Sensitization of Eriochromeazurol-B in Presence of Cetyldimethylethylammonium Bromide for the Microdetermination of Some Lanthanides

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Abstract: Cetyldimethylethylammonium bromide, a cationic surfactant has been used to decolorize eriochromeazurol B, an anionic triphenylmethane type of dye. Addition of specific lanthanide metal ion to this decolorized solution resulted into intense colored stable ternary complex with large bathochromic shift from 540 nm (binary complex) to 650 nm (ternary complex) with increase in absorbance values at shifted wavelength. CDMEAB thus decreases the color intensity of ECAB and increases the absorbance value of ternary complexes. This two fold advantage resulted into enhancement in molar absorptivities and sensitivities at shifted wavelength of ternary complexes with stoichiometric composition 1:(1:3)₂, [Ln : (R:S)] for all lanthanides under study namely yttrium, neodymium, europium, terbium and ytterbium. The ternary complexes at pH 6.0 exhibited absorption maxima at 650 nm with molar absorptivities 69000 L.mol⁻¹.cm⁻² for Y(III), 66000 L.mol⁻¹.cm⁻² for Nd(III), 69000 L.mol⁻¹.cm⁻² for Eu(III), 64000 L.mol⁻¹.cm⁻² for Tb(III), 70000 L.mol⁻¹.cm⁻² for Yb(III). Beer's law were obeyed in concentration range 0.11-0.94, 0.19-1.53, 0.2-1.41, 0.21-1.69 and 0.23-1.11 ppm for Y(III), Nd(III), Eu(III), Tb(III) and Yb(III) respectively. Conditional formation constants and various analytical parameters have been evaluated and compared the results of newly formed ternary complexes with binary complexes. Finally newly suggested modified method have been recommended for the microdetermination of lanthanides under study.

Keywords: Spectrophotometry, Eriochromeazurol B (ECAB), Cetyldimethylethylammonium bromide (CDMEAB), Europium (Eu), Neodymium (Nd), Terbium (Tb), Yttrium (Y), Ytterbium (Yb).

Introduction

The lanthanide metal ions have found an ever increasing use in many areas of research such as synthesis, co-ordination chemistry, material science, photonic devices, catalysis etc. The metals like europium and yttrium are used in the production of red phosphor that is found in all color television screens. Yttrium is also used in heating elements alloys, super alloys and high temperature semiconductors. Ytterbium can be alloyed with stainless steel to improve some mechanical properties in fiber optic cables where it can be used as an amplifier and doping agent. Terbium is used in X-ray machines and green phosphor activator. Neodymium appears in many electronics such as fluorescent lights and color televisions.

Organic reagents play very important role in analytical and complex chemistry of lanthanides for its determination. With increasing demand of more sensitive reagents for their use in determination of metal ions by spectrophotometric technique, the attempts have been made in the past to intensify the color using third component like surfactant by converting the binary complex of lanthanides to ternary complex. It was observed that the addition of surfactant to dye solution decreases the color intensity of the reagent. The addition of specific metal ion to this decolorized solution resulted into the formation of intense colored stable ternary complexes with bathochromic shift in the wavelength with heightened molar absorptivity and sensitivity which primarily decides the usefulness and importance of the reagents developed for spectrophotometric determination of metal ions.

Very few ternary or mixed ligand complexes appear in the literature for their spectrophotometric microdeterminations. The ternary complexes of gallium (III) and lead (II) were reported with pyrocatechol violet in presence of some cationic surfactants¹. Shokrollahi A. reported a spectrophotometric method for determination of sub-micro-molar amounts of aluminium (III) ion with eriochrome cyanine R in presence of DTAB as surfactant². Spectrophotometric determination of scandium (III) in monazite after separation in presence of reagent eriochrome cyanine R and surfactant CTAB have been reported by Chan-il-park and coworkers³. Application of chromeazuro S and benzyldodecyldimethylammonium bromide for gallium (III) determination in mineral fertilizers have been studied by Buhl F. and coworkers⁴. Spectrophotometric determination of uranium (VI) with pyrocatechol violet in cetyltrimethylammonium bromide and thorium (IV) and uranium (VI) with methyl thymol blue in presence of cetyl diethylammonium bromide have been reported earlier⁵⁻⁶.

