International Journal of Scientific Engineering and Research (IJSER)
ISSN (Online): 2347-3878
Index Copernicus Value (2015): 56.67 | Impact Factor (2017): 5.156

Potentiometric Titration of Manganese (II) with Potassium Ferricyanide using Mannitol as a Complexing Agent

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Abstract: ***A new method has been proposed for the potentiometric titration of manganese ion with potassium ferricyanide in the presence of mannitol as a complexing agent in a potassium hydroxide medium. The optimum conditions for potentiometric end-point detection were studied as a function of concentration of mannitol, concentration of potassium hydroxide and concentration of manganese(II), under the optimum conditions the titrations are fast and exhibit a reasonable potential change at the equivalence point. Thus, the addition of complexing agent increases the sharpness of 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 stastical methods. Overall mean recovery and the mean standard analytical errors obtained were 100.06% and 0.0097 respectively.***

Keywords: Redox reactions, Manganese determinations, mannitol, potassium ferricyanide

1. Introduction

Manganese plays a vital role in the steel industry, because of its great importance to the steel making, the determination of manganese has engaged the attention of several chemists, resulting in the accumulation of a vast and varied literature. The manganese minerals of great industrial importance are the oxides of manganese like pyrolusite, manganite, braunite, hausmannite and rhodonite. The most extensive use of manganese is a considerable tonnage of MnO_2 is used annually in the manufacture of dry cells. The principle ferroalloys of manganese are high carbon ferromanganese, low carbon ferromanganese, spiegeleisen and silico-spiegel. Manganese has a powerful effect on the harden ability of steel. It was therefore, considered worthwhile to determine manganese in the presence of mannitol and examine the precision and accuracy of the potentiometric procedure using conventional platinum electrode.

Many of the procedures recommended for the titrimetric determination of manganese(II) consist of treating the sample with an excess of an oxidizing agent at room temperature, with or without catalyst, removing the excess of the oxidizing agent, then titrating the manganese(VII) formed with a standard solution of a suitable reducing agent.

The oxidation of manganese(II) with the excess bismuth tetroxide, at room temperature was suggested by Schneider [1], the method has been improved by among others, Reddrop and Ramage [2], Ibbotson and Brearley [3], Blum [4], Cunningham and Coltman [5], who employed sodium bismuthate in a nitric acid medium in place of bismuth tetroxide. Bart Park [6] reported the oxidation of manganese(II) with excess of sodium bismuthate in sulphuric acid medium. A widely employed method consists of boiling the sample with excess of persulphate in a mixture of sulphuric and phosphoric acids in the presence of silver nitrate as a catalyst, and titrating the permanganic acid formed with a standard solution of a suitable reducing agent. These methods suffer from the disadvantage that some of the permanganic acid may decompose when the solution is boiled to destroy the excess of persulphate.

Willard and Thomson [7], boiled the manganese(II) sample with an excess of potassium periodate in a medium containing sulphuric and phosphoric acids. Willard and Merritt [8], proposed ozonized oxygen for the oxidation of manganese(II) perchlorate in a perchloric acid medium using silver nitrate as a catalyst. Tanaka [9] and Lingane and Dours [10] oxidized the manganese(II) with excess of silver(II) oxide in acid solution.

The methods proposed by Metzger and Marrs [11], Muller and Wahle [12] involve the oxidation of manganese(II) to manganese(III) by permanganate in a hydrofluoric acid medium to stabilize the manganese(III). Watters and Kolthoff [13] reported that manganese(II) can be oxidized to manganese(III) by treatment with excess lead dioxide in a pyrophosphate medium. Ingamells [14] proposed oxidizing manganese(II) to manganese(III) with nitric acid in a strong phosphoric acid-pyrophosphate medium.

Lingane and Karplus [15] developed a new method for the determination of manganese in the presence of pyrophosphate. Oxidation of manganous ions with potassium permanganate in the presence of fluoride has been investigated as a method for determination of manganese(II) [15-17]. According to serjeant [18], 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 present paper describes the effect of mannitol on the redox titration of Manganese(II) sulphate with potassium ferricyanide which effectively stabilize in solution thermodynamically unstable manganese(IV) ions.

