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Surfactant Induced Eriochrome Blue Black B-Metal Ion Interactions: Complexation and Analytical Studies

A.S. MAHAKALKAR
Department of Chemistry
Sevadal Mahila Mahavidyalaya, Nagpur-440 009, India

The chelation reactions of certain lanthanides and actinides in the presence of cetyltrimethyl-ammonium bromide (CTAB) have been studied in details. The complexes show a large bathochromic shift. The composition of the chelates of uranium, thorium, yttrium and europium with eriochrome blue black B was found to be 1 : 2 both in the absence and presence of CTAB. The stability constants of the complexes have been evaluated. The values of stability constants of ternary complexes of Th^{4+} and UO_2^{2+} have been found to be considerably increased in comparison to their corresponding binary complexes. The increased stability of ternary complex may be due to the stabilization of ternary complex in the surrounding atmosphere of cationic micelles of CTAB. The studies were extended to the analytical aspects of the complex equilibria and a suitable procedure has been recommended for the sensitive spectrophotometric determinations of metal ions under study. The effects of foreign ions on the systems was studied in the presence of large number of cations and anions. The extent of bathochromic shift in λ_{max}, considerable increase in the sensitivity and high stability of the complexes in the presence of CTAB shows the utility of this micelle forming cationic surfactant in the sensitization of colour reaction. The range of concentration for adherence to Beer's law and the effective photo range was calculated. The utility of these proposed methods have been established by evaluating the precision and the accuracy by employing suitable statistical methods.

Key Words: Eriochrome blue black B, Metal, Interaction, Complexation.

INTRODUCTION

In the earlier work the effect of the addition of surfactants to the acid base indicators showed[1–6] there is a considerable increase in the absorbance when the surfactant solution is added to the indicator solution. However, in some reactions a decrease in colour intensity of the organic dyes on addition of certain surfactants has been reported. In such cases, the modified reagents become much more suitable for the sensitization of colour reactions produced with metal ions. Subsequent development demonstrated that the addition of specific metal ions to these decolorized modified reagent solutions resulted in the formation of intense, water-soluble coloured ternary complexes. Much greater molar absorptivity and stability associated with these ternary complexes make them useful tools in the quantitative spectrophotometric determination of metal ions with an improved sensitivity.

We have reported earlier[7, 8] the results obtained in this regard with respect to our studies on the reaction between solochrome violet RS and eriochrome cyanine R with cetyltrimethyl ammonium bromide and its subsequent complexation and analytical studies.

In this communication, the results of the experiments carried out on the eriochrome blue black-B (EBBB) in the presence of cetyltrimethyl ammonium bromide (CTAB) and their interaction with UO_2^{2+}, Th^{4+}, Y^{3+} and Eu^{3+} are reported. Recently, these studies have found application in various applied analytical fields.

EXPERIEMENTAL

A UV-Shimadzu spectrophotometer UV-240, with glass cuvettes of 1 cm thickness was used for all absorption measurements. Distilled water was used as a reference for all spectral studies. The pH measurements were made with Elico pH-meter, LI-10 operated on 220 volts, with a glass-calomel electrode system. The instrument was standardized from time to time with potassium hydrogen phthalate buffer of pH 4.0 and borax buffer of pH 9.0.

All the chemicals used were of AnalaR grade. The dye solutions were prepared in double distilled water by dissolving their purified samples and the standard solutions of rare earth metals were prepared from oxide dissolved in hydrochloric acid. The surfactant, cetyltrimethyl ammonium bromide (CTAB) was prepared in 20% aqueous methanol and was standardized by usual procedures. Solutions of required concentration were prepared by appropriate dilution of these solutions.

The following general procedure was strictly followed in all the experiments. The order of mixing of reagents is very important. In all the experiments, TX or CTAB solution was added to the reagent solution which was kept for at least 20 min for maximum decolorizing effect. Metal ion solution was then added to the dye-surfactant solution and allowed to equilibrate for 30 min for complete complex formation. All the experiments were performed at room temperature.

RESULTS AND DISCUSSION

Absorption spectra of EBBB solution was recorded from pH 1.0 to 12.0. The spectral studies in the absence and presence of CTAB were made from pH 1.0 to 12.0. The absorption spectra of the reagent was noted from 350 to 650 nm in the absence and presence of surfactant. The λ_{max} values in the absence as well as in the presence of CTAB are summarized in Table-1.