Attempts have been made by using cationic surfactants like cetyltrimethylammonium bromide and cetylpyridinium bromide to improve the photometric sensitivity for the microdetermination of some lanthanides using some organic dyes⁷⁻¹². The ternary association of chromeazuro S and cetyltrimethylammonium ion in presence of triton-100 was useful for the sensitive spectrophotometric determination of lanthanide in mixtures and in hydroxide concentrates as reported by Preisler et al¹³. Spectrophotometric study of ternary complex forming systems of dysprosium (III) and holmium (III) with pyrogallol red and some lanthanide metal ions with eriochrome cyanine R in presence of cetylpyridinium bromide for microdetermination have been reported by A. S. Dhepe and A. B. Zade^{14, 15}. Magda Ali Akl et al have discussed the extraction, preconcentration and determination of microamounts of lanthanum and yttrium using alizarin red sulfonate (ARS) of a metal complex via surfactant-mediated phase separation¹⁶. The ternary interaction of naphthochrome green (NCG) with cetyltrimethylammonium bromide (CTAB) and lanthanides (Res: Yb, Dy, Er and Eu) has been investigated with the microsurface adsorption spectral correction technique (MSASC)¹⁷. The surfactant (CPB) sensitized analytical reaction of cerium (IV) with some triphenylformazan derivatives was studied by Ahmed and his coworkers¹⁸.

The present investigation describes the systematic study on the use of eriochromeazuro B (ECAB) as spectrophotometric reagent for the microdetermination of lanthanides i.e. yttrium (III), neodymium (III), europium (III), terbium (III) and ytterbium (III) in absence as a binary complex and in presence of cationic surfactant cetyldimethylethylammonium bromide (CDMEAB) as a ternary complex and has not been reported so far.

Experimental

Instrumentation and reagent solutions

All the chemicals used were of analytical grade purity. Eriochromeazuro B 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 for the determination of bromide ion content¹⁹. All the lanthanide oxides used were supplied by Indian Rare Earth Ltd., India, of 99.9% purity. The stock solutions of lanthanides, CDMEAB and ECAB were prepared of strength 1.0×10^{-3} M and subsequently diluted with double distilled water.

The CDMEAB solution was first added to ECAB 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 of desired concentration. Beckman model B spectrophotometer was used for the measurement of absorbance with glass cuvettes of light path 10 mm. All the experiments have been carried out at room temperature of $30 \pm 2^\circ\text{C}$.

Result and Discussion

Absorption spectra

It has been considered necessary to have prior information on the nature of interaction between anionic ECAB and cationic CDMEAB before evaluating the ECAB as a sensitive reagent for the estimation of lanthanides in presence of CDMEAB. Therefore absorption spectra of ECAB in absence and presence of CDMEAB, composition of dye-surfactant complex, absorption spectra of lanthanide 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 ECAB in absence and presence of CDMEAB

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

Absorption spectra of alkaline ECAB solution at pH 11.5 show a characteristic maximum at 600nm. After the addition of CDMEAB, this maximum decreases and second absorption peak appears at 440nm. Visually this change represents a discoloration of the original pale violet solution to pale grayish or in more dilute solution to almost colorless.

Notable shifts are observed in the acidic medium. At pH 1.0, λ_{max} 470nm shifted to 520nm. In the pH range 2.0 to 4.0 peaks shifted from 490 nm to 520 nm. There is no shifting of absorption maximum in the pH range 4.5 to 5.5. It has been observed that the absorbance value increases from pH 1.0 to 5.0 and then decreases up to pH 12.0. These

changes in absorbance maximum in presence of CDMEAB may be attributed due to interaction between anionic ECAB and cationic CDMEAB might be resulting into the possible formation of so called "Dye-Surfactant complex".

Table 1. Wavelengths of maximum absorbance of ECAB in absence and presence of CDMEAB.

ECAB		ECAB+CDMEAB	
pH	$\lambda_{\max}$ (nm)	pH	$\lambda_{\max}$ (nm)
1.0	470	1.0	520
2.0,3.0	490	2.9,6.0	520
4.0	490	4.0	520
4.5,5.0,5.5	510	4.5,5.0,5.5	510
6.0,6.5,7.0	430,600	6.0,6.5,7.0	440
8.0,9.0,10.0,11.0, 12.0	420,600	8.0,9.0,10.0,11.0, 12.0	440

Composition of ECAB-CDMEAB Complex

The effect of varying CDMEAB concentration on the absorbance of ECAB has been studied in acidic medium at pH 6.0 and alkaline medium at pH 11.5 at $\lambda_{\max}$ 600 nm where the maximum discoloration has been observed. The absorbance of different concentrations of ECAB solution is plotted against variable concentration of CDMEAB. The concentration of ECAB taken 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 is observed that the maximum decolorizing effect reached at the minimal ECAB: 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 $[\text{ECAB}(\text{CDMEAB})_3]$.

