



Scholars Research Library

Der Pharma Chemica, 2012, 4 (3):1226-1238
(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X
CODEN (USA): PCHHAX

Spectrophotometric study of ternary complex forming systems of some rare earths with bromopyrogallol red in presence of cetyldimethylethylammonium bromide for microdetermination

G. W. Belsare*, A. B. Zade**, Pawan P. Kalbende** and P. U. Belsare**

*P.G. Department of Chemistry, S. S. S. College, Akola- MS-444001, India.

**Professor of Chemistry, Laxminarayan Institute of Technology, R.T.M. Nagpur University, Nagpur, M.S.-440010, India.

ABSTRACT

The complexation reaction of trivalent yttrium, neodymium, europium, terbium and ytterbium with bromopyrogallol red, a member of triphenylmethane type of dye in presence and absence of micelle forming cationic surfactant cetyldimethylethylammonium bromide have been studied in detail though number of chromogenic reagents have been reported earlier to form water soluble colored complexes with various rare earths as a binary complexes for their microdetermination. Addition of cationic surfactant, cetyldimethylethylammonium bromide (CDMEAB) sensitizes the color reactions of Y(III), Nd(III), Eu(III), Tb(III) and Yb(III) with BPGR. Formation of water soluble, highly colored ternary complexes with a considerable bathochromic shift in presence of surfactant has been observed. Optimum reaction conditions and other analytical parameters were also evaluated. Stoichiometric ratio 1:2:4 of Ln: BPGR: CDMEAB are responsible for the observed rise in molar absorptivity and sensitivity. Beer's law was obeyed between 0.81 to 1.81 ppm. Effective photometric range and molar absorptivity of these ternary complexes have been calculated. A simple, rapid and highly sensitive spectrophotometric method has been proposed for the determination of metal ions under study.

Keywords: Spectrophotometry, Cetyldimethylethylammonium bromide (CDMEAB), Bromopyrogallol Red (BPGR), Ternary complexes, Rare earths.

INTRODUCTION

During past few years, considerable works have been reported on the use of BPGR as chromogenic reagent for the spectrophotometric determination of several metal ions. A detailed literature survey on its use as a spectrophotometric reagent as a binary complex for the determination of scandium [1] with λ_{\max} 610 nm at pH 0.1, titanium [2] with λ_{\max} 610 nm at pH 1-3, vanadium [3] with λ_{\max} 530 nm, cobalt [4] with λ_{\max} 533 nm at pH 12, antimony [5] with λ_{\max} 560 nm at pH 6.7, bismuth [6] with λ_{\max} 635 nm, germanium [7], indium [8] with λ_{\max} 570 nm at pH 3.5, silver [9] with λ_{\max} 635 nm, niobium [10, 11], zirconium [12], tungsten [13] with λ_{\max} 620 nm, molybdenum [14] with λ_{\max} 629 nm, thorium [15], uranyl ion [16] with λ_{\max} 620 nm at pH 5.0, some rare earth like neodymium with λ_{\max} 664 nm, at pH 6.2, ytterbium with λ_{\max} 620 nm at pH 6.2 [17], lead [18] at λ_{\max} 630 nm at pH 5.5,

lanthanum [19] with blue colored complex and cerium, aluminium [20] with λ_{\max} 525 nm at pH 3.8 has been reported as a binary complex using bromopyrogallol red as a reagent.

With increasing demand for the more sensitive reagents, the attempts have been made in the early 1970's for intensification of color of binary complex using third component like surfactants by converting binary complexes of some metal ions to ternary complex. It was observed that the addition of cationic surfactants to some of triphenylmethane dyes solution decreases the color intensity. The addition of specific metal ions to these decolorized solutions resulted into formation of deeply colored stable ternary complexes with a large bathochromic shift and heightened absorbance at a shifted wavelength which resulted into increased molar absorptivity and sensitivity.

Recently the ternary complexes of Mo(VI) [21, 22], W(VI) [21, 24], Cu(II) [23], Ti(IV) [23] and V(V) [24] have been reported with pyrogallol red and bromopyrogallol red in presence of CPB and OP-7. Determination of Co(II), Ni(II), Cu(II), Pd(II), Ru(II) and Mo(VI) have been carried out using sodium isoamylxanthate in presence of surfactants like sodium lauryl sulphate, triton X 100 and CTAB [25]. Sc(III) was determined spectrophotometrically using eriochrome cyanine R and CTAB [26] by Chan-il-park and coworkers. Determination of Zn(II) and Cd(II) were carried out spectrophotometrically with 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol in presence of cetylpyridinium chloride by Agnihotri K.[27] and with diphenylcarbazone in presence of Triton X 100 by Kaur V et al [28]. A simple spectrophotometric determination of Cd(II) using 1,5-diphenylthiocarbazone in presence of CTAB [29] and with 5-Br-PADAP in presence of CPC and HDPBA[30] have been reported.

Literature revealed that the attempts have been made to increase the sensitivity of binary complexes of some rare earths for their determination using cationic surfactants in early seventies. A 1:1:2 ternary complex was formed by yttrium, xylenol orange and tridodecylethylammonium bromide in xylene at pH 5.7 with λ_{\max} 604nm was studied by Shijo Y. [31]. The rare earths and yttrium formed ternary complexes with rhodamine B and 5, 7 - dibromo-8 hydroxy quinoline which was extracted with benzene at 550 nm [32]. Vekhande C. R. and co-worker reported the ternary complexes of rare earths with chrome azurol S in presence of cetylpyridinium bromide with λ_{\max} 620nm at pH 5.4 for the determination of lanthanum, praseodymium, neodymium, samarium, gadolinium or dysprosium [33]. Chromeazurol S and Zephiramine also reported ternary complex of lanthanum for the determination up to 2mg/ml showed λ_{\max} 510 nm at pH 6.5, studied by Horiuchi Y. and Nishida H. [34]. Methylthymol blue and cetylpyridinium bromide or cetyltrimethyl-ammonium bromide were used for the microspectrophotometric determinations of some rare earths [35]. Naixing Wang and coworkers studied fourth-derivative spectrophotometry method based on the absorption spectra of 4f electron transitions of the complex of neodymium with methylthymol blue and cetylpyridinium chloride [36]. Spectrophotometric determination of Th(IV) and U(VI) with chrome azurol-S in presence of cetyldimethylethylammonium bromide (CDMEAB) was reported by Upase A. B. and coworkers [37]. Dhepe A. S. and Zade A. B. [38] have studied spectrophotometric determination of some lanthanide metal ions with eriochrome cyanine R in presence of cetylpyridinium bromide (CPB). Recently selective and sensitized spectrophotometric determination of trace amounts of Ni (II) ion using alpha-benzyl dioxime in surfactant media have been reported [39].

