AMPEROMETRIC TITRATION OF TRACE AMOUNTS OF Sm^{3+} AND Gd^{3+} WITH METHYL THYMOL BLUE

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CONTENTS

ABSTRACT

A simple, convenient and selective amperometric method for the determination of Sm^{3+} and Gd^{3+} with methyl thymol blue (MTB) has been developed. MTB gives a polarographic wave at pH 5.8 in Britton-Robinson buffer and $\mu = 0.2$, under which conditions it also forms 2 complexes with Sm^{3+} and Gd^{3+}. An amperometric titration technique was used to determine these metal ions, at a plateau potential on the wave of MTB at -1.15 V vs. S.C.E.. The current-volume titration curves obtained were well defined, indicating a 1:1 stoichiometric ratio for metal reagent complexation in each case. The proposed method has been tested in the presence of several cations and anions. Microgram amounts may be determined with an error of ± 1.0%.

INTRODUCTION

Several studies on the complexation of metal ions with various sulphophthalein dyes using different physico-chemical methods have been described in the literature /1-5/. The use of Methyl Thymol Blue (MTB) as an indicator and reagent has also been reported /6, 7/. However, the literature is silent on its use as an amperometric titrant for the determination of rare earths. In continuation of our studies /8-11/, on the determination of trace and ultratrace amounts of rare earths by amperometric titration, the present paper deals with the results of determining Sm^{3+} and Gd^{3+} with MTB. The proposed method has been tested in the presence of several cations and anions.

EXPERIMENTAL

The chemicals used were of ANALAR or EXTRAPURE quality. Sm^{3+} and Gd^{3+} solutions were prepared by dissolving a calculated amount of each of the metal oxides in the minimum quantity of hydrochloric acid and making up the solution to the required volume with distilled water. A 0.005 M standard solution of MTB (Reanal, Hungary) was prepared by dissolving the calculated quantity with the appropriate amount of sodium carbonate so as to prepare a monosodium salt solution of the reagent. Britton-Robinson (BR) buffer solution was prepared in the usual way. The ionic strength (0.2M) was adjusted with the requisite quantity of potassium chloride solution.

Amperometric titrations were made on a manually operated polarograph with a multiflex galvanometer (sens.8.10×10^{-9} amp/div) using

the d.m.e. as the indicator electrode and a S.C.E. as the reference electrode. The d.m.e. used in these studies had the following capillary characteristics : m=2.373 mg/sec and t=3 sec/drop in airfree 0.5m potassium chloride solution at a mercury pressure (uncorrected for back pressure) of 41.0 cm (i.e. $m^{2/3}\ t^{1/6} = 2.136\ mg^{2/3}\ sec^{-1/2}$). An Elico digital pH meter (Model LI-120) was used for measuring the pH of the test solutions.

POLAROGRAPHY OF METHYL THYMOL BLUE

The polarographic studies of MTB were carried on a C.I.C. Baroda (India) pen recording polarograph. MTB gives /5/ one and two step reduction waves under different conditions of pH and ionic strength. The polarogram of MTB in BR buffer at pH 5.8 was recorded. The total diffusion current was found to be proportional to the concentration of MTB. The plateau potential for the second step was observed to be -1.15 V vs. S.C.E. The two step reduction wave of MTB is shown in Fig. 1-A.

AMPEROMETRIC TITRATIONS

Sets of solutions containing a known amount of Sm^{3+} or Gd^{3+} in the appropriate quantity of BR buffer at pH = 5.8 and μ = 0.2 M were prepared. For titration, each of the solutions was put in the titration cell and the plateau potential (-1.15 V vs S.C.E.) was applied. At this potential Sm^{3+} or Gd^{3+} do not produce diffusion currents /12/(Fig. 1-A and B). The solution of MTB (pH 5.8) was added drop by drop from a 1 cm^3 micro burette; an orange yellow coloured precipitate was observed to form. On plotting the galvanometer reading after making the necessary volume correction /13/ against the titrant volume a reversed L shaped curve was obtained (Fig. 2). The end-point indicated a metal to MTB ratio of 1:1.

