

Bromopyrogallol Red: A New Microanalytical Reagent for Amperometric Estimation of Dy(III) and Gd(III)†

G.P. SAHU and S.C. LAVALE*

Chemical Research Laboratory

J.H. Government Postgraduate College, Betul-460 001, India

Bromopyrogallol Red (BPR) has been extensively used as an indicator but its electro-reducibility has proved it to be a very useful amperometric reagent. BPR reduces on a DME in KNO_3 in the entire pH range 2.4 to 9.5. It produces single stage reduction wave below pH 4, but a two stage reduction wave in the basic range. Progressive ionization of hydroxyl group and distinct colour species of BPR, have also been studied using a Bausch and Lomb spectronic-20 spectrophotometer in order to support electroanalytical studies. On performing amperometric titrations of Dy(III) and Gd(III) with BPR at its plateau potential 1.0 V at pH 2.6 and $\mu = 0.4$, reversed L-shaped titration curves have been observed indicating metal to BPR ratio 1 : 1 and the colour changes from claret red to orange yellow. The reagents have been tested in presence of various diverse ions and tolerance limits have been computed. Na^+ , K^+ , Li^+ , Cl^- , ClO_4^- , CH_3COO^- , Pd^{2+} , Fe^{3+} ions did not interfere in the titrimetric procedure. However, small amounts of Bi^{3+} , Pb^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Mg^{2+} and rare earth metals have hampered the titrimetric estimations.

INTRODUCTION

Literature lacks references¹⁻³ on the polarographic behaviour and amperometric reagents such as bromopyrogallol red (BPR). Keeping this view in mind, the authors tried successfully to use BPR as a microanalytical amperometric reagent for the estimation of Dy(III) and Gd(III) along with the polarographic behaviour and spectrophotometric studies of this reagent at distinct pH and media.

EXPERIMENTAL

The chemicals used were of extra pure quality. The solution of reagent BPR (Loba) was freshly prepared for spectral as well as amperometric studies. Dy(III) and Gd(III) solutions were prepared by dissolving the requisite amounts of their oxides in minimum quantity of hydrochloric acid, and subsequent evaporation to dryness and finally the residue was extracted in double distilled water. The metal solution was standardized by usual methods^{4, 5}.

An automatic pen recording polarograph Elico model-101 was used to record the polarograms, The capillary characteristic was $m^{2/3}t^{1/6} = 2.13 \text{ mg}^{2/3} \text{ sec}^{-1/2}$. Systronic pH meter was used for measuring the pH of test solutions. Spectral studies were carried out on Bausch and Lomb spectronic-20 spectrophotometer. Amperometric titrations were carried out on manually operated polarograph with Polyflex galvanometer. DME was used as indicator electrode.

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Spectral and current-voltage behaviour of BPR

The current voltage behaviour of BPR was tested on Elico pen-recording polarograph. At $2.4 \leq \text{pH} \leq 4$ it produced single stage reduction wave. However, at $4 \leq \text{pH} \leq 9.5$ it produces two stage reduction wave (Fig. 1). This reduction behaviour in the entire range of pH was also confirmed using Bausch and Lomb spectronic-20 spectrophotometer. The progressive ionisation of hydroxyl group and distinct colour species of BPR are shown in Fig. 2.

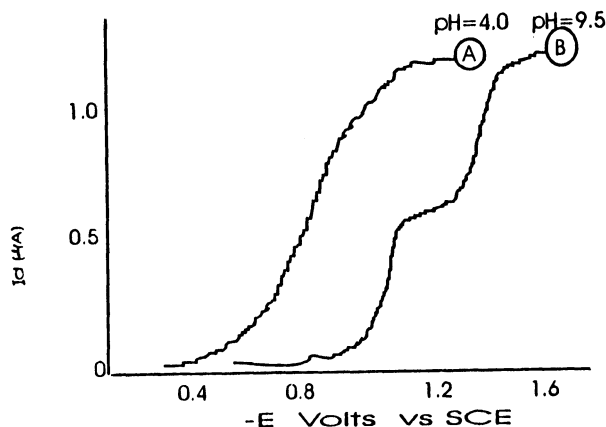


Fig. 1. Polarograms of BPR: A. acidic range of pH 4.0; B. basic range of pH 9.5

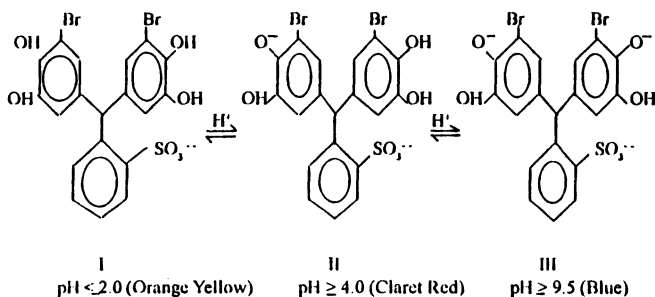


Fig. 2. Progressive ionization of hydroxyl group distinct colour species of BPR

RESULTS AND DISCUSSION

The set of solutions containing known amount of Dy(III)/Gd(III), $\mu = 0.4$ and $\text{pH} = 2.6$ were prepared. The test solution was taken in a titration cell. The plateau potential on the wave of BPR, *i.e.*, $-1.0 \text{ V vs. Hg pool}$ was applied (at which Dy(III) and Gd(III) do not give any diffusion current). The standard solution of BPR was added drop by drop from semi-microburette. The current was noted on Polyflex galvanometer. On plotting galvanometer reading against titrant volume, a reversed L-shaped curve was observed. The direct and reverse titration curves are shown in Fig. 3. The end point indicated metal to BPR ratio 1 : 1. The results