2. Reagents

All solutions were prepared using analytical grade reagents. Double distilled water was used throughout the present investigation. Standard solutions of 0.1M manganese(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. Mannitol (0.50 M) and potassium hydroxide (1.0 M) were prepared by dissolving an appropriate amount of salts in 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 manganese(II) with potassium ferricyanide

An aliquot of 0.01 M manganese(II) sulphate solution was transferred to the titration vessel followed by 20.0 mL of 0.50 M mannitol and KOH (2.0-6.0 mL, 1.0 M) was added and the resulting solution was diluted to 50.0 mL. The solution was then titrated against appropriately diluted potassium ferricyanide solution taken in a burette. Potential measurements were followed by using platinum as an indicator electrode and saturated calomel electrode as a reference electrode. The concentration of manganese was varied and six replicate titrations at each concentration were performed using platinum electrode.

3. Results and Discussions

The polarographic behavior of the complexes of di, tri and tetravalent manganese and other metals with mannitol were initially investigated to find out the structure of the complexes and their analytical use [16]. The results of the above investigation were utilized in polarographic analysis and in the oxidimetric determination of manganese(II) with hexacyanoferrate(III) [17].

Based on the results of the polarographic study of the manganese(II) oxidation at a dropping mercury electrode in an alkaline mannitol medium, they established that the following reactions should take place during the course of the reaction.

$$x\mathrm{Mn}^{2+} + y(\mathrm{mannitol}\text{-}n\mathrm{H})^{n-} + \mathrm{ZOH}^{-} \;\square\;\square\square\; (\mathrm{Mn}_{x}(\mathrm{mannitol}\text{-}n\mathrm{H})_{4}(\mathrm{OH})_{z})^{+2x-ny-z}$$

$$(\mathrm{Mn}_{x}(\mathrm{mannitol}\text{-}n\mathrm{H})_{4}(\mathrm{OH})_{z})^{+2x-ny-z} \;\square\;\square\square\; (\mathrm{Mn}(\mathrm{mannitol}\text{-}n\mathrm{H})_{4})^{+2-ny} + (\mathrm{Mn}_{z-1}(\mathrm{OH})_{z})^{+2(x-1)-z}$$

For $x = 1$ and $z = 2'$,

$$\mathrm{Mn}(\mathrm{OH})_{2} + y(\mathrm{mannitol}\text{-}n\mathrm{H})^{n-} \;\square\;\square\square\; (\mathrm{Mn}(\mathrm{mannitol}\text{-}n\mathrm{H})_{4})^{+2-ny} + 2\mathrm{OH}$$

In presence of mannitol, the Mn(II) gets oxidized to the Mn(IV)-mannitol complex with hexacyanoferrate(III) this is in well agreement with the results obtained by Dolexal et al., [19] who reduces the resulting manganese(IV)-mannitol complex with the iron(II) sulphate, to the manganese(III)-mannitol complex.

The present work is concerned with the potentiometric titration of manganese(II) with potassium ferricyanide in the presence of mannitol and the reaction were studied potentiometrically as a function of concentration of potassium hydroxide employed, concentration of mannitol and concentration of manganese.

3.1 Effect of potassium hydroxide concentration

During the potentiometric monitoring of the course of the manganese oxidation, the dependences on the concentrations of potassium hydroxide and concentration of mannitol were followed.

Manganese(II) solution of 2.75 mg of Mn(II) were added to 30.0-40.0 mL of 1.0-3.0 M potassium hydroxide and 0.50 M mannitol, oxygen was removed from the solution by passing nitrogen for 10-20 min and the solution was titrated against potassium ferricyanide. The best results were obtained in a medium 1.0-3.0 M in potassium hydroxide and 0.5 M in mannitol. The effects of the potassium hydroxide concentration on the reaction course are show in Figure 1. Potential values stabilize practically instantaneously in 1.0-3.0 M potassium hydroxide. If the hydroxide concentration is less than 1.0 M, the results of the oxidation always subject to a negative error, the value of which decreased with increasing hydroxide concentration.

3.2 Effect of mannitol concentration

The effect of mannitol concentration on the potentiometric titration curves of 3.30 mg of manganese(II) with potassium ferricyanide with 3.0 M in potassium hydroxide solution was examined in the range 1.0-0.03 M of mannitol solution. A potential break of 190 mV was observed for 0.5 M mannitol with 3.0 M potassium hydroxide solution. The potential break at the equivalence point increase linearly with the increase in the concentration of mannitol. The results are shown in Figure 2.

Titration of manganese(II) with potassium ferricyanide was carried out in mannitol medium using platinum electrode against saturated calomel electrode. The potential against volume plot gave S-shaped curves with large well defined potential change in the region of end point. (Figure 3).

