Spectrophotometric study of ternary complex forming systems of dysprosium(III) and holmium(III) with pyrogallol red in presence of cetylpyridinium bromide for microdetermination

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ABSTRACT

With the growing applications of lanthanoids in science and technology, the study of coordination compounds of these elements has received great attention. A large number of chromogenic reagents form soluble colored complexes with rare earths. Pyrogallol red has been reported to form blue colored complexes with rare earths and has been used for microdetermination of these metal ions. The addition of cationic surfactant, cetylpyridinium bromide (CPB), sensitizes the color reactions of Dy(III) and Ho(III) with pyragallol red. The formation of a water soluble ternary complex of stoichiometric ratio 1:1:4 (e.g. Dy(III)-R-CPB) is responsible for the observed enhancement in molar absorptivity at shifted wavelength, when a surfactant is present. The ternary complexes exhibit absorption maxima at 584nm with a bathochromic shift of about 35nm. Beer's Law obeyed between 0.5 to 6.30ppm. Effective photometric range and molar absorptivity of these ternary complexes have been calculated. The optimum reaction conditions and other analytical parameters were evaluated. The effects of interfering ions on determination of both the metal ions were studied. A simple, rapid and highly sensitive method for the determination of Dy(III) and Ho(III) with pyragallol red is proposed. © 2010 Trade Science Inc. - INDIA

INTRODUCTION

Dysprosium metal is used in permanent magnets for use in audio speakers and industrial applications as well as for magnetorestricitive alloys. The dysprosium metal can also be combined with vanadium and other rare earths to form an alloy used in laser manufacture. Dysprosium's thermal neutron absorption cross-section and high melting point make it ideal for combining with stainless steel in nuclear applications. Along with other small applications, dysprosium oxide has found use in nickel cement used for cooling nuclear reactor rods. Holmium is used as a dopant for yttrium-aluminum garnets used in laser surgery and is also used in to quench nuclear chain reactions in fission reactors. Holmium finds some use in alloy and phosphor production as well as in filters for UV spectrometer calibration. Lanthanum and yttrium are used in high technology applications, such as in superconductors, supermagnets, laser and alloys[1].

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The complexation of tungsten(VI), vanadium(V), molybdenum(VI), copper(II) and titanum(IV) with pyrogallol red(PGR) and bromopyrogallol red(BPGR) in presence of cationic surfactant like cetylpyridinium bromide and OP-7 were studied by A.M.Mamedeova and coworkers[2-4]. Spectrophotometeric determination of thorium, lanthanum, and yttrium in some geological and environmental samples was carried by using eriochrome cyanine R (ECR) in presence of TX-100 and CTAB[5]. The surfactant (CPB) sensitized analytical reaction of cerium (IV) with some triphenylformazan derivatives was studied by Ahmed and his coworkers[6]. Determination of trace amount of ruthenium (III) by the spectrophotometeric method with rhodamine B in micellar medium (CTAB) was studied by Mohsen Keyvanfard[7]. Samarium (III) was determined spectrophotometrically by using chrome azurol S in the presence of cetylpyridinium chloride[8]. Some of the rare earth elements with chromazurol S in the presence of cetyltrimethylammonium bromide and Triton X-100 were determined spectrophotometrically[9]. 2-Hydroxy-1-naphthaldehyde-*p*-hydroxybenzoic hydrazone as a spectrophotometric reagent was used for the determination of lanthanum (III) in presence of CTAB[10]. The ternary interaction of naphthochrome green (NCG) with cetyltrimethylammonium bromide (CTAB) and rare earths (REs: Yb, Dy, Er and Eu) has been investigated with the microsurface adsorption-spectral correction technique (MSASC)[11]. Cerium subgroup rare earths in nickel-base alloys in the presence of yttrium with *p*-acetylchlorophosphonazo and mixed surfactants were determined by spectrophotometric method[12]. Neodymium in mixed rare earths with semi-xylenol orange and cetylpyridinium chloride was determined by spectrophotometric method[13]. Rare earth elements (samarium, dyprosium, yttrium, gadolium, neodymium, praseodymium, lanthanum, and cerium) with xylenol orange in the presence of CPB were determined by spectrophotometric method[14]. Rare earth elements by flow injection analysis based on their reaction with xylenol orange in the presence of CPB were carried by spectrophotometric method[15]. Ciclopirox olamine was determined via ternary complex with Tb(III) and EDTA by spectrofluorimetric method[16]. The solution studies of ternary (1:1:1) complexes of Eu(III), Gd(III), and Tb(III) with benzoic acid/its derivatives and uracil/its