The anionic ECAB dye and cationic surfactant reaction may be anionic in nature forming a new ECAB surfactant complex. This newly formed complex is useful for further microdetermination of metal ions.

Absorption spectra of lanthanide complexes in absence and presence of surfactant

Series of solutions were prepared by keeping the ratio of Metal: ECAB: CDMEAB as 1:1:10 and 4:1:10. Number of sets was 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 400 to 700nm. Absorbance maxima of ECAB and its complexes with lanthanide in absence and presence of CDMEAB have been summarized at different pH values in Table 2.

Figure 1. Effect of CDMEAB on ECAB in alkaline medium.

Figure 2. Effect of CDMEAB on ECAB in acidic medium.

Table 2. Absorbance maxima (nm) of ECAB and its complexes in absence and presence of CDMEAB at different pH.

System	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5
ECAB	490	490	490	510	510	510	430	430
ECAB + CDMEAB	520	520	520	520	520	520	440	440
ECAB + Y	500	500	540	540	540	540	540	540
ECAB + CDMEAB + Y	530	530	550	650	650	650	650	650
ECAB + Nd	500	500	540	540	540	540	540	540
ECAB + CDMEAB + Nd	530	530	550	650	650	650	650	650
ECAB + Eu	500	500	540	540	540	540	540	540
ECAB + CDMEAB + Eu	530	530	540	650	650	650	650	650
ECAB + Tb	500	500	540	540	540	540	540	540
ECAB + CDMEAB + Tb	530	530	540	650	650	650	650	650
ECAB + Yb	500	500	540	540	540	540	540	540
ECAB + CDMEAB + Yb	530	530	540	650	650	650	650	650

In the pH range 3.0 to 3.5 in absence and presence of CDMEAB, the wavelength maxima of ECAB shows small change in λ_{max} and absorbance values; indicating poor complexation. However in presence of CDMEAB only one sharp peak has been observed at 650nm in the pH range 4.5 to 6.5 with high absorbance values. It has been observed that the maximum complexation takes place at pH 6.0 by comparing the absorption spectra and the absorbance values of the reagent and complex in absence and presence of CDMEAB as reported in the Table 2. But broad peak is observed in pH range 4.0 to 6.0 in the wavelength region around 540 nm indicating weak complexation in absence of CDMEAB for all lanthanides.

In Figure 3 to 7, the metal ions Eu (III), Nd (III), Tb (III), Y (III) and Yb (III) indicates binary complexation with ECAB and ternary with ECAB and CDMEAB at pH 6.0. Curve D represents the absorption spectra of ECAB alone at pH 6.0 showing a peak at 430 nm and second peak was also observed at 600 nm. ECAB in presence of CDMEAB has been indicated by curve C showing the $\lambda_{\max}$ at 440 nm (single peak). Curve B indicates a broad peak around 540 nm indicating weak complexation. Thus shifting in $\lambda_{\max}$ from 430 to 540 nm in absence for binary and from 440 to 650 nm in presence of CDMEAB for ternary have been observed indicating a bathochromic shift of 110 nm in absence and 210 nm in presence of CDMEAB for all lanthanides.

Thus the complex formation of lanthanides in presence of CDMEAB shows large bathochromic shift and increased absorbance value causing marked sensitization of above color reaction resulting into high molar absorptivity of ternary complex which may be applied as useful tool in microdetermination of metal ions understudy.

Effect of pH

In Figure 8 variation of $\lambda_{\max}$ of europium complex at different pH value was studied in absence and presence of ten fold excess of CDMEAB. Curve A represents variation of $\lambda_{\max}$ with change in pH of solution of ECAB in absence of CDMEAB. It shows $\lambda_{\max}$ at 510 nm in pH range 4.5 – 5.5 and suddenly decreases to 430 nm from where it remains constant upto 6.5. Curve B represents variation of $\lambda_{\max}$ with change in pH of the solution of ECAB in presence of CDMEAB show the constant $\lambda_{\max}$ at 520 nm in the pH range 4.0 to 5.5 which then shifted at 440 nm and remains constant upto pH 6.5. Curve C represent the variation of $\lambda_{\max}$ with change in pH of Eu complex in absence of CDMEAB. The horizontal portion of curve C in figure shows that the $\lambda_{\max}$ of binary complex remains constant in the pH range 4.0 to 6.5 indicating pH range of stability of constant wavelength of the complexes. Curve D represents variation of $\lambda_{\max}$ with change in pH of complexes of europium metal ion in presence of CDMEAB and indicate that the $\lambda_{\max}$ of ternary complex remains constant in the pH range 4.5 to 6.5 i.e pH range of stability of constant wavelength.

