AMPEROMETRIC ESTIMATION OF SOME RARE-EARTHS USING METHYL THYMOL BLUE

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ABSTRACT

The present paper deals with the amperometric titrations of some rare-earths (Tb^{3+}, Dy^{3+} and Er^{3+}) with methyl thymol blue at pH = 5.8 ± 0.02. The accuracy of the proposed method has been examined in the presence of some diverse foreign ions. The minimum amount of the titled metal ions which could be estimated by this titration procedure was 0.4 mg within an error limit of ± 0.4%. Spectrophotometric as well as the amperometric studies establish the metal:ligand ratio as 1:1.

INTRODUCTION

LITERATURE records many studies on the use of 3′,3″ bis [bis (carboxymethyl) amino] methyl derivative of thymolsuphonphthalein popularly known as methyl thymol blue (MTB) as an indicator[1–5] or a reagent for spectrophotometric determination[6–10] of a large number of metal ions. In continuation of our work on the use of MTB as an amperometric reagent[11], the present communication deals with the cathodic reduction of MTB on a DME and its use as an amperometric reagent for the trace determination of some lanthanides i.e. Tb^{3+}, Dy^{3+} and Er^{3+}. Absorption studies have also been made to establish the M:L stoichiometric ratio and formation constants of the complexes formed.

EXPERIMENTAL

AnalaR/BDH grade chemicals were used throughout the investigation. Oxides of Tb^{3+} and Dy^{3+} and Er-nitrate were used as source compounds. Stock solutions of metal Tb^{3+}, Dy^{3+} and Er^{3+}(0.01 M) were prepared and standardized[12]. Methyl thymol blue (0.005 M) was used as its mono sodium salt, which was prepared by dissolving a requisite quantity of MTB (Chroma, W. Germany) and sodium carbonate in carbon dioxide-free double distilled water and standardized[13]. Standard KCl solution (2 M) was used to adjust the ionic strength of test solutions. B. R. buffer prepared[14] by the addition of 40 ml of 0.2 N NaOH to 100 ml of acid mixture (gl.acetic acid, phosphoric acid and boric acid each of 0.04 M) was used to adjust the pH of test solution at 5.8 ± 0.02.

Amperometric titrations were performed on a manually operated polarograph. Current was read on a multiflex galvanometer (Sens. 8.10×10^{-9} amp./div.) DME and mercury pool were used as indicator and reference electrodes respectively. The DME had the following characteristics m = 2.373 mg/sec and t = 3 sec/drop at 40 cm effective height of mercury column. pH was measured on an Elico-digital pH-meter (model LI-120). A Tinsley potentiometer was used for potential adjustments whereas optical studies were made on a GCA-Mcpherson UV-VIS recording spectrophotometer (model EU-707-11).

Amperometry of titled metal ions:

Polarography of methyl thymol blue

Polarographic behaviour[15] of MTB has already been studied under varying conditions of pH and ionic strength. MTB gives a two-step reduction wave. Polarogram of MTB has been recorded in B. R. buffer (pH = 5.8 ± 0.02) at ionic strength μ = 0.1 M (KCl) and shown in figure 1. The total diffusion current for the second step reduction was proportional to MTB concentration.

Amperometric titrations

Titrations of MTB against rare-earths under study were performed at the plateau potential of MTB (i.e. at −1.25 V vs Hg pool). Sets of solutions containing different amounts of MTB were prepared in B. R. buffer (pH = 5.8 ± 0.02). Ionic strength of the test solutions was maintained constant at 0.1 M by the use of 2 M KCl. Each test solution thus prepared was taken in a titration cell. Standard solution of metal ion to be estimated (at pH = 5.8 ± 0.02) was then added drop-wise from a 1 cm^3 micro-burrette. An orange-red coloured precipitate was observed in the test solution and the complex formation was accompanied by bathochromic shifts[16]. Current readings were noted after each addition of the titrant. After making the necessary

