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Sensitized colour reactions of pyrogallol red in presence of cetyldimethylethyl ammonium bromide for the spectrophotometric determination of yttrium (iii), europium (iii), and terbium (iii)

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Abstract

The tripositive rare earth metal ions exhibit little tendency to form complexes with variety of normally powerful coordinating agents. Although this may be due to relatively large size of their cations. With the development of cheletometry in this context many new reagents have been introduced for the determination of rare earths in the recent past. In the present work the Cetyldimethyl ethyl ammonium bromide has been used to sensitize Pyrogallol Red (PGR) for the photometric determination of *Y(III)*, *Eu(III)* and *Tb(III)*. Cetyldimethylethyl ammonium bromide (CDMEAB), a cationic surfactant has been used to decolorized Pyrogallol Red(PGR), an anionic triphenyl methane dye. Addition of *Y(III)*, *Eu(III)* and *Tb(III)* to this decolorized solution resulted into intense coloured stable ternary complex. The shift in the λ_{max} with increased in the values of molar absorptivity and sensitivity have been observed in case of ternary complex(*Y(III)*, *Eu(III)* and *Tb(III)*-PGR-CDMEAB) as compared to binary complex(*Y(III)*, *Eu(III)* and *Tb(III)*-PGR). The analytical applications like Beer's law range and effective photometric range have been studied at pH 6.0 and at 550nm in absence and at 650nm in presence of CDMEAB.

Keywords: Pyrogallol Red (PGR), CDMEAB, Spectrophotometric determination, binary complex, ternary complex etc.

1. Introduction

Number of reagents has been proposed for spectrophotometric determination of rare earths [1-5]. The most widely used reagent for determination of rare earths is Xylenol orange [6, 7], although many others are applicable. Pyrogallol red i.e, Spiro [3H-2, 1-benzoanthiole-3, 9'-[9H] xanthene]-3', 4', 5', 6' Tetrol, 1-1-dioxide forms colored chelates with many metals [8-10]. Attempts have been made in the recent past to improve the sensitivity of some reagents for microdetermination of some rare earths using Cationic surfactants [2, 3, 4, 11, 12]. The colour forming reactions of thorium and uranium with Pyrogallol red (PGR), in the Presence and absence of Cetyldimethylethylammonium bromide has been studied spectrophotometrically by Upase at. al. [13] and palladium in presence of cetylpyridinium bromide has been studied by Kant at. al. [14]. Its color reactions and complex formation in presence of Cetyldimethylethylammonium bromide with *Y(III)*, *Eu(III)* and *Tb(III)* have not been reported so far. The present investigation describes the systematic study on the use of PGR as spectrophotometric reagent for *Yttrium(III)*, *Europium(III)*, *Terbium(III)*.

2. Materials and methods

All the chemicals used were of analytical grade purity. Pyrogallol red (PGR) used was supplied by Sigma Chemical Company, U.S.A. And Cetyldimethylethylammonium bromide (CDMEAB) by Aldrich Chemical Company, U.S.A. and its purity was estimated by argentometric titration [15] for the determination of bromide ion content. All the metal oxides used were supplied by Indian Rare Earth Ltd., India, of 99.9% purity. The stock solutions of rare earth, CDMEAB, and PGR were prepared of strength 1.0×10^{-3} M and subsequently diluted with double distilled water.

The CDMEAB solution was first added to PGR solution and was kept for half an hour. The 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 of solutions was maintained. Standard HCL and NaOH solutions were used for adjustment of pH Elico Li-10 pH meter, operated on

220 volts stabilizer with AC mains with glass and calomel electrodes assembly. All absorbance measurements were carried out by using Hitachi U 2001 spectrophotometer with matched quartz cell with 1.0 cm thickness at room temperature of 30 ± 2 °C. For all spectral studies deionised distilled water was used as a reference solution.

3. Results and discussion

It has been considered necessary to have prior information on the nature of interaction between PGR and CDMEAB before evaluating the PGR as sensitive reagent for the estimation of Rare earths in the presence of CDMEAB. Therefore, absorption spectra of PGR in absence and presence of CDMEAB, composition of dye-surfactant complex, absorption spectra of Rare earth chelates in absence and presence of CDMEAB, effect of pH, composition and stability constants of the chelates in absence and presence of CDMEAB, have been studied.

3.1 Absorption spectra of PGR in the absence and presence of CDMEAB

The color of PGR has been found to be different at different pH values. The addition of CDMEAB brings about a change in color of PGR at the same pH value. The absorption spectra of PGR, has been therefore, studied at different pH values (1.0 to 12.0) in the absence and presence of CDMEAB. The wavelength of maximum absorbance of PGR in the absence and presence of CDMEAB are summarized in Table 1.