Figure 3. Absorption spectra of Eu at pH 6.0, **A**-ECAB-CDMEAB-Eu-(Ternary complex), **B**-ECAB-Eu at(pH 6.0)-(Binary complex), **C**-ECAB-CDMEAB-(Modified reagent), **D**-ECAB-(Reagent).

Figure 4. Absorption spectra of Nd at pH 6.0, **A**-ECAB-CDMEAB-Nd-(Ternary complex), **B**-ECAB-Nd at(pH 6.0)-(Binary complex), **C**-ECAB-CDMEAB-(Modified reagent), **D**-ECAB-(Reagent).

Figure 5. Absorption spectra of Tb at pH 6.0, **A**-ECAB-CDMEAB-Tb-(Ternary complex), **B**-ECAB-Tb at(pH 6.0)-(Binary complex), **C**-ECAB-CDMEAB-(Modified reagent), **D**-ECAB-(Reagent).

Figure 6. Absorption spectra of Y at pH 6.0, **A**-ECAB-CDMEAB-Y-(Ternary complex), **B**-ECAB-Y at(pH 6.0)-(Binary complex), **C**-ECAB-CDMEAB-(Modified reagent), **D**-ECAB-(Reagent) .

Figure 7. Absorption spectra of Yb at pH 6.0, **A**-ECAB-CDMEAB-Yb-(Ternary complex), **B**-ECAB-Yb at (pH 6.0)-(Binary complex), **C**-ECAB-CDMEAB-(Modified reagent), **D**-ECAB-(Reagent).

In figure 9 Curve B represents the plot of absorbance of Eu complex of ECAB at the wavelength of maximum absorbance i.e. 650 nm in presence of CDMEAB with the changes in pH in the range 4.0-6.5. The curves clearly shows that the absorbance increases almost linearly in the pH range 4.0-5.5, however it attains the maximum value at 5.5 and remain constant upto pH 6.5 as indicated by straight line portion of the curves. This pH range where the absorbance of the complex at the $\lambda_{\max}$ is termed as optimum pH range of stability of complex formation. Curve A represents the plot of absorbance of lanthanide complexes at

540 nm in absence with changes in pH in the range 4.0 to 6.5. The curves in Figure 9 show range 6.0 – 6.5 as optimum pH range of constant absorbance.

The pH range of stability and optimum pH range of stability of all the lanthanide complexes of ECAB in absence and presence of CDMEAB under study are recorded in Table 3.

Table 3. pH range of stability of ECAB complexes in absence and presence of CDMEAB.

lanthanide complexes	$\lambda_{\max}$ of ECAB (nm)		pH range of stability of constant wavelength		pH range of stability of constant absorbance	
	Absence	Presence	Absence	Presence	Absence	Presence
Y(III)	540	650	4.0-6.5	4.5-6.5	6.0-6.5	5.5-6.5
Nd(III)	540	650	4.0-6.5	4.5-6.5	6.0-6.5	5.5-6.5
Eu(III)	540	650	4.0-6.5	4.5-6.5	6.0-6.5	5.5-6.5
Tb(III)	540	650	4.0-6.5	4.5-6.5	6.0-6.5	5.5-6.5
Yb(III)	540	650	4.0-6.5	4.5-6.5	6.0-6.5	5.5-6.5

Figure 8. Variation in $\lambda_{\max}$ with change in the pH of: A [ECAB]-(Reagent), B [ECAB+CDMEAB]-(Modified reagent), C [ECAB+Eu(III)]-(Binary complex), D [ECAB+CDMEAB+Eu(III)]-(Ternary complex).

Figure 9. Variation in absorbance at the $\lambda_{\max}$ with change in the pH of :
A- $\lambda_{\max}$, 540nm of ECAB-Eu (Binary complex)
B- $\lambda_{\max}$, 650nm of ECAB-CDMEAB-Eu (Ternary complex).