are tabulated in Table-1. The data clearly indicate that the method can be successfully applicable for the estimation of titled metal ion up to microgram level with an error less than $\pm 1\%$ with low values of coefficient of variation which was calculated from the replete sets of titrations.

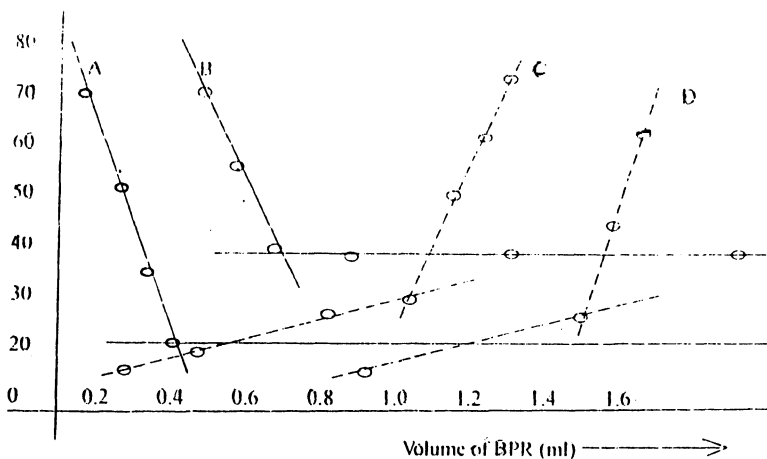


Fig. 3. Direct-reverse amperometric titration curve: (A) 0.0035 mM of BPR titrated against 0.01 M Dy(III); (B) 0.006 mM of BPR titrated against 0.01 M Gd(III); (C) 0.008 mM of Dy(III) titrated against 0.01 M BPR; (D) 0.02 mM of Gd(III) titrated against 0.02 M BPR;

TABLE-1
AMPEROMETRIC TITRATIONS OF Dy(III) AND Gd(III) WITH BPR PLATEAU
POTENTIAL = -1.0 V vs. SCE. $\mu = 0.4$; pH = 2.6 ± 0.02

Approx conc. (mM)	Amount of Dy(III),		%	C.V.*	Amount of Gd(III)		%	C.V.*
	Taken (mg)	Found (mg)			Error	Taken (mg)		
0.2	0.3008	0.2985	-0.79	0.66	0.3144	0.3152	+0.25	0.76
0.4	0.5556	0.5506	-0.88	0.34	0.5604	0.5640	+0.64	0.30
0.6	0.8334	0.8358	+0.28	0.41	0.8406	0.8352	-0.63	0.30
0.8	1.1112	1.1198	+0.77	0.69	1.1208	1.1267	-0.50	0.74
1.0	1.5040	1.5112	-0.47	0.42	1.5726	1.5685	-0.26	0.38
1.5	2.0835	2.0804	-1.16	0.66	2.1018	2.1270	+1.20	0.51
2.0	3.0080	2.9977	-0.34	0.50	3.1450	3.1342	-0.34	0.43
3.0	4.5120	4.5002	+0.26	0.31	4.7175	4.7018	-0.33	0.44

*Value of coefficient of variation obtained from the value of standard deviation taken from the replete sets of titrations.

Studies of effect of diverse ions: For interference studies known amounts of foreign ions were added to different concentrations of Dy(III) and Gd(III) solutions, and the metal was titrated following the procedure described above. Na^+ , K^+ , Cl^- , ClO_4^- , CH_3COO^- , Pd^{2+} , Fe^{3+} , Ga^{3+} ions did not interfere with the

titrimetric procedure up to 100-fold concentration. However, small amounts of Bi^{3+} , Pb^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Mg^{2+} and rare earth metals have hampered the titrimetric procedure (Table-2).

TABLE-2
AN AMPEROMETRIC ESTIMATION OF Dy^{3+} AND Gd^{3+} WITH BPR IN PRESENCE
OF DIVERSE METAL IONS TAKEN; $\text{Dy}^{3+} = 1.2032$ mg; $\text{Gd}^{3+} = 1.2576$ mg

Diverse ions added	Dy^{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
Pd^{2+} (30 mg)	1.2096	+0.53	1.2592	+0.12
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
Ga^{3+} (13.2 mg)	1.1804	-1.89	1.2822	+1.95
Fe^{3+} (10.7 mg)	1.2185	+1.27	1.2450	-0.92

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