halo derivatives in dioxane-water (30:70 v/v) medium (ionic strength $I = 0.1$ mol·dm^{-3} NaNO$_3$) have been performed[17]. The method is based on the luminescence sensitization of terbium (Tb^{3+}) by formation of ternary complex with IB in the presence of tri-*n*-octylphosphine oxide (TOPO) and tween-20 as surfactant[18]. Cationic surfactants, such as cetylpyridinium bromide (CPB), sensitize the color reaction of Nb(V) with 1-(2-benzothiazolylazo)-2-hydroxy-3-naphthoic acid (I$_a$), 5-(benzothiazolylazo)2,5-naphthalenediol (I$_b$), 5-(2-benzothiazolylazo)8-hydroxyquinoline (I$_c$) and 4-(2-benzothiazolylazo)2,2 -biphenyldiol (I$_d$) reagents[19]. Lanthanum, holmium and manganese in synthetic ceramics, (La$_{(0.8-x)}$Ho$_x$Sr$_{0.2}$MnO$_3$), by using chromogenic agent 5-Br-PADAP [2-(5-bromo-2-pyridylazo)-5-diethylaminophenol] and triton X-100 as a surfactant were determined by spectrophotometric method[20].

Color reaction of PGR and complex formation with Dy(III) and Ho(III) in presence of micelle forming cationic surfactant CPB have not been reported so far. Considering the increasing demand of more sensitive reagents, the present study has been planned for microdetermination of metal ions understudy. This primarily decides the usefulness and its importance for determination of metal ions. The results of the experiments carried out with PGR in presence of CPB and its interaction with Dy(III) and Ho(III) have been discussed in present investigation.

EXPERIMENTAL

All the chemicals used were of analytical grade purity. PGR supplied by Sigma chemical company (U.S.A.) and CPB by Aldrich chemical company were used. The purity of CPB was tested by argentometric titration for determination of bromide ion content[21]. Both the lanthanides used as their oxides and were supplied by Indian Rare Earth Ltd. India, of 99.99% purity. The stock solution of PGR of 1×10^{-2} M and CPB of 1×10^{-1}M strength were prepared. The lanthanide (III) ion solution of 1×10^{-2} M strength was prepared by dissolving respective oxides in minimum quantity of AR grade hydrochloric acid which were standardized by precipitating metal ions as their oxalates and were estimated volumetrically, by using bromopyrogallol red as a complexometric indicator. All subsequent dilutions

of desired concentration were made by using double distilled water.

Order of addition of reagent

The CPB solution was first added to PGR solution and was kept for half an hour. The metal ion solution was then added to this solution and again kept for half an hour to reach complete equilibrium. This order of mixing of solutions was maintained throughout the work. All the absorption measurements were made by using Beckman DU-2 model spectrophotometer with matched glass cells of 10mm light path working on its current supply (220V) device. The pH adjustment was done using Elico Model LI-10 pH meter with glass and calomel electrode assembly, and checked frequently with buffer solution of potassium hydrogen phthalate (pH 4.02) and borax. The pH of solution was so adjusted using hydrochloric acid and sodium hydroxide solution of suitable concentration.

RESULTS AND DISCUSSION

Absorption spectra of PGR

The absorption spectra of PGR solution show characteristic $\lambda_{max}(\varepsilon)$: 518nm (298) in low acidic medium (pH 5.5- 6.5) and $\lambda_{max}(\varepsilon)$: 545nm (302) in alkaline medium (pH 7.0 - 8.0) while in more acidic medium (pH 1.0 - 2.0) at $\lambda_{max}(\varepsilon)$: 475nm (385). On addition of CPB in more acidic medium, the absorbance decreases with appearance of new peak at 430nm causing color change from brown to light pink and in more diluted solution to almost colorless. This color change has been achieved in acidic medium due to early dissociation of protons in presence of CPB[22]. This decolorization might be attributed to the interaction between anionic dye and cationic surfactant as expected.