Dissociation constant (pK values) of EBBB: EBBB is a tribasic acid having three replaceable protons. Out of these one, due to the presence of $—SO_3H$ group would give pK_1, while the other two due to —OH groups will give pK_2 and pK_3 values of EBBB. The dissociation equilibria of EBBB can be written as:

$$H_3EBBB \overset{pK_1}{\rightleftharpoons} H_2EBBB^- \overset{pK_2}{\rightleftharpoons} HEBBB^{2-} \overset{pK_3}{\rightleftharpoons} EBBB^{3-}$$

The values recorded are summarized in Table–2.

TABLE-1
λ_{max} OF EBBB AT DIFFERENT pH VALUES

In the absence of surfactant		In the presence of CTAB	
pH	λ_{max} (nm)	pH	λ_{max} (nm)
1.0–3.0	515	1.0–3.0	540
4.0–6.0	525	4.0–6.0	540
7.0–11.0	570	7.0–11.0	650
12.0	540	12.0	540

TABLE-2
pK VALUES OF EBBB IN THE ABSENCE AS WELL AS IN THE PRESENCE OF CTAB

pK values	In the absence of CTAB	In the presence of CTAB
pK_1	2.2	2.0
pK_2	7.8	6.0
pK_3	11.0	10.6

The lowering observed in the pK values of EBBB in the presence of CTAB indicates definite interaction taking place between EBBB and CTAB where the surfactant facilitates the dissociation at a comparatively early pH.

Composition of EBBB–CTAB Complex: The effect of varying surfactant concentration on the absorption spectra of EBBB was studied at pH 6.0 and at 530 nm. At pH 6.0 if we compare the difference in the absorbance at 530 nm, we noticed more decrease in the absorbance and hence the composition of dye-surfactant was studied at pH 6.0 at 530 nm. In Fig. 1 the descending portion shows the increasing CTAB effect on EBBB and a horizontal section shows a constant absorbance. The intersection of these two lines represents the compositions of dye-detergent complex formation with ratio of EBBB : CTAB as 1 : 2.

Effect of mineral salts: The effect of mineral salts on the absorption spectrum of EBBB in the presence of CTAB was studied. The absorbance of EBBB in the alkaline medium is found to be changed by presence of higher amount of nitrates and slight change with chlorides.

In the acidic range no such significant changes were observed. Nitrates showed slight increase in the absorbance. Chlorides and sulphates showed nearly constant absorbance. This shows the negligible effect of mineral salts on the absorbance of the EBBB in the presence of CTAB. (Fig. 2) at pH 6.0.

The absorption spectra of EBBB, EBBB-metal ion, EBBB –CTAB and EBBB-metal ion –CTAB were recorded at pH of study. EBBB forms stable complexes with UO_2 (VI) and Y(III) in the absence as well as in the presence of CTAB and with Th(IV) and Eu(III) only in the presence of CTAB. A representative absorption spectrum is shown in Fig. 3 to indicate the pattern of change in λ_{max} in different conditions.

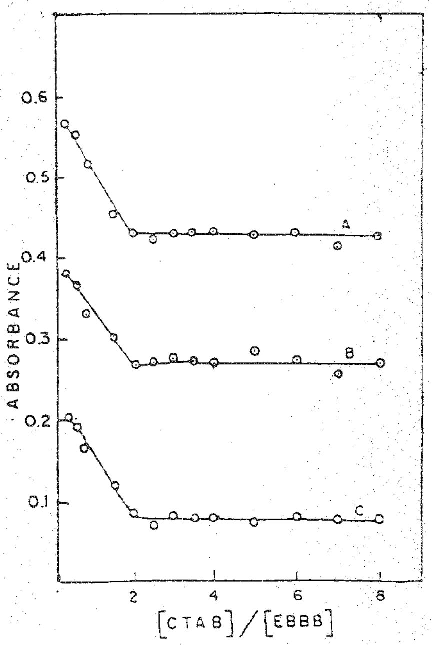

Fig. 1. Composition of EBBB-CTAB complex
pH = 6.0, λ = 530 nm
Final conc. of EBBB:
Curve A = 1.6×10^{-4} M
Curve B = 8.0×10^{-5} M
Curve C = 4.0×10^{-5} M

