STATISTICAL ASPECTS OF THE DETERMINATION OF MICRO AMOUNTS OF La(III) AND Ce(III) WITH METHYL THYMOL BLUE

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Methyl thymol blue has been extensively used as an indicator <1-5> and a reagent for the spectrophotometric estimation <6-10> of large number of metal ions, but there are divergent views regarding the nature of species in the solution and the chelating sites <11-12>. Polarographic reduction of methyl thymol blue (MTB) has been reported in the literature <13>. Here is reported the use of it as amperometric reagent in the estimation of La(III) and Ce(III).

EXPERIMENTAL

The chemicals used were of extrapure quality. MTB (Reanal) was purified as described <14>. The purity of the dye was tested by well known molar ratio method. The solution of the MTB was freshly prepared whenever required. La(III) & Ce(III) solutions were prepared by dissolving the requisite amount of the chlorides in required volumes of double distilled water and stzandardised <15>. Britton Robinson buffer was prepared. Ionic strength (0.2) was adjusted with required quantity of potassium chloride solution.

Amperometric titrations were done on manually operated polarograph with multiflex galvanometer; D.M.E used as indicator electrode had capillary characteristics $m^{2/3} t^{1/6} = 2.136\ mg^{2/3}\ sec^{-1/2}$ An Elico digital pH meter (Model Li 120) was used for measuring the pH of the test solution.

Current - Voltage Behaviour of MTB

The polarographic studies of MTB size carried on a C.I.C. Baroda (India) pen recording polarograph. The C-V behaviour has been tested under various experimental conditions (buffer, pH and μ)<16>. It is observed that MTB gives single and two stage reduction wave in BrittonRobinson buffer at pH 5 and pH 5.4 respectively. At pH 5.8 MTB gives two step reduction wave (Fig. 1), the diffusion current was found to be proportional to the concentration of MTB. At these pH value, MTB forms

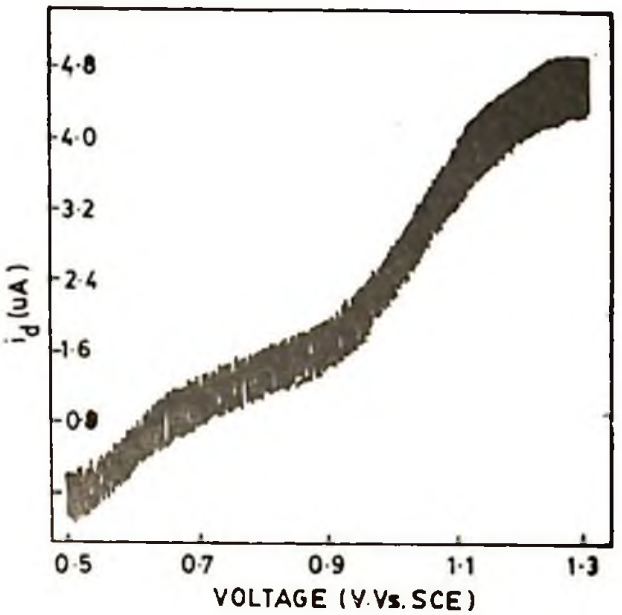


Fig. 1 Polarogram of 1 mM MTB in Br-buffer pH = 5.8 Temp = 25° C

a stoichiometric 1:1 complex and this pH is chosen for the amperometric titration.

Method

The solution containing known amount of La(III) or Ce(III) in appropriate quanity of BrittonRobinson buffer at pH 5.8 and μ = 0.2 were prepared. The test solution was taken in the titration cell. The plateau potential on the wave of MTB i.e.- 1.15 V vs SCE was applied (at which La (III) and Ce(III) do not give any diffusion current). The standard solution of MTB was added drop by drop from semimicro burette, orange yellow coloured precipitate was observed. The current was noted with multiflex galvanometer. On plotting galvanometer reading (after necessary volume correction) against titrant volume, reversed L shaped curve was obtained <17>. The end point indicated metal to MTB ratio of 1:1. For each set, replicate titrations have been performed and statistical method has been applied.