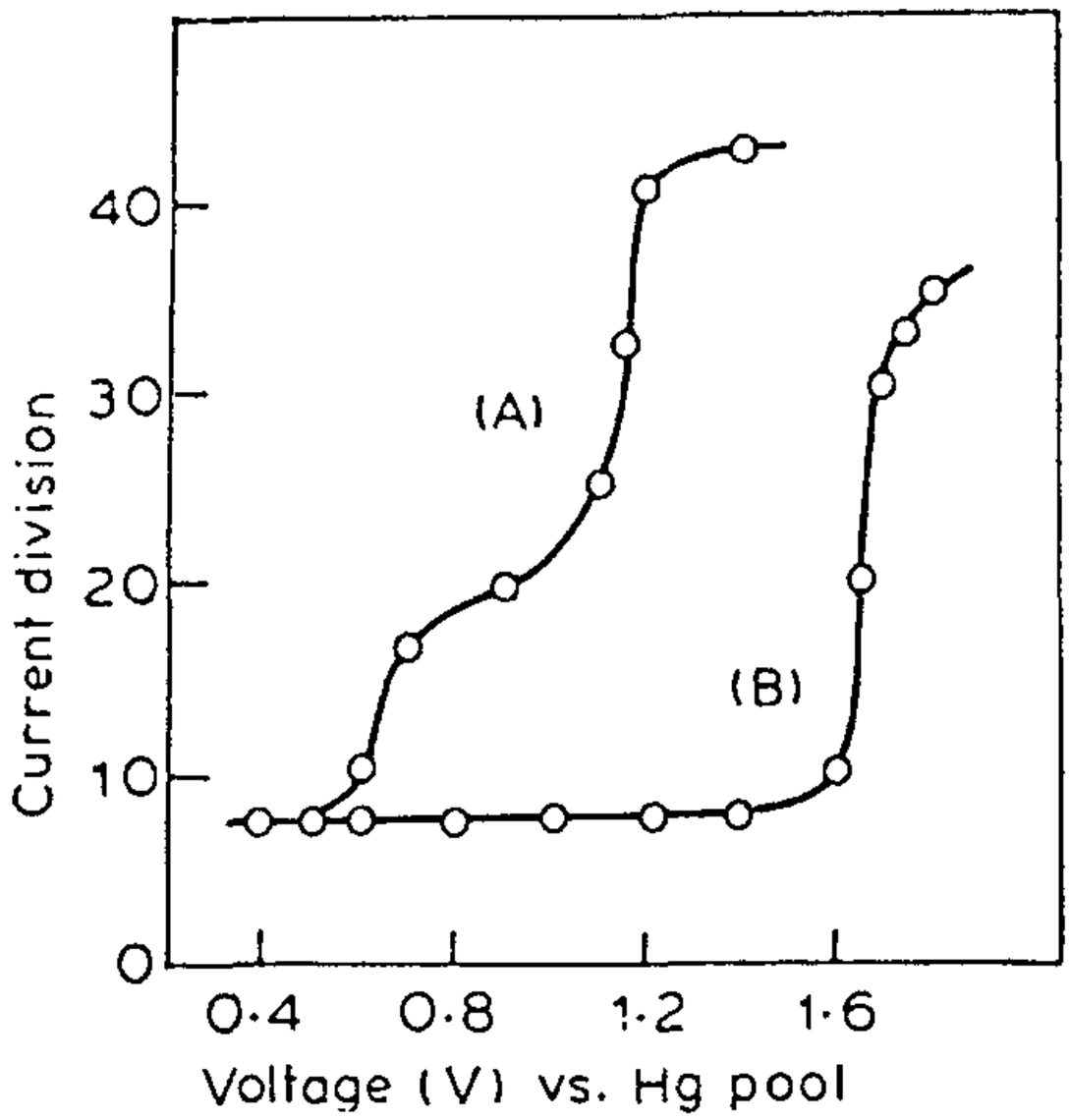

Figure 1. A. Polarogram of 1 mM MTB in B.R. buffer at pH = 5.8, μ = 0.1; **B.** Polarogram of 1 mM metal (Tb^{3+}, Dy^{3+} or Er^{3+}) at pH = 5.8.

volume corrections[17], current readings were plotted against the volume of metal ion solution added. The plot resulted in a L-shaped curve with each metal under study (figure 2). The end point as located by the graphical method, indicated rare-earth : MTB stoichiometric ratio of 1:1 which is in good agreement with the earlier reports[11,18,19].

