$$

This reaction is strongly affected by pH. In the pH range 7.0-8.0 or lower, manganese(II) is stable towards hexacyanoferrate(III). The oxidation of manganese(II) at pH 10.0 occur at the same potential as the oxidation of cobalt(II), no simultaneous determination of cobalt(II) and manganese(II) is possible. The interference of manganese(II) can be overcome in two ways. First the use of ethylenediamine, instead of ammonia results in a much larger potential change at the equivalence point because of an extra stabilization of the tervalent state of cobalt.

Second, in the absence of citrate, oxidation of manganese(II) no longer takes place when the pH is 8.0 or less, at this pH the concentration of ammonia is too small and no longer be used as a complexing agent for cobalt, so a used of amino acids instead of ammonia at pH 7.0 to 8.0 to prevent the interference of manganese.

When other metals like iron(III) present, auxiliary complexing agents were added to avoid the precipitation of hydroxides, fluoride was selected and it is found suitable to prevent the interference of iron(III), but in the presence of large amounts of manganese(II), however, cause precipitation of manganous fluoride.

Nickel(II) does not interfere in the determination when it is present in a 1000-fold amount.

3.3 Precision and accuracy

In order to study precision and accuracy of the proposed method, standard solutions containing eight different concentrations of cobalt were prepared and six titrations were performed with each standard solution and results obtained are given in Table 3.24. The overall mean recovery for 48 determinations was 99.81% while mean standard analytical errors were 0.0084, these statistical parameters reflect the reliability of the proposed method. Two-tailed student's t-test was applied for comparing the amount taken (μ) for analysis and the amount found ($\overline{x}$) at each concentration level. The mean value of student's t-value calculated for eight concentration levels was 1.26 which was less than the critical value of 2.57 at 5% level of significance and 5 degrees of freedom. It indicated the absence of any systematic error in the proposed method.

A significant test namely lack-of-fit test was performed to check whether the data fit a linear model indicating the agreement between the amount taken and found for the analysis. In the test, a hypothesis stating the data to fit a linear model is considered and an F-value is calculated. If the calculated value of F is less than the critical value, the hypothesis is retained. The calculated value of F for data given in Table 3.24 was 1.39 which was less than the critical value of 2.34 at 5% level of significance and 6, 40 degrees of freedom. In indicating the data to fit a linear model and the absence of any systematic error in the analysis.

Table 1: Potentiometric titration of cobalt(II) with $K_3[Fe(CN)_6]$ in the presence of ammonia
The calculated F-value in the lack-of-fit test was 1.39

S. No	Amount taken (mg)	Amount found (mg)	Mean ($\bar{\bar{x}}$) ± Std. Dev.	Mean recovery (%)	Standard analytical error	Student's t
1	0.29	0.29, 0.28, 0.29, 0.27, 0.28, 0.29	0.283 ± 0.008	97.70	0.0033	2.00
2	0.59	0.59, 0.56, 0.58,0.60, 0.58, 0.59	0.583 ± 0.001	98.87	0.0056	1.20
3	0.88	0.88, 0.90, 0.92, 0.87, 0.88, 0.90	0.891 ± 0.001	101.32	0.0075	1.56
4	2.95	2.94, 2.96, 2.97, 2.95, 2.99, 2.94	2.958 ± 0.001	100.28	0.0079	1.05
5	5.89	5.92, 5.88, 5.90, 5.89, 5.94, 5.88	5.901 ±0.002	100.20	0.0098	1.19
6	14.73	14.76, 14.70, 14.74, 14.73, 14.72, 14.77	14.736 ± 0.002	100.04	0.0105	0.63
7	29.47	29.49, 29.51, 29.45, 29.47, 29.50, 29.52	29.490 ± 0.002	100.07	0.0106	1.88
8	58.93	58.90, 58.92, 58.96, 58.94, 58.92, 58.98	58.936 ± 0.003	100.01	0.0120	0.56
			Mean…	99.81	0.0084	1.26

