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Use of Some Redox Indicators in Mn(IV) Oxidimetry

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The results of the titrimetric determination of reductants like ascorbic acid in phosphoric acid medium, potassium iodide and hydroquinone with Mn(IV) using sodium diphenyl amine sulphonate as an indicator, hexcyanoferrate(II) and iron(II) with Mn(IV) using N-phenyl anthranilic acid and thiazine dyes respectively in sulphuric acid medium are reported.

INTRODUCTION

Ascorbic acid is one of the potentially important vitamins in the human body. The numerous methods reported in the literature for the determination of the most important vitamin in the human body called vitamin C or ascorbic acid. Ascorbic acid solution can also be used instead of thiosulphate in a wide variety of iodometric determinations[1], variamine blue serves as indicator. The titration of iodide with silver nitrate in aqueous medium is more facile compared to that of chloride or bromide with most of the adsorption indicators. The reason for the facility especially with flourescein and azine type of indicators is due to the low solubility of silver iodide. The fluorescein derivatives are suitable for use as indicators in the determination of iodide[2, 3]. The indicator *p*-ethoxychrysoidine[4, 5] also functions excellently for the determination of iodide. The determination of hydroquinone is usually based on its reducing property. The redox potential of hydroquinone in equilibrium with quinone system at 25°C is reported to be 0.698 V in acid solutions. It is stable in weakly acid solutions. Murali Krishna *et al.*[6], reported a titrimetric method for the determination of hydroquinone and hexacyanoferrate(II) with Mn(IV) using nitrodiphenylamine as indicator. Rukmini *et al.*[7] used thiazine dyes and ferroin as indicators in sulphuric acid medium for the determination of hexacyanoferrate(II) with Mn(IV)[7]. Rukmini and Kavitha[8] developed a titrimetric method for the determination of iodide and ferrocyanide with Mn(IV) using thiazine dyes as indicators. A systematic study on the determination of reductants like ascorbic acid, in the presence of phosphoric acid medium, potassium iodide and hydroquinone in sulphuric acid medium with Mn(IV) using sodium diphenylamine sulphonate, hexacyanoferrate(II) and iron(II) in sulphuric acid medium with Mn(IV) using N-phenyl anthranilic acid and some thiazine dyes respectively has not been reported. Hence the authors attempted to develop conditions for the titrimetric determinations of the above reductants with Mn(IV) using redox indicators.

EXPERIMENTAL

A 0.02% solution of the sodium diphenylamine sulphonate is prepared in water. N-phenyl anthranilic acid[9] is prepared by dissolving 100 mg in 2 mL of 5% sodium carbonate and make it up to 100 mL with distilled water. A 0.05% of thiazine dyes (toluidine blue, new methylene blue, azure B and azure C) are prepared in deionized water.

A 0.025 M ascorbic acid solution is prepared and standardised[10]. A 0.05 M potassium iodide solution is prepared by the method of Rambabu *et al.*[11] A 0.05 M hydroquinone solution is prepared and standardised[12]. A 0.05 M solution of potassium hexacyanoferrate(II) is prepared and standardised[9].

0.05 N iron(II) solution is prepared and standardised[11].

0.05 M Mn(IV) is prepared and standardised[6].

Sulphuric acid, phosphoric acid and all other reagents employed in this investigation are of analytical grade quality.

RESULTS AND DISCUSSION

0.2 mL of the sodium diphenyl amine sulphonate (SDAS) indicator is treated with sufficient quantity of phosphoric acid and water to give the desired concentration in a total volume of 50 mL. To the solution a small quantity, about 0.02 mL of 0.05 M Mn(IV) sulphate is added. The results indicate that although the concentration of phosphoric acid/(H_2SO_4) medium is varied from 0.5–7.0N, the desired colour with the indicator developed instantaneously. To 50 mL of dilute phosphoric acid/(H_2SO_4) solution of desired strength containing the oxidised form of the indicator (0.2 mL solution of SDAS), 0.02 mL of ascorbic acid, potassium iodide and hydroquinone respectively are added. It is observed that the reaction between the oxidised form of the indicator and ascorbic acid, KI and hydroquinone respectively are instantaneous up to an acid concentration of 5.0 N in the case of SDAS. Hence the optimum acid range for the titration of ascorbic acid, KI and hydroquinone respectively with Mn(IV) using SDAS as indicator from 1.0–5.0 N, 0.25–1.5 N and 1–4 N respectively, is kept in all the determinations.

Dilute sulphuric acid and water are added to 0.2 mL of N-phenyl anthranilic acid (NPA) to get the desired concentration in a total volume of 50 mL. To the solution, 0.05 mL of Mn(IV) solution is then added. The appearance of pink colour is observed. The results indicate that the reaction between them is instantaneous in the acid range of 1.0–9.0 N. To 50 mL of dilute sulphuric acid solution containing the oxidised form of the indicator (NPA) 0.02 mL of hexacyanoferrate(II) is added. It is observed that the optimum acid concentration range for the determination of hexacyanoferrate(II) is 1–5 N.