Effect of CPB on PGR

The maximum decolorizing effect on PGR in presence of CPB has been observed in alkaline medium in 5.0-8.0 pH range showing minimal ratio 1:4 at the $\lambda_{max}(\varepsilon)$: 570nm (275). When this ratio was reached, the absorbance of the reagent remains unaltered even when five times excess of CPB has been added. Therefore, the tentative composition so called "Dye-Surfactant" association may be represented as [PGR (CPB)$_4$].

The direct proof of this association could not be collected in present investigation as all the attempts have been failed to isolate it from solution as concentration was very low. Similar results were obtained at pH 5.5 where further studies of complex formation have been carried out but the effects were less pronounced. The nature of absorbance spectra of the reagent was changed in presence of higher amount of mineral salts. The effects caused by the addition of chloride and sulphate ions were less as compared to nitrate ions.

Complex formation with Dy(III) and Ho(III)

Figure 1(a) and figure 1(b) show the comparative absorption spectra at pH 5.5. In figure 1(a), curve A for absorption spectra of PGR alone shows $\lambda_{max}(\varepsilon)$: 518nm (298), curve B for PGR in presence of CPB shows $\lambda_{max}(\varepsilon)$: 570nm (298), curve C is for PGR-Dy(III) complex at $\lambda_{max}(\varepsilon)$: 548nm (310) and curve D is for PGR-CPB-Dy(III) complex at $\lambda_{max}(\varepsilon)$: 584nm (462) indicating formation of strong ternary complex showing a bathochromic shift of 36nm.

In figure 1(b), the absorbance spectra of PGR and Ho(III) shows $\lambda_{max}(\varepsilon)$: 550nm (362) indicating very poor complexation which is shifted to $\lambda_{max}(\varepsilon)$: 584nm (469) in presence of CPB owing to the formation of strong ternary complex, showing a bathochromic shift of 34nm with increase in absorbance.

However, strong complexation in presence of CPB with a large bathochromic shift of ternary complexes which appeared to be convenient to study the analytical applications further. As the modified PGR reagent has considerable absorbance value at $\lambda_{max}(\varepsilon)$: 584nm (465) of the ternary complex, further studies have been made at pH 5.5 at 584nm for both the metal ions under study where maximum difference in absorbance between the reagent and ternary complex is observed. The interfering hydrolysis of the polyvalent metal ions in the weakly acidic medium has been suppressed due to increase in the stability of the complexes in presence of CPB.

Effect of pH

It has been found that $\lambda_{max}(\varepsilon)$: 550nm (330) of complexes remains constant in the pH range 5.0 to 6.0 in absence and $\lambda_{max}(\varepsilon)$: 584nm (465) of complexes remains constant in the pH range 5.0 to 9.0 in presence

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TABLE 1 : Comparative analytical parameter of the ternary complexes at pH 5.5, λ_{max} of PGR at pH 5.5 = 518nm

Parameter	Dy(III)	Ho(III)
λmax of binary complex(nm)	548	550
λmax of ternary complex(nm)	584	584
Bathochromic shift (nm)	36	34
pH range of stability	A 5.0-5.8 P 5.0-9.0	A 5.0-6.2 P 5.0-9.0
Effective pH range of stability	A 5.5-5.7 P 5.5-8.5	A 5.5-6.0 P 5.5-8.5
log K value	A 08.45 P 10.75	A 08.48 P 10.82
Beer's law range (ppm)	A 1.01-10.06 P 0.58-06.29	A 1.02-10.17 P 0.51-06.36
Effective photometric range (ppm)	A 1.51-07.55 P 1.01-05.03	A 1.52-07.63 P 1.02-05.09
Average molar absorptivity ($dm^3\ mol^{-1}\ cm^{-1}$)	A 44500 P 72400	A 47100 P 79600
Sandell's sensitivity ($\mu g/cm^2$)	A 0 .0036 P 0.0028	A 0.0044 P 0.0035