Bromopyrogallol red (BPGR) formed ternary complexes with aluminium and triethylhexyldecylammonium iodide [40] and the sensitizing effect of cetylpyridinium bromide and cetyltrimethylammonium bromide on BPGR-lead complex was studied [41]. The spectrophotometric sensitization is induced by cetyltrimethylammonium bromide in the niobium – BPGR-EDTA-CTAB system [42]. A much complicated procedure has been suggested by Kirillov and coworkers [43] for estimating uranyl as ternary complex with bromopyrogallol red and centrimide in hexamine buffer solution of pH 6.5. The spectrophotometric study of some rare earth complexes with BPGR in presence of cationic and anionic surfactants was studied earlier [44]. Earlier BPGR has been used with cetyltrimethylammonium bromide and cetylpyridinium bromide for the microdetermination of some rare earths by A. B. Zade and co-worker [45]. The 1:2:4 ternary complexes of rare earths with BPGR and hexadecyl pyridinium ion were extracted with isobutyl alcohol for measuring absorbance at 680 nm as reported by Poluektov N.S. et al [46]. In present investigation for the first time, a detailed study on the use of BPGR in presence of cationic surfactant cetyldimethylethylammonium bromide (CDMEAB) has been carried out for the determination of some rare earths.

MATERIALS AND METHODS

EXPERIMENTAL

Instrumentation and reagent solutions

All absorbance measurements were carried out by using Hitachi U 2001 spectrophotometer with matched quartz cell with 1.0 cm thickness. For all spectral studies deionised distilled water was used as a reference solution. The pH values of these solutions were adjusted using Elico Li-10 pH meter, operated on 220 volts stabilizer with AC mains with glass and calomel electrodes assembly. The pH scale was standardized and frequently checked with potassium hydrogen phthalate solution of pH 4.02 and borax solution of pH 9.20. Analytical grade hydrochloric acid and sodium hydroxide solutions of suitable concentration were used for pH adjustment. Bromopyrogallol Red (BPGR) and cetyldimethylethylammonium bromide (CDMEAB) were supplied by Sigma and Aldrich Chemical Company, USA respectively. Purity of CDMEAB was estimated by using argentometric titration for the determination of bromide ion content [45]. Y(III), Nd(III), Eu(III), Tb(III) and Yb(III) of analytical grade purity were supplied by British Drug House Company, England. Stock solutions of BPGR, CDMEAB and metal ions were prepared of strength 1.0×10^{-2} M and subsequently diluted to desire concentrations using double distilled water.

General procedure

All the experiments were carried out at room temperature of 30 ± 2 °C. The CDMEAB solution was first added to BPGR solution and kept for equilibration for half an hour. Metal ion solution was then added to dye surfactant solution and again kept for half an hour to reach complete equilibrium. This order of mixing the solutions was maintained throughout the investigation.

RESULTS AND DISCUSSION

Spectral study of CDMEAB-BPGR interaction

It is necessary to study the interaction between anionic BPGR and cationic CDMEAB before determining the BPGR as a sensitive reagent for the estimation of rare earth in presence of CDMEAB. Therefore absorption spectra of BPGR in absence and presence of CDMEAB, composition of dye-surfactant complex, absorption spectra of rare earth complexes in absence and presence of CDMEAB, effect of pH, composition and stability constants of the complexes in absence and presence of CDMEAB have been studied.

Study of absorption spectra of BPGR in absence and presence of CDMEAB

The absorption spectra of BPGR have been studied at different pH values (1.0-12.0) in absence and presence of CDMEAB. Addition of CDMEAB in the diluted solution of BPGR brings about a change in color at same pH value have been observed. Wavelength of maximum absorbance of BPGR in absence and presence of CDMEAB has been recorded in Table 1.

Table 1. Wavelength of maximum absorbance of BPGR in absence and presence of CDMEAB.

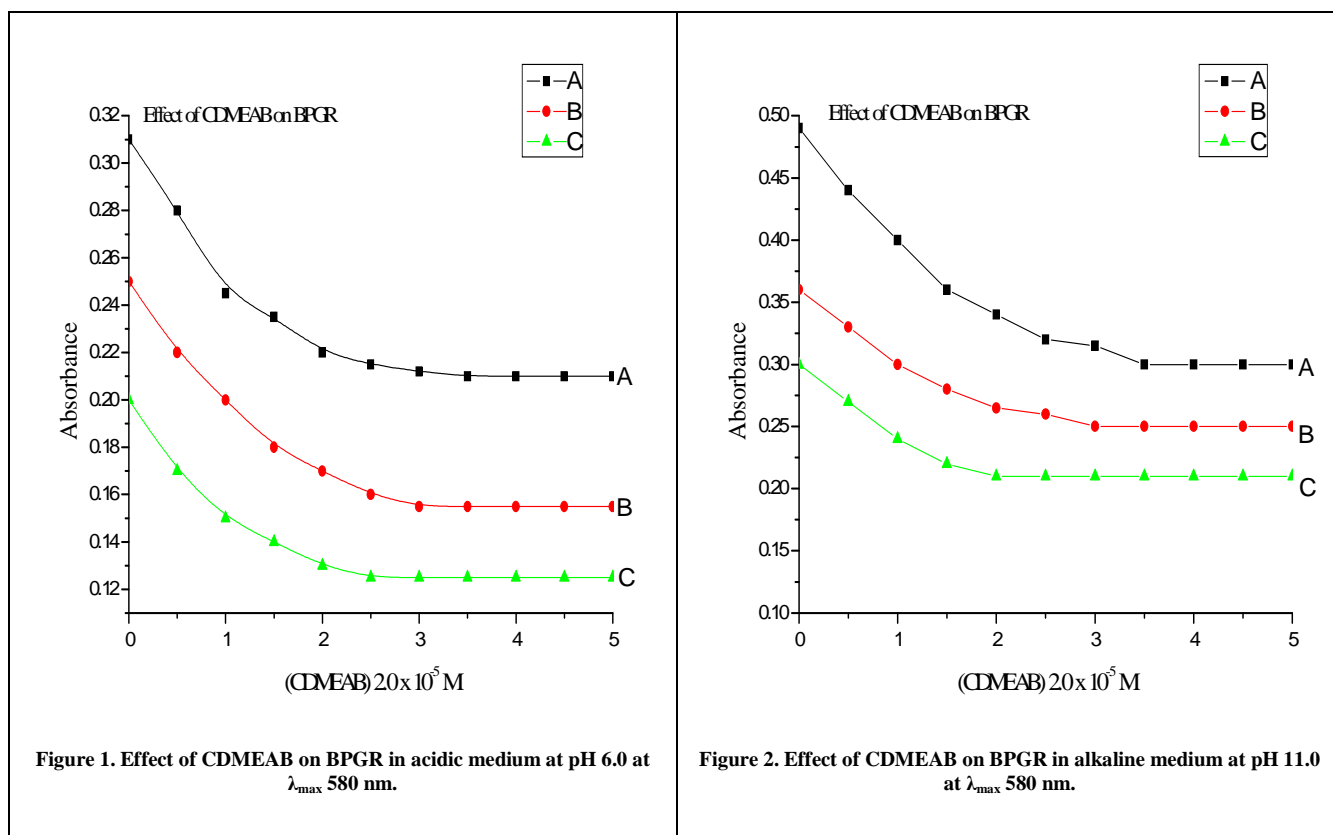
BPGR		BPGR + CDMEAB	
pH	λ_{\max} (nm)	pH	λ_{\max} (nm)
1.0	450	1.0	470
2.0	450	2.0	470
3.0-12.0	580	3.0-12.0	600

It has been observed that the maximum decolorizing effect of BPGR takes place at pH 11.0. However, the λ_{\max} 580 nm of BPGR at pH 11.0 in absence shifted to 600 nm in presence of CDMEAB showing a bathochromic shift of 20 nm with decrease in absorbance values from 0.480 at 580 nm to 0.300. Decrease in absorbance from 0.300 to 0.200 at pH 6.0 at 580 nm has been observed in presence of CDMEAB under the similar condition. Similar effect of decolorisation to the smaller extent has been observed in the pH range 3.0 to 5.5 in presence of CDMEAB. λ_{\max} remains constant in the pH range 1.0 to 2.0 at 450 nm in absence and at 470nm in presence of CDMEAB. Comparative study of these curves showed that the change in absorption maximum in presence of CDMEAB which may be attributed due to formation of possible "Dye-Detergent" complex.