The preliminary investigation of the authors indicates that the optimum amount of dye solution required for producing the precipitate colour change at the end point in a total volume of 50 mL is 0.1 mL. The indicator amount required is the same with all the dyes. Earlier work utilising Mn(IV) as titrimetric oxidant for iron(II) indicates that the reaction is rapid. In order to ascertain the nature and the speed of the dye by the oxidant in the sulphuric acid medium, the observations indicate that all the indicators are immediately oxidised by the oxidant solution in the range 1.0–12 N with a colour light blue to light orange and instantaneous in the case of toluidine blue, new methylene blue and colourless to light yellow, blue to light orange in the case of Azure B and Azure C respectively. The observations indicate that all the indicators are immediately oxidised by the oxidant solution in 1.0–12 N solution.

To 0.1 mL of the oxidised form of the indicator dye solution in acid concentration indicated, 0.02 mL of of iron(II) is added. The observations indicate that the reaction between the oxidised form of the dye indicators and iron(II) is rapid, almost instantaneous, in the acid range of 1–12 N with a colour change from light orange to colourless in case of toluidine blue, new methylene blue and light yellow to colourless, colourless to light violet for azure B and azure C respectively. The authors further observed that the speed of the reaction between thiazine dyes and Mn(IV) is not affected by the presence of iron(II).

Recommended Procedure

An aliquot of ascorbic acid (H_3PO_4), KI, hydroquinone, hexacyano ferrate(II), and iron(II) solutions respectively (0.126–0.504 mmoles) is taken in 250 mL conical flask, 1:1 sulphuric acid and water are added to give an overall acid concentration between 1.0–5.0 N, 0.25–1.5 N, 4.0 N, 5.0 N and 8.0 N respectively. Five drops of the indicators (SDAS, NPA and thiazine dyes correspondingly. 20.0 mL of acetone is added, diluted to 100 mL, for KI system only) are added to the respective reductants of reaction mixture and titrated with Mn(IV) solution. Appearance of permanent pink, violet, colourless to pink violet and pink respectively, blue to pink, blue to orange, colourless to orange and blue to pink in case of thiazine dyes—toluidine blue, new methylene blue, azure B and azure C respectively for the systems studied and colour violet makes the equvalence point of the titration. The indicator correction for 0.05M solution are negligible and the percentage reaction error was found to be 0.35 – 0.15. The results are recorded in table-1.

TABLE-1

RESULTS ON THE TITRIMETRIC DETERMINATION OF ASCORBIC ACID, POTASSIUM IODIDE, HYDROUQUINONE, HEXACYANOFERRATE(II) AND IRON(II) WITH Mn(IV) USING SODIUM DIPHENYL AMINE SULPHONATE, N-PHENYL ANTHRANILIC ACID AND THIAZINE DYES (TOLUIDINE BLUE, NEW METHYLENE BLUE, AZURE B AND AZURE C) AS INDICATORS CORRESPONDINGLY

S. No.	(1) Taken m. moles	(1) Found m. moles	% relative error
(1)	(2)		
Ascorbic acid + manganese(IV) using sodium diphenylamine Sulphonate			
1.	0.1260	0.1267	0.55
2.	0.1890	0.1901	0.32
3.	0.2520	0.2524	0.16

S. No.	(1) Taken m. moles	(1) Found m. moles	% relative error
4.	0.3150	0.3157	0.22
5.	0.3780	0.3770	–0.26
6.	0.5040	0.5047	0.13
	Potassium iodide + manganese(IV) using SDAS		
1.	0.2550	0.2560	0.39
2.	0.3825	0.3837	0.31
3.	0.5100	0.5116	0.31
4.	0.6375	0.6398	0.36
5.	0.7650	0.7682	0.42
6.	1.0200	1.0240	0.36
	Hydroquinone + manganese(IV) using SDAS		
1.	0.2560	0.2553	0.25
2.	0.3840	0.3819	0.52
3.	0.5120	0.5182	0.15
4.	0.6400	0.6384	0.25
5.	0.7680	0.7588	0.10
6.	1.0240	1.0183	0.55
	Hexacyanoferrate(II) + manganese(IV) using N-phenyl anthranilic acid		
1.	0.4760	0.4770	0.14
2.	0.7140	0.7100	–0.56
3.	0.9520	0.9510	–0.10
4.	1.1900	1.1850	–0.47
5.	1.4280	1.4320	0.28
	Iron(II) + Mn(IV) using toluidine blue		
1.	0.2650	0.2660	0.37
2.	0.3975	0.4003	0.65
3.	0.5300	0.5319	0.36
4.	0.6625	0.6588	-0.56
5.	0.7950	0.8003	0.66
6.	1.0600	1.0540	–0.56
	Iron(II) + Mn(IV) using new methylene blue		
1.	0.2650	0.2658	0.33
2.	0.3975	0.4000	0.62
3.	0.5300	0.5271	–0.54
4.	0.6625	0.6590	–0.53
5.	0.7950	0.7907	–0.51
6.	1.0600	1.0540	–0.56

S. No.	(1) Taken m. moles	(1) Found m. moles	% relative error
	Iron(II) + Mn(IV) using Azure B		
1.	0.2650	0.2635	–0.56
2.	0.3975	0.3962	–0.31
3.	0.5300	0.5320	0.37
4.	0.6625	0.6588	–0.56
5.	0.7950	0.7905	–0.59
6.	1.0600	1.0580	–0.19
	Iron(II) + Mn(IV) using Azure C		
1.	0.2650	0.2658	0.33
2.	0.3975	0.3953	–0.54
3.	0.5300	0.5271	0.54
4.	0.6675	0.6586	–0.59
5.	0.7950	0.7928	–0.28
6.	1.0600	1.0560	–0.38

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