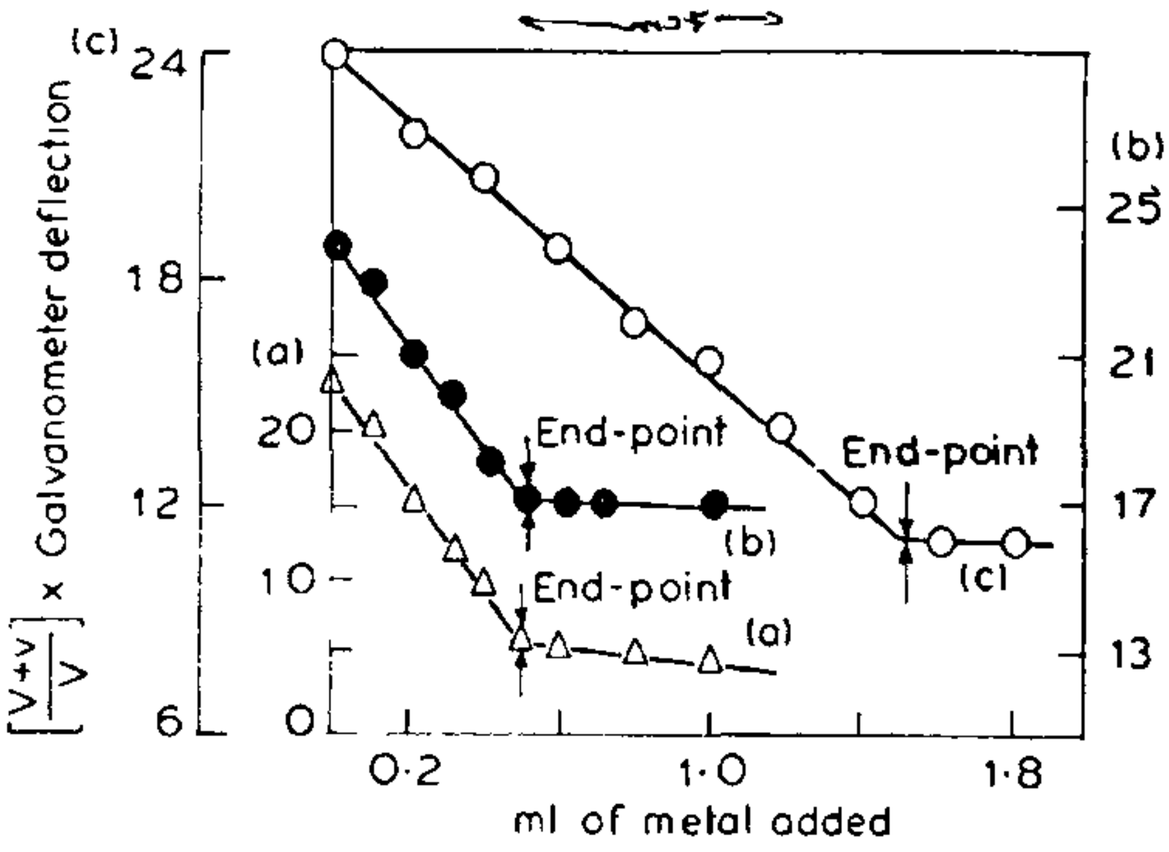

Figure 2. Amperometric titration curves of; **a.** 0.0025 mM/10 ml MTB against 0.005 mM/ml Tb (III), **b.** 0.005 mM/10 ml MTB against 0.01 mM/ml Er(III), **c.** 0.0075 mM/10 ml MTB against 0.005 mM/ml Dy(III)

Study of diverse ion effect

To test the viability of the proposed procedure in the presence of various cations and anions, a definite quantity of foreign ion was added to the test solution. Titrations were then performed as described earlier. It was observed that some trivalent metals like Fe^{3+}, In^{3+} and transition metals like Pb^{2+}, Zn^{2+}, Mn^{2+}, Cu^{2+}, Ni^{2+} and rare-earths seriously interfere with the titration procedure whereas ions like PO_4^{3-}, SO_4^{2-}, NO_3^-, Cl^-, I^-, ClO_4^- and CH_3COO^-do not affect the titrations even when present in fifty-fold excess to the metal ion under estimation. Ions like K^+, Na^+, Li^+, NH_4^+, Ca^{2+}, Ba^{2+}, $Mg^{2+}$and Bi^{3+} could be tolerated up to fifty-fold concentration to that of rare-earth to be estimated.

Accuracy and precision

The proposed method has been proved to be simple and convenient for determining the titled metal ions under study. The accuracy, sensitivity and precision of the proposed use of MTB as an amperometric reagent could be tested by estimating nearly 0.4–6.5 mg of each of Tb^{3+}, Dy^{3+} and Er^{3+} with an error not exceeding $\pm 0.4\%$ in each case. The calculated values of standard deviation and coefficients of variance are also in favour of the utility of the proposed method, and never exceeded 0.15% and 0.43 respectively.