A-in absence and P- in presence of CPB

of CPB indicating the pH range of stability of complex formation. The optimum pH range of stability was found to be 5.0 to 5.8 for Dy(III) and 5.0 to 6.2 for Ho(III) in absence; and 5.5 to 8.5 for both metals understudy in presence of CPB, where the absorbance remains nearly constant at λ_{max}(ε): 584nm (465) of the complex. Thus ternary complexation takes place in wider pH range as compared to binary complexes. This has been observed for both the metals understudy.

Composition of complexes

The stoichiometric composition of metal ion and PGR in absence and presence of ten times concentration of CPB have been found to be 1:1 at pH 5.5. It has been observed that PGR reagent at pH 5.5 exist as [PGR(CPB)$_4$] as four CPB ions are associated with PGR as discussed earlier and therefore, the composition of complexes in presence of CPB may be expressed as M[PGR(CPB)$_4$] for both the metal complexes. The composition of the complex was studied by the Job's method of continuous variation[23] and was further confirmed by Mole ratio method[24]. The formation of complexes may therefore be expressed by an equation (Omitting charges) as follows.

$$M + [PGR\ (CPB)_4] \rightarrow M\ [PGR\ (CPB)_4]$$
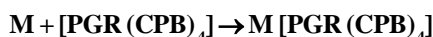
The values of log K evaluated by Job's method are shown in TABLE 1 which indicate that the ternary complexes are more stabilized.

Stability constant

Values of log K {where, K = [ML] / [M] [L]} of complexes of both the metal ions understudy in absence and presence of CPB show that the value for particular metal in presence of CPB is greater in presence than in absence of CPB. This is due to the formation of stable ternary complexes with modified reagent in presence of CPB.

Analytical applications of complexes of Dy(III) and Ho(III) in presence of CPB

The formation of intense colored ternary complexes with bathochromic shift at about 35nm for both metal ions and corresponding increase in absorbance values at shifted wavelength facilitates the analytical measurements for microdetermination of metal ions. Some important analytical parameters and applications for determination of metal ions have been summarized in absence and presence of CPB in TABLE 1.

Rate of color formation and stability of color at room temperature

Color formation does not depend on reaction time and is almost instantaneous. However the mixtures were kept for 30min. for equilibration before recording their absorbances in the present study. The stability of color was tested at room temperature by measuring the absorbance of complex at regular interval of time. The maximum absorbance was achieved in 5min. after the addition of reactants. The color is quite stable for more than 48h. at room temperature. The temperature was found to have no effect on color intensity of ternary complexes from 20°-60°C.