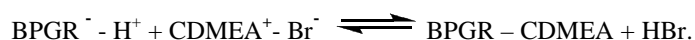
Composition of BPGR- CDMEAB complex

To find out the composition of BPGR-CDMEAB complex, effect of varying CDMEAB concentration on the absorbance of BPGR in acidic medium at pH 6.0 and also in alkaline medium at pH 11.0 at λ_{\max} of BPGR i.e. 580

nm have been studied and shown in Figure 1 and 2 respectively in which the absorbance of different concentrations of BPGR solution is plotted against variable concentration of CDMEAB.



The concentration of BPGR used were 2.0×10^{-5} M, 1.6×10^{-5} M and 1.33×10^{-5} M and have been represented by curve A, B and C respectively in Figures 1 and 2. It has been observed that the absorbance of BPGR decreases linearly with the addition of CDMEAB and remains constant at point when the ratio of BPGR-CDMEAB is reached to 1:2. When this ratio was attained the absorbance of reagent remains unaltered even after addition of five times excess of CDMEAB indicating the formation of specific species with composition $[\text{BPGR}(\text{CDMEAB})_2]$. The anionic BPGR and cationic surfactant CDMEAB reaction may be ionic in nature resulting into formation of new binary species. This newly formed species is useful for further microdetermination of metal ions as a ternary complex.



Study of rare earth [Y(III), Nd(III), Eu(III), Tb(III) and Yb(III)] complexes

Absorption spectra of rare earth complexes in absence and presence of CDMEAB

Absorption spectra of rare earth complexes were studied by keeping the ratio 1:1 and 4:1 for Metal: BPGR. For spectral studies in presence of surfactant tenfold excess of CDMEAB was added to the solution. The absorption spectra of rare earth complexes were taken in entire visible region i.e. 400 to 700 nm in the pH range 1.0 – 8.0. Wavelength of maximum absorbance of rare earth complex has been recorded in Table 2 in the pH range 3.0-6.5. The absorption spectra of BPGR show λ_{\max} at 580 nm in the pH range 3.0 – 6.5. The λ_{\max} shifted to 600 nm by the addition of CDMEAB in BPGR solution which resulted into the formation of dye - surfactant association. In the pH range 3.0 to 4.0, small change in λ_{\max} indicated poor complexation but broad peaks were observed in the pH range 4.5 – 6.5 at around 610 nm in absence of CDMEAB indicating the formation of binary complexes. In presence of CDMEAB, only one sharp peak with high absorbance values for all rare earth ternary complexes have been observed at 660 nm in the pH range 3.5 – 6.5 indicating the formation of strong and stable ternary complexes. Thus shifting of λ_{\max} of binary complex from 600 to 660 nm for ternary complex has been observed in presence of

CDMEAB. These ternary complexes show high absorbance values at shifted λ_{\max} as compared to maximum absorbance values at the λ_{\max} of binary complexes which clearly indicates the sensitization of colored reaction.

Table 2. Absorption maxima (nm) of BPGR and its complexes in absence and presence of CDMEAB at different pH values

System	pH	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5
BPGR		580	580	580	580	580	580	580	580
BPGR + CDMEAB		600	600	600	600	600	600	600	600
BPGR + Y		550	550	580	610	610	610	610	610
BPGR + CDMEAB + Y		580	660	660	660	600	660	660	660
BPGR+ Nd		550	550	580	610	610	610	610	610
BPGR + CDMEAB +Nd		580	660	660	660	660	660	660	660
BPGR +Eu		550	550	580	610	610	610	610	610
BPGR + CDMEAB +Eu		580	660	660	660	660	660	660	660
BPGR +Tb		550	550	580	610	610	610	610	610
BPGR + CDMEAB+ Tb		580	660	660	660	660	660	660	660
BPGR + Yb		550	550	580	610	610	610	610	610
BPGR + CDMEAB +Yb		580	660	660	660	660	660	660	660