Spectral studies

Spectral studies were used as supplementary tools for the result of amperometric studies. MTB gives a bathochromic shift on combination with titled metal ions[20]. The visible absorption spectra of MTB (2×10^{-4} M) in B.R. buffer (pH = 5.8 ± 0.02) consists of two peaks, at 415 nm and 490 nm respectively, while that of its complexes with titled rare-earths have only one at about 615 nm. This shift in λ_{max} values and change in absorption spectra may be attributed to complex formation in solution. Job's method[20] of continuous variation was applied to the M : L equilibria, which revealed the formation of 1 : 1 complexes of rare-earths to MTB (figure 3).

Spectrophotometric studies had to be completed within 1 hr of preparing the experimental sets, as on standing for more than 1 hr, a gelatinous precipitate appears in the test solution. Equilibrium constant values as calculated by the mole ratio method and nonlinear method of Job were 6.81, 7.08 and 7.47

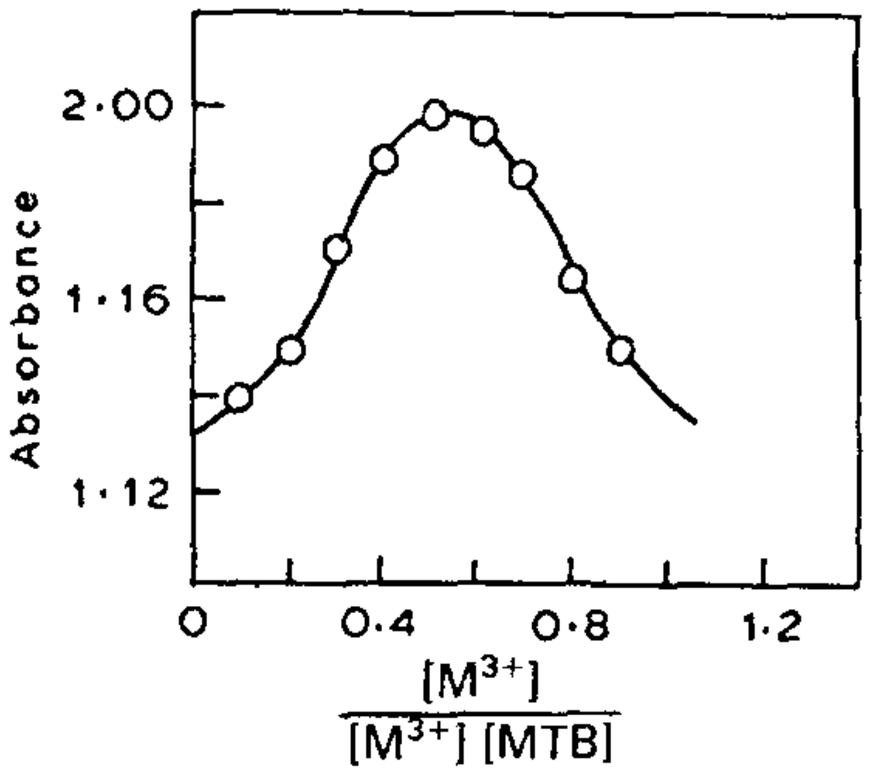

Figure 3. Job's Plot for rare-earth : MTB complexation at 615 nm.

for Tb^{3+}, Dy^{3+} and Er^{3+} complexes with MTB respectively.

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ANNOUNCEMENT

NATIONAL SEMINAR ON FRESHWATER AQUACULTURE IN INDIA

The above Seminar sponsored by the Univeristy Grants Commission, New Delhi and the Department of Zoology, Nagarjuna University, will be held during December 27–30, 1987 at the Department of Zoology, Nagarjuna University, Nagarjunanagar.

Areas of discussion of the Symposium are as follows: 1. Breeding and sprawning of culture organisms, 2. Management and cultural aspects of aquatic organisms, 3. Nutrition and feeding, 4. Predators, parasites, diseases and their control, and 5. Aquaculture education and training.

Details can be had from : Prof. Y. Radhakrishna, Convenor, Department of Zoology, Nagarjuna University, Nagarjunanagar 522 510.