3.3 Precision and accuracy

To study the precision and accuracy of the proposed method, standard solutions containing ten different concentrations of manganese(II) were prepared and six titrations were performed with each standard solution and results obtained are given in Table 1. The overall mean recovery for 60 determinations was 100.06% and mean standard analytical error were 0.0097. 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. Student's t-value was calculated at each concentration level by stating a hypothesis that mean of amount found by six replications $(\overline{x})$ was not significantly different from the amount taken for analysis (µ). The mean value of student's t-value calculated for ten concentration levels was 1.04 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.

The lack-of -fit test was applied to check whether the regression of the amount taken for the analysis vs the amount found by six replications at each concentration, fit a linear model. Calculated F-value in lack-of-fit test was 1.33 which was less than the critical value of 2.10 at 5% level of significance and 8, 60 degrees of freedom. It indicated the data to fit a linear model and the absence of any systematic error in the analysis.

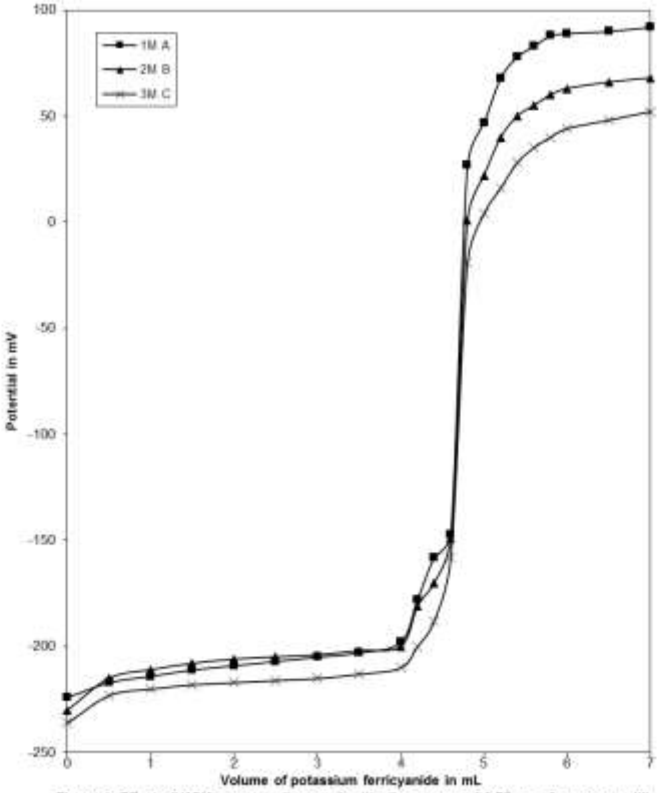

Figure 1: Effect of KOH concentration on the titration curves of 2.75 mg of manganese(II) with 1.06×10^{-2} M potassium ferricyanide in the presence of 0.5 M mannitol using platinum electrode.
Curve A 1.0 M; Curve B 2.0 M; Curve C 3.0 M;

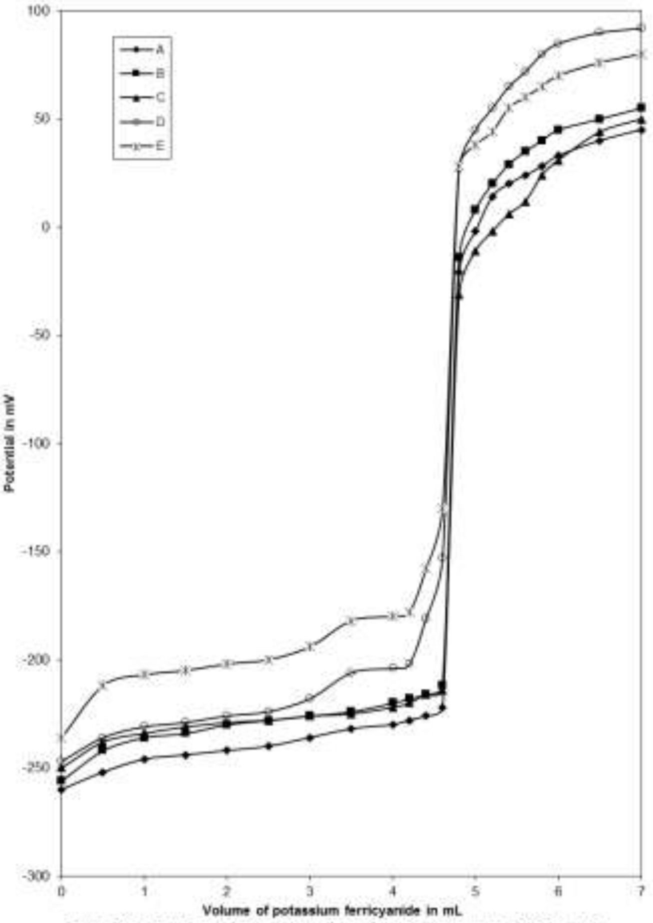

Figure 2: Effect of mannitol concentration on the titration curves of 3.30 mg of manganese(II) with 1.28×10^{-2} M potassium ferricyanide in alkaline medium. Curve A 1.0 M; Curve B 0.5 M; Curve C 0.1 M; Curve D 0.06 M; Curve E 0.01 M