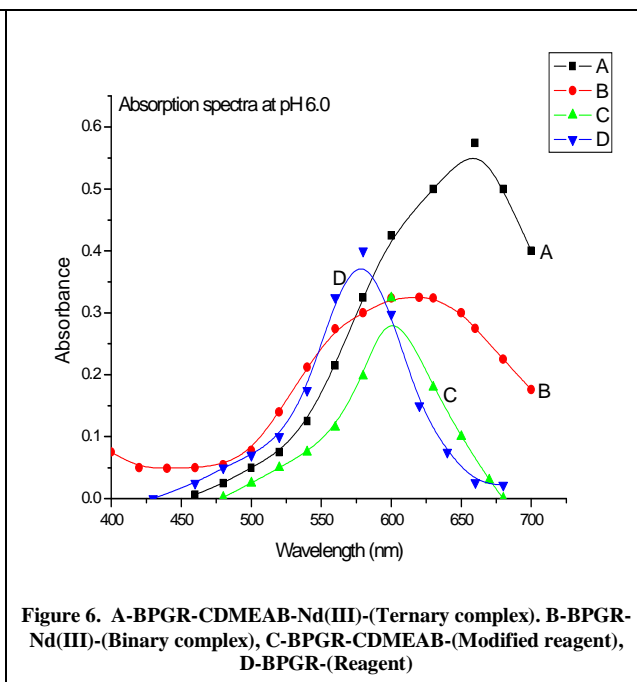
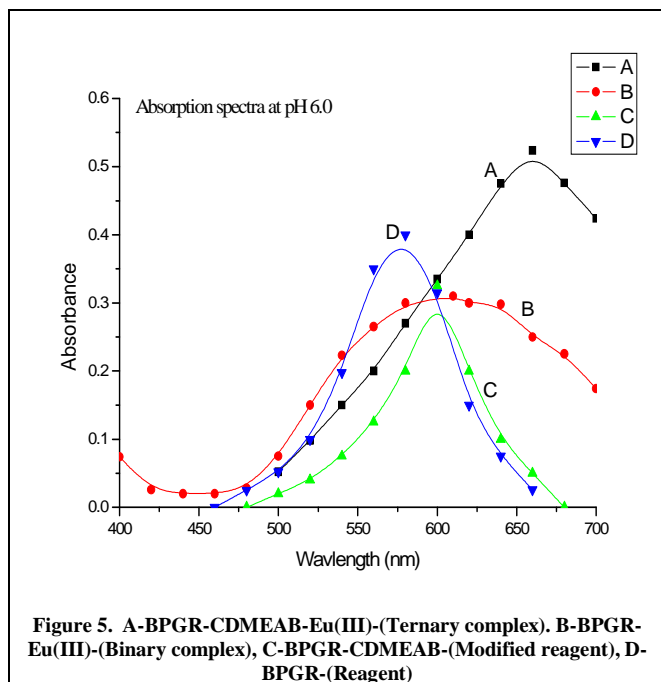
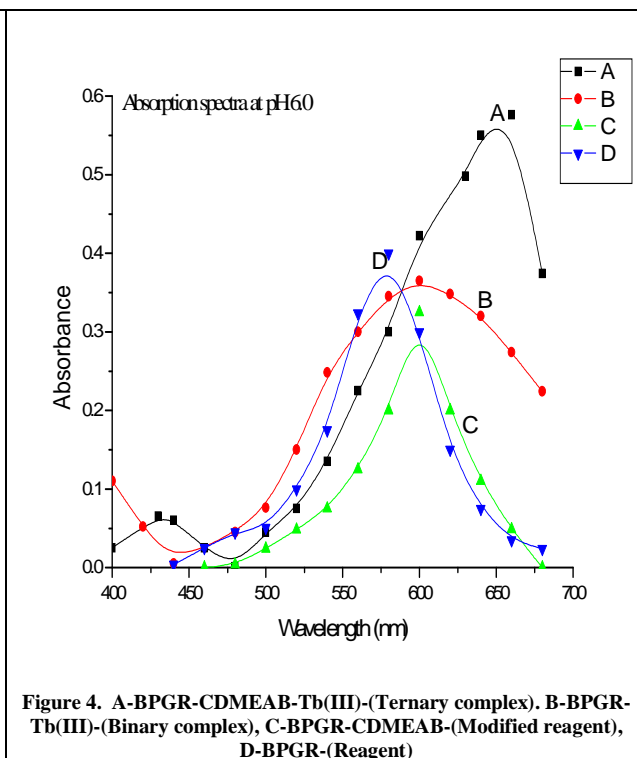
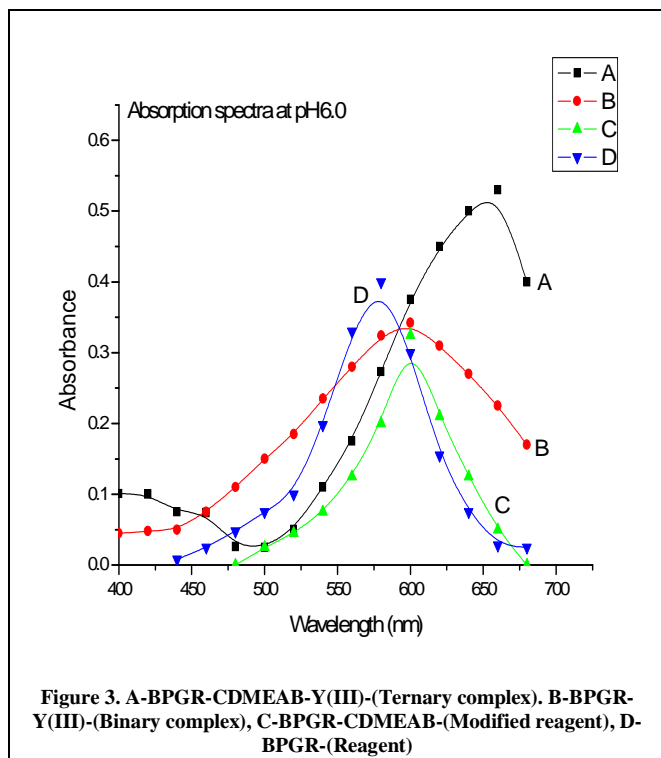
Comparing the absorption spectra and absorbance values of binary and ternary complexes maximum complexation has been observed at pH 6.0. Comparative absorption spectra at pH 6.0 for binary (B) and ternary complexes (A) of yttrium, neodymium, europium, terbium and ytterbium have been plotted in figures 3, 4, 5, 6 and 7 respectively. Figures also show absorption spectra of BPGR in absence (D) and presence of CDMEAB (C). The concentrations of different reactants in different curves are given in Table 3.

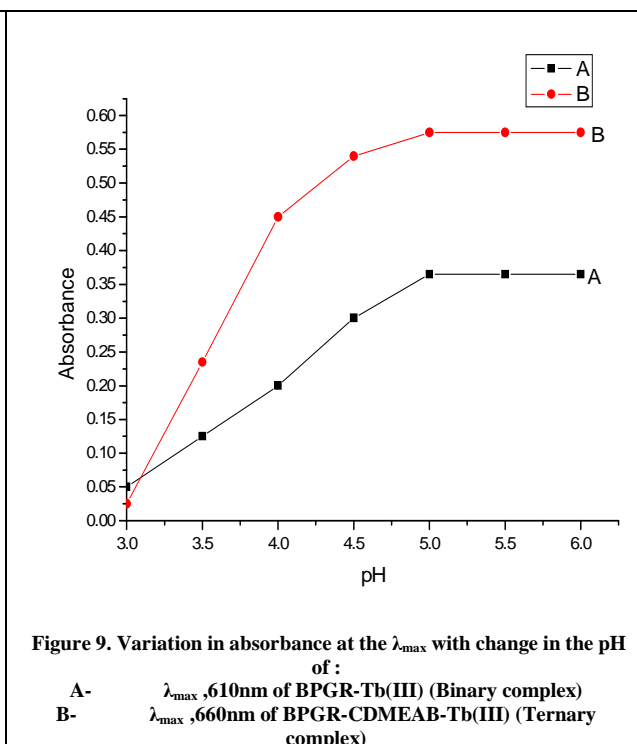
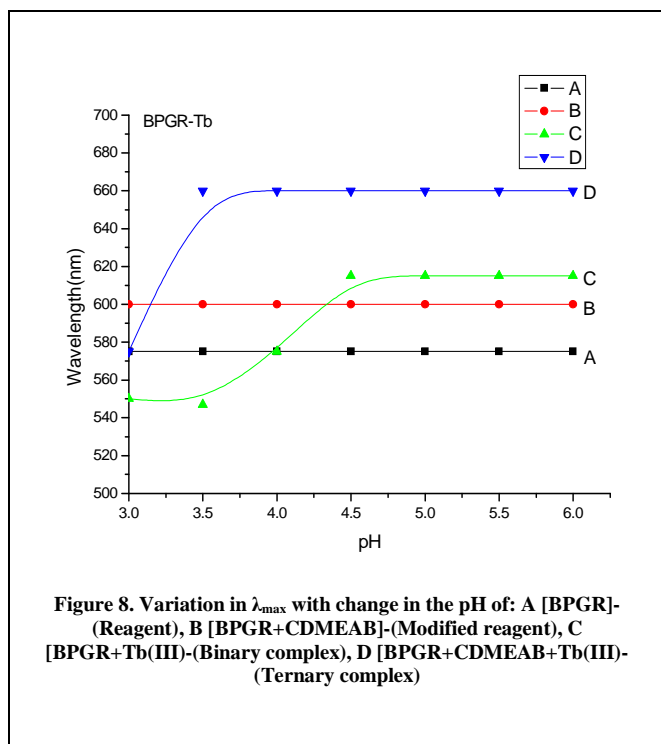
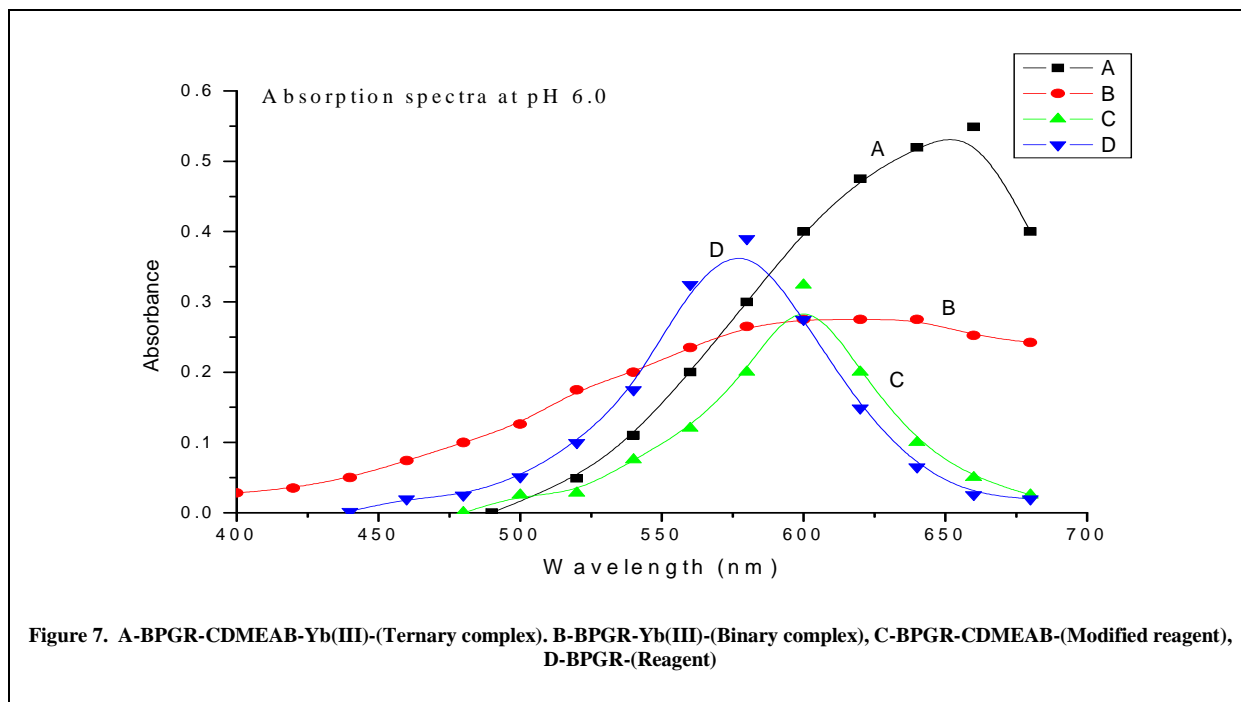
Table 3. Composition and concentration used in Figures 3 to 7