Composition of Complexes

Quantitative information on complex formation is obtained by determining its composition and stability constants of complexes formed. From the spectral studies, it has been found that the reagent ECAB forms only one type of complex with lanthanide metal ions under study. The composition of complexes has been studied by the Job's method of continuous variation²⁰ and it has been further confirmed by Mole ratio method. For Job's

method, solutions of lanthanide and ECAB have been taken in three equimolar concentrations of $2.5 \times 10^{-4} \text{ M}$, $2 \times 10^{-4} \text{ M}$, and $1.66 \times 10^{-4} \text{ M}$; five times excess of CDMEAB has been then added for studying the composition in presence of surfactant.

The stoichiometric composition between the metal ion and ECAB in presence and absence of CDMEAB has been found to be 1:2. It has been observed that ECAB reagent at pH 6.0 exists as $[\text{ECAB}(\text{CDMEAB})_3]$ and therefore the composition of complexes in presence of CDMEAB may be written as $\text{Ln}[\text{ECAB}(\text{CDMEAB})_3]_2$ for all lanthanide complexes. The composition has been further confirmed by Mole ratio method. This is just a tentative reaction and further studies in this regard is necessary for confirmation of the composition as the emphasis has been given in the present investigation on microdetermination of metal ions in presence of CDMEAB. The formation of complexes may therefore be expressed by equation (omitting charges).

Table 4. Composition and log K values of lanthanide complexes of ECAB in absence and presence of CDMEAB.

Complexes of ECAB	pH of study	Wavelength of study, nm	Composition Ln : R, Ln : (R:S)	Log K values by Job's method
Y(III)	A 6.0	540	1:2	10.19
	P 6.0	650	1:(1:3) ₂	10.46
Nd(III)	A 6.0	540	1:2	9.55
	P 6.0	650	1:(1:3) ₂	10.91
Eu(III)	A 6.0	540	1:2	9.88
	P 6.0	650	1:(1:3) ₂	10.91
Tb(III)	A 6.0	540	1:2	9.88
	P 6.0	650	1:(1:3) ₂	10.57
Yb(III)	A 6.0	540	1:2	10.08
	P 6.0	650	1:(1:3) ₂	10.43

A: Absence, P: Presence.

Stability Constant

Values of log K of complexes of lanthanides understudy in absence and presence of CDMEAB have been calculated from Job's method²⁰ are reported in Table 4. The result shows that the value of log K for particular metal ion in presence of CDMEAB is greater than in absence of CDMEAB. This increase in log K values in presence of CDMEAB is due to formation of stable complexes.

Analytical Applications of Ternary Complexes of Lanthanides (in Presence of CDMEAB)

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

Order of addition of reactants

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

Rate of color formation and stability of color at room temperature

The color formation does not depend on reaction time and is almost instantaneous in presence of CDMEAB. However the mixtures were kept for 30 minutes for equilibration. A mixture containing 2.5×10^{-4} M ECAB, 1.0×10^{-4} M ECAB, and 2.5×10^{-4} M lanthanide 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 20⁰ C to 60⁰ C.

Effect of reagent concentration

Different volumes of 1.0×10^{-4} M of ECAB 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 ECAB in all the cases of metal ions understudy 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.

Beer's Law and effective photometric ranges

The linearity between the absorbance of complexes 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 ECAB 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 absence of CDMEAB at 540 nm. However in presence of CDMEAB all the spectral measurements were 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 plot²¹ (log of metal ion concentration versus percentage transmittance). Thus the range as derived by the slope of curve is selected to be range for the effective photometric determination as given in Table 5.

Table 5. Photometric determination of lanthanides with ECAB in absence and presence of CDMEAB.

Complexes of ECAB	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	540	0.17-0.88	0.35-0.71	0.002	46000
	P 6.0	650	0.11-0.94	0.23-0.71	0.0012	69000
Nd(III)	A 6.0	540	0.28-1.44	0.57-1.15	0.003	37000
	P 6.0	650	0.19-1.53	1.15-2.69	0.0021	66000
Eu(III)	A 6.0	540	0.30-1.52	0.608-1.82	0.004	42000
	P 6.0	650	0.2-1.41	0.20-0.81	0.0022	69000
Tb(III)	A 6.0	540	0.31-1.90	0.63-1.58	0.0047	42000
	P 6.0	650	0.21-1.69	0.21-0.81	0.0024	64000
Yb(III)	A 6.0	540	0.31-1.73	0.69-1.38	0.0038	45000
	P 6.0	650	0.23-1.11	0.46-1.15	0.0024	70000

A: Absence, P: Presence.

