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II. CHEMISTRY

Analytical Chemistry

OXAZINE DYES AS INDICATORS IN BROMATOMETRY*

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The use of seven oxazine dyes, Capri Blue, Solochrome Prune AS, Gallamine Blue, Celestine Blue, Meldola's Blue, Cresyl Fast Violet Acetate and Resazurin as indicators in the bromatometric titrations of iron(II), arsenic(III), antimony (III), thallium (I), and hydrazine in sulphuric and hydrochloric acid media is described.

Keywords : Oxazine Dyes; Indicators; Bromatometry.

INTRODUCTION

RAO and Ramana (1977), Ramana *et al.* (1978) and Rao and Rao (1979) have recently reported the use of some dyes belonging to the azine and oxazine classes as indicators in bromatometry. The present study reports the results of our investigations on the use of seven oxazine dyes, Capri Blue (CB), Solochrome Prune AS (SPAS), Gallamine Blue (GB), Celestine Blue (CLB), Meldola's Blue (MB), (Colour Index Nos. 51015, 51040, 51045, 51050 and 51175 respectively), Cresyl Fast Violet Acetate (CFVA), and Resazurin (RSZ) as indicators in the bromatometric titrations of the analytes, iron(II), arsenic(III), antimony(III), thallium(I) and hydrazine in sulphuric and hydrochloric acid media. The advantages associated with these indicators are: (1) stability of the indicator solutions for about a year; (2) feasibility of performing the titrations at low acidities; and (3) sharp end points.

MATERIALS AND METHODS

Standard arsenic(III) solution (0.1 N) was prepared from E. Merck 'pro analysi' grade arsenious oxide. Solutions (0.1 N) of iron (II) (in 0.5 M H_2SO_4), antimony(III) (in 3.0 M HCl), thallium(I) carbonate, hydrazine sulphate and potassium bromate were prepared from reagent grade samples and standardised.

Indicator solutions of 0.1 per cent concentration were prepared in deionised water from the following samples : CB : Chroma; SPAS, GB, CLB, MB and CFVA: E. Gurr; RSZ : B.D.H.

All other chemicals employed were of reagent grade quality.

General Procedure:

The following general procedure is adapted for the titrations. The reductant solution (4 to 10 ml of 0.1 or 0.01 N) is treated with the requisite volume of 1 : 1 sulphuric or hydrochloric acid and the mixture diluted to 50 ml. To this solution,

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0.1 ml of 0.1 per cent CB, SPAS, GB, CLB, MB or CFVA or 0.05 ml of RSZ is added and the mixture titrated with 0.1 N (or 0.01 N) potassium bromate solution. Potassium bromide and osmic acid solutions are used and elevated temperatures are maintained wherever necessary.

The colour changes at the end points are sharp and are: green to colourless with CB, pink to colourless with SPAS, GB, CLB and RSZ, and violet to colourless with CFVA and MB, and the results obtained are in excellent agreement with those obtained by other methods. The conditions of titrations are mentioned below.

Titration of Iron(II): Titrations of iron(II) with potassium bromate using the oxazine dyes as indicators do not yield satisfactory results in hydrochloric or sulphuric acid medium. The indicators are bleached even after the addition of the first few drops of bromate.

Titration of Arsenic(III): Titrations of arsenic(III) with potassium bromate can be carried out in hydrochloric or sulphuric acid medium employing CB, SPAS, GB, CLB, MB and RSZ as indicators under the following conditions.

HCl medium: CB, SPAS, GB, CLB and MB: 1.5–2.0 M; RSZ: 0.75–1.5 M.

H_2SO_4 medium: CB: 1.75–2.0 M+3–4 drops of 0.25 per cent OsO_4;
SPAS, GB, CLB, MB and RSZ: 0.5–0.75 M+3–4 drops of 0.25 per cent OsO_4.

GB and MB in titrations in hydrochloric acid medium and all the indicators in titrations in sulphuric acid medium should be added towards the close of the titration.

CFVA does not function as indicator in this titration in any acid medium.