Curves	Composition	BPGR	CDMEAB	Rare earth metal ions
Curve A	BPGR + CDMEAB + Metal	2.0×10^{-5} M	2.0×10^{-4} M	8.0×10^{-5} M, 2.0×10^{-5} M
Curve B	BPGR + Metal	2.0×10^{-5} M	--	8.0×10^{-5} M, 2.0×10^{-5} M
Curve C	BPGR+CDMEAB	2.0×10^{-5} M	2.0×10^{-4} M	--
Curve D	BPGR	2.0×10^{-5} M	--	--

Curve 'A' represents the absorption spectra of rare earths complexes of BPGR in presence of CDMEAB show sharp peak at shifted wavelength 660 nm with high absorbance value of ternary complexes. Rare earth complexes showed broad peak in absence of CDMEAB at around 610 nm represented by curve B. Curve C represents absorption spectrum of modified reagents at λ_{\max} 600nm. Absorption spectrum of BPGR alone has been represented by Curve 'D'.

Thus a bathochromic shift of 50nm in the formation of binary complexes and 100nm in the formation of intense colored ternary complexes has been observed for all rare earths under study. The increase in absorbance values at the shifted λ_{\max} of ternary complexes resulting into increased molar absorptivity and clearly indicates the formation of strong and stable ternary complexes in wider pH range.





pH range of stability

Change in absorbance values with variation in λ_{max} at different pH values has been observed in absence and presence of CDMEAB. Variation in wavelength with change in pH values and change in absorbance at different pH at 540nm (λ_{max} of BPGR-Tb, binary complex) and at 650nm (λ_{max} of BPGR-CDMEAB-Tb, ternary complex) have been shown in Figures 8 and 9 respectively.

In Figure 8, Curve A represents the variation of λ_{\max} with change in pH values of BPGR solution shows constant λ_{\max} at 580 nm in the pH range 3.0 to 6.5. Curve B represents the variation of λ_{\max} with change in pH values of BPGR solution in presence CDMEAB, which shows constant λ_{\max} at 600 nm in the pH range 3.0 to 6.5. Curve C shows the constant λ_{\max} of rare earth complexes at 610 nm in the pH range 4.5 to 6.5 in absence of CDMEAB indicates pH range of stability of constant wavelength. But this range of constant wavelength for terbium complexes increases from 3.5 to 6.5 in presence of CDMEAB at λ_{\max} 660 nm with the addition of CDMEAB represented by curve D. Similar results have been obtained for other rare earths under study.

In Figure 9, curve A at 610nm indicates the absorbance of terbium complex increases slowly and remain constant in the pH range 5.0 – 6.0 in absence of CDMEAB. Curve ‘B’ represents the variation in absorbance of terbium complexes with change in pH value in presence of CDMEAB at 660 nm. The absorbance of complex increases linearly and remains constant in the pH range 5.0 – 6.5 indicates pH range of stability of constant absorbance at fixed wavelength.

Above pH ranges of stability indicate that stable ternary complexes are formed in wider pH range as compared to binary complexes and have been recorded in Table 4.

Table 4. pH range of stability of rare earth complexes in absence and presence of CDMEAB

Rare earth Complexes	λ_{\max} of BPGR (nm)		PH range of stability of constant wavelength		PH range of stability of constant absorbance	
	Absence	Presence	Absence	Presence	Absence	Presence
Y(III)	610	660	4.5-6.5	3.5-6.5	5.0-6.0	5.0-6.5
Nd (III)	610	660	4.5-6.5	3.5-6.5	5.0-6.0	5.0-6.5
Eu (III)	610	660	4.5-6.5	3.5-6.5	5.0-6.0	5.0-6.5
Tb (III)	610	660	4.5-6.5	3.5-6.5	5.0-6.0	5.0-6.5
Yb (III)	610	660	4.5-6.5	3.5-6.5	5.0-6.0	5.0-6.5

Composition of complexes

From the spectral study it was found that BPGR forms only one type of complex with all rare earth metal ions under study. The composition of complexes was studied by Job's method [47] of continuous variation at their optimum conditions. Again the rare earth metal ions and BPGR are mixed in such a way that total volume of reactants remains constant at 50 ml. Various concentration of three reactants used for studying the composition have been recorded in Table 5. The representative Job's curves for the europium have been shown in Figures 10 and 11 in absence and presence of CDMEAB respectively.

The composition 1:2 of M: BPGR has been observed in absence and presence of tenfold excess of CDMEAB. The composition between rare earth metal and BPGR in absence and presence of CDMEAB has been recorded in Table 6 respectively. Earlier it has been observed that BPGR reagent at pH 6.0 exists as $\text{BPGR}(\text{CDMEAB})_2$. Therefore, the composition of rare earth complex in presence of CDMEAB may be written as $\text{M}[\text{BPGR}(\text{CDMEAB})_2]_2$ or M : BPGR : CDMEAB as 1:2:4.