Sensitivities and Molar absorptivities

Molar absorptivities of the complexes have been determined by taking a constant amount of ECAB and different amount of excess of metal ions and five times excess of CDMEAB at pH 6.0. The values of molar absorptivities and Sandell's sensitivities²² of metal complexes in absence and presence of CDMEAB at the wavelength of study are given in Table 5. The increase in values of sensitivities and molar absorptivities of the ternary complexes than binary complexes again shows the sensitization of reagent in presence of CDMEAB.

Effect of Foreign ions

The effect of foreign ions has been studied by taking 28.84 μg of Nd (III) and determining its concentration in presence of large number of interfering ions. The method suffers from lack of selectivity but the interferences are not too many. The determination is possible in absence of metal ions such as Ag (I), Pd (II), Hg (II), In (III), Au (III), Th (IV), U (VI) and some transition metal ions. Anions such as nitrates, oxalates, citrates, succinates and EDTA which strongly interfere.

Procedure for Microdetermination

Adjust the pH of solution containing 0.5 to 4.5 ppm of lanthanide (III) metal ions to 6.0. Add about two fold excess of modified ECAB solution of same pH (The modified ECAB solution is prepared by adding about five fold excess of CDMEAB solution to ECAB solution and keeping it for at least 30 minutes for complete equilibration.) Dilute the solution to total volume of 50 ml with distilled water. Allow the mixture to stand for 30 minutes for full color development and equilibration. Measure the absorbance of this unknown solution at 650 nm against reagent blank prepared in the same manner. Compare the absorbance of this unknown solution from the calibration curve obtained under similar conditions. Results of the determination of individual metal ions have been reported in the table 6.

Table 6. Determination of Individual Metal Ion.

Lanthanides	Amount taken $\mu\text{g}/50\text{ ml}$	Amount found $\mu\text{g}/50\text{ ml}$	Standard average deviation
Y(III)	35.56	35.50	± 0.042
Nd(III)	25.84	25.97	± 0.04
Eu(III)	30.40	30.45	± 0.03
Tb(III)	42.37	42.42	± 0.03
Yb(III)	34.60	34.50	± 0.04

Conclusion

The spectrophotometric determination of lanthanides with eriochromeazuroI-B in absence and presence of cetyltrimethylammonium bromide have been studied. Following are the merits of modified method.

- 1) The sensitization of ECAB by addition of CDMEAB is clear from the fact that formation of stable ternary complexes with lanthanides occurs at pH 6.0 with bathochromic shift in the λ_{max} of metal ion-ECAB complexes in presence of cationic surfactant. This change is attributed due to formation of ternary complex system in presence of CDMEAB in acidic medium compared to the binary system in absence of CDMEAB.
- 2) The formation of stable ternary complexes with sharp peak in wider pH range as compared to weak binary complexes with broad shoulder in small pH range.
- 3) The increase in value of log K in presence of CDMEAB for particular metal ion is greater than in absence of CDMEAB shows the formation of stable complexes.
- 4) Due to the shifted λ_{max} towards higher wavelength (From 540 to 650 nm) and comparatively negligible absorbance of reagent gives the large difference in absorbance between the reagent blank (ECAB-CDMEAB) and its ternary complex which results in enhancement of sensitivities and molar absorptivities again indicates the sensitization of color reaction. In present investigation which was used for the determination of metal ions understudy when present in small concentration.
- 5) Further, the modified method requires smaller molar concentration of ECAB over the metal ion concentration for full color development and is instantaneous in presence of CDMEAB again indicates the stability of color reaction.
- 6) The modified reagent i.e. $[\text{ECAB}(\text{CDMEAB})_3]$ has also been found to be extremely useful in complexometric titration of lanthanide metal ions. This modified reagent act as sensitive metallochromic indicator giving a very sharp color change at the end point.
- 7) These observations suggest that a very useful application of these colored reactions in presence of ECAB or CDMEAB can be made in spectrophotometric determination of the metal ions with much enhanced sensitivity. It may be mentioned here that ECAB in presence of CDMEAB have been suggested for the first time as a sensitive reagents for spectrophotometric determination of metal ions understudy.

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