RESULTS AND DISCUSSION

The results of the amperometric titrations are shown in Table 1. 0.6 mg to 8.0 mg of the metal ions could be detected successfully with an error of less than ± 1.0%. The % standard deviation of the practical errors in the case of Sm^{3+} vs. MTB and Gd^{3+} vs. MTB are 0.22% and 0.16% respectively.

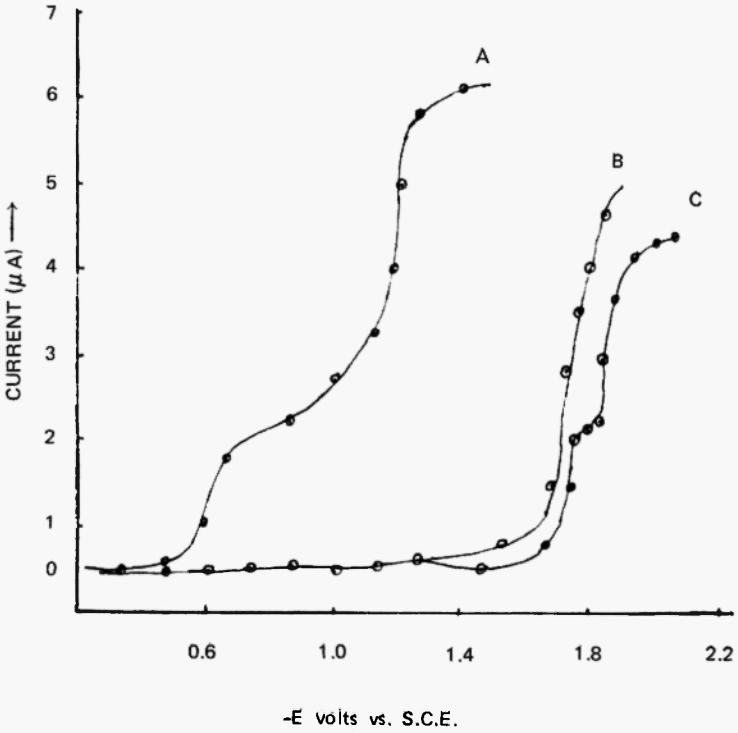

Fig. 1. A — Polarogram of 1 mM MTB in BR buffer at μ = 0.2. pH = 5.5
C & B — Polarogram of 2 mM Sm^{3+} and Gd^{3+} in 0.2 M KCl and at pH = 5.5 respectively.

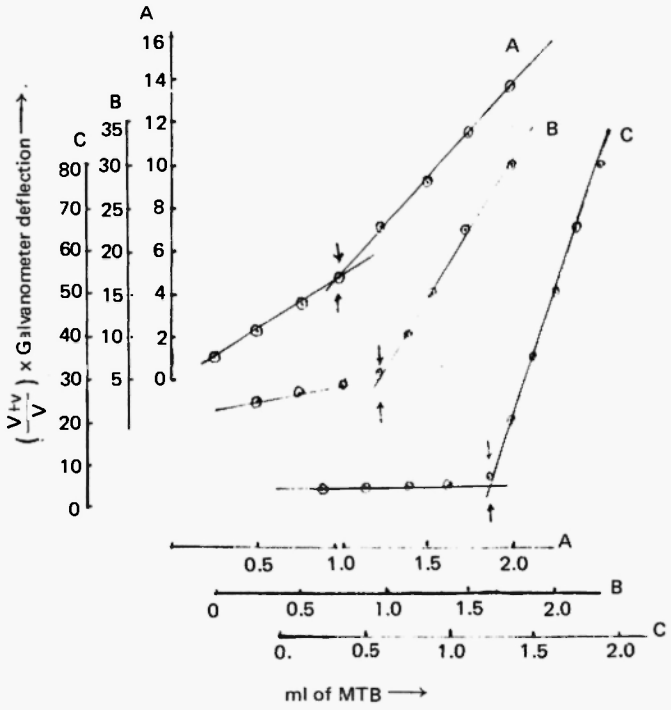

Fig. 2. Amperometric titration curve of Sm^{3+} and Gd^{3+} with MTB at pH 5.5 and μ = 0.2.