Titration of Antimony(III): The bromatometric titrations of antimony(III) can be carried out satisfactorily under the conditions mentioned below:

CB, SPAS, GB, CLB and MB: 1.0–2.0 M HCl or H_2SO_4;

CFVA: 1.0–2.0 M H_2SO_4; RSZ: 0.5–0.75 M HCl or H_2SO_4.

In these titrations, the indicators should be added near the end point and waiting for about 10–15 sec is necessary in the vicinity of the end point.

Titration of Thallium(I): Titrations of thallium(I) using the oxazine dye indicators should be performed at 50–60°C and under the following conditions:

HCl medium: CB: 3.0–4.0 M; SPAS: 2.0–2.5 M; GB, CLB and MB: 1.0–2.0 M; RSZ: 0.5–0.75 M.
CFVA is not suitable in this titration.

H_2SO_4 medium: SPAS, GB and CLB: 1.0–1.5 M+2.5 ml of 10 per cent KBr; RSZ: 0.4–0.5 M+2.5 ml of 10 per cent KBr.
CB, MB and CFVA do not serve as indicators in this acid medium.

Titration of Hydrazine: Suitable conditions for the titration of hydrazine with potassium bromate utilizing the oxazine dyes as indicators are as follows:

HCl medium: CB, GB, CLB and MB: 2.0–2.5 M; SPAS: 1.9–2.1 M; RSZ: 1.4–1.6 M.
CB should be added towards the close of the titration and waiting for about 1 min is required while using GB and RSZ.
CFVA is unsatisfactory in these titrations.

H_2SO_4 medium; CB and GB: 1.0–1.25 M; SPAS and CLB: 1.2–1.3 M+2.5 ml of 10 per cent KBr.

Waiting for about 10–15 sec near the end point is required while using GB as indicator.

MB, CFVA and RSZ are unsuitable in these titrations.

Titrations in Dilute Solutions: The following indicators are not suitable for titrations involving 0.01 N solutions of the reductants with bromate:

CB: Titrations of arsenic(III), antimony(III), thallium(I) and hydrazine in sulphuric acid medium.

SPAS, GB, CLB and MB: Titrations of arsenic(III) and antimony(III) in sulphuric acid medium.

CFVA and RSZ: Titrations of arsenic(III), antimony(III), thallium(I) and hydrazine in hydrochloric and sulphuric acid media.

Indicator Corrections: Titrations of 0.1 N solutions do not require any indicator correction whereas those involving 0.01 N solutions require the following indicator corrections:

CB: 0.04 ml; SPAS and MB: 0.18 ml; GB: 0.16 ml; CLB: 0.20 ml.

Results and Discussion

The fact that the colours of the dye solutions are discharged at the end points in all these titrations indicates that the mechanism of indicator action may involve production of the colourless leuco forms or some other derivatives of the dyes. Separate experiments have shown that bromine solution brominates the dyes yielding colourless solutions. It can, therefore, be concluded that the mechanism of indicator action of the dyes involves bromination of the dyes. In this connection, it may be mentioned that while working with some azine dyes as indicators in the titrations of arsenic(III) with bromine solution, Bognar(1974) has reported the formation of bromoderivatives of the azine dyes.

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References

Bognar, J. (1974) Reverzibilis bromometrias indikatorok Az arzen es antimon meghatarozasa. *Nehezip. Musz. Egy. Kozl.*, **20**, 11.

Ramana, P. V., Mohana Rao, K., and Rao, N. V. (1978) Bromatometric estimation of ascorbic acid using azine and oxazine dyes as indicators. *Ann. Conven. Chemists, Waltair*, Dec. 27–31.

Rao, N. V., and Mohana Rao, K. (1979) Oxazine dyes as indicators in bromatometry. *Ann. Conven. Chemists, Kurukshetra*, Sept. 23–27.

Rao, N. V., and Ramana, P. V. (1977) Azine dyes as new indicators in the bromatometric determination of arsenic(III). *Z. anal. Chem.*, **285**, 125.