Asian Journal of Chemistry Vol. 5, No. 4 (1993), 836–838

Oxazine Dyes as Complexometric Indicators

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The suitability of the oxazine dyes gallocyanine, solochrome prune AS, gallamine blue and celestine blue as indicators in the complexometric titration of bismuth (III), zinc (II), cadmium (II) and thallium (I) is examined and satisfactory conditions for their functioning are developed using EDTA and CyDTA as titrants. The colour changes at the equivalence point are very sharp and the results obtained are in agreement with those reported by other standard methods.

INTRODUCTION

Many oxazine dyes are reported as colorimetric reagents for the determination of various metal ions,[1,2] but the studies on the application of this class of dyes as complexometric indicators[3–6] are scanty. In this paper, the results of the investigations on the application of four oxazine dyes, gallocyanine, (GC) solochrome prune AS, (SPAS), gallamine blue (GB) and celestine blue (CB) (colour index numbers 51030, 51040, 51045 and 51050) as indicators in the complexometric titrations of bismuth (III), zinc (II), cadmium (II) and thallium(I) using ethylenediamine tetraacetic acid (EDTA) and 1,2-diaminocyclohexanone tetraacetic acid (CyDTA) are presented along with the conditions for the satisfactory titration. The application of tristimulus colorimetry[7] enabled to conclude that the quality of colour change of gallocyanine is superior to the other three indicators and the colour transition curve passes very close to the grey point indicating its ideal behaviour.

EXPERIMENTAL

0.01 M EDTA, 0.01 M solutions of Bi (III), Zn (II), Cd (II) and Tl (I) are prepared by dissolving the requisite quantities of reagent grade quality (BDH) samples in double distilled water. 0.1% Solutions of the dyes are prepared and 0.3–0.4 ml of these solutions are used as indicators in a total volume of 50 ml of the titrand.

Take an aliquot of the metal ion solution in a clean dry beaker and add 2 ml of buffer solution, 0.3–0.4 ml of the indicator solution and distilled water to make a total volume of 50 ml and titrate it with either EDTA or CyDTA solution until the colour change is observed. A representative set of results obtained are presented in Table-1.

TABLE 1
DETERMINATION OF Bi (III) WITH EDTA USING OXAZINE DYES AS INDICATORS

Taken	Bismuth (III), m moles			
	Found			
	Gallocyanine	Solochrome Prune AS	Gallamine Blue	Celestine Blue
0.02	0.0198	0.0200	0.0198	0.0198
0.04	0.0398	0.0402	0.0400	0.0398
0.06	0.0598	0.0600	0.0602	0.0600
0.08	0.0800	0.0798	0.0800	0.0802
0.10	0.1002	0.1000	0.1002	0.1000

RESULTS AND DISCUSSION

Titration of bismuth (III): A study of the variation of pH in the titration of bismuth (III) with EDTA showed that the complex formation between bismuth (III) and gallocynine is rather slow at a pH below 2.1 and resulted in lower titre values where as at pH values of 2.6 and above the colour transition is found to be sluggish., So, a pH range of 2.1–2.6 is recommended for the titrimetric determination of bismuth (III) with EDTA using oxazine dyes as indicators. In this titration colour change at the end point while using the oxazine dyes as indicators is from blue to pink, where as the colour change observed in the titration of EDTA with bismuth (III) (reverse titration) is from pink to blue. While using CyDTA as titrametric reagent, similar colour changes are observed in direct and reverse titrations. In the later case the titrations involving 0.001 M solutions provide a sharp colour change at the end point, where as in the former case (while using EDTA) higher titre values resulted because of slow colour change.

Titration of Zinc (II): The titration of zinc (II) with EDTA is found to be satisfactory in the pH range 9.8–10. The results obtained are not reproducible with GB, possibly due to the weak complex formed between the metal ion and the dye. So GB is not recommended as indictor in this titration. The colour change at the end point while using GC, SPAS and CB is from violet to blue. However, with CyDTA as titrant the pH ranges recommended for the titrations are 8.7–9.0 for GC and CB, 8.4–8.8 for SPAC and GB is not a suitable indicator in this titration. The titrations involving 0.001 M solutions are possible while using CyDTA as titrant.

Titration of Cadmium (II): While using EDTA as titrant the recommended pH range is 10.4–10.6 where as for CyDTA it is 10.0–10.4 (for GC, GB, CB) and 6.5 (for SPAS). The colour change at the end point is from pink to blue in titrations of 0.01 M solutions and also in 0.001 M solutions.

Titration of Thallium (I): The titration of thallium (I) with EDTA is found to be satisfactory in the pH range 10.8–11.3 for direct and reverse titrations and also for titrations involving 0.001 M solutions. The colour change observed with all

the studied indicators is from violet to blue. While using CyDTA as titrant (pH range 10.1–10.4) the titrations involving 0.001 M solutions alone are feasible where as in the titrations of 0.01M solutions large error is observed.

From a study of the trichromatic parameters, by the weighted ordinate method it is observed that GC is having a better quality of colour change in comparison with the other three studied indicators.

It has been observed that the following ions do not interfere even if present in thousand fold excess: Na^+, K^+, Hg^{2+}, Pb^{2+}, Mg^{2+}, As^{3+}, U^{6+}, Be^{2+}, Mn^{2+} and Ni^{2+}, in the titration of Bi (III) with EDTA,. However the following ions interference in this titration even if present in traces: Fe^{3+}, Zr^{4+}, Ga^{3+}, In^{3+}, Zn^{2+}, Al^{3+}, Tl^+, Th^{4+}, tartrate, phosphate, fluoride and citrate.

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(*Received*: 1 March 1992; *Accepted*: 5 February 1993) AJC–539.