Interferences

The effect of interferences have been studied on the method employed. The estimation of said rare metals are not in

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TABLE 1

AMPEROMETRIC DETERMINATION WITH MTB

pH = 5.8 μ = 0.2 Plateau = potential -1.15 V vs. SCE

Approximate molarity mM	Amount Taken	(mg) Found	%error*	Standard deviation**	Coefficient of variance
Lanthanum III					
0.4	0.5556	0.5506	-0.88	0.0019	0.34
0.5	0.6945	0.6907	-0.54	0.0040	0.58
0.6	0.8334	0.8358	+0.28	0.0035	0.41
0.8	1.1112	1.1198	+0.77	0.0078	0.69
1.0	1.3890	1.4002	+0.80	0.0058	0.41
1.5	2.0835	2.0804	-1.16	0.0138	0.66
2.0	2.7780	2.7825	+0.16	0.0147	0.52
3.0	4.1670	4.1438	-0.55	0.0204	0.48
5.0	6.9455	6.9130	-0.46	0.0425	0.61
6.0	8.3340	8.3702	+0.43	0.0607	0.72
Cerium III					
0.4	0.5604	0.5640	+0.64	0.0017	0.30
0.5	0.7007	0.6911	-1.37	0.0018	0.26
0.6	0.8406	0.8352	-0.64	0.0035	0.41
0.8	1.1208	1.1267	-0.50	0.0084	0.74
1.0	1.4012	1.3908	-0.74	0.0056	0.40
1.5	2.1018	2.1270	+1.20	0.0109	0.51
2.0	2.8024	2.7868	-0.55	0.0093	0.33
3.0	4.2036	4.1815	-0.52	0.0185	0.44
5.0	7.0060	7.0195	+0.19	0.0402	0.57
6.0	8.4072	8.3822	-0.29	0.0620	0.75

* Mean values obtained from set of six titrations.
** Values calculated from six different titrations for each set.

any way hampered by the presence of fairly large amounts of K(I), Na(I), Li(I), Mg(II), Ca(II), Ba(II), Bi(III). The tolerence limits has been reported in Table 3. The anions like Cl^-, ClO^-, NO_3^-, CH_3COO^-, I^-, SO_4^{2-} and PO_4^{3-} do not interfere in the titrimetric determination even when present in excess. However, a small amount of Cu(II), Pb(II), Zn(II), Mn(II), Ni(II), In(III) and Fe(III) etc. interfered seriously in the estimation of said rare earths.

RESULT AND DISCUSSION

The results of amperometric estimations are reported in Table 1 and 2. As little as 0.55 mg of La(III) Ce(III) has been successfully estimated with an error not exceeding 1.4%. Replicate observations were taken for each set of titrations. The mean values of the observed data with standard deviation. Coefficient of variation is found to be less than 0.74. The results revealed that the methyl thymol blue is a useful amperometric reagent under the prescribed experimental conditions for the estimation of La(III) and Ce(III).

TABLE 2

AMPEROMETRIC DETERMINATION OF La(III) AND Ce(III) IN PRESENCE OF DIVERSE ION.

Metal Taken:	La(III)=0.6945 mg		Ce(III)=0.7007 mg	
Diverse ion added mg*	found mg	% error	found mg	% error
K (98 mg)	0.6902	-0.62	0.7098	+1.29
Na (56 mg)	0.6915	-0.43	0.6925	-1.17
Li (35 mg)	0.7017	+1.02	0.7132	+1.78
Mg (27 mg)	0.6841	-1.49	0.7060	+0.75
Ca (25 mg)	0.6862	-1.19	0.6984	-0.32
Ba (15 mg)	0.6834	-1.60	0.6946	-0.87
Bi (9 mg)	0.7048	+1.48	0.7039	+0.45

* The amount within paranthesis shows the tolerence limit.

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