It has been observed that maximum decolorizing effect is observed at pH 11.0. However, the, λ_{\max} , 560nm at pH 11.0 in absence is shifted to 580nm in presence of CDMEAB showing bathochromic shift of 20nm a decrease in the absorbance value from 0.520 at the λ_{\max} of PGR(560nm) at pH 11.0 decreases to 0.375 in presence of CDMEAB. However, the decrease in absorbance from 0.290 at pH 6.0 at 560nm takes place to 0.205 in presence of CDMEAB under the similar condition. This change in absorbance maximum in presence of CDMEAB may be attributed due to the possible formation of a dye-surfactant complex.

Table 1: Wavelengths of maximum absorbance of PGR in the presence and absence of CDMEAB

PGR		PGR+CDMEAB	
pH	λ_{\max} (nm)	pH	λ_{\max} (nm)
1.0-3.0	480	1.0-3.0	480
4.0,4.5	520	4.0,4.5	550
5.0-6.0	560	5.0-6.0	580
7.0-12.0	560	7.0-12.0	580

3.2 Composition of PGR-CDMEAB complex

The effect of varying CDMEAB concentration on the absorbance of PGR has been studied in basic medium at pH 11.0, at λ_{\max} , 560nm where the maximum discoloration takes place. The absorbance of different concentrations of PGR is plotted against the variable concentration CDMEAB. The concentration of PGR taken were 2.5×10^{-4} M, 2.4×10^{-4} M, 1.66×10^{-4} M and 1.25×10^{-4} M. It is observed that the maximum decolorizing effect reached at the minimal PGR: CDMEAB ratio of 1:3. When this ratio was reach the absorbance of the reagent remains unaltered even when excess of five times of CDMEAB has been added. The modified reagent species thus formed, may therefore, be written as $[PGR (CDMEAB)_3]$.

3.3 Absorption Spectra of Rare earth Chelates in Presence and Absence of Surfactant.

A series of solutions were prepared keeping the ratio of Metal: PGR: CDMEAB as 1:1:10 and 4:1:10. A number of sets were prepared for each ratio and pH was adjusted to 3.0, 3.5, 4.0, 5.0, 5.5, 6.0, and 6.5. The absorption spectra were recorded in the entire visible region from 400nm to 700nm. Absorbance maxima of PGR and its complexes with Rare earths in the absence and presence of CDMEAB have been summarized at different pH values in Table 2.

Table 2: Absorbance Maxima (nm) of PGR and its Chelates in absence and presence of CDMEAB at different pH

SYSTEM	4.0	4.5	5.0	5.5	6.0	6.5
PGR	520	520	560	560	560	560
PGR+CDMEAB	550	550	580	580	580	580
PGR+Y	520	520	550	550	550	550
PGR+CDMEAB+Y	650	650	650	650	650	650
PGR +Eu	520	520	550	550	550	550
PGR+CDMEAB+Eu	650	650	650	650	650	650
PGR+Tb	520	520	550	550	550	550
PGR+CDMEAB+Tb	650	650	650	650	650	650

The absorption spectra of PGR shows peak at 580nm in the presence of CDMEAB in the pH range 5.0 to 6.5, but shows peak at 560nm in the pH range 5.0 to 6.5. in the pH range 5.5-6.5 purple coloured metal chelates show broad peak around 550nm in absence of CDMEAB indicating formation of binary complex. This purple colour of PGR complex changes to deep blue with high absorbance value in presence of CDMEAB indicating the involvement of micelles of CDMEAB in the formation of ternary complex. The increase in absorbance value at shifted λ_{\max} indicates the sensitization of colour reactions.

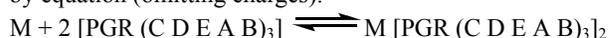
3.4 Effect of pH

Effect of pH on λ_{\max} and on the absorbance, of the Rare earth complexes of PGR in the absence and presence of tenfold excess of CDMEAB have been studied. It is found that the λ_{\max} of the complexes remain constant in the pH range 3.5 to 6.5 indicating pH range of stability of complex formation in presence of CDMEAB. However, in the absence of CDMEAB this range is from pH 5.0 to 6.5.

3.5 Composition of Chelates

The composition of the chelates has been studied by the Job's method of continuous variation and it has been further confirmed by Mole ratio method. For Job's method, solutions of Rare earths and PGR have been taken in three equimolar concentrations of 2.5×10^{-4} M, 2.4×10^{-4} M, and 1.66×10^{-4} M; Five times excess of CDMEAB has been then added for studying the composition in the presence of surfactant.

The stoichiometric composition between the metal ion and PGR in the presence and absence of CDMEAB has been found to be 1:2. It has been observed that PGR reagent at pH 6.0 exists as $[PGR (CDMEAB)_3]$ and therefore, the composition of complexes in the presence of CDMEAB may be written as $M[PGR(CDMEAB)_3]_2$ for all metal complexes. The composition has been further confirmed by Mole ratio method. The formation of complexes may therefore expressed by equation (omitting charges).



4. Analytical applications of PGR chelates

The large shift of 110 nm in absorption maximum of the complex from 540 nm in absence to 650 nm in presence of CDMEAB at pH 6.0 where the absorption of the reagent is comparatively negligible, facilitate the analytical measurements, making the reagent very sensitive for particular color reaction.