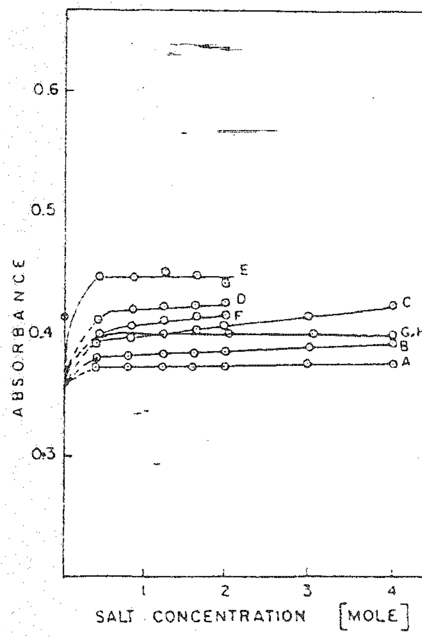

Fig. 2. Effect of mineral salt on EBBB in presence of CTAB
pH = 6.0; λ = 530 nm
Curve A = KCl, Curve B = NaCl
Curve C = NH_4Cl, Curve D = KNO_3
Curve E = $NaNO_3$, Curve F = NH_4NO_3
Curve G = Na_2SO_4, Curve H = $(NH_4)_2SO_4$

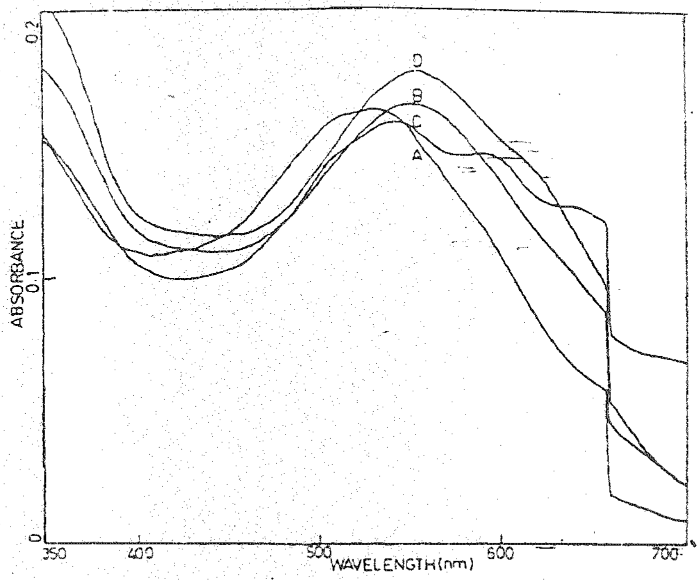

Fig. 3. Absorption spectra of UO_2 (VI) complex of EBBB
pH = 4.0
Conc. of EBBB = 4.0×10^{-5} M
Conc. of CTAB = 4.0×10^{-4} M
Conc. of UO_2(VI) = 1.6×10^{-4} M
Curve A = EBBB
Curve B = UO_2(VI) – EBBB
Curve C = EBBB – CTAB
Curve D = UO_2(VI) – EBBB – CTAB

TABLE-5

COMPOSITION AND log K VALUES OF CHELATES OF EBBB IN ABSENCE OF CTAB

Chelates	pH	Wavelength (nm)	Composition M : EBBB	log K values	
				Job's method	Mole ratio method
UO_2(VI)	4.0	555	1 : 2	8.90	9.13
Th(IV)	—	—	—	—	—
Y(III)	6.0	545	1 : 2	9.46	9.62
Eu(III)	—	—	—	—	—

TABLE-6

COMPOSITION AND log K VALUES (± 0.05) OF CHELATES OF EBBB IN PRESENCE OF CTAB

Chelates	pH	Wavelength (nm)	Composition M : EBBB : CTAB	log K values	
				Job's method	Mole ratio method
UO_2(VI)	4.0	560	1 : 2 : 4	10.16	10.10
Th(IV)	4.0	550	1 : 2 : 4	9.49	9.62
Y(III)	6.0	545	1 : 2 : 4	9.48	9.65
Eu(III)	6.0	545	1 : 2 : 4	10.47	9.90

The values of stability constants of ternary complexes of Th^{4+} and UO_2^{2+} have considerably increased over their corresponding binary complexes. The increase might be due to the attachment of two cations of CTAB to the reagent, EBBB which then forms a modified reagent $EBBB(CTAB)_2$. The increased stability of ternary complex may be due to the stabilization of ternary complex in the surrounding atmosphere of cations micelles of CTAB.

Analytical applications: In all the experiments CTAB solution was added to EBBB solution, which was kept for 1/2 h for complete formation of dye-detergent complex, to which the metal ion solution was then added. In the absence of CTAB, the order of addition of reactants was found to have no effect on the absorbance values.

The temperature was found to have no effect on colour intensity from 20° to 60°C in the presence as well as in the absence of CTAB containing a fourfold excess of reagent.