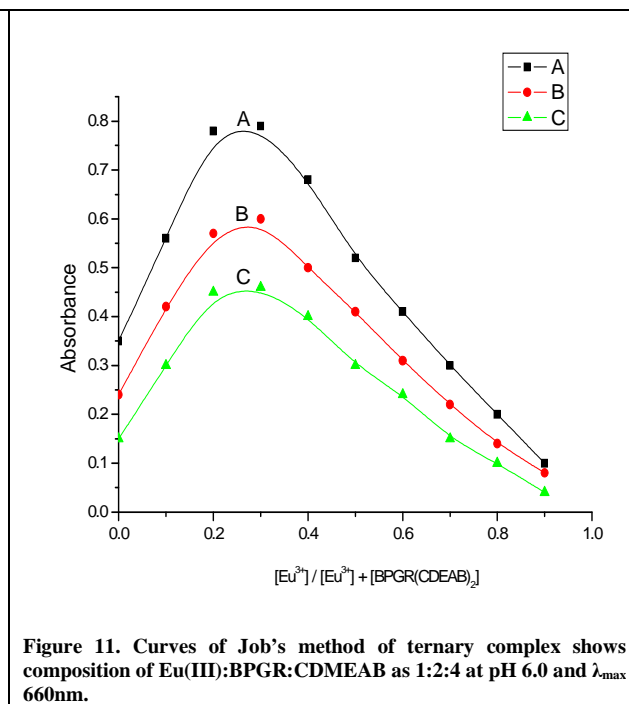
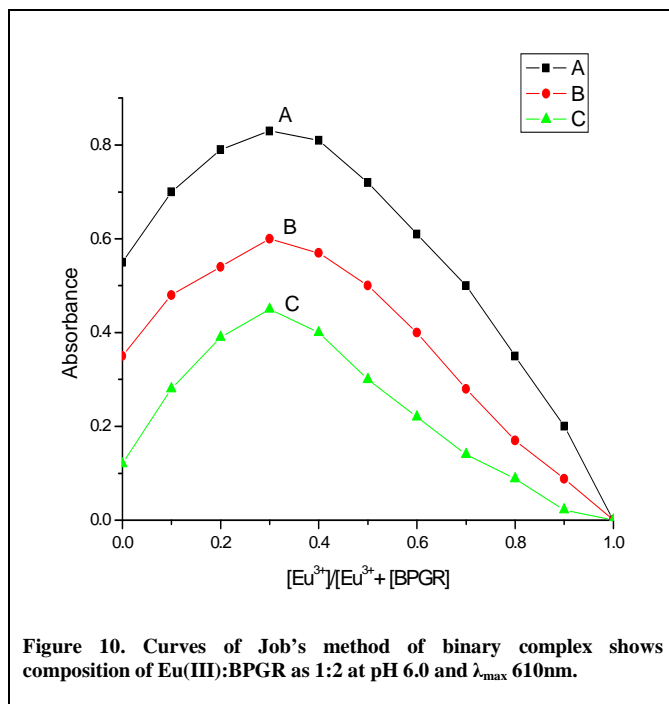


Figure 10. Curves of Job's method of binary complex shows composition of Eu(III):BPGR as 1:2 at pH 6.0 and λ_{max} 610nm.

Figure 11. Curves of Job's method of ternary complex shows composition of Eu(III):BPGR:CDMEAB as 1:2:4 at pH 6.0 and λ_{max} 660nm.

Table 5. Concentration of reagents used in Job's curve

Absence/Presence	Curve	BPGR	CDMEAB	Metal
Absence	A	$5.0 \times 10^{-4}M$	----	$5.0 \times 10^{-4}M$
	B	$2.5 \times 10^{-4}M$	----	$2.5 \times 10^{-4}M$
	C	$1.66 \times 10^{-4}M$	----	$1.66 \times 10^{-4}M$
Presence	A	$2.5 \times 10^{-4}M$	$2.5 \times 10^{-3}M$	$2.5 \times 10^{-4}M$
	B	$2.0 \times 10^{-4}M$	$2.0 \times 10^{-3}M$	$2.0 \times 10^{-4}M$
	C	$1.66 \times 10^{-4}M$	$1.66 \times 10^{-3}M$	$1.66 \times 10^{-4}M$

Stability constants of complexes

Considering the reaction between metals ion and reagent of the complex formation (omitting charges) for systems showing a composition 1:2, the complex formation may be expressed by the equation

In absence of CDMEAB



And in presence of CDMEAB



K can be calculated from equation (1)

$$K = \frac{x}{(a-x)(b-2x)^2} \quad (3)$$

Taking the two concentrations a_1 and a_2 , and b_1 and b_2 having the same absorbance value, i.e. the same value of x, we have

$$K = \frac{x}{(a_1-x)(b_1-2x)^2} = \frac{x}{(a_2-x)(b_2-2x)^2} \quad (4)$$

Knowing the value of x from the above equation, K can be calculated by putting the value of x in equation 3.

The above equations were used for the calculation of stability constant of the complexes. The values of stability constants of complexes in absence and presence have been calculated using Job's curves and are recorded in Table 6. Results show that the values of log K for particular metal ion in presence of CDMEAB are higher than in absence. This indicates that the ternary complexes are more stable than binary which might be due to the association of cationic micelles of CDMEAB with BPGR. Further it has been observed that the log K values decreases in presence of CDMEAB from Nd(III) to Yb(III) as the atomic radii decreases which might be due to attachment of bulky cationic surfactant ions to the anion of BPGR causing steric hindrance for smaller metal ions. It has also been observed that the log K values of Y(III) and Yb(III) are close to each other because of having almost same ionic radii.

Table 6. Composition and log K values of rare earth complexes by Job's method at pH 6.0 in absence at λ_{\max} 610 nm, and in presence of CDMEAB at λ_{\max} 660 nm

Rare earth complexes	Composition		Log K values	
	M:BPGR	M: (BPGR:CDMEAB)	Binary complex	Ternary complex
Y(III)	1:2	1: (1.2) ₂	9.76	10.17
Nd(III)	1:2	1: (1.2) ₂	9.69	10.81
Eu(III)	1:2	1: (1.2) ₂	9.72	10.50
Tb(III)	1:2	1: (1.2) ₂	9.74	10.44
Yb(III)	1:2	1: (1.2) ₂	9.76	10.20

Analytical applications of binary and ternary complexes

Formation of intense colored, stable ternary complexes with large bathochromic shift from 610 nm (binary complex) to 660 nm (ternary complex) with increase in absorbance values at shifted wavelength and comparatively negligible absorbance of the reagent resulted into increase in molar absorptivities as compared to binary complexes which has been considered as a useful tool in microdetermination of rare earths in the present investigation as a primary aim. The study of analytical measurements has been carried out at pH 6.0 and at λ_{\max} 660 nm for ternary complexes and at 610 nm in absence as a binary complex for comparison under similar experimental conditions. The result reported in the Table 7 and 8 for binary and ternary complexes respectively, proves that sensitization of the reagent takes place and the microdetermination of rare earths as a ternary complex found to be a superior method and has been reported for the first time for metal ions under study.

Order of addition of reagents

The sequence of addition of reagents has been followed strictly as usual in all the experiments. The CDMEAB solution was first added to BPGR solution of desired concentration. The solution was kept at least 30 minutes for the formation of so called BPGR - CDMEAB association for complete equilibration. To this modified reagents, metal ion solution was then added for complex formation and adjusted to a suitable pH in 50ml volumetric flask. The absorbance of the solutions was then recorded.