4.1 Order of addition of reactants

The sequence of addition of reactants must be followed strictly. In all the experiments, CDMEAB was first added to PGR solution. This solution was kept for at least 30 minutes for equilibration. To this solution of modified PGR, the metal ion solution was then added which again kept for 30 minutes for complete formation of the ternary complex.

4.2 Rate of color formation and stability of color at room temperature.

The color formation does not depend on reaction time and is almost instantaneous. However, the mixtures were kept for 30 minutes for equilibration. A mixture containing 2.5×10^{-4} M CAB, 1.0×10^{-4} M CAB, and 2.5×10^{-4} M. Rare earth solutions at pH 6.0 retained its absorbance value even after 24 hours standing at room temperature. The temperature was found to have no effect on color intensity of ternary complexes from 20-60 °C.

4.3 Effect of reagent concentration

Different volumes of 1.0×10^{-4} M of PGR were taken in

different flasks to which equal volume of 5.0×10^{-4} M CDMEAB was added. One ml of 1.0×10^{-4} M metal ions was then added in each flask. Total volume was maintained at 50 ml at pH 6.0. Absorbance readings were recorded at 650 nm. It was found that PGR, in case of all metal ions under study, must be present at least two times more than metal ion to have maximum color development. However, in absence of CDMEAB, reagent needed was six times that of metal ion for full color development.

4.4 Beer's law and effective photometric ranges

The linearity between the absorbance of the chelates and concentration of metal ion has been tested by taking the different volumes of metal ion solution (1.0×10^{-3} M in absence and 6.66×10^{-4} M in presence of CDMEAB). The final concentration of PGR taken was 2.0×10^{-4} M, of CDMEAB was 1.0×10^{-3} M. Total volume was kept constant at 50ml at pH 6.0. The absorbance values were measured in the absence of CDMEAB at 540 nm. However, in the presence of CDMEAB, all the spectral measurement was made at 650 nm. The range of Beer's law is given in table 4 in absence and presence of CDMEAB. The effective range for photometric determination was also calculated from these data by Ringbom plot of log of metal ion concentration versus percentage transmittance. Thus, the range as derived by the slope of the curve is selected to be range for the effective photometric determination as given in Table 3.

Table 3: Photometric Determination of Rare earths with PGR in the Absence and Presence of CDMEAB.

Chelates of PGR	pH of study	Wavelength of study (nm)	Beer's law Range (ppm)	Effective Photometric range (ppm)	Sendell's sensitivity	Molar Absorptivity
Y(III)	A 6.0	550	0.15-1.20	0.35-0.71	0.0042	21000
	P 6.0	650	0.088-0.80	0.088-0.53	0.0024	36000
Eu(III)	A 6.0	550	0.34-1.80	0.34-1.20	0.0060	25000
	P 6.0	650	0.15-1.21	0.15-0.91	0.0037	41000
Tb(III)	A 6.0	550	0.31-1.90	0.31-1.27	0.0075	21000
	P 6.0	650	0.12-1.69	0.21-0.81	0.0040	39000

A: Absence, P: Presence

4.5 Sensitivities and molar absorptivities

Molar absorptivities of the complexes have been determined by taking a constant amount of PGR and different amount of excess of metal ions and five times excess of CDMEAB at pH 6.0. The values of molar absorptivities and sensitivities of metal complexes in absence and presence of CDMEAB at the wavelength of study are given in Table 3. The increase in the values of the sensitivities and molar absorptivities of the ternary complex than binary complex again shows the sensitization of the reagent in presence of CDMEAB.

5. Conclusions

The spectrophotometric determination of metal ions under study with Pyrogallol red in the presence and absence of Cetyltrimethylammonium bromide has been studied. Following are the merits of modified method. The sensitization of PGR by the addition of CDMEAB is clear from the fact that the formation of stable ternary complexes with Rare earths occurs at pH 6.0 with bathochromic shift in the λ_{\max} of metal ion-PGR complexes in the presence of cationic surfactant. This change is attributed due to the formation of ternary complex system in the presence of CDMEAB in the acidic medium compared to the binary system in the absence of CDMEAB. Due to the shifted λ_{\max}

towards higher wavelength (From 550 nm to 650 nm) a large difference in the absorbance between the reagents blank (PGR-CDMEAB) and its ternary complex results in enhancement of the sensitivities and molar absorptivities again indicate the great sensitivity of color reaction.

Further, the modified method requires smaller molar concentration of PGR over the metal ion concentration for full color development and is instantaneous in the presence of CDMEAB, again indicates the stability of the color reaction. The modified reagent i.e., [PGR(C D E A B)₃] has also been found to be extremely useful in the complexometric titration of the Rare earth metal ions. This modified reagent act as sensitive metallochrome indicator giving a very sharp color change at the end of complexometric titration.

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