It was found that equilibrium is attained after 8–10 min. The absorbance was measured after regular time intervals and it was found that the colour remains constant even after 24 h of standing at room temperature. In all the determinations, measurements were made 30 min after mixing the reactants for full colour development.

Effect of reagent concentration: The effect of excess of reagent was determined in each system in the absence as well as in the presence of CTAB. It was observed that a three-fold concentration of the reagent is essential for maximum colour development, in the absence as well as in the presence of CTAB. After three-fold concentration, even if excess of reagent was added, the absorbance remained constant.

pH-range of stability of the absorbance of the systems: For this study metal : reagent was taken in 1 : 4 ratio and several sets were prepared with the same concentration for a chelate system for which different pH-values were adjusted. In the presence of surfactant, the ratio of reagent : CTAB was kept in 1 : 10 ratio. The absorbance was noted at the wavelength of study of the systems. The absorbance values remained constant within a certain pH range, which was considered as the stable pH range for the coloured systems. The pH range of stability for all the systems is recorded in Table-7.

TABLE-7
pH-RANGE OF STABILITY OF THE ABSORBANCE OF THE SYSTEMS

Systems	Wavelength of study (nm)	pH range of stability
UO_2(VI)-EBBB	555	3.7–5.0
UO_2(VI)-EBBB-CTAB	560	3.0–5.1
Th(IV)-EBBB-CTAB	550	3.0–6.0
Y(III)-EBBB	545	5.4–6.5
Y(III)-EBBB-CTAB	545	5.2–7.0
Eu(III)-EBBB-CTAB	545	4.5–6.5

Beer's law and photometric ranges: The conformity to Beer's law, *i.e.*, the linearity between the absorbance of the chelates in the absence as well as in the presence of CTAB was tested by keeping reagent concentration constant and varying metal ion concentration at the pH and wavelength of study selected for various chelate systems. The effective photometric range was evaluated by plotting Ringbom plot. The results are shown in Table-8.

TABLE-8
BEER'S LAW AND EFFECTIVE PHOTOMETRIC RANGE OF METAL IONS FOR THEIR SPECTROPHOTOMETRIC DETERMINATION WITH EBBB

Metal ions	Wavelength of study (nm)	pH of study	Beer's law range (ppm)	Effective photometric range (ppm)
In absence of surfactant:				
UO_2(VI)	555	4.0	1.9–16.7	3.2–11.2
Y(III)	545	6.0	1.4–12.5	2.5–6.3
In presence of CTAB:				
UO_2(VI)	560	4.0	1.4–15.7	4.5–11.2
Th(IV)	550	4.0	3.7–26.0	7.1–14.1
Y(III)	545	6.0	1.0–6.2	2.0–5.0
Eu(III)	545	6.0	0.9–9.1	1.0–3.2

Sensitivity and molar absorptivity: The sensitivity of the colour reactions of different metal ions with EBBB, as defined by Sandell and molar absorptivity of the systems, are given in Table-9.

TABLE-9
SANDELLS'S SENSITIVITY AND MOLAR ABSORPTIVITIES OF THE SYSTEMS

Systems	Wavelength of study (nm)	pH of study	Sandell's sensitivity $S \times 10^{-2}$	Molar absorptivity $Em \times 10^3$
UO_2(VI)-EBBB	555	4.0	4.7	3.5
UO_2(VI)-EBBB-CTAB	560	4.0	2.6	7.0
Th(IV)-EBBB-CTAB	550	4.0	4.0	3.7
Y(III)-EBBB	545	6.0	1.3	3.1
Y(III)-EBBB-CTAB	545	6.0	0.9	5.1
Eu(III)-EBBB-CTAB	545	6.0	2.5	7.2

Effect of foreign ions: The effect of foreign ions was tested by taking a constant concentration of metal ion and determining its concentration in the presence of a large number of foreign ions. Some metal ions interfere largely. Identical mixtures of EBBB, CTAB and metal ion were prepared at particular concentration to which variable amounts of foreign ions solution were added.

It was observed that metal ions VO^{2+} and Cr^{2+} interfere seriously. The determination was also affected by the presence of metal ions like Pb^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+} and Mn^{3+}. Few cations like La^{3+}, Mg^{2+}, Co^{2+}, Ni^{2+} do not interfere if not present in large excess. Anions like Cl^-, Br^-, I^- do not interfere while anions like tartarate, oxalate, citrate, fluoride interfere at all concentrations, in all the systems of EBBB with UO_2^{2+}, Th^{4+}, Y^{3+} and Eu^{3+} in the absence as well as in the presence of CTAB.