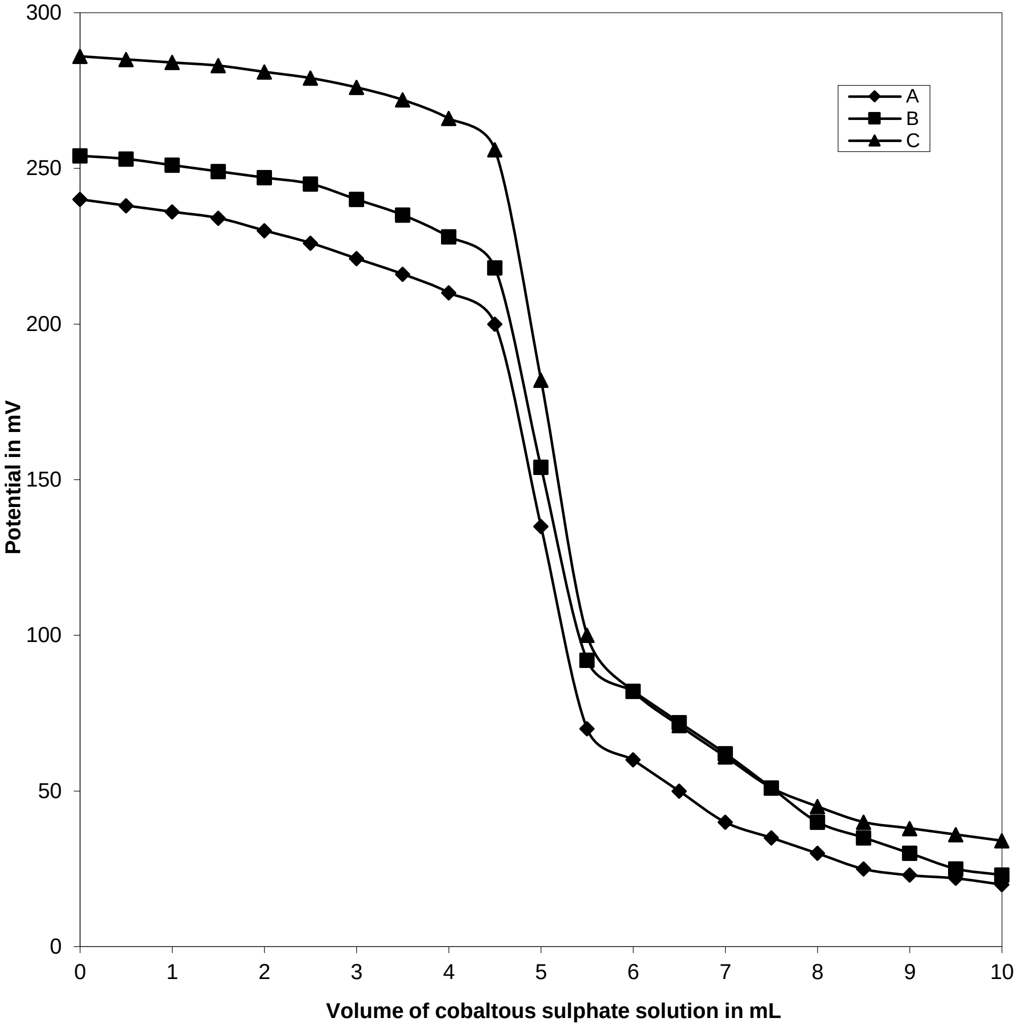

Fig. 1: Effect of ammonia concentration on the titration curves of 0.30 mg of Co (II) with 1.01×10^{-3} M of potassium ferricyanide at pH 10.0 using platinum as an indicator electrode. Curve A 1.0 M; Curve B 3.0 M; Curve C 5.0 M