A – 0.005 mM of Sm^{3+} titrated against 0.005 M MTB solution

B – 0.005 mM of Gd^{3+} titrated against 0.005 M MTB solution

C – 0.01 mM of Gd^{3+} titrated against 0.08 M MTB solution.

TABLE 1. Amperometric determination of Sm^{3+} and Gd^{3+} with Methyl Thymol Blue

pH = 5.8, μ = 0.2 and plateau = −1.15 Volt

S.No.	Approximate Molarity	Amount of Sm^{3+} Taken (mg)	Found (mg)	% error	Amount of Gd^{3+} Taken (mg)	Found (mg)	% error
1.	4.0×10^{-4}	0.6016	0.6031	+0.24	0.6288	0.6300	+0.18
2.	5.0×10^{-4}	0.7520	0.7450	−0.93	0.7860	0.7810	−0.76
3.	6.0×10^{-4}	0.9024	0.8952	−0.79	0.9432	0.9394	−0.40
4.	8.0×10^{-4}	1.2032	1.2076	+0.36	1.2576	1.2621	+0.36
5.	1.0×10^{-3}	1.5040	1.5112	+0.47	1.5726	1.5684	−0.26
6.	1.5×10^{-3}	2.2560	2.2489	−0.31	2.3589	2.3678	+0.37
7.	2.0×10^{-3}	3.0080	2.9878	−0.68	3.1450	3.1342	−0.34
8.	3.0×10^{-3}	4.5120	4.5002	+0.26	4.7175	4.7018	−0.33
9.	4.0×10^{-3}	6.0160	5.9702	−0.76	6.2900	6.3292	+0.62
10.	5.0×10^{-3}	7.5200	7.4848	−0.46	7.8625	7.9010	+0.49
		Average Mean Deviation = 0.21%			Average Mean Deviation = 0.12%		
		Standard Deviation = 0.22%			Standard Deviation = 0.16%		

TABLE 2. Amperometric titration of Sm^{3+} and Gd^{3+} with MTB in presence of diverse ions.

Metal taken: Sm^{3+} = 1.2032 mg; Gd^{3+} = 1.2576 mg.

Diverse Ion Added	Sm^{3+} found mg	% error	Gd^{3+} found mg	% error
K^+ (195 mg)	1.2076	+0.36	1.2492	−0.66
Na^+ (115 mg)	1.2004	−0.23	1.2458	−0.93
Li^+ (35 mg)	1.2186	+1.28	1.2725	+1.18
Mg^{2+} (36 mg)	1.2096	+0.53	1.2592	+0.12
NH_4^+ (21 mg)	1.2108	+0.26	1.2378	−1.57
Ca^{2+} (34 mg)	1.1804	−1.89	1.2810	+1.86
Ba^{2+} (20.4 mg)	1.1865	−1.38	1.2528	−0.38
Bi^{3+} (13.2 mg)	1.1804	−1.89	1.2822	+1.95

N.B. The figure in parenthesis shows the amount of foreign ion added.

EFFECT OF DIVERSE IONS

To study the tolerance limit of the method towards other ions, known amounts of foreign metal ions were added to a definite amount of metal (Sm^{3+} or Gd^{3+}) and this solution was titrated following the procedure described above. The titrations of Sm^{3+} or Gd^{3+} were not in any way hampered by the presence of fairly large amounts of the ions reported in Table 2. Moreover, fairly large amounts of Cl^-, ClO^-_4, NO^-_3, CH_3COO^-, I^-, SO^{2-}_4 and $(PO_4)^{3-}$ had no effect on the amperometric determination of Sm^{3+} or Gd^{3+}. However, it was observed that the ions Cu^{2+}, Fe^{3+}, In^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} interfered seriously.

CONCLUSIONS

1) Trace amounts of Sm^{3+} and Gd^{3+} could be estimated in dilute solutions with an error $< \pm 1.0\%$.

2) The stoichiometric ratio of the adduct formed by Sm^{3+} or Gd^{3+} with MTB is 1.

3) The method can be employed in presence of various diverse ions, but Cu^{2+}, Fe^{3+}, Mg^{2+}, In^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} cause serious interference.

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