Procedure for microdetermination: The pure sample of metal ion was suitably diluted so that it contains 1.0–5.0 ppm of metal ions under study. The modified EBBB solution was then added to it. Total volume was made up to 25 mL with distilled water and the pH was maintained. The absorbance was noted at the wavelength of study, against modified reagent solution as blank in the system where CTAB is present. The amount of metal ion present in unknown solution can be obtained by comparing from calibration curve obtained under similar conditions.

The mean absorbance, mean deviation and relative mean deviation are given in Table-10.

TABLE-10
SPECTROPHOTOMETRIC DATA FOR EBBB SYSTEMS IN ABSENCE AND IN PRESENCE OF CTAB

Systems	Mean absorbance	Mean deviation	Relative mean deviation (%)
UO_2(VI)-EBBB	0.245	0.0018	0.73
UO_2(VI)-EBBB-CTAB	0.251	0.0015	0.59
Th (IV)-EBBB-CTAB	0.182	0.0012	0.66
Y(III)-EBBB	0.211	0.0014	0.66
Y(III)-EBBB-CTAB	0.152	0.0010	0.60
Eu(III)-EBBB	0.155	0.0011	0.70

Statistical evaluation of proposed analytical methods

The data obtained during the proposed spectrophotometric investigations were analysed by determining:

(1) average or mean deviation (DM) and

(2) root mean square deviation or standard deviation (σ)

in the spectral absorbance data for ten replicate determinations with same amount of metal ion under exactly similar conditions. With small sample size, the confidence interval for the expected value is constructed by having recourse to *t*-distribution. The *t*-distribution holds for a random variable (for test statistics).

$$t = \frac{\overline{x} - \mu}{S/\sqrt{n}}$$

where x = arithmetical mean of observed data,
n = number of determination,
μ = most probable error,
S = sample standard deviation.

The value of the probable error in absorption measurement is expressed with the help of the equation

$$E = \pm t_{\alpha} \frac{\sigma}{\sqrt{n}}$$

where S = measure of precision of the analysis,
σ = root mean square deviation in absorbance measurements,
n = number of determinations,
t_{α} = confidence limit of analysis.

Conclusions can be drawn on the basis of the data given in Table-11 regarding (i) the root mean square deviation (σ), (ii) the most probable analytical error (E), the difference (Δ), between arithmetic mean ($\overline{x}$) and true or most expected (xt) value of absorbance for the systems studied.

TABLE-11
PRECISION DATA FOR ABSORBANCE MEASUREMENTS

Systems	$\overline{x}$	σ	E	$\overline{x} - E$	$\overline{x} + E$
UO_2(VI)-EBBB	0.245	0.0016	0.0021	0.243	0.247
UO_2(VI)-EBBB-CTAB	0.251	0.0009	0.0010	0.250	0.252
Th(IV)-EBBB-CTAB	0.162	0.0027	0.0032	0.179	0.185
Y(III)-EBBB	0.211	0.0015	0.0017	0.209	0.213
Y(III)-EBBB-CTAB	0.152	0.0016	0.0019	0.150	0.154
Eu (III)-EBBB-CTAB	0.155	0.0009	0.0010	0.154	0.156

The value of most probable analytical error, determined with root mean square deviation, σ, for ten replicate determinations ranges between 0.0009 to 0.0027 at the confidence limit of $t = 0.995$ or 99.5%. If the number of determinations are further increased that would subsequently decrease the value of t_{α}. Consequently a point would be reached when the increase in precision will be too small to justify the expenditure of labour time and reagents involved in increased number of determinations.

TABLE-12
ACCURACY OF DETERMINATIONS EXPRESSED IN TERMS OF ($\Delta < E$)

Systems	$\bar{x}$	x_t	$\Delta = x_t - \bar{x}$	E
UO_2(VI)-EBBB	0.245	0.246	0.001	0.0021
UO_2(VI)-EBBB-CTAB	0.251	0.251	0.000	0.0010
Th(IV)-EBBB-CTAB	0.182	0.182	0.000	0.0032
Y(III)-EBBB	0.211	0.211	0.000	0.0017
Y(III)-EBBB-CTAB	0.152	0.152	0.000	0.0019
Eu (III)-EBBB-CTAB	0.155	0.156	0.001	0.0010

The precision and accuracy data recorded reveal that the methods proposed are both precise as well as accurate.

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