ESTIMATION OF Ga(III), In(III) AND Tl(I) USING METHYL THYMOL BLUE AMPEROMETRICALLY

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Trace determination procedures for Ga(III), In(III) and Tl(I) have been put forward using various physico-chemical techniques under different experimental conditions [1,7]. In the present communication, the authors have reported an amperometric titration procedure for estimation of titled metal ions by taking advantage of cathodic reduction of MTB at electrode surface.

EXPERIMENTAL

Metal solutions (0.01 M) Ga(III), In(III) and Tl(I) were prepared by dissolving calculated quantities of their nitrates in carbon dioxide free double distilled water and standardised. Solution of MTB (0.005 M) was prepared by dissolving the requisite quantities of MTB (Chroma, West Germany) and sodium carbonate in carbon dioxide free double distilled water and standardised [9]. Britton-Robinson buffer [10] was prepared and pH measured using Elico digital pH meter (model LI-120). Ionic strength was maintained using KCl. All chemicals were of A.R.Grade.

A manual polarograph with a Tinsley Potentiometer and a multiflex galvanometer (sens 8.1×10^{-9} A/div) was used for recording polarograms. DME ($m^{2/3} t^{1/6} = 2.136\ mg^{2/3} sec^{-1/2}$ at 42 cm mercury height) and mercury pool were used as indicator and reference electrodes. Absorption studies were made on a GCA-Mcpherson UV-VIS recording spectrophotometer Model Eu-707-11

RESULTS

Polarographic behaviour of MTB have already been discussed. The current-voltage curve of MTB in BR buffer (pH = 5.5 ± 0.02) at constant ionic strength μ = 0.1 M KCl shows two steps with the second step having a plateau at -1.2 V and beyond. The height of the total step measured at - 1.25 V was found to be proportional to the MTB concentration.

To estimate the titled metal ions, a known amount of MTB in BR buffer of pH 5.5 ± 0.02 and of ionic strength 0.1 M (with KCl) was used as a titrand A dme and Hg pool were introduced and the potential of dme was set at -1.25 V vs Hg pool and the current reading in the galvanometer was noted. Titrant solution of the metal ion was then added gradually from a semi-micro burrette. Change in current after each addition of titrant was recorded. After necessary volume corrections [12], current reading were plotted against titrant volume. The titrations were repeated with a number of MTB test solutions, each containing different amount of MTB. The experiments were performed with each metal under study. The current-volume plots were V shaped (Fig. 1) because the metal ions as well as MTB are reducible at the applied voltage (i.e. at -1.25 V vs Hg pool). The results revealed stoichiometrically 1:1 complexes of MTB with each metal. The observed results are in good agreement with those reported in literature [13].

This was also checked by visible absorptiometric technique using Job's method of continuous variation as described by Vosburgh and Cooper [14]. Complexes of Ga(III), In(III) and Tl(I) with MTB in B.R. buffer (pH = 5.5 ± 0.02) were observed to have a single maximum in their absorption spectra, corresponding to 465 nm, 450 nm and 510 nm respectively showing different design of spectra and shift in λmax values in comparison to that of MTB (having two peaks at 415 nm and 490 nm respectively) under similar experimental conditions, which confirmed the formation of complexes. On applying Job's method to the spectral data obtained in each case the complexation ratio (M:L) was observed to be 1:1 which is in agreement with our observations using amperometric procedure. The M:L ratio and

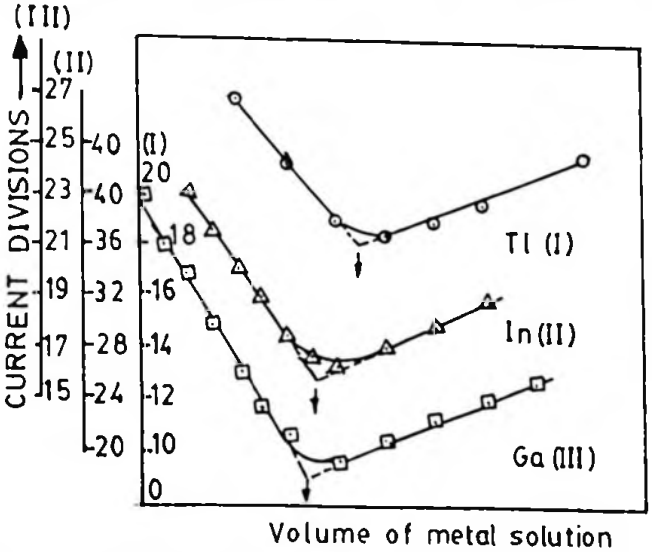


Fig. 1 Titration curves - current vs volume

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TABLE 1

AMPEROMETRIC DETERMINATION OF Ga(III), In(III) AND Tl(I) WITH MTB (METHYL THYMOL BLUE) PLATEAU POTENTIAL = 1.25 V vs Hg POOL, μ = 0.1, pH = 5.5 ± 0.02, TEMP = 28 ± 0.1°C.

Taken (mg)	Found (mg)	% Error
Amounts of Ga(III)		
0.2788	0.2762	-0.93
0.4182	0.4216	+0.81
0.6972	0.6958	-0.20
0.8364	0.8340	-0.28
1.1152	1.1204	+0.46
1.2546	1.2482	-0.51
1.3944	1.4018	+0.53
1.7430	1.7510	+0.45
Amounts of In(III)		
0.4592	0.4612	+0.43
0.6888	0.6866	-0.32
1.1482	1.1410	-0.62
1.3776	1.3804	+0.20
1.8368	1.8338	-0.16
2.0664	2.0612	-0.25
2.2964	2.2880	-0.36
2.8705	2.8828	+0.42
Amounts of Tl(I)		
0.8174	0.8138	-0.44
1.2261	1.2298	+0.30
2.0437	2.0498	+0.29
2.4522	2.4578	+0.22
3.2696	3.2594	-0.31
3.6783	3.6850	+0.18
4.0874	4.0620	-0.62
5.1092	5.1304	+0.41

Standard Deviation = 0.28%, 0.14%, 0.12%
Coefficient of variance = 0.61, 0.43, 0.45

formation constants of each complex is given below:-

Complexes	Ga: MTB	In : MTB	Tl : MTB
log K	13.17	13.74	10.48

Absorption studies had to be completed within an hour of preparing the experimental sets, On keeping the test solutions begins to precipitate.

Amounts of metal ions estimated have been shown in Table 1. It is found that titrations can be easily carried out using as low as 0.4 mM solution of metal ions. It was observed that ions like, Cl^-, I^-, NO_3^-, ClO_4^-, CH_3COO^-, SO_4^{2-}, NH_4^+, K^+, Ag^+, Co^{2+}, Mg^{2+}, Ba^{2+} do not hamper the titrations, whereas ions like Cu^{2+}, Ni^{2+}, Cd^{2+}, Pd^{2+}, Fe^{3+}, CO_3^{2-}, PO_4^{3-} caused serious interference.

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