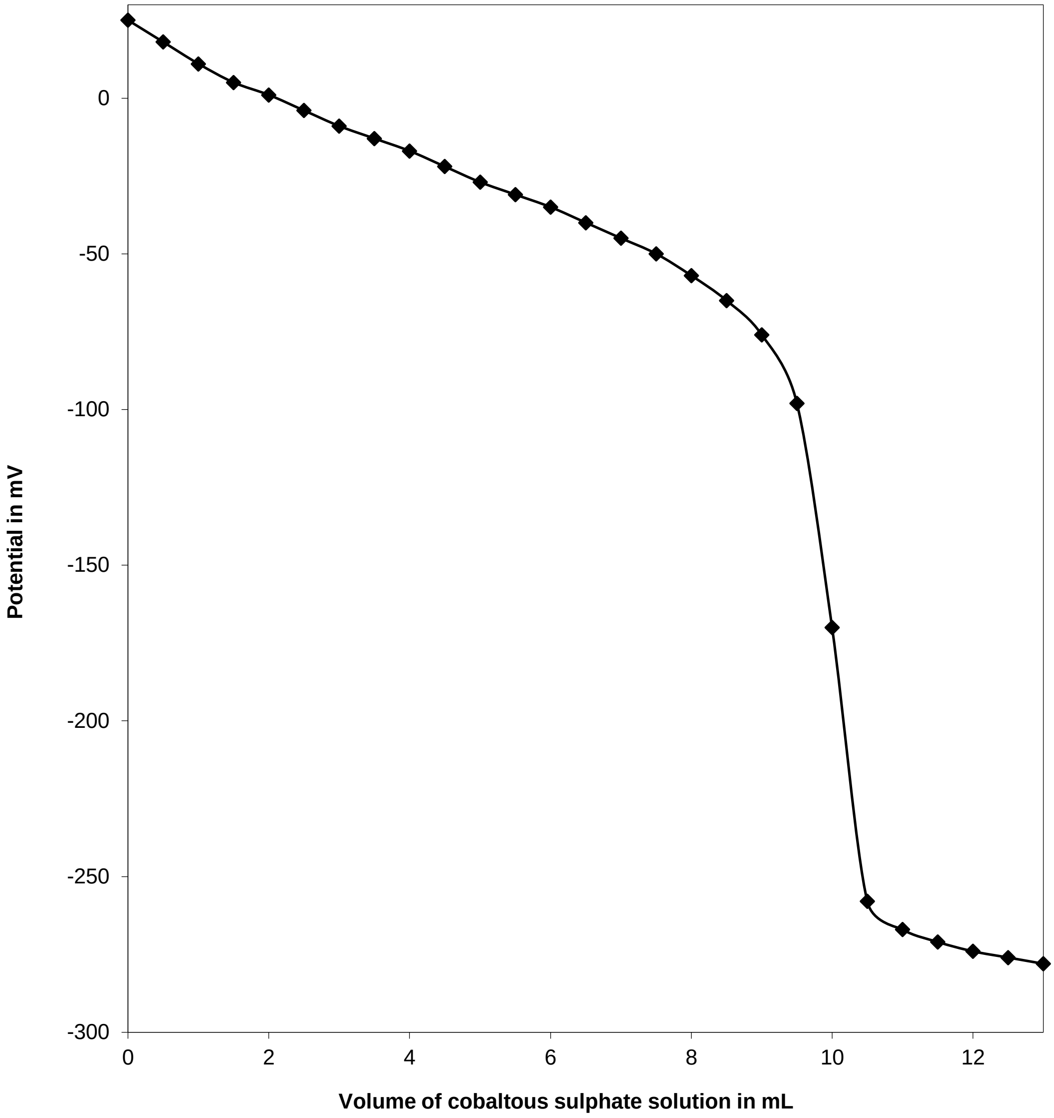

Fig. 2: Potentiometric titration of 5.89 mg of Co(II) with 9.75x10^{-3} M of potassium ferricyanide in the presence of ammonia at pH 10.0 using platinum indicator electrode.

4. CONCLUSION

The studied redox reaction of cobalt(II) with ferricyanide in the presence of complexing agent greatly improves the selectivity and sensitivity of the method. The studied redox reaction has several possible analytical applications. The method could be extended for the determination of cobalt in ore and steel samples.

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