Effect of time and temperature

5 ml. of M/1000 CDMEAB was added to freshly prepared BPGR solution (4 ml of M/4000). This solution was kept for at least 30 minutes for equilibration. To this modified reagent 1 ml of M/4000 rare earth metal ion solution was added. Total volume was adjusted to 6.0 pH in 50 ml. volumetric flask. The absorbance was measured after regular time interval and it was observed that the color formation was almost instantaneous in the formation of ternary complexes and remained constant for almost 24 hrs. However 1 hr time was required to attain complete equilibration for binary complexes. Effect of temperature has been studied in the range 20-60°C. The rate of reaction at higher temperature was faster in the formation of binary and ternary complexes.

Effect of reagent concentration

The effect of reagent concentration was studied in each system in absence and presence by mixing 5 ml of M/5000 metal ion solution and varying amount of M/5000 BPGR. Five times excess of CDMEAB was added to the BPGR solution for ternary complexes. The pH of solution was adjusted to 6.0 in absence and presence of CDMEAB. Total volume was adjusted to 50 ml. and absorbance was recorded at 610 nm in absence and at 660 nm in presence of CDMEAB. It was concluded that two fold excess in presence and six fold excess in absence of molar concentration of BPGR is required for maximum color development.

Beer's law and effective photometric ranges

Beer's Law and effective photometric ranges were studied in absence and presence of CDMEAB by adding varying amount of different concentration of rare earth metal ions. The metal ion solution was added to constant amount of BPGR (1 ml. of M/1000). Five time excess of CDMEAB was added for ternary complexation. Total volume was raised to 50 ml by addition of distilled water and pH was adjusted to 6.0. The absorbance was then measured at 610 nm for binary and 660nm for ternary. Validity of Beer's law was confirmed by plotting the absorbance against concentration of metal ion.

From the curves, the range of concentration for adherence to Beer's law was calculated. The effective ranges of photometric determination were also calculated using this data by Ringbom (3) plot [48] of negative log of metal ion concentration versus percentage transmittance. Thus, the range derived by slop of curves is selected to be the range for effective photometric determination.

Beer's law and effective photometric ranges for the determination of metal ions in absence and presence of CDMEAB have been recorded in Table 8 and 9 respectively. Lower values of photometric ranges in presence of CDMEAB indicate that the metal ion can be determined at very low concentration which is not possible by simple binary complexation. This proves the utility of CDMEAB in the formation of ternary complexes for the microdetermination of metal ions.

Sensitivities and molar absorptivities

The molar absorptivities in absence of binary and in presence of CDMEAB for ternary omplexes of rare earths were calculated by taking constant amount of metal ion solution and varying amount of BPGR solution at pH 6.0 and at 610 for binary and 660 nm for ternary complexation. The higher values of molar extinction coefficient and lower values of Sandell's sensitivity [49] again prove the utility of cationic surfactants in the microdetermination of metal ions.

Procedure for microdetermination

Place sample solution containing about 10 to 40 μg of metal ion in volumetric flask of 50 ml. Add about 2 ml of modified reagent solution prepared by mixing 1 ml each of M/1000 CDMEAB solution and M/5000 BPGR respectively. Keep it for at least 10 minutes for complex formation. Adjust the pH of the solutions to 6.0 and make up the final volume to 50 ml by adding water of same pH. Measure the absorbance of solutions at 660 nm. The amount of metal ion present in unknown sample solution can then be obtained by comparing the absorbance value from calibration curve obtained under similar conditions. Table 8 records the results of micro spectrophotometric determination of rare earths with BPGR in presence of CDMEAB by above procedure.

Table 7. Photometric ranges for the determination of rare earth as a binary complexes (pH of study = 6.0 and at λ_{max} = 610 nm)

Complex of BPGR	Beer's law Ranges (ppm)	Effective photometric ranges (ppm)	Molar absorptivities	Sandell's sensitivities $\mu\text{g}/\text{cm}^2$
Y(III)	0.11-.94	0.23-0.71	52000	0.0017
Nd(III)	0.19-1.53	0.38-1.34	53000	0.0024
Eu(III)	0.20-1.12	0.60-1.12	53000	0.0028
Tb(III)	0.21-1.69	0.63-1.69	52000	0.0030
Yb(III)	0.25-1.81	0.51-1.03	52000	0.0033

Table 8. Photometric ranges for the determination of rare earth as ternary complexes. (pH of study = 6.0 and at λ_{max} = 660 nm)

Complex of BPGR	Beer's law ranges (ppm)	Effective photometric ranges (ppm)	Molar absorptivities	Sandell's sensitivities $\mu\text{g}/\text{cm}^2$
Y(III)	0.088-0.62	0.17-0.44	72000	0.0012
Nd(III)	0.14-1.15	0.28-0.86	72000	0.0019
Eu(III)	0.45-1.36	0.45-1.26	72000	0.0020
Tb(III)	0.15-1.27	0.31-0.79	72000	0.0020
Yb(III)	0.17-1.12	0.34-1.03	72000	0.0023

CONCLUSION

Spectrophotometric determination of rare earths with bromopyrogallol red in absence and presence of cetyldimethylethylammonium bromide have been studied. Following are the merits of modified method.

- 1) The interaction between anionic BPGR and cationic CDMEAB takes place resulting into formation of so called Dye-Surfactant complex of specific composition 1:2.
- 2) The addition of specific rare earth metal ion resulted into the formation of intense colored stable ternary complexes with large bathochromic shift of 50 nm (610 for binary and 660nm for ternary complexes).
- 3) This change is attributed due to formation of deeply colored ternary complex system in presence of CDMEAB in acidic medium.
- 4) The formation of ternary complexes with sharp peak in wider pH range has been observed as compared to weak binary complexes with broad shoulder in small pH range.
- 5) Due to the shifted λ_{\max} towards higher wavelength and comparatively negligible absorbance of reagent resulted into the large difference in absorbance between the reagent blank (BPGR-CDMEAB) and its ternary complex. This resulted in enhancement of sensitivities and molar absorptivities again indicate the sensitization of color reaction.
- 6) Increase in values of log K in presence of CDMEAB for particular metal ion is greater than in absence shows the formation of stable complexes.
- 7) Higher absorbance values of ternary complexes and almost negligible absorbance of the reagent at 660nm resulted into increase in molar absorptivities about 20000 for different rare earths and lower values of sensitivities indicates the metal ion can be determined at low concentration.
- 8) Further, the modified method for determination of metal ion requires smaller molar concentration of BPGR over the metal ion concentration for full color development and is instantaneous in presence of CDMEAB.
- 9) The modified reagent i.e. [BPGR (CDMEAB)₃] has also been found to be extremely useful in complexometric titration of rare earth metal ions giving very sharp color change at the end point.

These observations suggest the utility of these colored reactions in presence of CDMEAB for spectrophotometric determination of the metal ions with heighten sensitivity. It may be mentioned here that BPGR in presence of CDMEAB have been suggested for the first time as a sensitive reagents for spectrophotometric determination of metal ions understudy. Attempts have been made to isolate the ternary complexes but invain being a colloidal nature and therefore the structure of binary and ternary complex suggested are tentative. Thus the method suggested in the present investigation is simple, rapid and highly sensitive for spectrophotometric determination of metal ions.