Effect of reagent concentration

Different volumes of 1.0×10^{-3} M of PGR were taken in different volumetric flasks to which equal volume of 1.0×10^{-2} M of CPB was added. 1ml of 1.0×10^{-3} M metal ions was then added in each flask and total volume was maintained at 25ml and adjusted at pH 5.5, and absorbance readings were recorded at 584nm. It was found that PGR should be present at least equal to metal ions concentration to have maxi-
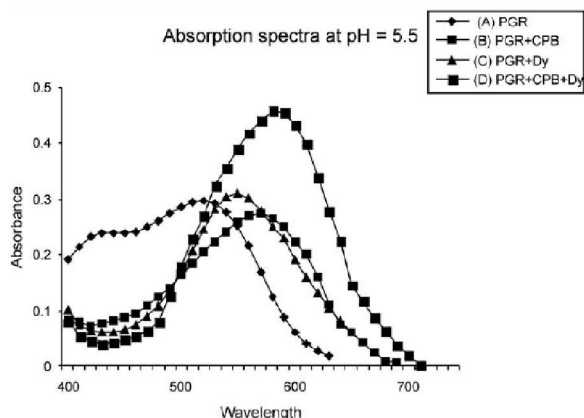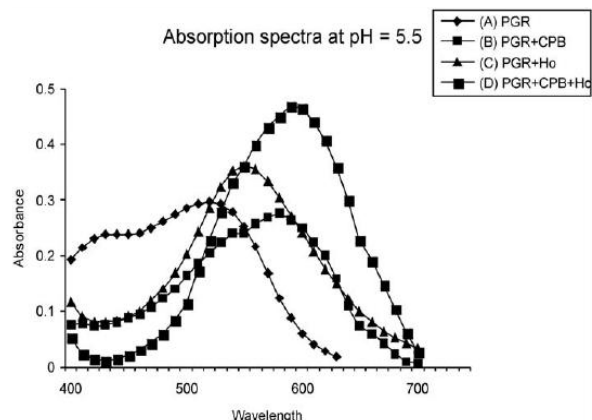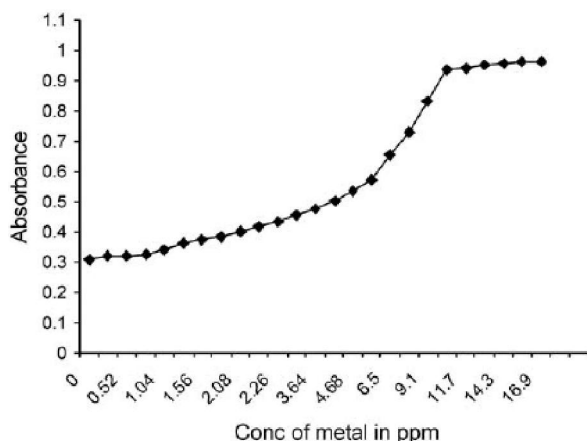
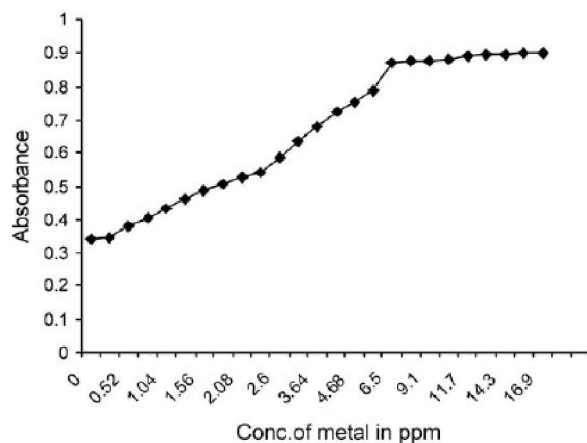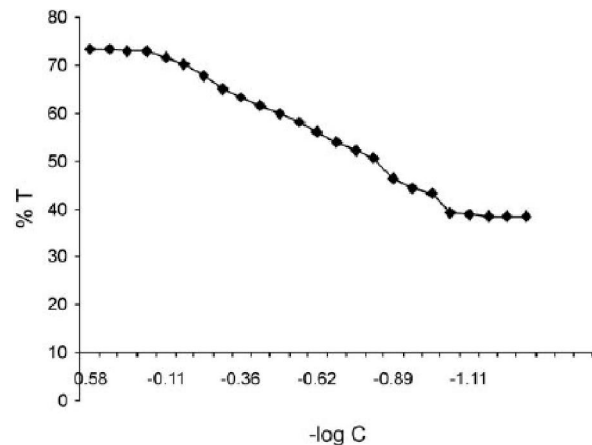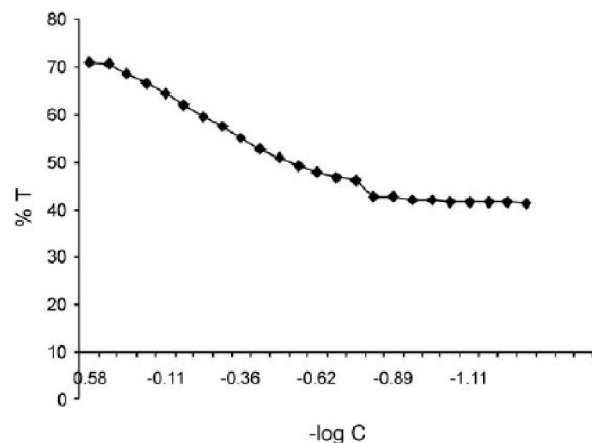**Figure 1(a) : Spectra at pH 5.5 for Dy**