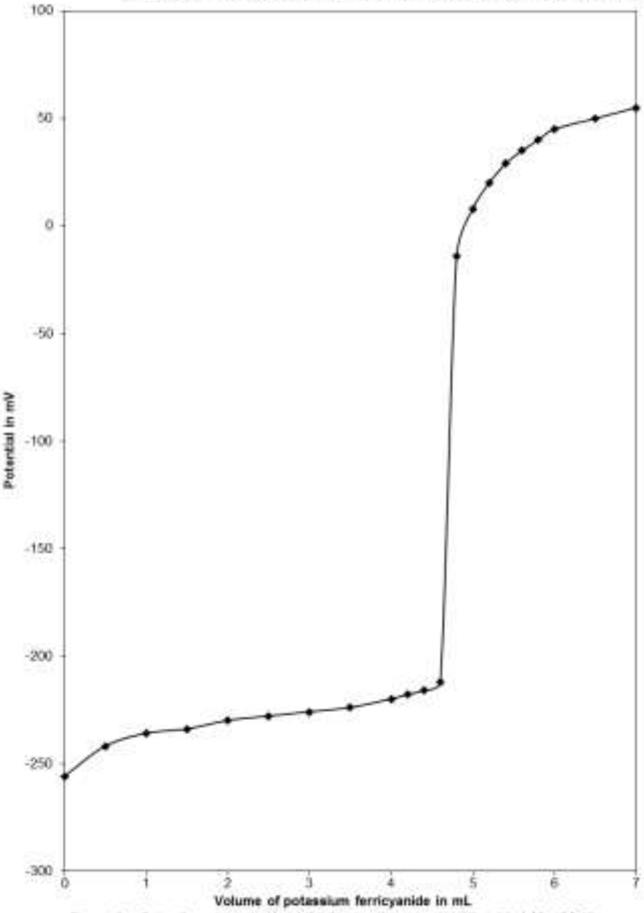

Figure 3: Potentiometric titration of 2.75 mg of manganese(II) with 1.06×10^{-2} M potassium ferricyanide in the presence of 0.5 M maannitol using platinum indicator electrode.

Table 1: Potentiometric titration of manganese(II) with potassium ferricyanide in the presence of mannitol**.**

S. No	Amount Taken (mg)	Amount Found (mg)	Mean ($\bar{x}$) ± Std.Dev.	Mean Recovery (%)	Standard Analytical Error	Student's t
1	1.65	1.65, 1.66, 1.64, 1.66, 1.65, 1.65	1.651 ± 0.007	100.10	0.0031	0.54
2	4.40	4.40, 4.41, 4.39, 4.41, 4.40, 4.41	4.403 ± 0.008	100.08	0.0033	1.00
3	6.60	6.62, 6.61, 6.61, 6.60, 6.62, 6.60	6.610 ± 0.008	100.15	0.0036	2.74
4	9.90	9.90, 9.92, 9.94 9.90, 9.90, 9.89	9.908 ± 0.018	100.08	0.0075	1.11
5	16.49	16.50, 16.51, 16.54, 16.52, 16.48, 16.49	16.506 ±0.022	100.10	0.0088	1.89
6	21.99	21.98, 21.99, 22.02, 22.04, 21.98, 21.99	21.992 ± 0.025	100.04	0.0100	1.00
7	32.98	32.97, 32.98, 33.04, 33.02, 32.96, 33.01	32.996 ± 0.031	100.05	0.0130	1.30
8	43.98	43.97, 44.02, 44.03, 43.94, 43.97, 43.99	43.986 ± 0.033	100.01	0.0140	0.48
9	65.98	65.96, 65.98, 66.03, 66.01, 65.94, 66.04	65.993 ± 0.039	100.02	0.0160	0.82
10	98.97	98.96, 99.03, 98.95, 98.94, 99.04, 99.02	98.990 ± 0.044 Mean…	100.02 100.06	0.0180 0.0097	1.09 1.04

4. Conclusion

The studied redox reaction of manganese (II) with ferricyanide in the presence of mannitol as a 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 manganese in ore and steel samples.

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