Acknowledgement

Authors are thankful to Prof. R. B. Mankar, Formar Director of Laxminarayan Institute of Technology, R.T.M. Nagpur University, Nagpur and presently Vice-Chancellor of Dr. Babasaheb Ambedkar Technical University, Lonere (MS) and Dr. M.K.N. Yenkie, Director In Charge, Laxminarayan Institute of Technology and Registrar of R.T.M. Nagpur University, Nagpur for constant encouragement and support.

REFERENCES

- [1] T. Shimizu, *Talanta*, **1967**, 14, 473-479; *Bull chem. Soc. Jap.*, **1969**, 42, 1561-1569.
- [2] D. Abromaityte, S. Ramonaite, N. Sidlauskienė, *Nauchn. Tr. Uyssh. Uchebn. Zaved. Lit. SSR. Khim. Khim. Tekhnol.*, **1972**, 14, 5.
- [3] M. N. Gordeeva, A. M. Ryndina, L. A. Khait, *Fiz. Khim.*, **1974**, 2, 149-151.
- [4] D. Costache and G. Popa, *Rev. Roum. Chim.*, **1970**, 15, 1349-1353.
- [5] D. H. Christopher, T. S. West, *Talanta*, **1966**, 13, 507-513.
- [6] V. Suk, M. Smetanova, *Collec. Czech. Chem. Commun.*, **1965**, 30, 2532-2537.
- [7] G. Popa, I. Parlescu, *Talanta*, **1968**, 15, 272.
- [8] T. Talipov, K. S. Abdullaeva, G. P. Gorkovaya, *Uzb. Khim. Zh.*, **1962**, 5, 16.
- [9] R. M. Dangnall, T. S. West, *Talanta*, **1964**, 11, 1533-1541.
- [10] T. V. Ramkrishna, S. A. Rahim, T. S. West, *Talanta*, **1969**, 16, 847-853.
- [11] A. I. Willims, *Analyst*, **1967**, 92, 43-46.
- [12] T. Sakai and Y. Funaki, *Bull. Chem. Soc. Jap.*, **1969**, 42, 2272.
- [13] M. Deguchi and T. Mamita, *Jap. Anal.*, **1976**, 25, 60-62.
- [14] M. Deguchi, M. Izaka and M. Yashiki, *Jap Anal*, 1974, **23**, 760-764.
- [15] V. D. Vasilenko, M. V. Shanya and V. I. Balbas, *Zh. Anal. Khim.*, **1967**, 22, 1818-1822.
- [16] V. F. Luk-vanov, E. P. Duderova, *Zh. Anal. Khim.* **1961**, 16, 60-62.
- [17] N. S. Poluektov, L. A. Ovchar, S. F. Ognichenko and R. S. Lauer, *Zavod Lab.*, **1971**, 37, 895-897.
- [18] S. C. Dhupar, K. C. Shrivastava and S. K. Banergee, *J. Chin. Chem. Soc. (Taipei)*, **1973**, 20, 145-150.
- [19] M. A. Sandu, N. S. Poluektov and R. S. Lauer, *Ukr. Khim. Zh.*, **1971**, 37, 820-826.

- [20] E. I. Bashirov and A. M. Ayubova, *Azerb. Khim Zh.*, **1971**, 4, 134-138.
- [21] V. M. Ivanov and A. M. Mamedova, *Journal of Analytical Chemistry*, **2006**, 61(3), 261-268.
- [22] V. M. Ivanov, A. M. Mamedova and S. A. Akhmedov, *Moscow University. Chemical Bulletin*, **2003**, 44(4), 253.
- [23] V. M. Ivanov, A. M. Mamedova and S. A. Akhmedov, *Moscow University. Chemical Bulletin*, **2003**, 44(5), 304.
- [24] A. M. Mamedova, V. M. Ivanov and S. A. Akhmedov, *Moscow University. Chemical Bulletin*, **2004**, 45(2), 117.
- [25] A. K. Malik, K. N. Kaul, B. S. Lark, W. Faubel and A. L. J. Rao, *Turk. J. Chemistry*, **2001**, 25, 99-105.
- [26] Chan- il Park and Ki-Won Chan, *Bull. Korean Chem. Soc.* **1999**, 20(12).
- [27] N. K. Agnihotri, S. Ratnani, V. K. Singh and H. B. Singh., *Analytical Sciences*, **2004**, 20, 955.
- [28] V. Kaur, A. K. Malik, N. Verma and A. L. Rao, *J. Indian Journal of Chemistry*, **2007**, 46A, 1432-1436.
- [29] H. Khan, A. Jamaluddin and M. I. Bhanger, *Indian Journal of Analytical Chemistry*, 2007, 6(2).
- [30] R. K. Banjare and M. K. Deb, *Indian Journal of Chemistry*, **2006**, 45A, 1408-1412.
- [31] Y. Shijo, *Jap. Anal.*, **1974**, 884-889.
- [32] N. S. Poluektov, V. T. Mishchenko Zh, *Anal. Khim.*, **1969**, 24, 1434-1436.
- [33] C. R. Vekhande, K. N. Munshi, *Indian J. Chem.*, **1976**, 14, 189-191.
- [34] Y. Horiuchi and H. Nishida, *Jap Anal.*, **1968**, 17, 1486-1491.
- [35] C. R. Vekhande, K. N. Munshi, *J. Indian Chem.*, **1975**, 52, 939-941.
- [36] Naixing Wang, Ping Qi and Kezheng Jiang, *Microchimica Acta*, **1994**, 116(4), 191-196.
- [37] A. B. Upase, A. B. Zade and P. P. Kalbende, *E-J.Chem*, **2011**, 8(3), 1132-1141.
- [38] A. S. Dhepe and A. B. Zade, *E-J.Chem*, **2011**, 8(3), 1264-1274.
- [39] M. Ghaedi, *Spectrochimica Acta Part A*, **2007**, 66, 295-301.
- [40] A. S. Arkhangelskaya, L. A. Molot, Manuscript No. 1743, Deposited at Vsesoyuznyi inst. Nauchnoi; Tekhnicheskoi, Informat, Moscow; **1974**.
- [41] P. T. Rao, T. V. Ramakrishna, *Talanta*; **1980**, 27, 439.
- [42] S. G. Jadhav, C. Venktewarlu, *Indian J. Chem.*, **1978**, 16A, 263.
- [43] A. J. Kirrillov, I. P. Golentovskaya and N. A. Vlasov, *Zavod lab*, **1975**, 41, 523-525.
- [44] Nemcova Irena, Plckova Pavla, Tron Hong con., *Collect. czech. Chem. Commun.*, **1982**, 47, 503.
- [45] A. B. Zade, K. N. Munshi "Surfacetants in solution" K. L. Mittal, Ed. **1989**, 9, 261.
- [46] N. S. Poluektov, L. A. Ovchar, R. S. Laueer and S. F. Potapova, *Zh. Anal. Khim*, **1975**, 30, 1106-1109.
- [47] P. Job, *Ann Chim*, 9, 113, *Chem. Abst.* **1928**, 22, 2120.
- [48] A. Z. Ringbom, *Anal Chem.* **1939**, 115, 332.
- [49] E. B. Sandell, *Colorimetric determination of trace metals 3rd Edition. Inter science Publishers Inc New York*, **1959**, 568.