Figure 1(b) : Spectra at pH 5.5 for Ho

Figure 2(a) : Curves of Beer's law for determination of Beer's law ranges of PGR chelates of Dy in absence of CPB at pH 5.5 and $\lambda_{max} = 548nm$

Figure 2(b) : Ringbom plot for photometric determination of PGR chelates of Dy in presence of CPB at pH 5.5 and $\lambda_{max} = 584nm$

mum color development in presence of CPB. However in absence of CPB, reagent needed was eight times as that of metal ion for full color development.

Beer's law and effective photometric ranges

The linearity between the absorbance of complex and concentration of metal ion was tested by taking the different volumes of metal ion solution of 2.0×10^{-4} M in absence and presence of CPB. The concentration of PGR and CPB solutions used were 5.0×10^{-4} M and 5.0×10^{-3} M respectively. The volumes of PGR and CPB solutions used were 4.0ml each. Total volume was kept constant at 25ml at pH 5.5. The absorbance values were measured at 548nm for Dy(III), and at 550nm

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for Ho(III) in absence and at 584nm for both the metal ions in presence of CPB. From a graph as shown in figure 2(a) of absorbance Vs metal ion concentration, the Beer's law ranges were then calculated and found to be 1 to 10ppm for binary complexes. However in presence of CPB, these ranges have been found to be 0.5 to 6.3ppm for ternary complexes. The most effective photometric ranges as derived from straight-line portion of the Ringbom plot as shown in figure 2(b) (i.e. -ve log of metal ion concentration versus percentage transmittance) have been found to adhere from 1.5 to 7.5ppm in absence of CPB. However in presence of CPB, these ranges have been found to be 1.0 to 5.0ppm. Thus the present values of photometric ranges are in well agreement with the values reported earlier for the metal ions understudy. Thus both the metal ions understudy can be determined by the present proposed method when present in low concentration.

Sensitivities and molar absorptivities

The average values of molar absorptivities of metal complexes in absence and presence of CPB at the wavelength of study are given in the TABLE 1. The increase in values of the sensitivities and molar absorptivities of ternary complexes which primarily decides the usefulness and importance of the present reactions for the microdetermination. Thus the present investigation shows that sensitization of the reagent in presence of CPB takes place and can be used for the microdetermination of both the metal ions understudy.

Effect of foreign ions

The method suffers from lack of specificity but with less interference. The determination is possible in absence of metal ions such as Sc^{3+}, Y^{3+}, Th^{4+}, Li^{1+}, other lanthanides, Ag^+, Pd^{2+}, Hg^{2+}, In^{2+}, Au^{3+} and anions such as nitrates, oxalates, citrates, succinates and EDTA strongly interfere.

Recommended procedure for microdetermination of individual Ho and Dy

To an aliquot containing 0.6 to 6.30ppm of above metal ions (Ho / Dy), add 8ml of the modified PGR solution, prepared by adding each of 4ml of PGR and CPB of concentrations 5.0×10^{-4} M and 5.0×10^{-3} M respectively in 25ml volumetric flask. Dilute the solu-

tion with distilled water to 25ml after adjusting pH 5.5. Allow the mixture to stand for about 5min. for full color development. Measure the absorbance of this unknown solution at 584nm for both the metal ions against reagent blank of the same pH prepared in the same manner. The amount of metal ions present in sample solution can be evaluated by comparing this absorbance from calibration curve obtained under similar condition. The results of ten determination of 45.30μg per 25ml for Dy(III) and 65.80μg per 25ml of Ho(III) showed standard average deviation of 0.048 and 0.081 respectively.

CONCLUSION

Thus the reagent reported in presence of surfactant CPB can be used as one of the most sensitive reagent for the spectrophotometric analysis of Dy(III) and Ho(III) when present in extremely small concentration. The increased stability has been achieved in presence of surfactant corresponding to a ternary complexation which is adequate for the analytical purposes. The developed procedure appeared to be quite sensitive, precise and reproducible. The commercial exploitation of these reactions needs further investigation.

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