

STUDY OF THE RATE OF ELECTROLYTIC OXIDATION OF Mn(II) To Mn(III) AND ITS REACTION WITH THIOSULPHATE USING FERROIN AS INDICATOR

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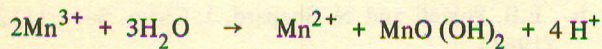
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The rate of electrolytic generation of Mn(III) in sulphuric acid medium and the shelf life of the so prepared solution have been studied. The prepared solution has been successfully used to standardise a method for the determination of thiosulphate potentiometrically, with Mn(III) as self indicator and ferroin as external indicator. The method reported here is convenient, practical, accurate and can be used for routine work also.

INTRODUCTION

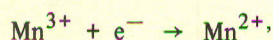
Since manganese (II) is highly stable in neutral or acidic aqueous solutions, all its compounds are strong oxidants in acidic media [1]. Disproportionation is greatly responsible for the deterioration of the stability of the manganese (III) solutions forming stable complexes with manganese (III) or by increasing the concentration of manganese (II) or of hydrogen ions [1].



Although diphosphate, phosphate and fluoride have often been used as complexing agents, yet in a number of cases the complexing properties of acetic, sulphuric and various polyaminocarboxylic acids have also been pressed into effect [2].

Manganese (III) usually oxidises many inorganic substances fast in direct titrations, whereas the oxidation of organic compounds is often slow [2]. Hence in the latter cases an excess of the reagent is usually added to increase the rate of the reaction and to make unambiguous, stoichiometric and quantitative studies so that the excess of the reagent is back titrated to determine its exact consumption.

Keeping in view the high redox potential value of about +1.4V of the system,



Mn(III) has been made use of in the present work [1]. Although the determinations of a variety of inorganic and organic substances has already been carried out using manganese (III) as volumetric titrant [1, 2], yet in the

present investigations its usefulness has been extended through the study of the rate of electrochemical generation of its diphosphate complex in sulphuric acid, stability of the diphosphate complex, introduction of Ferroin [1-10] phenanthroline iron (II) salt] (Ferroin) as a new redox indicator in its investigations on redox studies and the standardisation of a method for the determination of thio-sulphate. Some of the results of these investigations have been reported in this work.

EXPERIMENTAL

Reagents: In all these studies the water means double distilled water if not otherwise mentioned:

Manganese (II) sulphate. A 1.0M aqueous solution of manganese (II) sulphate ($\text{MnSO}_4 \cdot \text{HO}_2$) was prepared by dissolving 169.02 g of the substance (Merck) in one litre of water.

Sodium pyrophosphate (anhydrous). A 1.0 M solution of sodium pyrophosphate was prepared by dissolving 266.0 g of the substance (Merck) per litre.

Potassium dichromate. A 0.01N standard aqueous solution was prepared by dissolving 1.226 g of the substance (GR - Merck) in 250.0 ml of water.

Ferrous sulphate. Approximately 0.1 N solution of ferrous sulphate was prepared by dissolving 0.695 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (GR-Merck) in 250 ml of water in which 5 ml of concentrated H_2SO_4 (GR-Merck) was already added and the solution so prepared was standardised according to the conventional method.

Diphenylamine. A 1.0% solution in concentrated sulphuric acid was used during these studies.

Ferroin. A $\frac{1}{40}$ M Ferroin solution (Merck) was used as redox indicator.

Sodium thiosulphate. A 0.1N aqueous solution of sodium thiosulphate was prepared by dissolving 12.409 g

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Table 2. Showing the stability of the Mn(III) solutions prepared in 10 N and 15N H₂SO₄

Medium	Time (hours)	Mn(III) solution kept at	
		30° (N)	20° (N)
10N H ₂ SO ₄	0	0.0388	0.0388
	24	0.0270	0.0273
	48	0.0221	0.0242
	96	0.0125	0.0160
	120	0.0107	0.0141
	170	0.0087	0.0119
15N H ₂ SO ₄	0	0.0388	0.0388
	24	0.0275	0.0280
	48	0.0268	0.0275
	96	0.0262	0.0270
	120	0.0255	0.0263
	170	0.0250	0.0260

According to the Table 2, the rate of decrease of Mn(III) concentration is greater at higher temperature (30°) than at low temperature (20°) both in 10N and 15N H₂SO₄. But the decrease in the normality of Mn(III) in 10N H₂SO₄ is more than in 15N H₂SO₄ both at 20° and 30°

The determination of thiosulphate was carried out in 10N H₂SO₄ as medium using Mn(III) as self-indicator, Ferroin as external indicator and potentiometrically. From the results of these studies as reported in Table 3, it is obvious that thiosulphate can be easily determined within the range from 0.09 to 1.20 mg with a maximum error of -1.67% potentiometrically, -2.0% in case of Mn(III) as self indicator and -0.83% in case ferroin is used as indicator. The reaction proceeds very fast and one titration could be completed within 3-5 min. Therefore, any of the reported methods is quite convenient to follow the determination of thiosulphate. Even in case of the potentiometric end-point method the potential stabilisation is quite fast after each addition of the titrant.

Table 3. Showing the results of determination of thiosulphate in 10N H₂SO₄ medium

Thiosulphate taken (mg)	Thiosulphate found potentiometrically (mg)	Error (%)	Thiosulphate found with Mn(III) as self-indicator (mg)	Error (%)	Thiosulphate found with ferroin as indicator (mg)	Error (%)
1.20	1.18	-1.67	1.18	-1.67	1.19	-0.83
0.60	0.59	-1.66	0.59	-1.66	0.60	± 0.00
0.50	0.50	± 0.00	0.49	-2.00	0.50	± 0.00
0.21	0.21	± 0.00	0.21	± 0.00	0.21	± 0.00
0.16	0.16	± 0.00	0.16	± 0.00	0.16	± 0.00
0.10	0.10	± 0.00	0.10	± 0.00	0.10	± 0.00
0.09	0.09	± 0.00	0.09	± 0.00	0.09	± 0.00

time it was clear that after 120 hr of electrolysis time, the rate of oxidation of Mn(II) and the concentration of the solutions were almost equal with respect to Mn(III) content whether it is 10N or 15N H₂SO₄ or the current intensity is 0.3 Amp in the case of 10 N sulphuric acid or 0.1, 0.2 or 0.3 Amp in the case of 15N sulphuric acid.

REFERENCES

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2. J. Barek and A. Berka, *Use of Mn(III) in Titrimetry*, *CRC Crit. Rev. in Anal. Chem.*, May (1980).